The American Ceramic Society

12th Pacific Rim Conference on Ceramic and Glass Technology

ABSTRACT BOOK

May 21–26, 2017
Waikoloa, Hawaii

The
American
Ceramic
Society
www.ceramics.org

Introduction

This volume contains abstracts for over 1400 presentations during the 12th Pacific Rim Conference on Ceramic and Glass Technology in Waikoloa, Hawaii. The abstracts are reproduced as submitted by authors, a format that provides for longer, more detailed descriptions of papers. The American Ceramic Society accepts no responsibility for the content or quality of the abstract content. Abstracts are arranged by day, then by symposium and session title. An Author Index appears at the back of this book. The Meeting Guide contains locations of sessions with times, titles and authors of papers, but not presentation abstracts.

How to Use the Abstract Book

Refer to the Table of Contents to determine page numbers on which specific session abstracts begin. At the beginning of each session are headings that list session title, location and session chair. Starting times for presentations and paper numbers precede each paper title. The Author Index lists each author and the page number on which their abstract can be found.

MEETING REGULATIONS

The American Ceramic Society is a nonprofit scientific organization that facilitates the exchange of knowledge meetings and publication of papers for future reference. The Society owns and retains full right to control its publications and its meetings. The Society has an obligation to protect its members and meetings from intrusion by others who may wish to use the meetings for their own private promotion purpose. Literature found not to be in agreement with the Society's goals, in competition with Society services or of an offensive nature will not be displayed anywhere in the vicinity of the meeting. Promotional literature of any kind may not be displayed without the Society's permission and unless the Society provides tables for this purpose. Literature not conforming to this policy or displayed in other than designated areas will be disposed. The Society will not permit unauthorized scheduling of activities during its meeting by any person or group when those activities are conducted at its meeting place in interference with its programs and scheduled activities. The Society does not object to appropriate activities by others during its meetings if it is consulted with regard to time, place, and suitability. Any person or group wishing to conduct any activity at the time and location of the Society meeting must obtain permission from the Executive Director or Director of Meetings, giving full details regarding desired time, place and nature of activity.

Diversity Statement: The American Ceramic Society values diverse and inclusive participation within the field of ceramic science and engineering. ACerS strives to promote involvement and access to leadership opportunity regardless of race, ethnicity, gender, religion, age, sexual orientation, nationality, disability, appearance, geographic location, career path or academic level.

The American Ceramic Society plans to take photographs and video at the conference and reproduce them in educational, news or promotional materials, whether in print, electronic or other media, including The American Ceramic Society's website. By participating in the conference, you grant The American Ceramic Society the right to use your name and photograph for such purposes. All postings become the property of The American Ceramic Society.

During oral sessions conducted during Society meetings, **unauthorized photography, videotaping and audio recording is prohibited.** Failure to comply may result in the removal of the offender from the session or from the remainder of the meeting.

Registration Requirements: Attendance at any meeting of the Society shall be limited to duly registered persons.

Disclaimer: Statements of fact and opinion are the responsibility of the authors alone and do not imply an opinion on the part of the officers, staff or members of The American Ceramic Society. The American Ceramic Society assumes no responsibility for the statements and opinions advanced by the contributors to its publications or by the speakers at its programs; nor does The American Ceramic Society assume any liability for losses or injuries suffered by attendees at its meetings. Registered names and trademarks, etc. used in its publications, even without specific indications thereof, are not to be considered unprotected by the law. Mention of trade names of commercial products does not constitute endorsement or recommendations for use by the publishers, editors or authors.

Final determination of the suitability of any information, procedure or products for use contemplated by any user, and the manner of that use, is the sole responsibility of the user. Expert advice should be obtained at all times when implementation is being considered, particularly where hazardous materials or processes are encountered.

Table of Contents

GOMD Symposium 1: Fundamentals of the Glassy State

GOMD Symposium 2: Glasses in Healthcare: Fundamentals and Applications

GOMD Symposium 3: Optical and Electronic Materials and Devices: Fundamentals and Applications

GOMD Symposium 5: Professor Jacques Lucas Honorary Symposium

PACRIM Symposium 02: Virtual Materials Design and Ceramic Genome

PACRIM Symposium 03: Novel, Green, and Strategic Processing and Manufacturing Technologies

PACRIM Symposium 07: Porous Ceramics: Innovative Processing and Advanced Applications

PACRIM Symposium 11: Engineering Ceramics: Processing and Characterizations

PACRIM Symposium 17: Advanced Functional Ceramics and Critical Materials Perspective

PACRIM Symposium 19: Transparent Ceramic Materials and Devices

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

PACRIM Symposium 25: Ceramics for Next Generation Nuclear Energy

PACRIM Symposium 27: Ceramics for Enabling Environmental Protection: Clean Air and Water

PACRIM Symposium 28: Advanced Materials and Technologies for Electrochemical Energy Storage Systems

PACRIM Symposium 29: Advances in Polar, Magnetic and Semiconductor Materials: Extending Temperature Limits

PACRIM Symposium 31: Advances in Bioceramics: Biomineralization and Bioinspired Materials

GOMD Award Lectures

GOMD Symposium 1: Fundamentals of the Glassy State

GOMD Symposium 3: Optical and Electronic Materials and Devices: Fundamentals and Applications

GOMD Symposium 4: Glass Technology and Crosscutting Topics

GOMD Symposium 5: Professor Jacques Lucas Honorary Symposium

PACRIM Third International Richard M. Fulrath Symposium on Discontinuous Progress for Ceramic Innovations

PACRIM Symposium 02: Virtual Materials Design and Ceramic Genome

PACRIM Symposium 03: Novel, Green, and Strategic Processing and Manufacturing Technologies

PACRIM Symposium 07: Porous Ceramics: Innovative Processing and Advanced Applications

PACRIM Symposium 11: Engineering Ceramics: Processing and Characterizations

PACRIM Symposium 17: Advanced Functional Ceramics and Critical Materials Perspective

PACRIM Symposium 19: Transparent Ceramic Materials and Devices

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

PACRIM Symposium 25: Ceramics for Next Generation Nuclear Energy

PACRIM Symposium 28: Advanced Materials and Technologies for Electrochemical Energy Storage Systems

PACRIM Symposium 29: Advances in Polar, Magnetic and Semiconductor Materials: Extending Temperature Limits

PACRIM Symposium 31: Advances in Bioceramics: Biomineralization and Bioinspired Materials

GOMD Symposium 1: Fundamentals of the Glassy State

GOMD Symposium 2: Glasses in Healthcare: Fundamentals and Applications

GOMD Symposium 4: Glass Technology and Crosscutting Topics

GOMD Symposium 5: Professor Jacques Lucas Honorary Symposium

PACRIM Third International Richard M. Fulrath Symposium on Discontinuous Progress for Ceramic Innovations

PACRIM Symposium 02: Virtual Materials Design and Ceramic Genome

PACRIM Symposium 03: Novel, Green, and Strategic Processing and Manufacturing Technologies

PACRIM Symposium 07: Porous Ceramics: Innovative Processing and Advanced Applications

PACRIM Symposium 11: Engineering Ceramics: Processing and Characterizations

PACRIM Symposium 17: Advanced Functional Ceramics and Critical Materials Perspective

PACRIM Symposium 19: Transparent Ceramic Materials and Devices

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

PACRIM Symposium 25: Ceramics for Next Generation Nuclear Energy

PACRIM Symposium 28: Advanced Materials and Technologies for Electrochemical Energy Storage Systems

PACRIM Symposium 29: Advances in Polar, Magnetic and Semiconductor Materials: Extending Temperature Limits

PACRIM Symposium 31: Advances in Bioceramics: Biomineralization and Bioinspired Materials

GOMD Award Lectures

GOMD Symposium 1: Fundamentals of the Glassy State

GOMD Symposium 3: Optical and Electronic Materials and Devices: Fundamentals and Applications

GOMD Symposium 4: Glass Technology and Crosscutting Topics

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium

PACRIM Symposium 07: Porous Ceramics: Innovative Processing and Advanced Applications

PACRIM Symposium 10: Multifunctional Nanomaterials and Their Heterostructures for Energy and Sensing Devices

PACRIM Symposium 11: Engineering Ceramics: Processing and Characterizations

PACRIM Symposium 12: Design, Development, and Applications of Ceramic-Matrix Composites

PACRIM Symposium 14: Novel Spray Coatings

PACRIM Symposium 16: Geopolymers: Low-Energy and Environmentally-Friendly Ceramics

PACRIM Symposium 17: Advanced Functional Ceramics and Critical Materials Perspective

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

PACRIM Symposium 25: Ceramics for Next Generation Nuclear Energy

PACRIM Symposium 28: Advanced Materials and Technologies for Electrochemical Energy Storage Systems

PACRIM Symposium 29: Advances in Polar, Magnetic and Semiconductor Materials: Extending Temperature Limits

PACRIM Symposium 31: Advances in Bioceramics: Biomineralization and Bioinspired Materials

PACRIM Young Investigators Forum: Design and Application of Next-Generation Multifunctional Materials-Addressing the New Millennium's Societal Challenges

GOMD Award Lectures

GOMD Symposium 1: Fundamentals of the Glassy State

GOMD Symposium 3: Optical and Electronic Materials and Devices: Fundamentals and Applications

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium

PACRIM Symposium 08: Additive Manufacturing and 3-D Priniting Technologies

PACRIM Symposium 09: Ceramic Integration and Joining Technologies

PACRIM Symposium 10: Multifunctional Nanomaterials and Their Heterostructures for Energy and Sensing Devices

PACRIM Symposium 12: Design, Development, and Applications of Ceramic-Matrix Composites

PACRIM Symposium 14: Novel Spray Coatings

PACRIM Symposium 17: Advanced Functional Ceramics and Critical Materials Perspective

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

PACRIM Symposium 23: Materials for Solar Thermal Energy Conversion and Storage

PACRIM Symposium 26: Advances in Materials and Technology for Perovskite and Next Generation Solar Cells

PACRIM Symposium 30: Glasses and Ceramics for Nuclear and Hazardous Waste Treatment

PACRIM Symposium 32: Nanostructured Bioceramics and Ceramics for Biomedical Applications

PACRIM Young Investigators Forum: Design and Application of Next-Generation Multifunctional Materials-Addressing the New Millennium's Societal Challenges

GOMD Award Lectures

GOMD Symposium 1: Fundamentals of the Glassy State

GOMD Symposium 3: Optical and Electronic Materials and Devices: Fundamentals and Applications

GOMD Symposium 4: Glass Technology and Crosscutting Topics

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium

PACRIM Symposium 01: Characterization and Modeling of Ceramic Interfaces: Structure, bonding, and Grain Growth

PACRIM Symposium 04: Polymer-Derived Ceramics (PDCs) and Composites

PACRIM Symposium 05: Advanced Powder-Processing and Manufacturing Technologies

PACRIM Symposium 10: Multifunctional Nanomaterials and Their Heterostructures for Energy and Sensing Devices

PACRIM Symposium 13: Advanced Structural Ceramics for Extreme Environments

PACRIM Symposium 14: Novel Spray Coatings

PACRIM Symposium 15: Advanced Wear-Resistant Materials: Tribology and Reliability

PACRIM Symposium 18: Microwave Dielectric Materials and Their Applications

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

PACRIM Symposium 22: Direct Thermal to Electrical Energy Conversion Materials and Applications

PACRIM Symposium 26: Advances in Materials and Technology for Perovskite and Next Generation Solar Cells

PACRIM Symposium 30: Glasses and Ceramics for Nuclear and Hazardous Waste Treatment

PACRIM Symposium 32: Nanostructured Bioceramics and Ceramics for Biomedical Applications

GOMD Symposium 1: Fundamentals of the Glassy State

GOMD Symposium 4: Glass Technology and Crosscutting Topics

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium

PACRIM Symposium 01: Characterization and Modeling of Ceramic Interfaces: Structure, bonding, and Grain Growth

PACRIM Symposium 04: Polymer-Derived Ceramics (PDCs) and Composites

PACRIM Symposium 05: Advanced Powder-Processing and Manufacturing Technologies

PACRIM Symposium 06: Synthesis and Processing of Materials Using Electric Currents and Pressures

PACRIM Symposium 13: Advanced Structural Ceramics for Extreme Environments

PACRIM Symposium 18: Microwave Dielectric Materials and Their Applications

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

PACRIM Symposium 21: Solid Oxide Fuel Cells and Hydrogen Technologies

PACRIM Symposium 22: Direct Thermal to Electrical Energy Conversion Materials and Applications

PACRIM Symposium 24: Photovoltaic and Related Materials and Technologies

PACRIM Symposium 30: Glasses and Ceramics for Nuclear and Hazardous Waste Treatment

PACRIM Symposium 32: Nanostructured Bioceramics and Ceramics for Biomedical Applications

GOMD Award Lectures

GOMD Symposium 1: Fundamentals of the Glassy State

GOMD Symposium 4: Glass Technology and Crosscutting Topics

PACRIM Symposium 01: Characterization and Modeling of Ceramic Interfaces: Structure, bonding, and Grain Growth

PACRIM Symposium 04: Polymer-Derived Ceramics (PDCs) and Composites

PACRIM Symposium 06: Synthesis and Processing of Materials Using Electric Currents and Pressures

PACRIM Symposium 13: Advanced Structural Ceramics for Extreme Environments

PACRIM Symposium 18: Microwave Dielectric Materials and Their Applications

PACRIM Symposium 21: Solid Oxide Fuel Cells and Hydrogen Technologies

PACRIM Symposium 22: Direct Thermal to Electrical Energy Conversion Materials and Applications

PACRIM Symposium 24: Photovoltaic and Related Materials and Technologies

PACRIM Symposium 30: Glasses and Ceramics for Nuclear and Hazardous Waste Treatment

Monday, May 22, 2017

PacRim Plenary Session
Room: Monarchy
Session Chair: Dileep Singh, Argonne National Lab

9:00 AM

(PACRIM-PL-001-2017) Bio-process Inspired Synthesis and Processing for New Structures and Functions

Z. Fu*[1]

1. Wuhan University of Technology, State Key Lab of Advanced Technology for Materials Synthesis and Processing, China

In studying and mimicking the well-defined structures or unique functions of biomaterials, scientists have succeeded in designing and synthesizing bio-inspired materials or bio-inspired functions. Furthermore, the fantastic structure-forming process in biological systems is also evolution results of many billions of years, which efficiently and accurately fabricate biomaterials under environmentally benign conditions, in contrast to our present technological world where harsh conditions are commonly prerequisites. Hence, the natural structure-forming processes in bio-mineralization, photo-synthesis and other biological systems, are also worth learning by scientists to develop new synthesis and processing techniques, which is refereed as 'bio-process inspired synthesis and processing'. In this talk, I will report the research work and results about natural organism directed synthesis of new materials and functions; Genetically engineered living organism directed synthesis of new structures and functions; Organized and confinement controlled structure formation directed by rationally designed multi-functional proteins; Artificial synthesis inspired by photo-synthesis. The bio-process inspired approach extends present chemical methodology to produce materials, especially under environmentally benign conditions.

GOMD Symposium 1: Fundamentals of the Glassy State

Mechanical Properties of Amorphous Solids I
Room: Kona 4
Session Chair: Yunfeng Shi, Rensselaer Polytechnic Institute

1:15 PM

(GOMD-S1-001-2017) Bridging from Atoms to Continua in the Mechanics of Amorphous Solids (Invited)

A. Hinkle[1]; S. Patinet[4]; M. L. Falk*[1]; M. Shields[3]; C. Rycroft[2]

1. Johns Hopkins University, Materials Science & Engineering, USA
2. Harvard University, SEAS, USA
3. Johns Hopkins University, Civil Engineering, USA
4. ESPCI, France

Amorphous solids, which lack crystal structure, find wide application from consumer goods to photovoltaics and are ubiquitous in the natural world as glasses, but issues quantifying disorder have stymied reliable mechanical constitutive laws for these materials. Quantitatively predicting strain localization, a limiting failure process in high-strength metallic glasses and other amorphous materials, requires adequately capturing fluctuations in material structure and their role in the material's mechanical response. We focus on using atomic-scale models to quantify fluctuations in the glass structure correlated with deformation in shear. We then directly cross-compare molecular dynamics simulations and continuum representations of these same materials in order to test and validate constitutive theories relating disorder and plasticity.

1:45 PM

(GOMD-S1-002-2017) Development of micro-mechanical glass model in finite element method based on molecular dynamic simulation input

E. Dobroslavskaia*[1]; J. Luo[2]; P. Gorelchenko[2]; B. Zhang[2]; G. Hu[2]

1. Corning Scientific Center, Science & Technology, Russian Federation
2. Corning Incorporated, Science & Technology, USA

In general glass is treated as a brittle material with a purely elastic behavior. At a micro-level, however, a molecular dynamic (MD) modeling predicts that glass may demonstrate non-linearity like plastic material response at some stress-states. MD simulation allows carrying out a variety of simple material tests to define glass yield surface. The aim of this work is to develop a glass material model for finite element (FE) analysis that can accurately reflect the glass behavior at micro-scale level. FE method can be used for problems of any scale and can help to define conditions of glass contact cracking. Due to the lack of suitable material models in commercial software, the material model is implemented as a user-defined subroutine in LS-DYNA. FE simulation of simple material tests is used to demonstrate how the new user defined model performs in comparison with commonly used material models for glass. Finally a material model performance is evaluated with a glass indentation model and compared with MD simulation results.

2:00 PM

(GOMD-S1-003-2017) Understanding glass fracture from its elasticity

Y. Shi*[1]

1. Rensselaer Polytechnic Institute, USA

Glasses are usually brittle, seriously limiting their practical usages. Recently, the intrinsic ductility of glass was found to increase with the Poisson's ratio (v), with a sharp brittle-to-ductile (BTD) transition at v_{BTD}=0.31-0.32. Such a correlation between far-from-equilibrium fracture and near-equilibrium elasticity is unexpected and not understood. Four families of glasses (metallic glasses, amorphous silicon, silica, and polymeric glasses) with systematically controlled bonding, processing, and testing conditions were studied using molecular dynamics simulations. We show glasses with low v exhibit brittle fracture behavior and vice versa. In addition, nanocomposites with amorphous matrix and crystalline second phase show BTD transition, that is also accompanied by a corresponding change in the Poisson's ratio. These results indicate that the Poisson's ratio, albeit defined elastically, is sensitive to atomic structure, bonding, or even microstructures.

2:15 PM

(GOMD-S1-004-2017) Unveiling the distinct features of inherent heterogeneity in metallic glass

P. Guan*[1]

1. Beijing Computational Science Research Center, China

Heterogeneity is commonly believed to be intrinsic to metallic glasses. Nevertheless, how to distinguish and characterize the heterogeneity in atomic level is still debated. Based on extensive molecular dynamics simulations that combine isoconfigurational ensemble and atomic pinning methods, we directly reveal that metallic glass contains flow units and an elastic matrix which can be well distinguished by their distinctive atomic-level responsiveness and mechanical performance. The microscopic features of the flow units, such as the shape, spatial distribution dimensionality, and correlation length, are characterized from atomic position analysis. Furthermore, the correlation between the flow units and the landscape of energy state, free volume, atomic-level stress, and especially the local bond orientation order parameter is discussed.

2:30 PM

(GOMD-S1-005-2017) A double-edge sword: Nanocrystallite in toughening and embrittling metallic glasses

B. Deng*[1]; Y. Shi[1]

1. Rensselaer Polytechnic Institute, Materials Science & Engineering, USA

Monolithic bulk metallic glasses (BMGs) are featured by their near theoretical strength and large elasticity limit. However, they exhibit limited amount of global plasticity prior to failure via highly localized shear bands propagation. Recently, experimental results have shown that it could be mitigated via incorporating soft crystalline dendrites to promote strain location in multiple sites. Here we present a systematic MD simulation work to study the role of nanocrystallites (both in-situ and ex-situ synthesized) in tuning the ductile to brittle (BTD) transition of BMGs. We observed that the overall mechanical property and BTD transition of the metallic glass composite significantly hinge on the volume fraction, size, crystal orientation, and hardness of the crystal phase. Moreover, the ductility of these composite samples is highly related to Poisson's ratio (v), with high value for ductile samples, and vice versa.

2:45 PM

(GOMD-S1-007-2017) Assessing sealing glass equivalency based on viscoelastic behavior

R. Jamison*[1]; B. Elisberg[1]; K. Troyer[1]; M. Stavig[3]; K. Ewsuk[2]

1. Sandia National Laboratories, Component Science & Mechanics, USA
2. Sandia National Laboratories, Electronic, Optical, and Nano, USA
3. Sandia National Laboratories, Organic Materials Science, USA

Sealing glasses are used to make high reliability hermetic electrical feedthroughs for a variety of applications. Corning 9013 has long been an industry benchmark sealing glass used to make compression seals. As Corning has largely exited the market, a number of companies have developed and marketed alternate, "equivalent" sealing glasses based largely on the average linear coefficient of thermal expansion (CTE). While CTE is an important sealing glass material parameter, recent analysis has shown that the viscoelasticity of the glass is also critical to accurate residual stress predictions. In this study, dynamic and thermal mechanical experiments were performed on a six equivalent sealing glasses to determine their thermophysical properties and viscoelastic behavior. These data were used to populate a nonlinear viscoelastic material model for use in a FE model. Results for a simple, model compression seal will be presented. An assessment of sealing glass equivalency as it relates to the predicted residual stress state in the glass after manufacturing and aging will be discussed. Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

3:00 PM

(GOMD-S1-008-2017) Deformation and indentation cracking behavior of Na_2O-TiO_2-SiO_2 glasses (Invited)

L. Huang*[1]; G. Scannell[1]; T. Rouxel[2]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA
2. Université of Rennes 1, Glass and Mechanics Department, France

Effects of composition on deformation and cracking behavior of Na_2O-TiO_2-SiO_2 glasses were studied by using a combination of elastic measurements and micro-hardness indentation experiments. Na_2O-TiO_2-SiO_2 glasses with titania contents of 4-10 mol% and sodium oxide contents of 10-25 mol% were prepared through a traditional melt-quench process. Elastic properties were measured using Brillouin light scattering experiments. Indentation experiments were conducted using a Vickers indenter with loads ranging from 10 mN to 49 N. Volumes of densification and shear flow around indents were measured using atomic force microscopy (AFM). Critical loads for crack initiation and cracking patterns were systematically investigated and correlated with the elastic properties of glass. In this ternary system concerning a relatively large range of Poisson's ratio, a minimum in critical crack initiation load was observed at Poisson's ratio of 0.21-0.22. No correlations were observed between hardness, average crack length, or fracture toughness with the critical crack initiation load. A correlation between the minimum in crack initiation load and a change in deformation mechanisms over the same Poisson's ratio range was observed.

3:45 PM

(GOMD-S1-009-2017) Effects of network modifiers on pressure induced structural transformations and elastic properties variation in boroaluminosilicate glasses

A. Tandia*[1]; S. Goyal[1]; J. Luo[1]

1. Corning Incorporated, Modeling & Simulation, USA

WITHDRAWN

4:00 PM

(GOMD-S1-010-2017) Large Elastic Recovery During Indentation of Alkali Metaphosphate Glass Above Glass Transition Temperature

J. Endo*[1]; S. Inaba[1]; H. Muto[2]; S. Ito[1]

1. Asahi Glass Co., Ltd., Japan
2. Toyohashi University of Technology, Japan

We found that the $(Li, Na, K, Cs)_2O{\cdot}P_2O_5$ glass compressed under uniaxial stress showed an unusually large recovery of its shape above its glass transition temperature (T_g). To clarify the phenomenon, the viscous, elastic, and plastic behavior in the glass transition region were evaluated by a depth-sensing indentation method. From the load-displacement (P–h) curves, an unusual recovery of the depth displacement was found during unloading above T_g. By analyzing the P–h curves with a viscous–elastic–plastic model, the recovery was derived from elastic deformation lager than viscous deformation even above T_g. We concluded that the large shape recovery can be attributed to entropic elasticity related to relaxation to the randomly oriented -P-O-P- chain structure from the oriented chain structure formed under compression in the metaphosphate glass.

4:15 PM

(GOMD-S1-011-2017) Novel functional glass with high nitrogen content fabricated by containerless processing

C. Xu*[1]; X. Liu[1]; J. Qiu[2]

1. Zhejiang University, School of Material Science and Engineering, China
2. Zhejiang University, College of Optical Science and Engineering, China

There has been a constant search for glasses with excellent mechanical properties, i.e., high elastic moduli and hardness. Among oxide glasses, Ta_2O_5-Al_2O_3 system glass fabricated by aerodynamic levitation demonstrates superior mechanical properties. We show here that the hardness of glass can be increased dramatically with the incorporation of nitrogen into the network structure. The aerodynamic levitation allows the containerless synthesis of $46Ta_2O_5$-xAl_2O_3-$2(54-x)AlN$ glass, where Al_2O_3 is partly replaced with the AlN. This novel oxynitride glass possesses higher elastic moduli and hardness compared with the oxide glass. Nano indentation, thermodynamic analysis (DTA), Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) and Raman spectra are used for the examination of the inner structure and stability of the novel glass system. Our results may have important implications for the fabrication of glass with higher elastic moduli and hardness that can be applied in cell phone screen, windows, etc.

4:30 PM

(GOMD-S1-012-2017) The Structural Chemistry of B_2O_3

A. Wright*[1]

1. University of Reading, United Kingdom

The structural chemistry of B_2O_3 has been the subject of considerable controversy in the literature, especially in the case of the vitreous phase. The present paper reviews the present state of knowledge concerning the structures of crystalline, liquid and vitreous B_2O_3 from an historical perspective, and it is concluded that the key to the structural chemistry of B_2O_3 lies in understanding that of the liquid. This is governed solely by the equilibrium reaction between $B_3O_3Ø_3$ boroxol groups and independent $BØ_3$ basic structural units (i.e. those not in boroxol groups), since there are no thermodynamically-accessible crystalline phases available to the ambient-pressure anhydrous super-cooled melt, due to the high activation energy involved in the break-up and reforming of boroxol groups. Structural explanations are given for the anomalous properties of B_2O_3, such as the extremely low viscosity of the liquid, and the wide variation of the densities and glass transition temperatures reported for vitreous B_2O_3.

GOMD Symposium 2: Glasses in Healthcare: Fundamentals and Applications

Larry L. Hench Memorial session on Bioactive Glasses

Room: Waikoloa 3
Session Chairs: Ashutosh Goel, Rutgers University;
Toshihiro Kasuga, Nagoya Institute of Technology

1:15 PM

(GOMD-S2-001-2017) Multi-Function Bioactive Glasses for Musculoskeletal Tissue Repair (Invited)

P. Hatton*[1]; M. Santocildes-Romero[1]; J. Fernandes[2]; C. Miller[1]; A. Crawford[1]; R. Pires[2]; I. M. Reaney[3]; R. Reis[2]

1. University of Sheffield, School of Clinical Dentistry, United Kingdom
2. University of Minho, 3Bs Research Group, Portugal
3. University of Sheffield, Department of Materials Science & Engineering, United Kingdom

There is a pressing unmet clinical need for an innovative biomaterial that is able to enhance bone tissue regeneration while combating infection in orthopaedic and related surgical interventions. Bioactive glasses appear ideally placed for further development to address this challenge, as small modifications to glass design may substantially alter properties including biocompatibility and antimicrobial activity. This paper will consider recent progress in the field of developing truly multi-functional bioactive glasses, focusing on compositional changes that both enhance osteoconduction and increase inhibition of microbial growth. Using data from Sheffield's laboratories, the effect of inorganic modification (e.g. substitution of Ca with Sr) will be demonstrated with respect to bone cell response, while the results of collaborative research with the University of Minho will provide evidence to support new strategies to introduce antimicrobial activity. The paper will conclude with an assessment of the potential for development of true multi-functional bioactive glasses for applications in bone surgery. Acknowledgements: This work is associated with the UK EPSRC Centre for Innovative Manufacture in Medical Devices (MeDe Innovation, EP/K029592/1) and was supported partly by the Portuguese Foundation for Science and Technology (PhD Grant BD/73162/2010).

1:45 PM

(GOMD-S2-002-2017) Thermodynamic evaluation and experimental validation of the crystallization behavior of bioglass 45S5

B. S. Pföss*[1]; R. Conradt[1]; C. Roos[1]

1. RWTH Aachen University, Insitute for Mineral Engineering, Germany

Silica based bioactive glasses are known to have a strong crystallization tendency, which is a challenge for the variety of manufacturing techniques available. However, it is the amorphous nature that makes up for their outstanding properties as a biomaterial. A number of different analyzing techniques were combined to study the crystallization behavior of bioactive glasses. A transmission microscope with a heating unit allows to observe and record the nucleation, growth, morphology and melting of crystals up to 1400°C. In addition to this information, data from differential thermal analysis provides a thermochemical description, via the onset and peak crystallization temperature. Crystals nucleated and grown in the melt were prepared as single crystals and powders for XRD and identified as combeite (Na2O*2CaO*3SiO2). A thermodynamic approach, based on the crystalline reference system yields the relative crystallization velocity of individual crystalline reference phases as a function of tem- perature. The results are related to relevant peak temperatures of up- and downscan differential thermal analysis. Combeite, which is a major phase in the crystalline reference system, is also experimen- tally identified as the kinetically predominant phase and moreover reveals a high relative crystallization velocity.

2:15 PM

(GOMD-S2-003-2017) PILP-releasing cements for dental repair (Invited)

S. Habelitz*[2]; H. Nurrohman[1]; J. Seto[2]; S. Girn[3]; K. Saeki[2]; S. Marshall[2]; T. Le[3]; G. Marshall[2]; L. Gower[4]

1. Missouri School of Dentistry & Oral Health, USA
2. University of California, PRDS, USA
3. University of California, OFS, USA
4. University of Florida, USA

Recent advances in mineralization of collagen fibrils produced novel methods to reintroduce apatite mineral. The polymer-induced liquid precursor system (PILP) involves the use of a charged polymer, e.g. poly-Aspartic Acid (pAsp), which stabilizes saturated solutions as ion clouds of calcium and phosphate form around pAsp. These nanodroplets attach to collagen and release their ion content into fibrils to subsequently transform into oriented apatite. PILP-treatments recovered of mechanical properties of demineralized dentin by 60-100% in extracted teeth. Here we tested novel cement formulations for their ability to continuously release PILP-nanodroplets at the dentin-cement interface and to restore dentin properties. Methods: Two types of glass-ionomer cements were used and supplemented with 0, 20 and 40% of pAsp: Product A) Biocem (Nu-Smile Inc.); B) Glass Powder (GP). Effect of pAsp on setting time was evaluated. Artificial lesions were covered with cement and stored in SBF for 14 days. Results: Biocem and GP form stable cements with the addition of pAsp. Nanomechanical profiles indicate that both Biocem and GP remineralize dentin collagen as indicated by an increase in modulus from 0.3 to above 4 GPa after 14 days of remineralization. Conclusions: Additions of pAsp to glass ionomer cements may present a viable approach to remineralize carious lesions, recover portions of the natural tissue reducing the risk of pulp exposure.

2:45 PM

(GOMD-S2-004-2017) The Influence of Solution Composition on In Vitro Dissolution of Bioactive Glasses

L. Hupa*[1]; L. Aalto-Setälä[1]; L. Björkvik[1]; O. Karlström[1]; D. S. Brauer[2]; S. Fagerlund[3]

1. Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Finland
2. Friedrich-Schiller-University Jena, Otto Schott Institute of Materials Research, Germany
3. Paroc Group Oy, Finland

The release of inorganic ions from bioactive glasses is decisive for their tissue regenerative capability. Usually, the ion dissolution in vitro is studied in static solutions while the information from dynamic systems simulating the body environment is sparse. We compare the influence of solution composition on the dissolution kinetics of bioactive glasses 45S5 and S53P4 in a continuous flow measurement system. The pH of the initial solutions varied from pH 2 to pH 7.4. The solutions used in the immersion of the glass particles were the simulated body fluid, Tris-buffer, Tris-buffer enriched with ions dissolved from the glass, water, HAc/NaAc-buffer, lactic acid, and HCl. The ion concentrations in the solutions were measured using ICP-OES. The ion release was extensive in the acidic systems; in the solutions buffered at the body pH, clearly lower dissolution was measured. The solution composition also affected the overall dissolution mechanisms of the glasses. The presence of similar ions in the solution decreased their release from the glasses. The results imply that local conditions around a bioactive glass particle affects its dissolution albeit the solution flow is constant throughout a bed of particles. The results may help in estimating e.g. the osteostimulative effects of bioactive glasses or their resorption in vivo.

3:00 PM

(GOMD-S2-005-2017) Glasses for Healthcare: Research, Development and Industrialization (Invited)

Q. Fu*[1]; J. C. Mauro[1]; M. N. Rahaman[2]

1. Corning Incorporated, USA
2. Missouri University of Science & Technology, Ceramic Engineering, USA

Since the discovery of 45S5 bioactive glass by Hench in 1969, numerous studies have been conducted on the use of bioactive glasses for the repair of hard and soft tissues. However, limited progress has been achieved in the commercialization of bioactive glass as medical products, with the most successful ones being 45S5-based Perioglas®, Novabone® and NovaMin®. This indicates that a gap exists between academic research and industrial scale-up. Our work attempts to provide a preliminary study on the two well-known bioactive glasses, 45S5 and 13-93, to evaluate their suitability for mass production in an industrial platform. Glass properties including strain, annealing, and softening points, thermal expansion, density, and liquidus temperature are characterized. Our results show that both glasses have a substantially lower liquidus viscosity than soda lime silicate (SLS) glass, suggesting that melting and forming them in an industrial continuous-unit melting system could be challenging. Innovations in bioactive glass compositions by delving into literature, referencing relevant phase diagrams, conducting design of experiments (DOE), and utilizing modeling tools are needed. Furthermore, joint research between academia and industry on the development of new forming techniques is critical to meet the increasing demand for bioactive glass in a variety of sizes and geometries.

3:45 PM

(GOMD-S2-006-2017) Qsqr_glcb Pcjc_qc md @gm_argtc Amknmslbq dpmk _ Bms`jc+J_wcpcb L_lm A_ppgcp tg_ _ @gmbcep_b_`jc Nmpmsq Nmjwkcp+Acp_kga Gknj_lr (Invited)

I. Manavitehrani[1]; A. Schindeler[2]; F. Dehghani*[1]

1. The University of Sydney, School of Chemical and Biomolecular Engineering, Australia
2. The Children's Hospital at Westmead, Orthopaedic Research & , Biotechnology, Australia

The controlled release of bioactive compounds such as growth factors from a biodegradable implant influences the integration between the biomaterial and the surrounding tissues. In addition, a porous structure provides the required interface for cell migration into the scaffold and tissue regeneration. In this study, mesoporous silica nanoparticles were synthesized by the sol-gel method. a model protein, fluorescein-conjugated bovine serum albumin (FITC-BSA) was applied to the silica nanoparticles using optimized conditions. These amine-functionalized nanoparticles were uniformly distributed in a hydrogel. The resulted hydrogel was loaded inside a biodegradable scaffold. The Scaffold was fabricated by gas foaming technique by modulating the pressure, temperature, and depressurization rate to generate a high pore interconnectivity and an average pore size ranging from ~100-500 μm. Spectrometry revealed that double-layered nanocarrier (FITC-BSA loaded nanoparticles inside the hydrogel) released the protein from porous scaffold implants with a first order kinetic profile. These results demonstrate that such an implant design is capable of sustained release of bioactive molecule with a broad range of potential applications for tissue engineering.

4:15 PM

(GOMD-S2-007-2017) Bioactive glasses with controlled ionic compositions and microstructures for bone and skin tissue regeneration (Invited)

C. Wu*[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, Biomaterials and Tissue Engineering Research Center, China

Regeneration of large-size bone and skin tissue defects represents a significant challenge clinically, which requires the used scaffolds with multifunction, such as anti-bacterial activity, and stimulation of osteogenesis and angiogenesis. Mesoporous bioactive glasses (MBG) possess excellent bioactivity and drug-delivery ability as well as effective ionic release in the body fluids microenvironment due to its specific mesoporous structure and large surface area. For these reasons, functional ions (e.g. Li, Sr, Cu and B) and drug/growth factors (e.g. dexamethasone, VEGF and BMP) have been incorporated into MBG, which shows high loading efficiency and effective release. The release of therapeutic ions and drug/growth factors from MBG offers it multifunctional properties, such as improved osteogenesis, angiogenesis, anti-bacterial/cancer activity. Therefore, in this talk, we mainly focused on the new advances for the functional effect of delivering therapeutic ions and drugs/growth factors on the ostegeogenesis, angigogenesis and antibacterial activity. It is expected that the talk will offer new concept to develop multifunctional biomaterials for bone and skin tissue regeneration by the synergistic effect of therapeutic ions and drug/growth factors from newly-developed bioactive glasses.

4:45 PM

(GOMD-S2-008-2017) Antibacterial and Osteo-stimulatory Effects of a Borate-based Glass Series Doped with Strontium Ions

Y. Li*[1]; W. Ston[2]; E. H. Schemitsch[3]; P. Zalzal[4]; M. Papini[1]; S. Waldman[5]; M. Towler[1]

1. Ryerson University, Mechanical and Industry Engineering, Canada
2. Ryerson University, Chemistry and Biology, Canada
3. St. Michael's Hospital, Keenan Research Centre, Canada
4. Oakville Memorial Hospital, Canada
5. Ryerson University, Chemical Engineering, Canada

This work considered the effect of incubation time and increasing strontium content (up to 25 mol%) on the antibacterial and osteo-stimulatory effects of the B_2O_3-P_2O_5-$CaCO_3$-Na_2CO_3-TiO_2-$SrCO_3$ glass series, where B_2O_3 is replaced with $SrCO_3$ in 5 mol% increments. Discs of each glass (2.2x6.4Φ mm) were immersed in de-ionized water for 1, 7 and 30 days and the water extracts used to determine release profiles and cytotoxicity of the ions eluting from the glasses. The addition, and subsequent release, of Sr^{2+} retarded the solubility of the glasses by inhibiting the release rate of Na and Ca ions. Greater than 20 mol% Sr^{2+} incorporation into the glasses resulted in increased osteoblast cell (MC3T3-E1) proliferation. The glasses, except for the one containing the highest Sr content (25 mol% Sr^{2+}), were bacteriostatic against Staphylococcus aureus after both 1 and 7 days exposure, a result of the combined or individual effect of BO_3, Sr, Na and Ca ions released from the glasses.

5:00 PM

(GOMD-S2-009-2017) Glass Polyalkenoate Cements Designed for Cranioplasty Applications: An Evaluation of Their Physical and Mechanical Properties

B. A. Khader*[1]; D. J. Curran[1]; S. Peel[2]; M. Towler[1]

1. Ryerson University, Mechanical and Industrial Engineering, Canada
2. University of Toronto, Division of Oral & Maxillofacial Surgery & Anaesthesia, Faculty of Dentistry, Canada

Glass polyalkenoate cements (GPCs) have been used in restorative and luting applications in dentistry and have potential for skeletal cementation. Unfortunately, commercial GPCs all contain, and subsequently release, aluminum ions, which have been implicated in degenerative brain disease. The purpose of this research was to create a series of aluminum-free GPCs constructed from silicate, calcium, zinc and sodium containing glasses mixed with polyacrylic acid (PAA) and to evaluate the potential of these cements for cranioplasty applications. Three glasses were formulated based on the SiO2-CaO-ZnO-Na2O parent glass (KBT01) with 0.03 mol % (KBT02) and 0.06 mol % (KBT03) germanium (GeO2) substituted for ZnO. Each glass was mixed with 50wt % of a patented SiO2-CaO-ZnO-strontium (SrO) glass composition and the resultant mixtures were reacted with aqueous PAA200 with an M_w of 210,000 (50wt % addition) to produce three GPCs. The incorporation of Ge in the glass phase resulted in decreased working (142 s to 112 s) and setting (807 s to 448 s) times. Compressive and biaxial flexural strengths of the cements were examined at 1, 7 and 30 days post mixing and increased with both maturation and Ge content. The results of this research indicate that Ge-Si based GPCs have suitable handling and mechanical properties for cranioplasty fixation.

5:15 PM

(GOMD-S2-010-2017) Bioactive Borosilicate Glass as a Carrier for Nanoceria

K. S. Ranasinghe*[1]; D. E. Day[2]; R. Singh[1]

1. Kennesaw State University, Physics, USA
2. Missouri University of Science & Technology, USA

A bio active borosilicate glass doped with different concentrations of cerium oxide was investigated as a potential carrier for nanoceria. Nanoceria exhibit coexistence of Ce^{3+} and Ce^{4+} ions and the Ce3+/Ce4+ ratio plays an important role in determining its anti-oxidant activity in a biological system. A borosilicate glass doped with 3-6 wt% cerium oxide was used to produce cerium oxide nano particles. These nano particles as well as the glass that contained the nanoparticles was examined using SEM, Raman, XRD, and DSC. The release of cerium by the bioactive borosilicate glass into simulated body fluid was also determined by ICP

GOMD Symposium 3: Optical and Electronic Materials and Devices: Fundamentals and Applications

Charge and Energy Transport in Disordered Materials

Room: Kona 2

Session Chair: Krishna Muralidharan, University of Arizona

1:15 PM

(GOMD-S3-001-2017) Relationships between ionic conductivity and structure in Li-based sulfide glasses (Invited)

D. Le Coq*[1]; S. Cozic[1]; T. Usuki[2]; L. Cormier[3]; E. Bychkov[4]

1. University of Rennes 1, ISCR - Glass and Ceramic Team, France
2. University of Yamagata, Japan
3. University Pierre and Marie Curie, France
4. University of Littoral Côte d'Opale, France

Glassy electrolytes for batteries based on lithium and sulfur are very promising. In this contribution, the GeS_2-Ga_2S_3 system was chosen as glass-matrix since this system is known to be both very stable and a good host to incorporate alkali ions. More accurately, addition of LiCl in three different series, $0.7GeS_2$-$0.3Ga_2S_3$, $0.8GeS_2$-$0.2Ga_2S_3$, and $0.9GeS_2$-$0.1Ga_2S_3$ were studied to evaluate the influence of the LiCl content on the conductivity. Whatever the series, the conductivity shows an Arrhenius-type behavior for each composition and the evolution of the room temperature conductivity is standard. In order to well establish the relationships between the electrical conductivity and the structure, the short- and intermediate-range order of prepared glasses have been investigated by the mean of various complementary structural analysis techniques including Raman scattering and high scale facilities. The powerful complementarity of Neutron and High-Energy X-ray diffractions is used to bring out the changes due to the LiCl addition in the glassy network and to underline the affinity of Cl for Ga. Also, in order to better estimate the coordinence and the environment of the lithium in these glasses, a Neutron Diffraction with Isotopic Substitution using ^{7}Li and ^{6}Li isotopes has been also undertaken and the main results will be given in this presentation.

1:45 PM

(GOMD-S3-002-2017) Structural Characterization and Fast Li ion Conduction of Stoichiometric Li_2S-Ga_2Se_3-$GeSe_2$ Glasses

M. A. Marple*[1]; S. Sen[1]; B. Aitken[2]

1. University of California Davis, Chemical Engineering and Materials Science, USA
2. Corning Incorporated, USA

The structure of homogeneous glasses in the mixed-chalcogen pseudo-ternary system Li_2S-Ga_2Se_3-$GeSe_2$ are characterized using Raman and 1- and 2-dimensional ^{6}Li, ^{77}Se, and ^{71}Ga nuclear magnetic resonance (NMR) spectroscopy and can be described as a charge-compensated network predominantly consisting of corner sharing $(Ga/Ge)(Se,S)_{4/2}$ tetrahedra. The atomic structure is heavily influenced by the Li_2S:Ga_2Se_3 ratio R where charge compensation is accommodated by the formation of different structural units and preferential chemical ordering for S atoms. Glasses with R<1 are deficient in chalcogens required to satisfy the tetrahedral coordination of Ga and consequently form ethane-like X_3Ge-GeX_3 (X=S, Se) units and S atoms preferentially participate in these structural units. The structure of chalcogen-excess glasses with R>1 are characterized by the formation of non-bridging Se (NBSe) and S (NBS) sites. The Se atoms show a preference for these non-bridging sites while the S atoms preferentially bond to Ga, resulting in the formation of $GaS_{4/2}$ tetrahedra. Ionic conductivity of these glasses is measured using electrical impedance spectroscopy and is found to monotonically increases with increasing Li concentration. The composition dependence of the glass transition temperature and Li ion conductivity are consistent with the corresponding evolution of the atomic structure of these glasses.

2:00 PM

(GOMD-S3-003-2017) The Mixed Glass Former Effect in Glassy Solid State Electrolytes: The Structure and Properties of the $0.67Na_2S + 0.33[xSiS_2 + (1-x) PS_{5/2}]$ glass system

D. Watson*[1]; S. Kmiec[1]; S. W. Martin[1]

1. Iowa State University, Materials Science and Engineering, USA

The mixed glass former effect (MGFE) in ternary glass systems have been studied because of their potential to be candidates for glassy solid electrolytes in all solid state batteries. The phenomena, where the varying of two glass formers in the presence of a constant modifier concentration, leads to a maximum or minimum in the properties of the glass such as the ionic conductivity. The MGFE in the $0.67Na_2S + 0.33[xSiS_2 + (1-x)PS_{5/2}]$ glass system, a highly modified mixed glass former (MGF) system exhibiting high ionic conductivities and a wider thermal working range than normally expected for sulfide glass systems is reported here. Structural characterization using Raman and infrared spectroscopies with ^{29}Si and ^{31}P Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) reveal a new behavior from the previously studied y=0.50 sodium thiosilicophosphate system and the binary sodium thiosilicates. Alkali thiosilicates possess edge sharing character which dictates the short range order found in the network. The ^{29}Si MAS NMR reveals that the y=0.67 series deviates from its expected edge sharing behavior in the presence of the sodium thiophosphate glass.

2:15 PM

(GOMD-S3-004-2017) Lithium Oxythioborate Glasses for Solid-State Electrolytes

M. R. Hoyt*[1]; S. W. Martin[1]

1. Iowa State University, Materials Science & Engineering, USA

High modifier $yLi_2S + (1-y)[(1-x)B_2S_3 + xB_2O_3]$ ion-conductive glasses (LiSBOs) were characterized to evaluate their suitability as electrolytes for lithium batteries. Samples prepared at $0.60 < y < 0.74$ were either splat-quenched or annealed at 140-160 °C in a brass mold and cooled at 1 °C/min to 30 °C. Increasing the B_2O_3 mole fraction resulted in increasing crystallization and opacity of the quenched LiSBO samples. Yet, powder x-ray diffraction showed some amorphous structure retention past complete sample opacity. Differential scanning calorimetry on the glassy sulfide $yLi_2S + (1-y)B_2S_3$ samples (LiSBs) showed a local maximum $\Delta T = T_c - T_g$ of over 100 °C at y = 0.65. Infrared and nuclear magnetic resonance spectroscopies on LiSBs revealed an increasing B_4/B_3 ratio as the Li_2S modifier fraction decreased. An accompanying increase in isolated BS_3^{-3} units with decrease of modifier was observed by Raman spectroscopy.

2:30 PM

(GOMD-S3-005-2017) Structure of Sodium Thioborosilicate Glassy Solid State Electrolytes

B. Curtis*[1]; S. W. Martin[1]

1. Iowa State University, Materials Science and Engineering, USA

Solid state batteries are of growing interest due to their high energy density and safety. As this interest grows, so does the interest for an optimal solid state electrolyte. Glassy solid state electrolytes prove to be an advantageous competitor due to the relatively low manufacturing costs and increased safety. In addition, properties of these electrolytes (i.e ionic conductivity, density, glass transition temperature, etc.) can be modified due to the mixed glass former effect (MGFE) which occurs when varying the ratio of glass formers from one binary system to the other through a ternary system. Physical and electrochemical properties vary in a non-linear, non-additive trend as the composition, and subsequently the structure, is changed. The structure of the glass system, $0.6Na_2S + 0.4[xBS_{3/2} + (1-x)SiS_2]$ has been examined in an attempt to understand the MGFE. The glass structure was examined through Raman, infrared and NMR spectroscopies.

2:45 PM

(GOMD-S3-006-2017) Glass Formation and Structural Analysis of the Sodium Oxy-Thio Phosphate Glass System $67Na_2S + 33P_2S_xO_{(5-x)}$

S. Kmiec*[1]; S. W. Martin[1]

1. Iowa State University, USA

An investigation of the short range order (SRO) structures in $67Na_2S + 33P_2S_xO_{(5-x)}$, $0 \leq x \leq 5$, glass system was conducted on samples prepared using the planetary ball milling technique. The structure of these glasses were probed using XRD, and Raman, Fourier Transform infrared (FT-IR), and ^{31}P Magic Angle Spinning NMR (MAS NMR) spectroscopies to develop an understanding of how oxygen is incorporated into the sulfide structure. The results show a disproportionation reaction in which the pyro-phosphate (P^1) units undergo a transformation to form ortho-phosphate (P^0) and meta-phosphate (P^2) structures such that there is a conservation of Na^+ charge. As seen in other mixed oxy-sulfide glass forming systems, the stronger Lewis base $O^=$ is present in the P^2 groups in the form of bridging oxygens (BO) whereas the weaker Lewis base $S^=$ is present predominantly in the P^0 groups in the form of non-bridging oxygens. Using a combination of charge balance, the value of x, and the quantitative ^{31}P MAS NMR techniques, a complete composition map of all of the SRO structures present in these glasses has been proposed. This structural transformation plays a large effect on the physical properties of the glass which can be seen in the increased glass transition temperature and decreased ionic conductivity of the glass with increasing oxygen content.

3:00 PM

(GOMD-S3-007-2017) Elastic Properties and Activation Energy for Modifier Cation Migration in Mixed-Network Former Glasses

W. Wang*[1]; R. Christensen[2]; B. Curtis[2]; S. W. Martin[2]; J. Kieffer[1]

1. University of Michigan, Materials Science and Engineering, USA
2. Iowa State University, USA

Glass electrolyte materials have increasingly attracted attention due to their outstanding mechanical stability, wide redox window and open structure. In this study, we investigate two mixed network former glasses, sodium borosilicate $0.2Na_2O + 0.8[xBO_{1.5} + (1 - x) SiO_2]$ and sodium borogermanate $0.2Na2O + 0.8[xBO_{1.5} + (1 - x) GeO_2]$ for their elastic properties and ionic conductivity. We use Brillouin light scattering and dielectric impedance spectroscopy to characterize their elastic moduli and ionic conductivity. We developed a reaction equilibrium model that in combination with NMR data allows us to determine the concentrations of all SRO structural units, including the ones for Germanium. Our results reveal linear relationship between the elastic modulus and the number density of highly coordinated structural units, the tetrahedral and octahedral units. Ionic conductivity of the glasses demonstrates non-linear, non-additive mixed glass former behavior. We found that elastic deformations of the structure surrounding the migrating cation are almost purely hydrostatic. Furthermore, our analysis suggests that in mechanically stiffer structures, fewer atoms tend to be involved in a cation jump, which requires higher-frequency phonons to focus the thermal energy onto these participating atoms. Consequently, the activation energy is high and cation mobility low.

3:15 PM

(GOMD-S3-008-2017) Fractoluminescent Glasses and Interfaces

M. Dejneka*[1]; J. Walter[1]; J. Kohl[1]

1. Corning Incorporated, USA

While some crystalline materials are known to fluoresce when fractured (fractoluminescence) like sugar, especially when doped with wintergreen oil (Wint O Green Lifesavers®), the phenomenon has never been reported in glasses, until now. We have found that certain rare earth containing glasses fluoresce brightly when hit with a hammer. Further investigation revealed that fluorescence only occurred when the glass was mechanically separated from a few specific metals. The fractoluminescence spectra of the glass was the same as the photo induced luminescence spectra. The glasses, dopants, energy transfer, and metals that give rise to fractoluminescence will be presented.

3:45 PM

(GOMD-S3-009-2017) Transition metal oxides doped tellurite glasses

C. Mugoni*[1]; M. Lassinantti Gualtieri[1]; M. Affatigato[2]; C. Siligardi[1]

1. University of Modena and Reggio Emilia, Italy
2. Coe College, Department of Physics, USA

Oxide glasses containing transition metals exhibit unique optical and electrical properties which make them appealing for electrical energy storage systems, in particular as cathode materials in batteries. Among oxide glasses, vanadium tellurite glasses have relatively higher electronic conductivity than other vanadium-containing oxide glasses such as phosphates, borates, and silicates. In this work, glasses belonging to the $CuO-V_2O_5-TeO_2$ system were synthesized by a melt quenching method and investigated by means of density, differential thermal analyses, Raman spectroscopy and electrical measurements. The physical and structural characterizations showed a less compact structural arrangement substituting CuO by V_2O and the network forming character of vanadium at high concentration. An increased amount of vanadium oxide resulted in an increase in conductivity while the V-V distance and the activation energy decreased. Hence, the conduction mechanism was attributed mainly to small polaron hopping between the vanadium ions. Moreover, nucleation and growth of crystalline phases induced by post-quenching thermal treatments were shown to enhance the electronic conductivity of the glass matrix that probably contains higher concentration of redox pairs (V^{4+}-V^{5+}). The crystallization process was investigated by means of In-Situ high temperature X-Ray diffraction and the date were correlated to the observe electrical properties.

4:00 PM

(GOMD-S3-010-2017) A Solid-state NMR Study of Tellurite-based Glass Materials

M. Garaga Nagendrachar*[1]; U. Werner-Zwanziger[1]; S. Feller[2]; J. Zwanziger[1]

1. Dalhousie University, Chemistry, Canada
2. Coe College, Physics, USA

Tellurite-based glasses have attracted much attention in view of application to optical devices, especially for fiber technology. It is important to understand the structure and related properties of pure tellurite glass (a-TeO_2) in order to develop other binary and ternary tellurite-based glasses. Complementary to quantum chemical calculations and diffraction techniques, solid-state nuclear magnetic resonance (NMR) is a powerful tool to study the local structure around Te atoms in a glassy or crystalline framework. Here we use multi-nuclear NMR of ^{125}Te, ^{17}O, and ^{39}K to establish the structure of a-TeO_2 and K_2O-TeO_2 glasses. In particular, NMR parameters such as the isotropic chemical shift (δ_{iso}), the chemical shift anisotropy ($\Delta\delta$) and the asymmetry parameter (η) extracted from ^{125}Te NMR spectra indicate the presence of distinct structural units. ^{39}K NMR shows the distribution of K^+ ions in an amorphous tellurite network. On the basis of neutron diffraction data it has been suggested that glassy TeO_2 contains both $TeO_{4/2}$ and $TeO_{3/2}$ units. In order to search for these we synthesized O-17-enriched samples, which enables acquiring 2D ^{17}O MQMAS NMR. This gives valuable information about the nature of bridging and non-bridging oxygen atoms and hence the existence of $TeO_{4/2}$ and $TeO_{3/2}$ units, respectively.

4:15 PM

(GOMD-S3-011-2017) Ionic to electronic conductivity in $0.50[xAg_2O(1-x)V_2O_5]0.50P_2O_5$ glasses

A. Martins Rodrigues*[1]; J. Díaz Marín[1]

1. Federal University of Sao Carlos, Materials Engineering, Brazil

Mixed ionic-electronic conductors are applied as cathode material in batteries or electrochemical devices. This work presents the electrical characterization of the $0.50[xAg_2O(1-x)V_2O_5].0.50P_2O_5$ ($0 \leq x \leq 1$) glass system. In this system, Ag^+ ions ensure ionic conductivity while the presence of vanadium, which present two oxidation states, V^{4+} and V^{5+} ensures electronic conductivity. Thus, by varying x it is obtained a series of material, from purely ionic (x=1) to purely electronic, (x=0). For intermediary values of x, it is supposed to have a mixed ionic-electronic conductivity. The electrical characterization of glassy samples was conducted by impedance spectroscopy, from room temperature up to 200°C, in a frequency range from 1 MHz to 100 mHz. The Nyquist diagrams show, for samples tich in V_2O_5, the absence of electrode polarization at low freqency (characteristic of ionic conduction), confirming that electronic conduction predominates in those samples. Compositions with high concentration in Ag_2O show higher values for both activation energy and pre-exponential factor, which reflect the characteristics of ionic conduction. Compositions with high concentration in V_2O_5 present lower activation energy and pre-exponential factor, reflecting the characteristics of electronic conduction by small polaron, as predicted by the Mott equation.

4:30 PM

(GOMD-S3-012-2017) Heat Generation during Electric Field-induced Softening of Alkali Silicate Glasses

C. McLaren*[1]; C. Kopatz[2]; N. J. Smith[2]; H. Jain[1]

1. Lehigh University, Materials Science and Engineering, USA
2. Corning Incorporated, USA

Recently, electric field-induced softening (EFIS) of alkali disilicate glasses has been reported, indicating that application of DC voltages significantly lowers the furnace temperature for glass softening compared to conventional radiative heating. EFIS has been observed to occur with the application of moderate externally-applied voltages and mechanical pressures. Mechanisms have been identified as alkali ion migration, electrolysis, charge injection, Joule heating and thermal dielectric breakdown. A key remaining question concerns the local temperature of the sample. Accordingly, the role of alkali ion migration in thermal generation has been investigated using two binary alkali (lithium and sodium) disilicate glasses and two mixed alkali lithium-sodium disilicate glasses of varying electrical resistivities. Heat generation during EFIS has been measured in-situ via thermal imaging, and modeled using finite element analysis (FEA). An alkali ion depletion layer near the anode creates a high internal electric field conducive for thermal dielectric breakdown during EFIS and subsequently leading to glass softening. Thermal imaging has confirmed that heat generation near the anode induces an increase in sample temperature exceeding furnace temperatures required for glass softening.

4:45 PM

(GOMD-S3-013-2017) Mechanisms of electric field-induced softening of alkali silicate glasses

C. McLaren*[1]; M. Balabajew[2]; B. Roling[2]; R. Raj[3]; H. Jain[1]

1. Lehigh University, Materials Science and Engineering, USA
2. University of Marburg, Department of Chemistry, Germany
3. University of Colorado, Department of Mechanical Engineering, USA

Electric field-induced softening (EFIS) has been suggested as an innovative glass processing technique to reduce the furnace temperature required for softening of alkali silicate glasses. Although its preliminary mechanism was proposed previously, further investigation is required to fully understand the early stages of the EFIS processing parameters, starting at the initial polarization. Accordingly, we have investigated the effect of external DC voltages across glass on thermally stimulated currents (TSC) during EFIS. The role of alkali ion migration has been studied using two binary alkali (Li^+ and Na^+) disilicate glasses and two mixed alkali Li^+-Na^+ disilicate glasses of varying electrical resistivities. Characterization of TSC between single and mixed-alkali disilicate glasses have delineated the role of alkali ion migration and charge transport. Activation energies corresponding to polarization mechanisms and charge transport processes have been calculated from experimental data. Further characterization of the alkali ion depletion layer composition and thickness were investigated by SEM, EDS, ToF-SIMS, and XPS. The observed complex viscous flow response of glass during EFIS is a result of the formation of an alkali ion depletion layer, development of large internal electric fields, electrolysis and charge injection processes followed by dielectric breakdown subsequently leading to Joule heating.

5:00 PM

(GOMD-S3-014-2017) Heat flow control by spin thermal conductivity materials having ordered/disordered structures

N. Terakado*[1]; R. Takahashi[1]; Y. Yamazaki[2]; Y. Takahashi[1]; T. Fujiwara[1]

1. Tohoku University, Japan
2. IMRAM, Tohoku University, Japan

Lately, thermal energy has been regarded as one of new energy resources; however, reuse of it seems not to be achieved sufficiently. This is because the thermal energy, particularly that in a small space such as electronic devices, is easy to diffuse, which gives rise to difficulty of efficient energy conversion. Therefore, we have studied novel thermal management materials and those structures in order to control heat flow and prevent heat diffusion in such a small scale. Here we report on heat flow control focusing on $SrCuO_2$ and $La_5Cu_9Cu_{24}O_{41}$, which have low-dimensional antiferromagnetically-coupled spin arrangement yielding high, anisotropic heat conduction by spins. Preparation of the materials by sputtering on amorphous substrate causes inhomogeneous structures including amorphous and/or submicron partially-oriented grains, but successive laser irradiation (patterning) and heat treatment provide ordered structures which give the high, anisotropic thermal conduction paths. Structural and thermal properties, and additionally possibility of active heat flow control by laser irradiation, will be reported.

5:15 PM

(GOMD-S3-015-2017) The Contribution of Propagons and Diffusons in Heat Transport Through Calcium-Silicates

M. Abdolhosseini Qomi*[1]

1. University of California, Irvine, CEE, USA

Whether it is glass, ceramics, cement or concrete, minimizing thermal conduction through disordered materials is a determining factor when it comes to reducing the energy consumption of cities. In this work, we explore underlying physical processes involved in thermal conduction through the disordered glue of cement, calcium-silicate-hydrates (CSH). We find that at 300K, phonon-like propagating modes in accordance with Boltzmann transport theory, propagons, account for more than 30\% of the total thermal conductivity, while diffusons, described via Allen-Feldman theory, contribute to the remainder. The cumulative thermal conductivity proves to be close to both equilibrium molecular dynamics calculations and experimental values. These findings help us establish different strategies, such as localization schemes (to weaken diffusons) and scattering mechanisms (to constrainpropagons), for reduction of thermal conductivity of CSH without sacrificing its mechanical properties.

Rare Earth Doped Fibers, Fiber Lasers, and Related Glass Systems

Room: Kona 3
Session Chair: Setsuhisa Tanabe, Kyoto University

1:15 PM

(GOMD-S3-016-2017) The optical materials requirements for high power mid-infrared fibre lasers (Invited)

S. Jackson*[1]; A. Fuerbach[2]; D. Hudson[2]

1. Macquarie University, Department of Engineering, Australia
2. Macquarie University, Physics and Astronomy, Australia

Optical fibre lasers continue to grow in many ways. Demonstrations have involved high efficiency moderate power output, high peak power ultrashort pulse generation, single longitudinal mode operation and broad tunable emission. All the successful demonstrations are based on the access to high quality glasses that can be drawn into optical fibre. In this review, I will focus on the glasses and fibres that have been used create the record performance and I will highlight what the major technological steps were that lead to these demonstrations. I will also discuss the major challenges and the opportunities for further research.

1:45 PM

(GOMD-S3-017-2017) Progress in mid-infrared fiber lasers

A. B. Seddon*[1]; Z. Tang[1]; D. Furniss[1]; L. Sojka[2]; S. Sujecki[1]; E. Barney[1]; T. Benson[1]

1. University of Nottingham, Mid-Infrared Photonics Group, George Green Institute for Electromagnetics Research, United Kingdom
2. Wroclaw University of Technology, Telecommunications and Teleinformatics Department, Poland

The mid-infrared spectral region spans 3 to 50 microns' wavelength. This paper reviews progress towards mid-infrared fiber lasers: narrow-line rare earth ion doped direct emission fiber lasers; narrow-line Raman fiber lasers and wide-band supercontinuum fiber lasers. To date no narrow-line rare earth ion doped fiber laser beyond 3.9 microns wavelength has been demonstrated. Mid-infrared photoluminescent characteristics of praseodymium, dysprosium and terbium rare earth ion doped bulk glasses and fiber will be reviewed and a critical analysis of glass quality of these discussed. The general characteristics of demonstrated mid-infrared Raman lasers will be compared with potential performance of mid-infrared rare earth ion doped fiber lasers. Mid-infrared supercontinuum fibre lasers have now been demonstrated and prospects for improving average power out and wavelength coverage will be discussed. The great potential for real-time chemical and biomedical sensing using new mid-infrared fiber lasers will be addressed.

2:00 PM

(GOMD-S3-019-2017) Recent advances on Nd^{3+}-doped laser glass and filter glass for high power laser system in SIOM (Invited)

D. He*[1]; L. Hu[1]

1. Shanghai Institute of Optics and Fine Mechanics, China

Due to its high doping concentration and capacity of obtaining large size, laser glass has a more leading advantage in the large energy laser

field such as Inertial confinement fusion (ICF), pumping source for OPCPA system or mixed glass laser for PW system and laser peening system of industry. In this work, the latest research and development of neodymium phosphate laser glass and Sm^{3+}-doped filter glass in SIOM, China has been addressed. The continuous melting and edge cladding technology have been developed and successfully used for the fabrication of large aperture N31 neodymium phosphate laser glass slab. NAP2 and NAP4 glass with high thermal shock resistance have been developed for using in laser peening fields and as pumping source for OPCPA system. Nd:Silicate and Nd:Aluminate glasses with peak emission wavelength at 1061nm and 1067nm, effective emission bandwidth of 34nm and 50nm, respectively, are developed for Exawatt-class laser system application. Sm^{3+}-doped filter glass and glass ceramics were developed in high average power laser system by adjusting the emission spectra of Xenon lamp.

2:30 PM

(GOMD-S3-020-2017) Photo-thermo-refractive glass with sensitivity to visible and near IR radiation

F. Kompan[1]; G. Venus[2]; L. Glebova[3]; H. Mingareev[1]; L. Glebov*[1]

1. University of Central Florida, CREOL, USA
2. IPG Photonics, USA
3. OptiGrate, USA

Conventional photo-thermo-refractive glass (PTR-glass) is a multi-component silicate glass doped with a photosensitizer Ce^{3+}. This glass permanently changes its refractive index after exposure to UV radiation followed by thermal development. It is extensively used for recording of trivial holograms (volume Bragg gratings) operating in visible and near IR spectral regions. Ability to record complex holographic structures in PTR glass is of utmost interest as it would be advantageous for imaging and laser beam control applications. However, since photosensitivity of PTR glass is limited to the UV region, complex holograms for visible and IR applications could not be recorded in PTR glass. To extend PTR glass sensitivity towards longer wavelengths the same glass matrix was doped with terbium, and then excited state absorption mechanism was used for two-step excitation of the $5d^14f^7$ band of Tb^{3+} ions by concurrent illumination with one of the long wavelengths (449, 522, 808 or 975 nm) and UV (375 nm) beams. For the first time refractive index modulation exceeding 2×10^{-4} was observed after exposing the material to blue, green and near IR laser radiation. Complex holograms operating in blue and green spectral regions were recorded in Tb-doped PTR-glass.

2:45 PM

(GOMD-S3-021-2017) Radiation dosimetry using Tb^{3+}-doped fluoride phosphate optical fibres

C. Kalnins[1]; H. Ebendorff-Heidepriem*[1]; N. Spooner[2]; T. Monro[3]

1. University of Adelaide, Institute for Photonics and Advanced Sensing and School of Chemistry and Physics, Australia
2. Defence Science and Technology Group, Australia
3. University of South Australia, Australia

Fluoride phosphate (FP) glasses have been developed for radiation dosimetry based on the mechanism of optically stimulated luminescence (OSL), these fibres have applications in environmental radiation monitoring. Doping of the FP glass with Tb^{3+} was found to increase the intensity of the OSL response. Glasses were doped with Tb^{3+} by remelting in both oxidising and reducing atmospheric conditions. Thermoluminescence and OSL measurements were performed following exposure to ionising radiation. Optical fibres were fabricated from undoped and doped glasses melted under both reducing and oxidising conditions. Following loss characterisation, OSL measurements were performed under both beta and X-ray irradiation. TL measurements show the formation of deep traps at 300 °C in Tb^{3+}-doped samples, which are not present in undoped samples. OSL measurements show an increase in intensity from 8.8×10^5 cnts/g/Gy to 812.3×10^5 cnts/g/Gy for glasses remelted in oxidising conditions and an increase from 12.3×10^5 cnts/g/Gy to 60.3×10^5 cnts/g/Gy for reducing conditions. OSL measurements were performed on optical fibres along lengths of up to 2.6 m under beta and X-ray irradiation. In conclusion, radiation dosimetry was successfully performed using OSL within optical fibres of Tb^{3+}-doped FP glass. Remelting under oxidising conditions produced samples with the most intense OSL response to both beta and X-ray irradiation.

3:00 PM

(GOMD-S3-022-2017) Enhanced Infrared Emission from Rare-Earth Ions in YF_3 Co-Doped Oxyfluoride Glass-Ceramics

Z. Zhao*[1]; C. Liu[1]; J. Han[1]; X. Zhao[1]

1. Wuhan University of Technology, State Key Laboratory of Silicate Materials for Architectures, China

With the formation of fluoride nanocrystals with low-phonon energies in the nearly oxide glass matrices, oxyfluoride glass-ceramics have been considered as the promising host materials for rare-earth (RE) ions to realize the efficient infrared emission. However, due to the preferential incorporation of RE ions into the fluoride nanocrystals, energy transfer processes among RE ions is easy to occur, leading to the quenching of infrared emission. To achieve efficient infrared emission, it is necessary to control the distribution or decrease the effective concentration of RE ions inside the fluoride nanocrystals. Since RE ions are the nucleation centers, one possible method is to introduce optical non-active RE ions as the nucleation and dilution agents. In addition, the crystallization process and microstructure of fluoride nanocrystals should be optimized. In this work, YF_3 was introduced into the glasses to promote the formation of fluoride nanocrystals while decreasing the effective concentration of Er^{3+} (Tm^{3+}) ions inside the fluoride nanocrystals. Formation of RE ions incorporated nanocrystals were confirmed by the XRD patterns, EELS analysis and absorption spectra. As a result, enhanced ~2.73 μm (~1.46 μm) emission from Er^{3+} (Tm^{3+}) ions were observed, indicate that this type of co-doping method in glass-ceramics has great potentials for RE ions to realize efficient infrared emission.

Glass Compositions, Structure, and Properties

Room: Kona 3

Session Chair: Maxime Cavillon, Clemson University

3:45 PM

(GOMD-S3-023-2017) Rare-earth–doped chalcogenide glasses for infrared photonics (Invited)

J. Adam*[1]; F. Starecki[2]; A. Braud[2]; R. Chahal[1]; C. Boussard-Pledel[1]; V. Nazabal[1]

1. University Rennes - CNRS, France
2. ENSI Caen - CNRS, France

Vitreous materials based on chalcogen elements (S, Se, Te) show large transparency windows that extend from the visible up to 12-15 μm in the infrared, depending on their compositions. This is due to the lower phonon energies of chalcogenides, which are also responsible for enhanced luminescence of rare-earth ions embedded in such matrices. As a result, they possess a high potential for applications as infrared sources, where rare-earth-doped oxide glasses cannot operate. As far as shaping is concerned, specific chalcogenide glass compositions can be obtained in the form of optical fibers, thin films or planar waveguides. The presentation deals with the latest results in terms of mid-infrared luminescence of Pr^{3+}, Dy^{3+}, and Er^{3+} ions in sulphide glass optical fibers or micro-waveguides, with the aim to develop new integrated optical sensors.

4:15 PM

(GOMD-S3-024-2017) Local Environment Dependence on the Luminescence of Rare Earth Doped Chalcohalide Glasses and Glass Ceramics

J. Zhang*[1]; L. Meng[1]; C. Liu[1]; X. Zhao[1]

1. Wuhan University of Technology, State Key Laboratory of Silicate Materials for Architectures, China

In present research, the effect of alkali halide addition on the luminescence properties of rare earth ions will be systemically investigated. Nd3+, Ho3+, Er3+ single doped Ge-Ga-S-CsX (X=Cl, Br, I) chalcohalide glass, and Nd3+/Tm3+, Nd3+/Pr3+ co-doped chalcohalide glasses were prepared by conventional melt-quenching method. The micro-structure changes due to alkali halide addition were characterized by Raman spectroscopy. The results indicated that a new peak formed originated from Ga-X bond vibration in [GaS3/2X]- group. The visible upconversion luminescence bands from Nd3+, Er3+ intensity was enhanced, and novel upconversion from Ho3+ was observed. Moreover, different energy transfer processes were varied with different CsX content in chalcohalide glasses. The near infrared luminesce also observed from chalcohalide glasses, changed with different alkali halide and their content. The nanocrystals were fabricated in chalcohalide glasses. Visible upconversion and infrared luminescence were further enhanced. X-ray diffraction (XRD) patterns and transmission electron microscopy images proved that Ga2S3 nanocrystals were in glass matrix, with diameters ~20nm – ~100 nm. The distributions of rare earth ions were directly observed using electron energy loss spectroscopy (EELS). And the local surroundings were confirmed.

4:30 PM

(GOMD-S3-025-2017) Energy transfer in Tb^{3+}/Eu^{3+} doped borate and fluorozirconate glasses

M. Mungra[1]; F. Steudel[2]; A. Evans*[3]; R. L. Leonard[3]; J. Johnson[3]; B. Ahrens[1]; S. Schweizer[1]

1. South Westphalia University of Applied Sciences, Department of Electrical Engineering, Germany
2. Branch Lab of Fraunhofer Institute for Microstructure of Materials and Systems IMWS, Fraunhofer Application Center for Inorganic Phosphors, Germany
3. University of Tennessee Space Institute, Department of Mechanical, Aerospace, and Biomedical Engineering, USA

Tb^{3+} single- and Tb^{3+}/Eu^{3+} double-doped borate as well as fluorozirconate glasses were investigated for their photoluminescence and energy transfer properties based on the concentration of the dopants. The double-doped glasses consist of a constant concentration of Tb^{3+} ions and an increasing Eu^{3+} concentration, ranging from 0.05 to 0.5 at.%. Upon direct excitation of only Tb^{3+} at 490 nm, the emission spectra of the double-doped glasses demonstrate an enhancement of typical Eu^{3+} emissions, thus validating the energy transfer from Tb^{3+} to Eu^{3+} in both glass systems. While the spectral composition of the emissions of both borate and fluorozirconate glasses are mostly similar, borate glasses are found to have faster radiative decay than fluorozirconate glasses. The energy transfer efficiency in each glass system is calculated based on the radiative decay measurements. The mechanism of multipolar interaction underlying the energy transfer is determined to be mostly due to dipole-dipole interaction. With increasing Eu^{3+} concentration, a gradual shift in photoluminescence color from green to orange/red is recorded. It is found that besides variation in Eu^{3+} concentration, color-tunable photoluminescence can also be achieved by modulating the excitation wavelength.

4:45 PM

(GOMD-S3-026-2017) Structural Studies of Fluoroborate Laser Glasses by Solid State NMR and EPR Spectroscopies

R. Zhang*[1]; J. Ren[1]; L. Zhang[1]; H. Eckert[2]

1. Shanghai Institute of Optics and Fine Mechanics, Key Laboratory of Materials for High Power Laser, China
2. University of Muenster, Germany

The structure of glasses in the system (100-x)B$_2$O$_3$-xPbF$_2$ (x = 30, 40, 50) and 50B$_2$O$_3$-(50-x)PbO-xPbF$_2$ (x = 5, 10, 15, 20, 25, 20, 35, 40 and 45) has been studied by solid state NMR and EPR spectroscopies. Based on ^{11}B and ^{19}F high resolution solid state NMR as well as on ^{11}B/^{19}F double resonance results, we develop a quantitative structural description on the atomic scale. ^{19}F NMR results indicate a systematic dependence of the fluoride speciation on PbF$_2$ content: At low x-values, F$^-$ ions are predominantly found on BO$_{3/2}$F$^-$ units, whereas at higher x-values, fluoride tends to be sequestrated into amorphous domains rich in PbF$_2$. In addition, both pulsed EPR studies of Yb^{3+} doped glasses and photophysical studies of Eu^{3+} doped samples indicate a mixed fluoride/borate coordination of the rare-earth ions and the absence of nanophase segregation effects.

5:00 PM

(GOMD-S3-027-2017) Mechanism of photoionization of photo-thermo-refractive glass

L. Glebov*[1]; C. Magon[2]; J. Gonzalez[2]; J. Lima[2]; H. Eckert[2]; E. Dutra Zanotto[3]; H. Mingareev[1]; L. Glebova[4]; F. Kompan[1]

1. University of Central Florida, CREOL, USA
2. Univesity of Sao Paulo, Institute of Physics, Brazil
3. Federal University of Sao Carlos, LAMAV, Brazil
4. OptiGrate, USA

Photo-thermo-refractive glass is a Na$_2$O-ZnO-Al$_2$O$_3$-SiO$_2$-NaF-KBr glass doped with a photosensitizer (Ce) plus Ag, Sn and Sb. After exposure to UV radiation followed by thermal treatment close to the glass transition range, this glass shows a permanent change of refractive index. Therefore, it is a photosensitive material widely used for volume hologram recording. The refractive index change results from a sequence of photoinduced and then thermally stimulated structural transformations in the glass volume. While the initial and final processes are well-known (photoionization of Ce^{3+} and precipitation of NaF crystals), a chain of structural transformations in the process of hologram recording is still far from detailed understanding. We examine the initial stages of this process, including photoionization and valence change of Ce, Sb and Ag, which results in the formation of a latent image. A number of PTR-like glasses with different combinations of dopants were synthesized and exposed to optical excitation in the absorption bands of the PTR glass matrix and matrix with different dopants. Absorption and luminescence spectra, continuous-wave and pulsed X-band electron paramagnetic resonance spectroscopy were used for this study. We found that UV exposure of PTR glass produces intrinsic color centers and changes the valent states of cerium, antimony and silver. A mechanism of photoinduced transformations is proposed.

5:15 PM

(GOMD-S3-028-2017) Cerium redox state in silicate glasses and melts: Implications for property changes and structural roles

M. Cicconi*[1]; D. de Ligny[1]; D. R. Neuville[2]; A. Veber[1]; W. Blanc[3]; F. Baudelet[4]

1. Friedrich-Alexander-Universityet Erlangen-Neurnberg, Materials Science and Engineering, Germany
2. IPGP, France
3. Université Nice Sophia Antipolis, CNRS LPMC, France
4. Synchrotron SOLEIL, France

The detection and the quantification of redox species dissolved in glasses have a strong impact in many fields, and among REE-doped glasses, Ce is widely used in laser technology, fast scintillators, white emitting LEDs... In glasses, Ce is stable with two oxidation states

(3+ and 4+), but whilst Ce^{3+} species show efficient luminescence in the UV-Vis region, Ce^{4+} species do not show luminescence. Thus, the understanding of the factors influencing Ce redox, and the detection of the different species, are crucial for applications. In this study we want to enhance the understanding of the factors influencing Ce redox, and provide a method to detect and quantify the Ce^{3+}/Ce^{4+} ratio in silicate glasses/melts, and to relate it to changes in glass structure and properties. Ce-bearing melts were studied by using "in-situ" Dispersive-XAS and we obtained Ce redox kinetics for different melt compositions. The frozen melts obtained, with well-defined Ce valences, were also studied by Raman and Photoluminescence spectroscopy. The data obtained show that Ce content, Na/Al ratio, and glass polymerization have a strong influence on the Ce^{3+}/Ce^{4+} ratio. Moreover, it was observed that the two species affect the Raman signals in a different way, implying that the role played by them is different. Applications to Ce-doped SiO_2 optical fiber pre-forms will be discussed.

5:30 PM

(GOMD-S3-029-2017) Expanding the range of action of water-dispersible lanthanide-based luminiscent nanothermometers: Towards NIR-II and NIR-III

A. Benayas*[1]; A. Skripka[1]; E. Hemmer[1]; F. Vetrone[1]

1. Institut National de la Recherche Scientifique, Energie Matériaux Télécommunications, Canada

Real-time biosensing is a crucial tool for the investigation of biological phenomena and in the diagnosis of diseases such as cancer. Herein, the need for nanosized light-emitting probes, which can act as more accurate, efficient, non-invasive and fast detection tools, both for imaging and sensing purposes has been greatly increased. The use of near-infrared (NIR) light in the range of the second biological window (NIR-II: 1.00-1.35 um) and even third (NIR-III: 1.5 -1.75 um) provides the advantage of deeper penetration depth into biological tissue, better image contrast, avoiding competing tissue-autofluorescence, reduced phototoxicity and photobleaching. Moreover, remote (non-invasive) temperature sensing can be used as an early diagnosis tool, and is also essential for temperature monitoring in real time during the application of thermal treatments against many diseases, including cancer. Here we present our latest work in NIR-II and NIR-III carefully engineered core/shell nanothermometers describing several outstanding assets, upon optical excitation of them in NIR-I, 750-950nm. It is here fully described their performance as all-optical nanothermometers (non-contact tracking of fluorescence emission, lifetime or even ratiometric nanothermometry when building a hybrid nanostructure from them).

GOMD Symposium 5: Professor Jacques Lucas Honorary Symposium

Chalcogenide

Room: Kona 5

Session Chair: Shibin Jiang, AdValue Photonics Inc

1:30 PM

(GOMD-S5-001-2017) Chalcogenide liquids over the decades with Jacques: Simple glassformers and now supercrystallizers (Invited)

C. A. Angell*[1]; P. Lucas[2]; S. Wei[3]

1. Arizona State University, School of Molecular Sciences, USA
2. University of Arizona, Materials Science and Engineering, USA
3. Technische Universität München, Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II), Lichtenbergstr. 1, Germany

My collaboration with Jacques began in the days of fluoride glasses, and later involved joint summer months with Connie Moynihan and the Rennes group that were both personally very enjoyable and phenomenologically rich. This was during the transition in focus to the much more compositionally versatile chalcogenide glassformers, which have proved of great value for IR optical applications. The chalcogenides show wide variations of liquid fragility which are of interest and also controversy in relation to constraint theory vs. chemical theory. Then we turn to our newest interest in these systems which lies in their conversion from glassformer to fast crystallizer by change of As for Sb in the Te-based ternary system. This brings us to the domain of phase change materials (PCMs) concerning which we have recently argued for a special role for metal-to-semiconductor transitions in enhancing the crystallization kinetics. An intriguing relation to water physics will be discussed.

2:00 PM

(GOMD-S5-002-2017) Molecular Ge-doped As Sulfide Glasses (Invited)

B. Aitken*[1]; O. Gulbiten[1]; S. Sen[2]

1. Corning Incorporated, USA
2. University of California-Davis, USA

Chalcogenide glasses from the Ge-As-S system are characterized structurally by networks that have a continuously rising degree of polymerization with decreasing S content due to the increase of the average atomic coordination number. In terms of their physical properties, this increase in network connectivity is manifested by the concomitant rise in characteristic temperatures, including the glass transition temperature T_g. As a result, S-deficient glasses in this system have T_g ranging from 200 to 450ºC depending on the As:Ge ratio. However, certain As-rich S-deficient glasses have T_g near room temperature due to the collapse of the typical polymeric network structure in response to the stabilization of cagelike As_4S_3 molecular species that are interlinked through only van der Waals interactions. Despite their molecular nature and low T_g, these materials persist indefinitely in the glassy state. Raman spectroscopy of a representative molecular glass at high pressure reveals a reversible transition to a high density polymerized amorphous phase near 2 GPa and, providing sufficient densification, the high pressure network phase can be quenched to ambient pressure. ^{31}P NMR spectroscopy of P-doped glasses show that the $(As,P)_4S_3$ molecules execute tumbling motion at temperatures well below T_g. Finally we also present new data on the viscosity and fragility of these zero-dimensional glasses as measured by DSC along with beam bending viscometry.

2:20 PM

(GOMD-S5-003-2017) Chalcogenide glass-ceramics transparent in the infrared: a review (Invited)

L. Calvez*[1]

1. University of Rennes 1, Institut des Sciences Chimiques de Rennes, France

Chalcogenide glass shows excellent IR transmission ranging from 0.8 µm up to 20 µm, thus becoming a valuable building block in IR optics. However, the advantages of chalcogenide glasses are largely inhibited by their relatively weak thermo-mechanical properties. At the University of Rennes 1, we focused our studies to enhance thermo-mechanical properties of chalcogenide glasses. Fortunately, glass-ceramics with crystal phases of different physico-chemical properties give a route for the enhancement of mechanical properties, meanwhile keeping the usual advantage of fabrication versatility. The crystallization behavior and related physicochemical properties of nontoxic $Ge(S/Se)_2$-$Ga_2(S/Se)_3$ based glasses were studied. However, chalcogenide GC are not only dedicated to the enhancement of mechanical properties. In fact, depending on the glass composition, 'a la carte' properties can be obtained. Thus, the possibility to strongly increase the luminescence efficiency by controlled crystallization within chalcogenide GC doped with rare-earth will be developped. Moreover, by controlling the generated crystalline species, some chalcogenide GC present outstanding properties such as photo-carrier generation, potentially leading to novel generation of photosolar cells. Finally, the possibility to fasten

the crystallyzation process by using sintering process such as Spark Plasma Sintering will be demonstrated.

2:40 PM

(GOMD-S5-004-2017) Chalcohalide Glasses (Invited)

J. Heo*[1]; W. Chung[2]; Y. Choi[3]

1. Pohang University of Science and Technology(POSTECH), Materials Science and Engineering, Republic of Korea
2. Kongju National University, MSE, Republic of Korea
3. Korea Aerospace University, MSE, Republic of Korea

Chalcohalide glasses refer to glasses composed of both chalcogen and halogen components. Large amount of research effort have been focused to develop glasses with a wide infrared window as well as to enhance the emission properties by doping rare-earth ions. One of the major issues is to reduce the multiphonon relaxation from the emission level of rare-earth ions through the addition of halogen into chalcogenide glasses. For instance, author's group has reported the significant improvement on the spectroscopic properties of many rare-earth ions in Ge-Ga-S glasses through the addition of alkali halides. Intensity of the 1.31um emission from Dy^{3+} increased sharply when the appropriate amount of alkali halides were added, at the expense of the 1.75um emission intensity. Analysis on the molecular structure of glasses indicated that alkali halides were added to Ge-Ga-S glasses modified the phonon vibration through the formation of $[GaS_{3/2}Br]^-$ subunits that directly affect the non-radiative transition in rare-earths.

Materials for Photonics

Room: Kona 5
Session Chair: Kathleen Richardson, University of Central Florida

3:15 PM

(GOMD-S5-005-2017) High-purity chalcogenide glasses for mid-IR photonics (Invited)

V. Shiryaev*[1]; M. Churbanov[1]

1. Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, Russian Federation

Waveguides based on chalcogenide glasses are promising for the transfer of mid-IR radiation, creation of remote sensors, spatial filters, couplers, fiber lasers, opto-electronic and non-linear devices. The methods for preparation of high-purity As-Se, Ge-As-Se-(Ga,In), As-Se-Te, Ge-Se-I, Ge-Sb-Se-(Ga,In), and Ge-As-Se-Te glasses, including the samples doped with rare earth elements, have been developed. The optical transmittance of the produced glasses, their structure, physico-chemical properties and the content of limiting impurities were determined. The prepared glass samples have ultra-low content of limiting impurities (in ppmwt): oxygen - <0.1, carbon - <0.5, hydrogen - <0.02, silicon - <0.1, transition metals - <0.05. Using the double crucible technique, the multimode and single-mode optical fibers were prepared, their optical and mechanical properties were investigated. Minimum optical losses in multimode fibers were <100 dB/km in the mid-IR. Minimum optical losses in Pr^{3+}-doped Ge-As-Ga(In)-Se glass fibers were about 500 dB/km. The 1000-3000 ppmwt Pr^{3+}-doped bulk glasses and fibers exhibited an intensive photoluminescence in the spectral range of 3 – 6 μm. The maximum measured lifetime of emission at 4.7 μm was > 10 ms. The tests on the use of obtained optical fibers for photonics devices were carried out. This work was supported by the Russian Science Foundation (Grant No. 16-13-10251).

3:35 PM

(GOMD-S5-007-2017) Highly nonlinear soft glass optical fibers and their applications (Invited)

Y. Ohishi*[1]

1. Toyota Technolological Institute, Japan

Highly nonlinear optical fibers have attracted much attention in recent years because they paved the way for the development of compact nonlinear devices for applications such as supercontinuum (SC) generation, wavelength conversion, pulse compression, parametric amplification, etc. Among nonlinear applications of highly nonlinear fibers, SC generation is attractive one. Studies on SC in optical fibers have been very active in recent years, because it has excellent properties, such as wide spectral bandwidth, high coherence, high brightness and potential compactness. For improving the applications of SC, continuous efforts to extend the SC spectral range to the mid-infrared (MIR) region have been made in the past several years. Fiber optical parametric amplification (FOPA) is another important application of highly nonlinear fibers. However, the potential of FOPA for soft glass highly nonlinear fibers have not yet been studied in details. We have fabricated microstructured optical fibers (MOF) made of tellurite and chalcogenide glass to control chromatic dispersion and shown that highly nonlinear soft glass MOFs are promising as MIR SC generation and FOPA media. Here, we report the new status and prospect of soft glass highly nonlinear optical fiber research.

3:55 PM

(GOMD-S5-008-2017) Fiber Optics R&D at the NRL (Invited)

J. Sanghera*[1]; B. Shaw[1]; C. Baker[1]; J. Friebele[2]; S. Bayya[1]; V. Nguyen[1]; L. Busse[1]; C. McClain[3]; D. Gibson[1]; R. Gattass[1]; F. Kung[3]; R. Miklos[2]; D. Rhonehouse[3]; R. Thapa[2]; I. Aggarwal[2]

1. Naval Research Lab, USA
2. Sotera Defense Solutions, USA
3. University Research Foundation, USA

As silica fiber laser technology moves into the eye safer wavelength region beyond 1.4 um, there is a need to attain higher power and efficiency. We solved the problems of clustering and OH absorption/multiphonon quenching of Er and Ho, respectively, using nanoparticle doping. We will describe synthesis of the NP's, their incorporation into silica fibers and our results highlighting high efficiency lasing beyond 1.4 um, respectively. Crystal fiber lasers represent a paradigm shift in high power fiber lasers, combining the thermo-physical advantages of crystals with fiber geometry to enable heat mitigation, and potentially increase output power per fiber by >10X. We will report on the fabrication of small core diameter single crystal fiber with claddings and demonstrate lasing. Infrared chalcogenide glass fibers exhibit transmission in the infrared wavelength region and have many passive and active applications. Various applications, including multimode beam combiners, mid-infrared supercontinuum sources, fiber Bragg gratings, and fiber bundles for IR imaging, are described. A new class of hollow fibers has emerged, called anti-resonant or negative curvature fibers that transmit with upto 1000x lower loss than the material loss. We describe our latest results in this area, clearly demonstrating fibers with record low optical losses in the infrared.

4:15 PM

(GOMD-S5-009-2017) S-band gain and blue upconversion characteristics in Tm-doped fiber amplifier by dual-wavelength pumping (Invited)

S. Tanabe*[1]

1. Kyoto University, Japan

Gain characteristics of Tm-doped fiber amplifier were investigated by pumping with 1.05 μm or 1.41 υm and tunable L-band lasers. Red-shift and improved gain were observed by the pumping wavelengths in the 1.54–1.65 lm range. The gain values in the 1.44–1.50 μm range were improved by optimized pumping wavelengths and the optimized wavelengths were varied with the signal wavelength.

4:35 PM

(GOMD-S5-010-2017) Advances in laser induced cooling in rare earth-doped low phonon glasses (Invited)

J. Fernandez*[1]; R. Balda[1]; J. Adam[2]

1. University of the Basque Country, Applied Physics, Spain
2. Institut des Sciences Chimiques de Rennes UMR CNRS 6226 - Université de Rennes 1, France

The investigation of new hosts for rare earth ions with low phonon energies appears to be a promising way to find efficient cooling materials. In this work we discuss the anti-Stokes laser-induced cooling of low phonon glass matrices doped with Yb^{3+} and Er^{3+}. In order to assess the presence of internal cooling in these systems we used photothermal deflection and conventional excitation spectroscopic techniques, whereas the bulk cooling in the Er^{3+}-doped materials was detected by means of a calibrated thermal sensitive camera. The experimental results for the Yb^{3+}-doped glasses are in good agreement with the predictions of a model based on the presence of a second order process in the cooling mechanism. The fluorescence excess shown by the excitation spectra of Yb^{3+}-doped sample obtained at high fluencies has been explained in the framework of the configurational coordinate model by considering that the frequencies of the vibrational modes in the ground and excited states change at high pumping intensities. In the case of Er^{3+} ion, it is worthwhile to mention that the cooling was observed in the spectral region where some upconversion processes that initiate at the pumped $^4I_{9/2}$ level occur. Together with the spectroscopic characterization, a short discussion on the experimental and theoretical background of the cooling process including the possible influence of upconversion processes is presented.

4:55 PM

(GOMD-S5-011-2017) Rare-Earth Doped Glass Fibers for Lasers (Invited)

S. Jiang*[1]

1. AdValue Photonics Inc, USA

Our progress on rare-earth doped multi-component glass fibers for laser applications will be presented.

PACRIM Symposium 02: Virtual Materials Design and Ceramic Genome

Modeling of Amorphous Ceramics

Room: Kohala 4
Session Chair: Isao Tanaka, Kyoto University

1:15 PM

(PACRIM-S2-001-2017) Mixed alkali effect and chemical strengthening in bulk silicate glass and its surface (Invited)

W. Ching*[1]

1. University of Missouri-Kansas City, USA, USA

We report the structures and properties on models of alkali-doped silicate glass using first-principles method. Based on the simulation of five models of alkali-doped silicates in a continuous random network of $(X_2O)_{20}(SiO_2)_{80}$ (X = Li, Na, K), it is shown that both the structures as well as the electronic, mechanical and optical properties depend sensitively on the alkali elements and their mixtures. Using total bond order density (TBOD) as a quantum mechanical metric, we quantitatively characterize and explain these differences. The presence of alkali ions results in the formation of a wide range of relatively strong ionic X-O bonds with bond strength in the order of Li-O > Na-O > K-O due. Isolated formation of strong Si-Si and weaker O-O bonds are also identified. The change in the trend for TBOD is partly attributed to the increase of the cell volume. Simulation is extended to larger alkali-doped surface models to investigate the effect of surface and the specific changes between bulk and surface models.

1:45 PM

(PACRIM-S2-002-2017) Compressing Amorphous Boron Nitride at High-Pressure using Constant-Pressure Ab-initio Molecular Dynamic Simulations (Invited)

P. Kroll*[1]

1. UT Arlington, USA

We investigate the structure development of amorphous boron nitride as a function of pressure using via constant pressure (NPT) ab-initio molecular dynamic (aiMD) simulations. Models comprise 256 and 512 atoms, and simulation times extend over 40-200 ps. At low pressures, a-BN transform into planar, "turbostratic" BN, which is consistent with the structure formation observed at high-temperature and low pressures. At pressures exceeding 13 GPa a-BN transforms into (predominantly) cubic-BN with some structural defects. Both Al and C as "alloying" elements have significant impact on the computed pressure of a "phase boundary" between planar (sp^2-like) and cubic (sp^3-like) BN. Substitution of AlN for BN yields to lower pressures of cubic-BN(AlN) formation, while C substitution in a-BN increases the pressure needed to form cubic-BN(C).

2:10 PM

(PACRIM-S2-003-2017) Structural design of oxyfluoride glasses and glass-ceramics from atomistic simulations: From phase separation to nanocrystallization (Invited)

J. Du*[1]

1. University of North Texas, Materials Science and Engineering, USA

Oxyfluoride glass-ceramics possess intriguing optical properties due to their capability to combine the superior optical properties of fluoride crystals due to their low phonon energy with thermal stability and chemical durability of the oxide glass matrix. In this talk, I will present our study of oxyfluoride glasses using large scale classical molecular dynamics simulations to understand the glass structures as a function of glass composition in fluoro-silicate and fluoro-aluminosilicate glasses. From these simulations, for the first time, we observe initial stages of phase separation and the evolution of structures with and evolution with glass composition and temperature. These results were correlated with experimental structural characterization and optical photoluminescence measurements. The results show that combining computer simulations at the atomic scale with experimental structural study and property measurements can be used to design new glass-ceramic compositions with large optical emission efficiency based on the understanding of the structure-property relationships in glasses and glass-ceramic materials.

2:35 PM

(PACRIM-S2-004-2017) Glass Chemical Durability: From Laboratory to Industry (Invited)

A. Li*[1]

1. Corning Incorporated, Characterization Science, USA

Chemical Durability is an important attribute in glass industry and it is used in nearly every stage of a glass product's lifetime. This includes manufacturing, storage, applications of glass products, all the way to disposal of the product. In this presentation, we will start giving an overview of the capabilities of Corning's Chemical Durability group, including various durability tests and cutting-edge techniques used to support Corning business. In particular, we will highlight a method for determining glass thickness during wet etching and the applicable etch rate and its applications. After that, we will give a few examples to demonstrate how we leverage statistical tools and expertise in glass corrosion in the lab to solve real problems in industry.

3:00 PM

(PACRIM-S2-005-2017) Mechanical properties of ion-exchanged glasses based on moleular dynamics simulations

S. Urata*[1]

1. Aasahi Glass Co., Ltd., USA

Chemically strengthened glass is now widely applied to various devices, such as mobile phones, tablet computers, navigation systems and so on. The toughness of ion-exchanged glasses has been modified, nevertheless further improvement is still demanding. It is thus important to understand relation between the toughness and glass compositions from atomistic view point, in order to design more appropriate glass materials. In this study, we examine mechanical properties of a variety of glass compositions by using molecular dynamics simulations. Moreover we shall discuss how to extend our approach to macroscale analysis.

3:15 PM

(PACRIM-S2-006-2017) Modeling and simulation approaches to elucidate nucleation in glass

M. E. McKenzie*[1]; I. Dutta[1]; J. C. Mauro[1]

1. Corning Incorporated, Science & Technology, USA

Well-known limitation to the classical nucleation theory is that the critical cluster nuclei size is based on macroscopic properties. Understanding critical nuclei formation, both the kinetic and thermodynamic aspects, will elucidate the important mechanisms involved during this metastable process. In this work, we compare similar atomistic modeled systems of liquid to solid nucleation of vitreous silicates using different simulation methods. These methods include metadynamics, seeding, enhanced sampling, and bias sampling in molecular dynamics (kinetic information) and monte carlo (thermodynamics) frameworks. By studying a similar system, each technique's strengths allows for a unique insight into the formation of the critical nuclei. Unexpectedly, it was found that these sub-critical clusters do have regions of local stability. We explore these configurations and formulate a nucleation pathway.

Novel modeling Concept and Method

Room: Kohala 4

Session Chair: Wai-Yim Ching, University of Missouri-Kansas City, USA

3:45 PM

(PACRIM-S2-007-2017) Real and virtual screening for materials discovery through first principles calculations (Invited)

I. Tanaka*[1]

1. Kyoto University, Materials Science and Engineering, Japan

Recently, challenges for accelerated discovery of materials with the aid of data science have been well demonstrated. One of the approaches uses materials database that is generated by first principles density functional theory (DFT) calculations. A large number of DFT calculations can be made with the accuracy comparable to experiments, which can be used for "real screening". In order to construct a database by DFT calculations, we need to have a priori knowledge of their structures as in ICSD (Inorganic Crystal Structure Database). Alternatively, we need to restrict our search space within prototype structures. Here we will show an example to discover novel Sn(II)-based oxide compounds suitable for daylight-driven photocatalysis using prototype structures registered in ICSD and real screening. Another approach called "virtual screening" uses machine-learning techniques to select predictors for making a model to estimate the target property. The whole library can then be screened. Verification process is required to examine the predictive power of the model. Models and the quality of the screening can be improved iteratively through Bayesian optimization process. The virtual screening is useful when real screening based upon the DFT data is not practical. Discovery of new low lattice thermal conductivity (LTC) crystals through the virtual screening technique will be shown as an example.

4:15 PM

(PACRIM-S2-008-2017) Multiscale modelling of reactive metal oxide interfaces (Invited)

K. Hermansson*[1]

1. Uppsala University, Department of Chemistry-Angstrom, Sweden

Chemically active metal oxide surfaces and interfaces, such as catalysts, sensors, and electrodes, play crucial roles in our society and in the development of new technologies. Modelling such complex systems is by no means easy, and the computational scientist needs to make shrewd decisions about both the choice of structural model for the interface and the choice of total-energy method. I will discuss some of our efforts to develop multiscale modelling protocols for metal oxide surfaces, nanoparticles and interfaces (e.g. Ceria and ZnO), with and without interacting molecules. We combine a range of theoretical methods including DFT, tight-binding-DFT, and reactive force-field models. A key question here is: Is it possible to model redox-active metal oxides without including the electrons? Adequate models for post-processing of simulation data is as important as the data generation itself, since the post-processing links directly to experimental methods for, e.g., surface characterization, such as spectra and images. I will also discuss some of our efforts in this field.

4:45 PM

(PACRIM-S2-009-2017) Accurate functionals for the design of complex oxides: A high-throughput DFT study (Invited)

S. F. Yuk*[1]; J. T. Krogel[1]; V. R. Cooper[1]

1. Oak Ridge National Laboratory, Materials Science and Technology Division, USA

Density functional theory (DFT) has been widely used to study both the structural and dynamic properties of relevant materials. However, significant variations in DFT-predicted properties are often observed due to the treatment of exchange and correlation effects. Thus, evaluating the accuracy of DFT exchange and correlation (XC) functionals is practically important when computationally screening new classes of materials for a particular application. In this work, we present a high-throughput DFT study of the computed properties of various oxides obtained with different types of XC functionals. Interestingly, the non-local van der Waals density functional with C09 exchange (vdW-DF-C09), which was designed to treat soft matter, performs similarly to the revised Perdew-Burke-Erzenhoff functional which was developed specifically for bulk solids (PBEsol). Such performance in vdW-DF-C09 can be closely related to the behavior of its exchange enhancement factor comparable to the gradient expansion approximation for small reduced gradients. Our results allow us to explore the overall effects of XC on predicted material properties. Research was sponsored by the US DOE, Office of Science, BES, MSED and Early Career Research Programs and used resources at NERSC and OLCF.

5:10 PM

(PACRIM-S2-010-2017) High Throughput Screening for Rare Earth Silicates as Environmental/Thermal Barrier Coating Materials (Invited)

J. Wang*[1]

1. Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, High-performance Ceramics Division, China

Silicon-based ceramics and composites are enabling high temperature structural materials for a wide range of components in extreme environments. Environmental barrier coating plays a crucial role to protect the silicon-based materials from water vapor and CMAS corrosions attacks at high temperatures. A strategic perspective is to develop integrated environmental/thermal barrier coating (E/TBC) systems in the future protective system. Trial-and-error approaches were typically explored to recognize proper RE-silicate as E/TBC candidates. However, the intrinsic mechanical, thermal and chemical properties of dense materials in extreme environments are still not fully understood. The missing knowledge blocks the breakthroughs on optimal properties which would trigger significant modification of the performances of protective coatings. To promote the high throughput screening for advanced E/TBC candidates, a comprehensive informatics is critically needed on the mechanical and thermal properties, as well as high temperature corrosion resistance of dense and phase-pure RE-silicates in harsh environments. The presentation clearly describes the dependences of properties on crystal chemistry, namely chemical composition and crystal structure. The results would initiate high-efficient materials design and selection of RE-silicates for advanced E/TBC applications.

PACRIM Symposium 03: Novel, Green, and Strategic Processing and Manufacturing Technologies

Novel, Green, and Strategic Processing I

Room: King's 3
Session Chairs: Francis Cambier, Belgian Ceramic Resaerch Centre; Hisayuki Suematsu, Nagaoka University of Technology

1:15 PM

(PACRIM-S3-001-2017) Processing and Properties of Anisotropic Hierarchical Porous Ceramics Electrodes for High Performance Li-Ion Batteries (Invited)

R. Bordia*[1]; M. Azami-Ghadkolai[1]

1. Clemson University, Materials Science and Engineering, USA

Porous electrodes are critically important for high performance Li-ion batteries. This application demands optimization of a multitude of properties, which have conflicting requirements on the microstructure. Using available models for the effect of the porous microstructure on the important battery performance characteristics, it will be shown the electrodes with designed anisotropic and hierarchical microstructures have the potential to optimally address the different performance requirements. Results will be presented on two processing approaches to make these designed microstructures. Both tape cast and partially sintered bulk electrodes have been investigated. With the developed processing protocols, it will be shown that it is possible to independently control several relevant microstructural parameters. The 3D microstructure has been characterized at relevant length scales and these results will be presented. The electrochemical performance of the designed porous electrodes will be compared to that of the uniformly porous isotropic electrodes. It will be shown that, compared to uniform porosity electrodes, due to reduced tortuosity leading to deeper electrolyte access, the electrode thickness can be increased leading to high energy density without significant capacity fade at higher charge/discharge rate.

1:40 PM

(PACRIM-S3-002-2017) Silicon Nitride-Hydroxyapatite Bioactive Composite (Invited)

P. Sajgalik*[1]

1. Institute of Inorganic Chemistry, Slovak Academy of Sciences, Ceramic Department, Slovakia

Silicon nitride-based ceramics are characterised especially by high chemical resistance, superior combination of fracture toughness, hardness and bio-inertness. However, the biological applications often require additional properties, e.g. bioactivity enabling stronger bonding to the host tissue. In this work silicon nitride porous substrate is covered by the hydroxyapatite thin layer in order to change the composite from bio-inert to bio-active. Hydroxyapatite coating prepared by sol-gel route, which provides pure, stable and nano-crystalline product is one of the ways to achieve bioactivity of bio-inert ceramics. Therefore silicon nitride-hydroxyapatite composites were prepared by infiltration of hydroxyapatite precursor sol into the silicon nitride based porous ceramics. The conditions of sol preparation were optimised to be appropriate for pure HA synthesis: ageing at elevated temperature (85 °C) and calcinations at 500 °C for 1 h. Cytotoxicity and in vitro bioactivity of Si_3N_4-HA composites were tested in order to verify the effect of hydroxyapatite addition on the biological properties of composite. After immersion of porous composite into simulated body fluid (SBF) for 21 days, calcium phosphate layer was formed on the surface of silicon nitride-hydroxyapatite composites, indicating their bioactivity.

2:05 PM

(PACRIM-S3-003-2017) Aqueous Processing and Characterization of Lead-Based Piezoceramics for Multilayer Electronic Component Applications

W. Sakamoto*[1]

1. Nagoya University, Institute of Materials and Systems for Sustainability, Japan

Recently, the demand for environmentally friendly ceramic processing has increased for the development of miniaturized electronic ceramic components with high performance. For this, one of the solutions is the aqueous manufacturing process using well-dispersed aqueous slurries. On the other hand, lead-based piezoceramics such as $Pb(Zr,Ti)O_3$ has extensively been applied to various electronic components because of their excellent piezoelectric properties. In this study, aqueous $Pb(Zr,Ti)O_3$-based material slurry processing has been mainly investigated. Dispersibility of $Pb(Zr,Ti)O_3$-based ceramic particles in aqueous slurries with various pH was elucidated by characterizing the sedimentation density, viscosity of slurries and amount of adsorbed dispersant. The microstructures of the green and sintered ceramic sheets fabricated using aqueous slurries were affected by the dispersion state of ceramic particles in slurries. The addition of dispersant greatly improved dispersibility of the aqueous $Pb(Zr,Ti)O_3$ slurries, leading to the enhancement of dielectric and piezoelectric properties of the resultant ceramic bodies. Furthermore, casting and drying conditions of the green sheet were also found to strongly influence the sintering behavior of the sintered ceramic sheet.

2:20 PM

(PACRIM-S3-004-2017) Development of Lithium Ion Conducting Glasses Containing Boron, Silicon, and Sulfur

M. P. Aguilar*[1]

1. Iowa State University, Materials Science and Engineering, USA

A high demand for battery powered electronics and sustainable energy has propelled research into longer lasting, safer, and higher energy dense lithium ion batteries. In order to achieve these goals, a highly conductive solid state electrolyte must be developed that remains chemically stable with the electrodes, has a long cycle life, and is safe if exposed to air. Glass based electrolytes form strong networks that can allow for speedy ion transport while remaining structurally and chemically stable, and potentially making it possible to use lithium metal electrodes due to dendrite blocking properties. In this research, a glassy electrolyte containing a lithium, boron, silicon, and sulfur with the composition $0.5Li_2S + 0.5[xBS_{3/2} + (1-x) SiS_2]$ prepared via melt quenching will be explored and characterized using infrared spectroscopy, differential scanning calorimetry, and impedance spectroscopy.

2:35 PM

(PACRIM-S3-005-2017) Role of Freezing Rate on Templated Pore Structures in Dense Freeze Cast Ceramics

S. Pinches*[1]; G. Franks[1]; C. Tallon[2]

1. University of Melbourne, Chemical Engineering, Australia
2. Virginia Tech, Department of Materials Science and Engineering, USA

Presently, few processes are suitable for the shaping of complex-shaped dense ceramics. Existing processes that can produce such shapes are slow, costly, and impractical for mass production, while current mass-production ceramic shaping processes are limited to simple geometries. This study investigates freeze-casting as a technique for producing complex near-net shaped dense ceramic parts. Previous work producing porous ceramics identified the rate of freezing as a major factor affecting the distribution and morphology of pores produced via freeze casting. Presented in this work is the effect of freezing-rate on microstructures that were observed via SEM and micro-CT in freeze-dried green samples. Samples were prepared from dispersed non-aqueous ceramic suspensions with high solids loadings, and were freeze-cast in cylindrical moulds at temperatures between -20 and -80°C. In addition, the initial freezing rate was further controlled by casting in moulds prepared at either ambient or pre-chilled temperatures. Altering the freezing rate produced a range of microstructural features across various length scales. Variations were observed in both the distribution and size of the features, which included crack-like voids alongside templated pores. Heat transfer modelling was applied to evaluate the local freezing front velocity and overall freezing rate of the samples frozen at different temperatures.

2:50 PM

(PACRIM-S3-006-2017) Pt Nano Particles Supported by Lingzhi Spores- Derived Microporous Carbon as the High -Performance Electrocatalyst for Oxygen Reduction Reaction

P. Ma*[1]; Y. Yu[1]; X. Zou[1]; X. Ma[1]; Z. Fu[1]

1. Wuhan University of Technology, China

The oxygen reduction reaction (ORR) is a critical technology for developing high-performance fuel cells. At present, synthesizing high-surface- area carbon as the support for costly platinum-based catalysts is still a prerequisite for the commercial application of this technology. Carbonizing biomass evolved from natural selection to obtain carbon -based electrocatalyst materials with high specific surface area and introduction of heteroatoms have been paid more attention. In this research, Lingzhi Spores with hard double-layers as the candidate resource were transformed to microporous carbon materials with a high N- doping quantity and specific surface area of 2582.52 m^2/g via combination technologies of direct carbonization and KOH activation. The obtained carbon materials preserving the self - supporting double –layers microstructure are used as the substrate for Pt nano particles. The as-prepared Pt/C electrocatalysts show excellent performance for ORR and good stability, which are comparable to the Pt/N-doped graphene materials. A high proportion of microspore with appropriate pore size, N doping and highly-dispersed Pt nano particles contribute to the excellent ORR activities in the well - defined structures.

3:05 PM

(PACRIM-S3-008-2017) Combustion Joining of Refractory and Dissimilar Materials (Invited)

A. Mukasyan*[1]

1. University of Notre Dame, USA

Refractory ceramics with melting point above 2000°C is difficult to join. Same conclusion stands for dissimilar materials (i.e., ceramic-metal) that have large differences in their structural and physical properties. In this work, the combustion joining (CJ) method, which is based on the use of the self-sustained heterogeneous gasless reaction, was applied for “welding” of the refractory and dissimilar materials. More specifically, CJ was applied for bonding of the carbon-carbon composites, as well as silicon carbide ceramics to aluminum alloy. It was shown that under optimized conditions the crack – free joining can be achieved in both cases. It is more important that the mechanical properties of the joint layers appeared to be much higher than those for the materials. Thus it was demonstrated that CJ is an effective method for reactive “welding” of matereails, which are difficult or even impossible to join using other conventional techniques.

3:45 PM

(PACRIM-S3-009-2017) Metal hydroxides as platform for interfacial functionalities (Invited)

M. Takahashi*[1]

1. Osaka Prefecture University, Japan

Metal hydroxides are an important class of inorganic materials as solid state catalysts, electrodes, precursor for variety of oxides and others. A variety of nano sized metal hydroxides are also reported so far. They are characterized by the accommodation of hydroxyl group as a counter anion for metal cations which brings surface basicity and structural flexibility. The authors have been working on the preparation and application of metal hydroxide nano materials, especially for 1D nano rods, tubes, and belts. The fundamental interest is focused on the control of shape and size of the micro structures in nano to meso scales. Such nano hydroxides possess a large surface area where a large number of hydroxyl group is aligned according to the crystal structures. The surface hydroxyl group can be further used for scaffold to grow different materials. Recent achievements of our group on the preparation and application of 1D metal hydroxides for variety of interfacial applications will be presented. Topic includes: 1. Formation of hierarchically porous hydroxides as adsorbents of toxins in environments 2. Vertically oriented nanotubes for superhydrophobic surface with a switchable adhesion of water 3. Metal hydroxides as a scaffold for metal organic frameworks.

4:10 PM

(PACRIM-S3-010-2017) From waste CRT glasses to foam glass for green applications

F. O. Mear*[1]; R. Lebullenger[2]

1. Lille 1 University, France
2. Rennes 1 University, France

Necessity of recycling industrial wastes figures among daily environmental and economic priorities. Glass is known as an “eternal” recyclable material. Generally, glass cullet is re-used in the container and window glass industry. For cathode ray tube (CRT) glass, the situation is different. This work is devoted to search of possible applications for waste cathode-ray tubes (CRTs) glasses. Heavy elements contained in the glasses are required be buried land field by producers and recyclers of CRT’s. Foam glass seems to be the most promising for waste CRT glasses recycling. Today, commercial foam glasses are used for thermal and acoustic insulation applications resulting of their porous structure. The foam glass is obtained after heat treatment of a powder mixture of the CRT glass and reducing agent such as titanium nitride or silicon carbide. The basic principle of foam glass manufacture is to generate a gas, by reaction with the reducing agent. The gas expands thus producing a structure of cells to form a porous body.

4:25 PM

(PACRIM-S3-011-2017) Sintering of Boron Carbide Ceramics without Grain Growth by Plastic Deformation as Dominating Densification Mechanism

W. Ji*[1]; Z. Fu[1]; W. Wang[1]; H. Wang[1]; Y. Wang[1]; J. Zhang[1]; Z. Fan[1]

1. Wuhan University of Technology, China

Dense and fine grain structure is the goal of ceramic sintering. However, common sintering processes with high sintering temperature and long soaking time lead to inevitable grain growth, and attempts of new sintering methods also have some drawbacks such as energy dissipation. A new ceramic sintering approach employing plastic deformation as the dominant mechanism is proposed, at low temperature close to the onset point of grain growth and under high pressure. High performance Boron Cabide ceramics with full density without grain growth were fabricated based on the technologies. This idea and method provide both time and energy efficient ways for B_4C, and will also facilitate preparation of other advanced ceramics for practical applications.

4:40 PM

(PACRIM-S3-012-2017) Novel Route to Pollucite Ceramic through Geopolymer Precursor with Adjustable Thermal Expansion Behavior

J. Yuan*[1]; P. He[1]; D. Jia[1]

1. Harbin Institute of Technology, School of Materials Science and Engineering, China

A series of lithium-substituted cesium-based geopolymers, $\mathrm{Cs}_{(1-x)}\mathrm{Li}_x$GP (where x = 0, 0.1, 0.2, and 0.3), were prepared and heated at 1300 °C for 2 h to obtain the corresponding ceramic products. Phase composition, microstructure evolution and thermal expansion behaviors of the ceramics derived from the geopolymers were characterized. All the geopolymer specimens exhibited similar thermal evolutionary trends. With increasing of sodium substitution, $\mathrm{Cs}_{(1-x)}\mathrm{Li}_x$GP ceramics became much denser, and contained a large number of spherical particles surrounded by a glassy matrix, and the particle size of pollucite grain gradually coarsened. The introduction of Li results in two-step sintering behavior for the lithium-substituted cesium-based geopolymers. The average thermal expansion coefficient (CTE) of $\mathrm{Cs}_{(1-x)}\mathrm{Li}_x$GP ceramics decreased from $4.80 \times 10^{-6}\ \mathrm{K}^{-1}$ (x = 0) to $3.61 \times 10^{-6}\ \mathrm{K}^{-1}$ (x = 0.3) with increases in lithium substitution. The reason can be attributed to the presence of spodumene after thermal treatment, which has a relatively low thermal expansion coefficient compared with pollucite. Meanwhile, molten spodumene could serve as a buffer phase between pollucite crystals also conducive to the decline of CTE of this system.

4:55 PM

(PACRIM-S3-013-2017) Thin film deposition using rarefied gas jet

S. Pradhan*[1]

1. Indian Institute of Science, Department of Chemical Engineering, India

The rarefied gas jet of aluminium is studied at Mach number Ma = (U_j / \sqrt{kb T_j / m}) in the range 0.01 < Ma < 2, and Knudsen number Kn = (1 / (\sqrt{2} \pi d^2 n_d H) in the range 0.01 < Kn < 15, using two-dimensional (2D) direct simulation Monte Carlo (DSMC) simulations to understand the flow phenomena and deposition mechanisms in a physical vapor deposition (PVD) process for the development of the highly oriented pure metallic aluminum thin film with uniform thickness and strong adhesion on the surface of the substrate in the form of ionic plasma, so that the substrate can be protected from corrosion and oxidation and thereby enhance the lifetime and safety. The variation of the local fluxes along the streamwise direction away from the jet are studied. The qualitative nature of the local flux at high Mach number (Ma = 2) is similar to those in the incompressible limit (Ma = 0.01). These include the initial fast decay, then slow variation, and finally rapid decay near the substrate. However, there are important differences. The amplitudes of the local flux increase as the Mach number increases. The flux decreases by an order of magnitude before reaching to the substrate. There is significant velocity and temperature slip ((Pradhan & Kumaran, J. Fluid Mech-2011); (Kumaran & Pradhan, J. Fluid Mech-2014)) at the solid surfaces of the substrate.

PACRIM Symposium 07: Porous Ceramics: Innovative Processing and Advanced Applications

Innovations in Processing Methods & Synthesis of Porous Ceramics I

Room: King's 2

Session Chairs: Manabu Fukushima, National Institute of Advanced Industrial Science and Technology (AIST); Enrico Bernardo, University of Padova

1:15 PM

(PACRIM-S7-001-2017) Highly Porous Geopolymer Components from Foaming and Additive Manufacturing (Invited)

P. Colombo*[1]; G. Franchin[1]; C. Bai[1]; P. Scanferla[1]

1. University of Padova, Industrial Engineering, Italy

Open cell alkali or acid-based geopolymer foams were produced by direct foaming using different fabrication approaches. Potassium-based foams with a porosity up to 85 vol% were obtained from metakaolin, potassium silicate and potassium hydroxide, while metakaolin and phosphoric acid were used to fabricate foams containing an aluminum phosphate crystal phase already after synthesis at room temperature, and a total porosity of ~80 vol%. The strength of the foams depended on the porosity of the components as well as the heat treatment temperature. Geopolymer formulations were used to fabricate scaffold with controlled porosity and morphology, using Additive Manufacturing technologies (mainly, Direct Ink writing). The rheological properties of the inks were investigated in detail, and we studied the effect of different water content and different type and amount of additives in order to enhance the Bingham pseudo-plastic behavior of the inks. Such optimization resulted in the ability to fabricate components with overhangs and spanning features, including highly porous 3D lattices.

1:45 PM

(PACRIM-S7-002-2017) Nitridation behavior of silicon powder compacts with various thicknesses (Invited)

C. Matsunaga*[1]; Y. Zhou[1]; D. Kusano[2]; H. Hyuga[1]; Y. Yoshizawa[1]; K. Hirao[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Structural Materials Research Institute, Japan
2. Japan Fine Ceramics Co., Ltd., Japan

Silicon nitride ceramics with high thermal conductivity are expected to be used as promising substrate materials for the next-generation power devices. Our recent studies found that silicon nitride with both high thermal conductivity and good mechanical properties could be fabricated by a route of sintering of reaction-bonded silicon nitride (SRBSN), and nitridation was a key process for the SRBSN method. Moreover, while preparing silicon nitride substrates, effect of thickness of silicon compacts during the SRBSN process cannot be neglected. Therefore, in this work, effect of nitriding parameters and thickness of Si powder compacts on nitridation was investigated. A high purity silicon powder doped with Y_2O_3 and MgO additives was formed into pellets with a diameter of 15 mm and thicknesses ranging from 3 mm to 9 mm by die-pressing and cold isostatic pressing. Nitridation of the pellets were conducted in a nitrogen atmosphere. Effects of a variety of parameters such as nitriding temperature and holding time and thickness of the pellet specimens on the nitridation behavior of silicon were studied through examining the nitridation rates, analyzing the phase compositions and observing the microstructures of the nitrided compacts.

2:05 PM

(PACRIM-S7-003-2017) Mechanical and thermal properties of porous boron nitride/silicon oxynitride ceramic composites prepared by pressureless sintering

Y. Sun*[1]; Z. Yang[1]; D. Cai[1]; D. Jia[1]; Y. Zhou[1]

1. Harbin Institute of Technology, China

Porous boron nitride/silicon oxynitride (BN/Si_2N_2O) composites were successfully fabricated by pressureless sintering. The influence of sintering aids Li_2O and BN on microstructure, mechanical and thermal properties of the resulting porous BN/Si_2N_2O composites were investigated. The mechanical properties increased or decreased with increasing Li_2O or BN contents and the addition of BN effectively enhances the machinability of these ceramics. Almost all samples' Vickers hardnesses are lower than that of machinable mica-glass-ceramic (3 GPa). Increasing Li_2O contents facilitated densification and decomposition of Si_2N_2O into Si_3N_4. The apparent porosity of the composites increases with increases in BN and Si_2N_2O grain growth is restrained by the dispersed BN particles. The thermal conductivities (TC) were affected mainly by porosity. The flexural strength and elastic modulus of sample with 2~10 mol% Li_2O and 0~25 mol% BN were 110~280 MPa and 49~141 GPa. Porous BN/Si_2N_2O ceramic composites exhibit good mechanical and thermal performance, suggesting utility as high-temperature structural/functional materials.

2:25 PM

(PACRIM-S7-004-2017) Porous silicon nitride ceramics with designed porosity and pore structure

D. Yao*[1]; Y. Zeng[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Porous silicon nitride (Si_3N_4) shows superior properties in strength, toughness, thermal shock resistance due to the formation of interlocking microstructure. In order to fabricate porous Si_3N_4 ceramics with high porosity and high strength, several molding methods were investigated. Porous Si_3N_4 ceramics with porosity of 35~55% and with mono pore size distribution were obtained by controlled die molding pressure and pressureless sintering. Furthermore, high porosity of 70~90% can be achieved by freeze drying and foaming method. Gradient porous Si_3N_4 ceramics has been fabricated by the combination of slip casting and vacuum foaming methods. With the pressure decrease from 80KPa to 9KPa, the porosity increased from 59.01% to 80.85% and the gradient structure became more clearly.

2:45 PM

(PACRIM-S7-005-2017) Porous SiC ceramics prepared with a modified gelcasting and solid state sintering

Y. Zeng*[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

With starch as pore forming agent, porous silicon carbide (SiC) ceramics were fabricated by gelcasting. The novel and simple gelling system of isobutylene and maleic anhydride (Isobam) that can work in air at room temperature. The rheological behaviors of SiC slurries were investigated as a function of starch content. The gelled SiC green bodies were then sintered at 2050–2150ºC through solid state sintering with B_4C and carbon as sintering additives. Porosity of the porous SiC ceramics sintered at 2100 ºC was well controlled from 34.20 to 42.68% with the starch content increasing from 0 to 20wt%. With increasing the sintering temperature from 2050 to 2150 ºC, flexural strength and porosity of porous SiC ceramics with 20wt% starch varied from 61.0 to 128.0 MPa and 48.14 to 34.17%, respectively. The porous SiC ceramics fabricated with 20wt% starch addition and sintered at 2100 ºC were proved to have excellent thermal shock resistance, the flexural strength increased from 86.7 to 95.8 MPa after quenching at 1500 ºC.

3:05 PM

(PACRIM-S7-006-2017) Processing - Microstructure - Properties in Ceramic insulators prepared by gelation freezing process

M. Fukushima*[1]; H. Hyuga[1]; C. Matsunaga[1]; S. Tsuda[1]; T. Ohji[1]; Y. Yoshizawa[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

We will report fabrication process and properties of cellular ceramics through gelation and freezing route, investigating the effect of processing factors of content of gelation agent, ice binding additives, slurry preparation and freezing condition on porosity, pore interconnection, thermal conductivity and compressive strength of resultant ceramic insulators. In addition to that, we conducted the image based modelling techniques for mechanical properties and thermal conductivities of the insulators, by using three dimensional microstructures measured by X-ray computed tomography.

Innovations in Processing Methods & Synthesis of Porous Ceramics II

Room: King's 2
Session Chairs: Paolo Colombo, University of Padova;
Chika Matsunaga, National Institute of Advanced Industrial Science and Technology (AIST)

3:40 PM

(PACRIM-S7-007-2017) Silicate foams from engineered alkali activated suspensions (Invited)

E. Bernardo*[1]; A. Rincon Romero[1]; H. Elsayed[1]

1. University of Padova, Dept. of Industrial Engineering, Italy

The progressive hardening of suspensions associated with inorganic polymerization offers interesting possibilities for the development of highly porous foams. In fact, air may be easily incorporated by vigorous mechanical stirring, with the help of surfactants. The cellular structure is stabilised by the increase of viscosity caused by the same curing reactions, configuring an 'inorganic gel casting'. The present paper is aimed at extending the approach to a series of silicate ceramic foams, obtained by the thermal treatment of engineered alkali activated suspensions. In a first case study, pure mullite foams were achieved by gel casting of a suspension for Na-geopolymer enriched with reactive γ-Al_2O_3 powders. Sodium was extracted by ionic exchange with ammonium salts, before ceramization at 1300 °C. In a second case study, glass and glass-ceramic foams were achieved by gel casting of alkali activated suspensions of only glass powders. In a second case study, gels from the formation of calcium silicate hydrates were found instead of zeolites like gels, developed from conventional geopolymer-yielding suspensions, but a good control of foaming, by mechanical stirring, was preserved. Finally, the foams were subjected to viscous flow sintering, with or without concurrent crystallization, at 700-1000 °C, depending on the composition (from recycled soda lime glass to bioactive glass-ceramics).

4:10 PM

(PACRIM-S7-008-2017) Tailored surface porosities on ceramic foams

A. Shimamura[1]; M. Fukushima[1]; T. Ohji*[1]; N. Kondo[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Novel ceramic foams with tailored surface porosities have been prepared by direct blowing of powder compact, and followed by modulated gas release from the blown bodies. The processing methodologies to produce precisely controlled pore configuration have been discussed in terms of: the direct blowing of powder compacts with a phenoric resin, to form an array of interconnected spherical pores with various unique surfaces comprised of relatively denser, zebra-stripe type (denser and porous) and highly oriented grains, to provide improved mechanical strength and sufficient fluid permeability, that has been created by using one-pot blowing process. These simple and versatile approaches can be used to tailor pore configurations, and fabricate macroporous monoliths with various distinct characteristics.

4:30 PM

(PACRIM-S7-009-2017) Processing of ceramic bone mimic structures and their influence on mechanical resistance and cell invasion

A. L. Leriche*[1]; S. Chamary[1]; E. Meurice[1]; F. Bouchart[1]; J. Hornez[1]; D. Hautcoeur[2]; F. J. Cambier[2]; M. Fernandes[3]; F. Monteiro[4]

1. University of Valenciennes, France
2. Belgian Ceramic Research Centre, Belgium
3. University of Porto, Faculty of Dentistry, Portugal
4. University of Porto, INEB, Portugal

For the last decade, a lot of researches were focused on the development of new ceramic shaping methods able to mimic the complex structure of natural bone. In this paper, three different processing methods applied to home-made calcium phosphate powders will be compared. The first process consists on ceramic slurry impregnation of an organic skeleton made of PMMA glued beads, allowing the development of isotropic spherical porous structure with pore diameter size ranging between 250 and 600 μm. The second process is a casting method based on ceramic slurry ice-templating producing tubular pores characterized by ellipsoidal shape and smaller diameters (100 to 300 μm). The third process is the UV micro-stereolithography of ceramic/resin mixture allowing to perform any porosity shape and size. Finally, a dual core-shell structure with large core porosity and elongated porosity outside to mimic the bone structure has also been developed. The PMMA bead scaffold replica method was used for the core and the ice-templating method for the shell. These various scaffolds with quite similar pore size but differently shaped and arranged porosity were compared on compressive mechanical behavior and cell colonization occurring inside the macroporosity.

4:50 PM

(PACRIM-S7-010-2017) Connectivity and Flow through Freeze-Cast Microstructures

M. Naviroj[2]; T. Fey[3]; K. Faber*[1]

1. California Institute of Technology, USA
2. Northwestern University, USA
3. Friedrich-Alexander University Erlangen-Nürnberg, Germany

Two of the likely applications for directionally freeze-cast ceramics are catalyst supports and filtration membranes. Both require through-thickness alignment and connectivity in the porous phase. In this work, we have explored various strategies to tailor the degree of alignment and hence, the flow characteristics of the materials. We firstly will compare the permeability and connectivity of solution freeze-cast SiOC prepared using a range of organic solvents with a siloxane preceramic polymer. Secondly, we will report on a grain-selection templating technique which provides enhanced nucleation control during freeze casting to increase alignment, and consequently, permeability. Permeability results will be compared to connectivity profiles from X-ray computed tomography.

5:10 PM

(PACRIM-S7-011-2017) Mixed-Oxide Sorbents Produced by 3D-printing for the Removal of Hydrogen Sulfide from Bio-Syngas

K. Chen*[1]; Y. Chen[1]; W. Wei[1]

1. National Taiwan University, Materials Science and Engineering, Taiwan

Removal sulfur in biofuel is important for the use of renewable energy in solid oxide fuel cells. The purification and reforming of hydrocarbon fuels are currently conducted to prevent poisoning of the oxide electrodes. This research reports previous formulation technique of ceramic/polymer kneading of several polymers with ceramic powders (ZnO, Θ-Al_2O_3, and CaO and $CaCO_3$), and extruding to produce feedstock of wire shape in order to form catalytic ceramic supports. The effects of Ni+CeO_2 catalyst is used to simultaneously remove of H_2S and hard particles, and reform CH_4 in the temperature range of 650–800 °C by using mixed-oxide sorbents. The pore size of ceramic supports shows two different distributions, due to polymer burnt-out and its stacking configuration. The shape of the sorbents is designed and manufactured by 3D printing tending to create turbulent flow and to improve the retention of raw gas. The performance of the modified sorbents is discussed in terms of the testing by the syngas from the gasification of several biomass sources.

PACRIM Symposium 11: Engineering Ceramics: Processing and Characterizations

Innovative Processing

Room: King's 1
Session Chairs: Takashi Goto, IMR Tohoku University;
Ralf Riedel, TU Darmstadt

1:15 PM

(PACRIM-S11-001-2017) Melt-solidification of ultra-high-temperature ceramics (Invited)

T. Goto*[1]

1. IMR Tohoku University, Japan

Since ultra-high-temperature ceramics (UHTCs) have too high-melting point, melt-solidification process has hardly been employed to fabricate UHTCs. On the other hand, high-temperature technology using laser and electron beam has been developing, and a high-temperature around 2000 to 3000 K is able to be produced readily, and thus UHTCs may be melted by laser. The melting point can be further decreased by eutectic reactions, and well-controlled self-assembled eutectic composites can be synthesized by melt-solidification using laser. The authors have synthesized various binary and ternary UHTCs composites by employing eutectic reactions. SiC-ZrB_2 composite has the eutectic composition of 41 mol%ZrB_2 with a labyrinth texture. SiC-B_4C composite has the eutectic composition of 47 mol%B_4C. B_4C-TiB_2 composite has the eutectic composition of 20 mol%TiB_2 with a rod-like texture. By using Nd:YAG laser, UHTC eutectic composites were melted and solidified forming fine micro-structure. SiC-CrB_2 has a relatively low melting temperature, and SiC-CrB_2 sintered body was melted by laser forming a typical laminar eutectic texture. The microstructure changed depending on laser scanning speed, i.e., solidification rate, and a uniform eutectic texture was formed 80 to 100 μm in thickness. Below the melt-solidified layer well-sintered layer was obtained.

1:45 PM

(PACRIM-S11-002-2017) SiBCN-Based Ceramics: Assessment of the Status Quo after 25 Years of Research (Invited)

R. Riedel*[1]

1. TU Darmstadt, Department of Materials, Germany

Ceramics based on silicon nitride and carbide are strong and stable at high temperatures, and have been therefore of great fundamental and technological interest for the fabrication of motor and turbine parts. But silicon nitride decomposes at about 1,400 °C in vacuum and 1,775 °C in 0.1 MPa nitrogen, limiting the high-temperature range of its technological uses. At the beginning of the 1990ies, a boron-containing silicon nitride/carbide-based ceramic that does not degrade at temperatures up to 2,000 °C even in nitrogen-free environments had been discovered and considered as a candidate material for ultra-high temperature applications. In particular, the synthesis of this novel material via a polymer-to-ceramic transformation process from a single source precursor, namely a newly developed polymeric polyborosilazane precursor, opened the unique opportunity to fabricate advanced silicon based non-oxide fibers. The amorphous nature of the SiBCN ceramic even at elevated temperatures far beyond 1400 °C was discussed as an advantageous feature over the well-known polycrystalline SiC-fibers. Since the discovery of the SiBCN-ceramic, 25 years of intense studies regarding its synthesis, microstructure and high-temperature properties followed. This presentation highlights the historic development of SiBCN and discusses and evaluates its technological outcome and future perspective.

2:15 PM

(PACRIM-S11-003-2017) Single-Source-Precursor Approach towards Advanced Silicon-Based Ceramic Nanocomposites: Synthesis, Properties and Applications (Invited)

Z. Yu*[1]

1. Xiamen University, China

Silicon carbide (SiC) and silicon carbonitride (SiCN) based ceramic nanocomposites modified with in-situ formed or incorporated carbon nanophase are effectively synthesized via the polymer-to-ceramic-transformation technique starting from suitable single-source-precursors. In this lecture, the phase composition of different SiC and SiCN-based systems will be discussed. The developed single-source-precursor approach allows to homogeneously disperse nanocarbon phase in ceramic matrices, which exhibits significant advantage over the physical blending method. The carbon nanophase plays a critical role in their dielectric properties. The relationship between the obtained nano/microstructure of the synthesized SiC- and SiCN-based ceramics and their property features will be highlighted. Moreover, due to the enhanced dielectric properties, our Si-based ceramic nanocomposites possess outstanding electromagnetic (EM) properties and versatile designability from EM absorbing to shielding behavior, which shows substantial progress beyond the state of the art.

2:45 PM

(PACRIM-S11-004-2017) Creating 3D multifunctional polymer derived ceramic-graphene composites

B. Román-Manso[1]; D. Pérez-Coll[1]; M. Belmonte[1]; P. Miranzo[1]; M. I. Osendi*[1]

1. Institute of Ceramics and Glass, CSIC, Spain

Cellular materials have attracted considerable attention due to the realm of potential uses, for example as biomaterials, in energy conversion systems, for thermal management or in catalysis. Here we show possibility of constructing hybrid ceramic/graphene structures with designed patterns from a preceramic polymer precursor and graphene oxide (GO). We present spanned structures of GO created from water based inks and diverse polyelectrolytes that provide the required stability and viscosity to make them printable. Partial drying and freezing steps were followed by the structure lyophilisation, required to avoid severe shrinkage and cracking of the GO assemblies during freezing. The limit solid concentration achieved in the inks was around 5 wt.%. These highly porous structures were readily impregnated with liquid polysilazane, a polymeric precursor to Si_3N_4, and subsequently pyrolyzed at temperatures of 800-1100 °C under N atmosphere. The rods of the 3D structures were entirely impregnated developing a connected network of reduced GO embedded in an amorphous matrix containing Si and N atoms. The buried graphene sheets add a desirable electric conductivity to these hybrid composites. Consequently, conducting 3D Si_3N_4/graphene composites are built using aqueous dispersions and relatively low temperatures.

3:00 PM

(PACRIM-S11-005-2017) In situ growth of lamellar BN(C) toughened Si-B-C-N monoliths by spark plasma sintering

B. Liang*[1]; Z. Yang[1]; D. Jia[1]; Y. Zhou[1]

1. Harbin Institute of Technology, Materials Science & Engineering, China

La-containing Si-B-C-N ceramic monoliths were prepared by mechanical alloying followed by spark plasma sintering. Addition of LaB_6 promotes in situ growth of lamellar BN(C) grains thereby increasing greatly composite toughness by 40% (from 5.6 to 7.8 $MPam^{-1/2}$). Multiple toughening mechanisms including pull-out, crack deflection, branching and bridging operate in BN(C) and SiC grain toughening. The dissolution of La ions in BN(C) promotes preferential growth of BN(C) along the (002) plane causing formation of lamellar BN(C).

Sintering and Microstructure Control

Room: King's 1

Session Chairs: Yu Zhou; Kaline Furlan, Hamburg University of Technology

3:45 PM

(PACRIM-S11-006-2017) Structure Evolution During Sintering of Oxide-based Inverse Opals Produced by Atomic Layer Deposition (Invited)

K. P. Furlan*[1]; R. Pasquarelli[1]; R. Zierold[2]; K. Nielsch[2]; G. Schneider[1]; R. Janssen[1]

1. Hamburg University of Technology, Institute of Advanced Ceramics, Germany
2. Institute for Nanostructure and Solid State Physics, University of Hamburg, Germany

Porous ceramics present many technologically promising applications, such as bio-ceramics, filters, catalysts and heat insulators. The performance of a porous ceramic is not only defined by geometry and number of pores, but also by its size and type of interparticle connections. Regarding this the conventional methods to fabricate porous ceramics, such as are partial sintering, sacrificial template methods and pore-forming agents generate structures with an uneven distribution of pores and pore size, which may reduce application properties. Here, we demonstrate that ordered self-assembly of monosized spheres followed by atomic layer deposition (ALD) can be used to produce inverse opals, which heat treated generate a more homogeneous porous structure, both in alumina and titania opals. Synthesis method as well as microstructural evolution of oxide-based inverse opals will be approached and implications for ordered porous structure suitable to serve at high temperatures discussed. Special emphasis will be given to application as photonic materials, but a prospective application in catalysis will also be addressed.

4:15 PM

(PACRIM-S11-007-2017) Textured ceramics and their anisotropy (Invited)

Y. Zhou*[1]; D. Jia[1]; X. Duan[1]; Z. Yang[1]

1. Harbin Institute of Technology, China

Most of ceramics are polycrystalline material, made up by many random arrangement of small single crystals and intergranular phase compositions. From a statistical standpoint, the overall performances of ceramic are the average values in all directions, so it shows the isotropic properties at the macroscopic level. If the external physical conditions, such as stress field, electromagnetic field or temperature gradient field, are applied during the preparation process, the grains can be arranged along a certain direction or the crystallographic axis orientation probability increasing in certain directions, then the so-called "textured ceramics" are obtained. In this presentation, the preparation methods of textured ceramics are systematically introduced, such as template method, electromagnetic field method, pressure assisted sintering method, etc. In addition, a variety of textured ceramic systems are reviewed, including Al_2O_3, SiO_2, TiO_2, Si_3N_4, h-BN, $BaTiO_3$, MAX phase, etc. Furthermore, the application of typical textured ceramic with obviously anisotropic properties are also introduced in this presentation, such as textured h-BN ceramics with directional thermal leading, textured Si3N4 ceramics with obvious strengthening and toughening effect, etc. The development of textured ceramics, enriched the basic theory on ceramic materials, has provided more wide development platform for practical application of ceramic materials.

4:45 PM

(PACRIM-S11-008-2017) Ultra-hard and transparent spinel with grain sizes below 10nm produced by modified Spark Plasma Sintering

D. Ferreira Muche*[1]; J. W. Drazin[1]; J. Mardinly[2]; S. Dey[1]; R. Castro[1]

1. University of California, Davis, Materials Science and Engineering, USA
2. Arizona State University, LeRoy Eyring Center For Solid State Science, USA

Magnesium aluminate spinel is a strategic ceramic for application as transparent armor. Typical processing of spinel to full densities leads to significant grain growth, not allowing exploitation of benefits coming small grain sizes, such as increase in hardness. Here we report a modification in the Spark Plasma Sintering (SPS) process in which nanopowders can be sintered with minimal grain growth, allowing grain sizes below 10 nm in truly fully dense pellets. The process makes use of the high heating rates and pressures of SPS, but relies on a deformable punch design, which allows it to transfer transversal momentum to the sample at high temperatures. This leads to destabilization of isolated pores at the final stage of sintering, allowing densification without associated grain enlargement. By using this method, transparent spinel with grain sizes ranging from 188nm to 7.1 nm were produced and showed an increase in hardness from 17.2 GPa to 28.4 GPa (surpassing sapphire hardness), respectively, following the well-known Hall-Petch relationship, without apparent deviations.

5:00 PM

(PACRIM-S11-009-2017) Submicronic yttria-stabilized zirconia ceramics densified by SPS: Relation between microstructure and physical-chemical properties

F. Ahmad[1]; G. Chevallier[1]; A. Weibel[1]; C. Elissalde[2]; F. Mauvy[2]; C. Estournes*[1]

1. CIRIMAT, LCMIE, France
2. ICMCB-CNRS, France

Ceramics exhibit interesting mechanical and thermo-mechanical properties (hardness, stiffness, wear resistance,...) but are penalized by their low toughness (K_{Ic}). However, some zirconia based ceramics (ZrO_2) were described as "ceramic steel" because, while retaining the usual properties of ceramics, they exhibit exceptionally high toughness which paved the way for many applications, particularly in the field of aeronautics and biomaterials. Spark Plasma Sintering (SPS) allows to densify materials, at lower temperature and with shortest sintering time, leading to nanoscale microstructures non-obtainable by natural sintering or hot pressing methods. This technique is thus well suited to produce nanostructured zirconia ceramics particularly interesting for biomedical applications (hip and dental implants), energy storage (SOFC…) and aeronautics (thermal barriers…). Recently, using SPS, we have densified 3Y-ZrO_2 ceramics which exhibit grain size around 200 nm and high mechanical properties (fracture strength $s_f = 692$ MPa and toughness $K_{Ic} = 10.3$ MPa.m$^{1/2}$). Varying the SPS parameters (dwell time, temperature setpoint and applied pressure…) ceramics with different microstructures have been obtained. Their mechanical and electrical properties will be discussed according to their microstructures.

5:15 PM

(PACRIM-S11-010-2017) The role of manganese in lowering densification temperatures of yttria-stabilized zirconia

H. Li*[1]

1. University of California, Davis, Materials Science and Engineering, USA

The effect of Mn as a sintering aid for yttria-stabilized zirconia (YSZ) was systematically studied from both kinetic and thermodynamic perspectives. YSZ and Mn doped YSZ nanopowders were prepared using coprecipitation method and sintered using fast-firing. Mn increased densification rate of YSZ, allowing it to reach 95% of the theoretical density at 1100 °C within only 5 min. of processing, signifying a decrease of 200 °C with respect to temperatures required for YSZ to achieve similar densities. This was a consequence of the reduction in the activation energy for solid-state sintering from 202.15kJ/mol for YSZ to 69.53kJ/mol for YSZ containing 3 mol% Mn, likely due to segregation of Mn to the grain boundaries to activate densification mass transport mechanisms. The effect Mn on the surface and grain boundary energies was also studied by means of microcalorimetry and revealed the Mn segregation to the interfaces also leads to a change in the dihedral angle of YSZ, thermodynamically favoring pore elimination.

5:30 PM

(PACRIM-S11-011-2017) Using Thermo-Optical-Measurement technique TOM to characterize sintering and melting behavior of ceramic and glass parts under atmospheric control

A. Diegeler*[1]

1. Fraunhofer ISC, Center of Device Development, Germany

Thermo-optical measurement devices have been developed at the Fraunhofer ISC during the last 12 years - recently also with atmospheric control (TOM-AC). Thus it is possible to follow shrinkage or warpage of oxide and non-oxide ceramic parts during the whole temperature cycle inside the furnace. However, this method allows to follow changes in the shapes of samples (up to 50mm in diameter) with an accuracy of about 0.3 micron by contact-less measurements. Due to the purely optical detection samples of any shape can be monitored inside the furnace. A sophisticated algorithm detects the contour of samples - and thus dimensional changes. Possible applications include simply measuring the shrinkage or shape distortions of ceramic parts in a contact-less manner as well as measuring the wetting angle of melts, especially on glass. By a computer controlled program we realized full atmospheric control, i.e. changing the gas atmosphere inside the furnace (inert gas at different pressures, forming gas or vacuum) during the sintering process. We present several examples of experiments with ceramic and glass parts of unusual shapes where e.g., nevertheless, shrinkage curves can be obtained and compared to those taken for the same material with a standard dilatometer.

PACRIM Symposium 17: Advanced Functional Ceramics and Critical Materials Perspective

Advanced Functional Ceramics and Critical Materials Perspective I

Room: Kohala 2
Session Chairs: Nobuhito Imanaka, Osaka University;
Takaaki Tsurumi, Tokyo Institute of Technology;
Shinji Tamura, Osaka University

1:15 PM

(PACRIM-S17-001-2017) Domain Structure propagation of tensile-strained {100}-oriented epitaxial tetragonal Pb(Zr, Ti)O_3 films (Invited)

H. Funakubo*[1]; D. Ichinose[1]; T. Sato[1]; T. Shimizu[1]; O. Sakata[2]; T. Yamada[3]

1. Tokyo Institute of Technology, Japan
2. National Institute for Materials Science (NIMS), Japan
3. Nagoya University, Japan

Thin films of ferroelectric materials have been widely investigated for the wide variety of applications. The ferroelectric and piezoelectric properties are strongly affected by the film orientation and domain structure. Mixed orientation of (100) and (001) were obtained for {100}-oriented ferroelectric films with a small in-plane strain. In this study, we investigated the temperature dependence of the domain structure in this strain region. The $Pb(Zr_{0.05}Ti_{0.95})O_3$ films has the in-plane tensile (0.4%) strain at the deposition temperature of 600°C, while $Pb(Zr_{0.22}Ti_{0.78})O_3$ has the in-plane compressive strain (0.5%). $Pb(Zr_{0.22}Ti_{0.78})O_3$ film formed (001) orientation, then (100) orientation appear under the cooling process after the deposition. On the other hand, with the decrease in temperature, diffraction spots of $Pb(Zr_{0.05}Ti_{0.95})O_3$ split into two ones, indicating (100) orientation formation by the phase transition. Then, diffraction spot of the (001) orientation is appeared. These data show that the formation process of the domain structure depend on the tensile or the compressive strain as predicted by the strain – temperature diagram. In my presentation, we demonstrate the domain structure difference between the films grown under the tensile and compressive strain. This work was partially supported by the JSPS KAKENHI Grant Numbers 26220907 and 15H0421.

1:35 PM

(PACRIM-S17-002-2017) Development of tunable device using Barium Strontium titanate thin films (Invited)

K. Morito*[1]; D. Ishii[1]; M. Natsume[1]; S. Sekiguchi[1]

1. Taiyo Yuden Co., Ltd., Research and Development Lab., Japan

Highly AC power resistance tunable devices using Barium Strontium titanate (BST) thin film are developed. The tunable device consists of BST thin film metal-insulator-metal (MIM) parallel plate configuration capacitors and tantalum nitride base thin film resistors. These films are deposited on Si based substrates using RF magnetron sputtering. The capacitance of a BST MIM capacitor is set by the value of a DC bias potential which is applied to the BST MIM capacitors typically between 0 and 3 volts via thin film resistor. We are going to intruduce tunable impedance matching circuit device as a tunable application.

1:55 PM

(PACRIM-S17-004-2017) The Energy Storage Behavior of $Bi(M_I, M_{II})O_3$-$BaTiO_3$ Dielectric Ceramics (Invited)

S. Zhang*[1]; H. Hao[2]; H. Liu[2]

1. University of Wollongong, ISEM, Australia
2. Wuhan University of Technology, China

Electrical energy storage has become a key for an effective implementation of the electricity generated from renewable energy sources, in order to maintain the sustainable development of the ecological society. Dielectric capacitors as an electrical energy storage technology belong to passive electronic components that store energy in the form of an electrostatic field and have been widely applied in electronic circuit. Up to now, the driving force for dielectric capacitor applications is attributed to the significantly increased consumer electronics market. Typical features of dielectric capacitors which intrinsically exhibit a high energy density and a fast charge/discharge performance compared to Li-ion batteries or fuel cells make them promising candidates for energy storage devices in some specific areas. In this presentation, recent developments on $Bi(M_I, M_{II})O_3$-$BaTiO_3$ based dielectric ceramics will be surveyed, the impacts of dielectric constant, dielectric loss, dielectric breakdown strength on the energy storage and reliability will be studied, which are associated with the microstructures, including density, porosity, defects, grain size and grain boundary, in addition, the phase coexistence and core-shell structure will also be discussed.

2:15 PM

(PACRIM-S17-005-2017) Ferroelectric properties and Domain Structure of $0.77Bi_{0.5}Na_{0.5}TiO_{3\text{-}0.23}SrTiO_3$ Based Ceramic-Ceramic Composite (Invited)

J. Cho*[1]

1. KICET, Republic of Korea

Ceramic-ceramic composites of Fe2O3 modified 0.77Bi0.5Na0.5Ti1-xFexO3-0.23SrTiO3 ceramics and another ceramics were prepared by using a conventional solid-state reaction method. The ferroelectric properties, microstructure and domain morphology were investigated with field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). 0.77Bi0.5Na0.5TiO3-0.23SrTiO3 exhibited a core-shell structure, including a large volume of domain. With increasing Fe modification content, the volume of core domain reduced. For the sample with x=0.04, ~approximately 30% of the grains display a core-shell structure. From the TEM study, the crystal structures of core and shell were identified as Rhombohedral with space group R3c and Tetragonal with space group P4bm, respectively. The large strain 0.12% and low hysteresis of 0.77Bi0.5Na0.5Ti0.96Fe0.04O3-0.23SrTiO3 ceramics sintered at 1150oC for 2h were obtained at an applied electric field of 2kV/mm. For the composition of x=0.04, the enhanced normalized strain of 550 pm/V was obtained by core shell structure under an applied electric field of 2 kV/mm.

2:35 PM

(PACRIM-S17-006-2017) Visualization of Chemical Bonding in Functional Ferroelectrics and Their Solid Solutions by SXRD (Invited)

Y. Kuroiwa*[1]

1. Hiroshima University, Department of Physical Science, Graduate School of Science, Japan

The advent of the 3rd generation synchrotron radiation facility enables us to determine the crystal structure at the electron charge density level. Our group has been devoted to visualizing the electron charge density distribution of ferroelectrics by analyzing the synchrotron-radiation X-ray powder diffraction (SXRD) data measured at SPring-8 using the maximum entropy method (MEM)/Rietveld method. The MEM is efficient in analyzing accurately the electron density at the low level. The atomic positions of the H and

Li atoms in ferroelectrics, even for their disordered states, can be determined by MEM. Recently, we have developed the method to evaluate the valence electron density distribution purely from the SXRD data. Basically, the valence electron density distribution is more informative in many cases from the viewpoint of chemistry of chemical bonding. We have succeeded in visualizing the charge density distribution of the lone electron pairs in the Pb^{2+} and Bi^{3+} ions in ferroelectrics. In this symposium, the results of our electron charge density studies to reveal the characteristic chemical bonding and the local disordered atomic arrangement which govern the emergence of polar lattice distortion associated with the ferroelectric phase transition are introduced for various functional ferroelectrics and their solid solutions.

2:55 PM

(PACRIM-S17-007-2017) Coupled Electromechanical and Thermal Breakdown in Piezoelectric Films (Invited)

S. Trolier-McKinstry*[1]; B. Akkopru Akgun[1]

1. Pennsylvania State University, Materials Science and Engineering, USA

Lead zirconate titanate (PZT) thin films are of interest for piezoelectric microelectromechanical systems. In this application, however, the films are typically driven to electric fields and order of magnitude higher than would be characteristic of bulk materials. Thus, the failure mechanisms at high electric fields are essential to an understanding of the device lifetime. In this paper, the lifetimes of PZT films with donor and acceptor doping levels are compared in terms of the stability of properties as well as highly accelerated lifetime testing conditions. It was found that while acceptor-doped films produce improved stability in the properties, they are also associated with strong anisotropy in the lifetimes under dc field. Thermally stimulated Depolarization Currents suggest that at least part of this asymmetry is associated with the migration of oxygen vacancies. Donor doped films show much smaller internal bias fields, as well as less asymmetry in the lifetime under dc field. Finally, the link between thermal and electromechanical failure events will be demonstrated for films as a function of thickness, orientation, and doping levels.

3:15 PM

(PACRIM-S17-008-2017) Tunable Colossal Piezoelectric Properties induced in Bi-based lead-free piezoceramics via Polarization Engineering (Invited)

W. Jo*[1]

1. Ulsan National Institute of Science and Technology, School of Materials Science and Engineering, Republic of Korea

Extensive research over the last decade in response to the demand on sustainable materials in the field of piezoelectricity has discovered that at least in the case of large-stroke actuator applications, lead-free piezoceramics have advantages with incipient piezostrains over their lead-based counterparts. However, few breakthroughs, if any, have been made in enhancing the direct piezoelectric effect, yet. One of the major reasons for the absence of breakthroughs is that the inherent piezoelectric properties of lead-free ceramics are inferior to those of lead-based ones. This means that to overcome the inherent inferiority of lead-free piezoceramics, one should come up with a novel way to harness the maximum possible properties for a given condition. In this report, we demonstrate that our recently developed processing technique realizing 'seed-induced constrained polarization' be a highly effective way to tailor piezoelectric properties in both the direct and the converse mode. Details of the processing as well as related mechanism will be discussed.

3:50 PM

(PACRIM-S17-009-2017) Texturing of BNKT piezoelectric ceramics by RTGG process using BNT and BNT15 templates (Invited)

J. Jeon*[1]; H. Cha[1]

1. Korea Institute of Materials Science, Nano-Functional Materials, Republic of Korea

The mechanism by which $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) and $Bi_{4.5}Na_{0.5}Ti_4O_{15}$ (BNT15) templates are synthesized via a topochemical microcrystal conversion method using $Bi_4Ti_3O_{12}$ (BiT) precursor and TiO_2 particles was investigated based on their crystal structures. The BNT template consisted of a mixture of plate-like and equiaxed particles, whereas the BNT15 template consisted only of plate-like particles. The size of the plate-like and equiaxed particles was dependent on the size of the BiT precursor and TiO_2 particles, respectively. The Lotgering factor and piezoelectric constant of textured $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$ (BNKT) ceramics prepared using the BNT template were lower than those of the textured BNKT ceramics prepared from the BNT15 template. This can be attributed to the small amount of plate-like particles in the BNT template caused by the inevitable co-existence of equiaxed particles.

4:10 PM

(PACRIM-S17-010-2017) Nanoscale Origins of Small Hysteresis and Remnant Strain in BNT-Based Lead-Free Ceramics

M. Mao*[1]; H. Qian[1]; Z. Yu[1]; Y. Liu[1]; Y. Lyu[1]

1. Nanjing Tech University, China

High precision devices are vital in the premium field of modern industry. In this regard, $BiAlO_3$-doped $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$ (BA-doped BNT-BKT) ceramics are greatly concerned due to their sufficient electric-field-induced strain with small hysteresis and remnant strain. Specially taken 0.96(0.75BNT-0.25BKT)-0.04BA for instance here, it exhibits a large strain of 0.21% at ~70 kV/cm, a small strain hysteresis of only 24% with a small hysteresis in P-E loop and a near-zero remnant strain. Using the structural analysis especially the high-resolution transmission electron microscope (HRTEM), the antiferroelectric nano-domains composited by three variants of in-phase $a^0a^0c^+$ octahedral tilting, coexisting with the remnant ferroelectric nano-domains of anti-phase $a^-a^-a^-$ octahedral tilting, are directly identified, which reveals the nanoscale inducement underlying the excellent properties. According to the structural features, a continuous tilting model is proposed to interpret the gradually transitional tilting between distinct tilting systems and the reversible local phase transition involving nano-domains, leading to a small hysteresis and a near-zero remnant strain. Based upon this, further optimizing the properties through creating stable antiferroelectric nano-domains in BNT-based ceramics and the analogues may pave a way for the future design of advanced high precision devices.

4:25 PM

(PACRIM-S17-011-2017) The potential impact of environmental protection legislation on the piezoelectric ceramics market (Invited)

A. J. Bell*[1]

1. University of Leeds, School of Chemical and Process Engineering, United Kingdom

In the light of European Directives potentially limiting the lead content of products and the fact that some lead-free alternatives to PZT are close to market, product managers in device and systems companies may now be considering whether to specify a lead-free material in their next generation products. Consideration of this question may also provide some insight into the future of the piezoelectric materials industry. The issue is, of course, complex and raises several subsidiary questions concerning the commercial viability of switching to a new material: 1. Does the material meet the performance requirements for the intended use ? 2. Is it legal ?

3. Does it meet the company's sustainability policy ? 4. Is it available, now and in the future ? 5. What will it cost to revise device designs to match the new material ? This presentation will examine the range of responses that may result. Under current assumptions concerning the future course of the legislation, a "mixed economy" of lead-based, lead-free and non-piezoelectric solutions is proposed, depending upon the performance, market volume and strategic nature of the products concerned.

PACRIM Symposium 19: Transparent Ceramic Materials and Devices

Transparent Ceramic Materials and Devices I

Room: Kohala 3
Session Chair: Byung-Nam Kim, National Institute for Materials Science

1:15 PM

(PACRIM-S19-001-2017) Yb^{3+}-doped CaF$_2$-LaF$_3$ ceramics for high power ultrashort pulse lasers (Invited)

A. Shirakawa*[1]; S. Kitajima[1]; K. Yamakado[1]; K. Ueda[1]; H. Ishizawa[2]

1. University of Electro-Communications, Institute for Laser Science, Japan
2. NIKON Corporation, Japan

Today Yb^{3+}-doped calcium fluoride (Yb:CaF$_2$) attracts growing attention. It has many advantages suitable for ultrashort pulse lasers: the broad and smooth fluorescence spectrum, the favorite thermal property, and the long fluorescence lifetime. Recently fabrication of rare-earth doped CaF$_2$ ceramics have been investigated extensively. Here we report the laser operation of Yb^{3+}-doped CaF$_2$-LaF$_3$ ceramics fabricated from nanocrystals. Our fabrication process is based on the hot isostatic pressing (HIP) method. Three type of fluoride nanocrystals which are CaF$_2$ and two kinds of rare-earth fluoride particles synthesized by a chemically process are mixed. In this work, we choose the Yb-ions and La-ions. Incorporation of small amount of lanthanum fluoride modified the lattice structure of CaF$_2$ and suppresses the formation of Yb^{2+} ions. The fluorescence spectrum changes by the doping concentration of Yb^{3+} ions. As the Yb ion doping concentration increases, the fluorescence spectrum becomes broader and smoother. The CW operation of Yb:CaF$_2$-LaF$_3$ ceramics was demonstrated with the simple two-mirror cavity setup. A 2%La1%Yb sample marked the highest slope efficiency of 73.1% and a 2%La3%Yb sample marked the highest maximum output power of 3.97 W. We are also challenging mode-locked laser operation of those ceramics.

1:45 PM

(PACRIM-S19-002-2017) Mico-/nano-structural design approaches for anisotropic transparent ceramics (Invited)

J. E. Garay*[1]

1. University of California, San Diego, Dept. of Mechanical and Aerospace Engrg., USA

Light scattering has prevented the use of polycrystalline ceramics with anisotropic optical properties in applications such as laser gain media. However, continued development of processing technology has allowed for very low porosity and fine grains, significantly improving transparency and is paving the way for polycrystalline ceramics to be used in demanding optical applications. We will discuss the important microstructural features that contribute to the optical properties and some processing techniques that allow for microstructural control. Specifically, we will discuss the role of point defects as purposely added dopants and unwanted contaminants as well as secondary phases in oxides and nitrides. We will also show results from on going efforts to develop ceramics for light emitting (photoluminescence) and light controlling (electro-optic) applications. An important theme for the electro- optic work is developing powder formulations that allow one to lower densification temperatures. In the photoluminescence case we discuss the role of dopant concentrations and dopant agglomeration on the optical properties.

2:15 PM

(PACRIM-S19-003-2017) Synthesis and characterization of yttria-based powders for the fabrication of highly transparent ceramics (Invited)

D. Kim*[1]

1. Korea Advanced Institute of Science and Engineering (KAIST), Dept. of Mater Sci & Eng, Republic of Korea

Transparent ceramics have attracted considerable interest and investigated for the applications such as lasers and cutting tools, night vision devices, armor windows and nose cones for heat seeking missiles. The yttria-based transparent ceramics is one of the most promising transparent materials as the infrared-domes and solid-state laser host because of its high melting point, high corrosion resistance and broad range of IR transparency. The fabrication of transparent ceramics at lower temperature is possible with the advanced ceramic technique. As increasing demand for high-end optical applications, there are remained problems in ceramic processing which should be solved to improve the optical performance. Above all, the preparation of high quality raw powder is crucial for the high sinterability to make full density ceramics. It is still required to study on the powder characteristics of crystallinity, particle size and particle density and effects on spectral properties of the sintered products. In this study, we synthesized and characterized the Y$_2$O$_3$, YAG and Y$_2$O$_3$-MgO nanocomposite powders under the various conditions. The effect of characteristics of initial powder on the optical properties of the transparent ceramics is discussed.

2:45 PM

(PACRIM-S19-004-2017) Processing of transparent ceramics for LASER and ballistic protection applications

A. L. Leriche*[1]; C. Gajdowski[2]; M. Lagny[2]; J. Boehmler[2]; Y. Lorgouilloux[1]; S. Lemonnier[2]; E. Barraud[2]

1. University of Valenciennes, LMCPA, France
2. ISL, France

For last years, transparent polycristalline ceramics can be found in a various range of domains, such as medical, industry, defense and security. The development of these materials requires a poreless microstructure without impurities to avoid light scattering. As seen in the literature, transparency can be obtained by the application of a loading during the sintering step, such as Hot Press or Spark Plasma Sintering (SPS), or the combination of a pressureless sintering and Hot Isostatic Pressing (HIP). On one hand, SPS process allows to obtain high optical quality in one step without post-treatment. Moreover, an additive helps to remove graphite contamination due to SPS tools. On the other hand, pressureless sintering followed by a post-treatment by HIP is a suitable method to produce numerous and large ceramics of complex shape without the use of sintering aids. Nevertheless, this procedure requires considerable time. Advantages and drawbacks of the two approaches to elaborate transparent ceramic will be illustrated with two examples: Er:YAG ceramic by SPS for LASER applications and MgAl$_2$O$_4$ spinel for ballistic protection of vehicles and soldiers.

3:00 PM

(PACRIM-S19-005-2017) DSMC Simulations of Leading Edge Flat-plate Boundary Layer Flows at High Mach Number

S. Pradhan*[1]

1. Indian Institute of Science, Department of Chemical Engineering, India

The flow over a 2D leading-edge flat plate is studied at Mach number Ma = (U_{inf} / \sqrt{k_B T_{inf} / m}) in the range 3 < Ma < 10, and at Reynolds number number Re = (L_T $U_{inf}\rho_{inf}$)/ μ_{inf} equal to 10^4 using two-dimensional (2D) direct simulation Monte Carlo

(DSMC) simulations to understand the flow phenomena of the leading-edge flat plate boundary layer at high Mach number. The variation of streamwise velocity, temperature, number-density, and mean free path along the wall normal direction away from the plate surface is studied. The qualitative nature of the streamwise velocity at high Mach number is similar to those in the incompressible limit (parabolic profile). However, there are important differences. The amplitudes of the streamwise velocity increase as the Mach number increases and turned into a more flatter profile near the wall. There is significant velocity and temperature slip ((Pradhan and Kumaran, J. Fluid Mech-2011); (Kumaran and Pradhan, J. Fluid Mech-2014)) at the surface of the plate. It is interesting to note that for the highest Mach numbers considered here, the streamwise velocity at the wall exceeds the sound speed, and the flow is supersonic throughout the flow domain. The subsonic region near the wall, expected when a no-slip boundary condition is applied, is not present when there is wall slip at sufficiently high Mach number.

3:15 PM

(PACRIM-S19-006-2017) NIR luminescence of Bi_2O_3-GeO_2 and Bi_2O_3-SiO_2 binary system: Glass and glass-ceramics

J. Xu*[1]; J. Liu[2]; N. Li[1]

1. Tongji University, Department of Physics, China
2. Tongji University, School of Materials Science and Engineering, China

Bi-doped materials have received great interest at home and abroad since 2001, owing to their ultra broad IR luminescence properties in the wavelength region from 1000 to 1700 nm with a FWHM up to about 300 nm. The bismuth-doped materials have the potential to become the next great wide-band optical amplifier. In most Bi-doped materials, bismuth was introduced as dopant of a small amount. We reported on the NIR luminescent properties in bismuth germinate (Bi_2O_3-GeO_2) and bismuth silicate (Bi_2O_3-SiO_2) binary system in this paper. In binary system, Bi_2O_3 is introduces both as one of the matrix members and active center. It has a wide concentration range of $Bi_2O_{3.}$ Bi_2O_3-SiO_2 and Bi_2O_3-SiO_2 glass and glass ceramics were prepared. XRD, near-infrared and VIS luminescence spectra, excitation spectra and fluorescence decay curves were measured. Apparent differences of NIR luminescence and decay properties manifest the co-existence of more than one active center in these two binary systems. Bi^{2+} and Bi^{+} are proposed as the emission centers of the photoluminescence peaks at 1060 nm and 1300 nm, respectively.

3:45 PM

(PACRIM-S19-007-2017) Transparent electronics: A dream that becomes reality

E. Fortunato*[1]; R. Martins[1]; P. Barquinha[1]

1. FCT-UNL, Materials Science, Portugal

The evolution from rigid silicon-based electronics to flexible electronics requires the use of new materials with novel functionalities that allow non-conventional, low-cost and environmental friendly processing technologies. Among the alternatives, metal oxide semiconductors have brought to attention as backplane materials for the next generation of flat panel displays. After the huge success and revolution of transparent electronics and with the worldwide interest in displays where metal oxide thin films have proved to be truly semiconductors, display backplanes have already gone commercial in a very short period of time, due to the huge investment of several high profile companies: SHARP, SAMSUNG, LG and BOE. These materials have demonstrated exceptional electronic performance as active semiconductor components and can be tuned for applications where high transparency/electrical conductivity is demanded. The new paradigm of transparent electronics has attracted much interest as a novel technical solution in the field of the next generation of consumer electronics. The ultimate goal of this "see-through" device is to realize an integrated system equipped with ubiquitous functions of information storage, image display and networking, which strongly demands an embeddable transparent array of non-volatile memory.

4:00 PM

(PACRIM-S19-008-2017) Recent Progress in Ceramic Scintillators for Nuclear Detection, Medical Imaging and Radiography (Invited)

M. R. Squillante[1]; C. Brecher[1]; M. Breen[1]; D. Chartier[1]; J. Glodo[1]; R. Shawgo[1]; Y. Wang[1]; K. S. Shah[1]; R. Hawrami*[1]

1. RMD, Inc, USA

Many high-tech applications require large transparent materials. Conventionally, these needs are met using single crystals grown from the melt. Ceramic processing, however, can provide a number of important benefits over single crystal growth, including lower cost, higher yield, and relaxed constraints on size and shape. The ceramic approach can produce material of higher purity with better control of composition, higher dopant levels, and greater uniformity. Ceramics are also generally more robust than single crystals toward thermal or mechanical shock. This article discusses recent progress at RMD on the fabrication of transparent ceramic scintillator materials used for nuclear detection, medical imaging and radiography. Materials studied include rare earth garnets and oxides.

4:30 PM

(PACRIM-S19-009-2017) Advanced IR Materials and Devices (Invited)

W. Kim*[1]; G. Villalobos[1]; C. Baker[1]; B. Shaw[1]; S. Bayya[1]; J. Frantz[1]; M. Hunt[1]; V. Nguyen[1]; L. Busse[1]; D. Boyd[1]; D. Gibson[1]; R. Gattass[1]; J. Myers[1]; I. Aggarwal[2]; J. Sanghera[1]

1. Naval Research Laboratory, Optical Science Division, USA
2. Sotera Defense Solutions, USA

We highlight our recent progress in the development of optical materials including transparent ceramics, crystal fibers, and chalcogenide glasses for IR applications. We have developed low loss spinel as an exit window aperture for HEL and space applications. We also report high optical transparency from a spinel ceramic fabricated by microwave sintering process. High efficiency laser oscillations from various rare-earth sesquioxides are also presented. In addition to solid state ceramic lasers, we show a fabrication of crystal fibers drawn from these high purity rare-earth sesquioxides ceramic feed by LHPG method. High gain from glass or crystal cladded crystal core fibers is reported. Antireflective surface structures were fabricated directly onto the surface of various substrates including transparent ceramics, single crystals, glasses, and fibers to show low reflection losses and high laser damage thresholds. Furthermore, these structures can be chemically modified to impart superhydrophobic character to the surface that is very important for various commercial and military applications. We review our recent research progress to develop chalcogenide glass fibers for applications in the mid- and long-wave IR wavelength region. Various applications of these high quality fibers, including multimode beam combiners, mid-infrared supercontinuum sources, fiber Bragg gratings, fiber bundles for IR imaging, and modal filters, are described.

5:00 PM

(PACRIM-S19-010-2017) Hybrid Ceramic/Polymer Phosphor Films for Solid State Lighting

H. Menkara*[1]

1. PhosphorTech, USA

A novel type of ceramic/polymer color conversion hybrid films will be discussed with a wide range of applicability to various LED components and fixtures. This technology can be used to easily produce various colors using existing blue, UV, and even white LEDs from direct die-level attachment to remote phosphor lamps. It eliminates the need for conventional ceramic powder handling, processing, dispensing, and enables unique spectral control wih a high degree of flexibility. Products can be customized for low, medium, and high power LED applications and can be manufactured using various polymers and substrate materials ranging from conventional plastics to high temperature glass and ceramics. High light extraction and overall optical gains have been demonstrated and LED light sources with ultra-high color rendering indices (CRI) have been achieved in both cool and warm white colors.

5:15 PM

(PACRIM-S19-011-2017) Scalable and formable tellurite-based transparent ceramics for near infrared applications

G. Delaizir*[1]; A. Bertrand[1]; M. Allix[2]; S. Chenu[1]; J. Carreaud[1]; P. Thomas[1]; J. Duclere[1]

1. SPCTS, UMR 7315 CNRS, France
2. CEMHTI, France

Innovative transparent tellurite polycrystalline ceramics are demonstrated to be simply elaborated by full and congruent crystallization of the $75TeO_2$-$12.5Bi_2O_3$-$12.5Nb_2O_5$ parent glass. The low temperature tellurite glass elaboration and its stability both enable the preparation of scalable tailor-shaped ceramics with high refractive index, transmission in the near infrared range up to 5.5 μm and promising mechanical/thermal properties. This proof of concept paves the way for new type of optical and photonic ceramics in the near infrared range.

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

Semiconductor

Room: Kohala 1
Session Chair: Elvira Fortunato, FCT-UNL

1:15 PM

(PACRIM-S20-001-2017) Development of low resistivity 4H-SiC crystals for power device application (Invited)

N. Ohtani*[1]

1. Kwansei Gakuin University, School of Science and Technology, Japan

In the last decade, significant progress in the quality improvement of silicon carbide (SiC) single crystals made the fabrication of high performance SiC power devices a reality. 100 and 150 mm diameter 4H-SiC epitaxial wafers with a low dislocation density have already been brought to market. However, widespread commercialization of SiC power devices is still hindered by technological issues related to SiC crystal growth, and thus it is abundantly clear that further successful development of SiC semiconductor technology relies on achieving an understanding of SiC crystal growth process and, based on it, improving the technologies of manufacturing large high-quality SiC crystals. In this presentation, I will talk about the stacking fault formation in heavily nitrogen-doped 4H-SiC crystals. By optimizing the growth conditions, 4H-SiC crystals with resistivities as low as 1–3 mWcm have been grown; however, they are not commercially available. This is due to structural instability of the crystals during high temperature treatment. The structural changes have been attributed to a 4H to 3C polytypic transformation that is induced by the formation and expansion of double layer Shockley-type stacking faults during high temperature treatment. I will review several important aspects regarding the stacking fault formation and discuss the formation mechanism in terms of the so-called quantum well action model.

1:45 PM

(PACRIM-S20-002-2017) Artificial photosynthesis anode electrode composed of nano particulate photocatalyst film in visible light responsive GaN-ZnO solid solution system (Invited)

Y. Imanaka*[1]; T. Anazawa[1]; T. Manabe[1]; H. Amada[1]; R. Ishikawa[2]; Y. Ikuhara[2]

1. Fujitsu Laboratories Ltd., Japan
2. University of Tokyo, Japan

Artificial photosynthesis technology known as Honda-Fujishima effect which produces oxygen and hydrogen or organic energy from sunlight, water, and carbon dioxide, is an ultimate energy and environmental technology. The key device for the higher efficiency of this reaction system is the anode electrode, generally composed of a photocatalyst formed on glass substrate with an electrically conductive FTO. To obtain the highly efficient electrode, the dense film composed of nano particulate visible light responsible photocatalyst having usually complicated multi-elements composition need to be deposited and adhered on the FTO. In this study, we discovered a method capable of controlling electronic structures of a film by controlling the aerosol-type nano particle deposition (NPD) condition and thereby forming films of materials with a smaller band gap than prepared raw material powder, and succeeded in extracting a higher current from the anode electrode. As a result, we confirmed that a current approximately 100 times larger than currents produced by conventional processes could be obtained using the same material. This effect can be expected not only from the materials discussed (GaN-ZnO) in this paper but also from any photocatalyst, particularly materials of solid solution compositions.

2:15 PM

(PACRIM-S20-003-2017) Vertical Bridgman Growth of High Purity Mg_2Si and Fabrication of IR Detector (Invited)

U. Haruhiko*[1]

1. Ibaraki University, Electrical & Electronic Eng., Japan

Anti-CaF_2 type semiconducting magnesium silicide, Mg_2Si is an interesting material for a Si-based infrared photo detector operated in the short wavelength infrared (SWIR, 0.9 – 2.5 um) and the mid wavelength infrared (MWIR) region, because it has an indirect band gap with the gap energy of $E_g = 0.61$ eV at room temperature, and the E_g can be controlled between 0.3 eV and 0.61 eV by making the $Mg_2Si_{1-x}Sn_x$ alloy compound. Richness and non-toxicity of the materials are also suitable for mass consumption. Recently, we have succeeded in growing the high purity Mg2Si bulk single crystal by the vertical Bridgman method and demonstrated the photoresponse below 2.1 um from the Mg_2Si pn-junction photodiodes. In this presentation, we will report the growth technique for obtaining the high purity Mg_2Si, results of the crystal characterizations and the performance of Mg_2Si pn-junction photodiodes.

2:45 PM

(PACRIM-S20-004-2017) Zinc Oxide Thin Films and Nanostructures for Biomedical Sensing Applications (Invited)

D. J. Rogers*[1]; F. Teherani[1]; P. Bove[1]; E. Sandana[1]

1. Nanovation, France

Zinc Oxide (ZnO) is a remarkable direct wide bandgap (Eg ~3.4eV) semiconductor material with a distinctive and highly tuneable property set. With Scopus recording over 8000 publications on ZnO in 2015 it has become one of the hottest research topics in materials science. Amongst the various strongpoints of ZnO is an excellent biocompatibility which has allowed it to become a platform for a huge range of biomedical applications. In particular, ZnO is emerging for biosensing (piezoelectric, electrochemical, optical or field effect transistor based transduction). This is because good electrical conductivity, chemical stability, a biomimetic nature, the potential for surface functionalisation and a high isoelectric point (which facilitates immobilization of biomolecules) make ZnO an attractive biosensor matrix. Due to their small dimensions, increased sensing surface and strong binding properties nanostructures offer faster responses and can achieve single-molecule detection. Ongoing trials should pave the way to commercialisation of implantable, miniature point-of-care biosensors compatible with CMOS/MEMS technology for wireless telemedicine. In this talk we will give an overview of this topic illustrated with some of our work in the domain.

3:15 PM

(PACRIM-S20-005-2017) High electromechanical coupling thick ScAlN piezoelectric films for ultrasonic generation in low frequency of 80MHz

K. Sano*[2]; R. Karasawa[2]; T. Yanagitani[1]

1. Waseda University, JST PRESTO, Japan
2. Waseda University, Advanced Science and Engineering, Japan

Large piezoelectricity in 43% Sc doped ScAlN thin film has been recently reported. The thickness extensional mode resonant frequency, where ultrasonic generation efficiency become large, is inversely proportional to the thickness of films. A Bulk ScAlN thick plates are attractive for the low frequency high power ultrasonic applications such as actuators and medical ultrasonics because ScAlN possess lower mechanical and dielectric losses compared with PZT. However, the thick ScAlN films has not been reported. In this study, 43 μm thick ScAlN films were grown on Ti electrode/silica grass substrate by the RF magnetron sputtering using ScAl alloy (Sc:43%). The growth rate was approximately 2.0 μm/h when RF power density of 3.3-5.5 W/cm^2. The electromechanical coupling coefficient k_t^2 was determined by comparing the experimental ultrasonic generation efficiency measured by a network analyzer and theoretical one simulated using equivalent circuit model. k_t^2 was determined to be 19% using the thickness extensional mode at 81 MHz which is extremely low compared to well-reported ScAlN thin films in the GHz ranges. In contrast to the low Tc of 360 °C in PZT, ScAlN can operate above 1000 °C. ScAlN thick films are promising for various acoustic device applications because they will be grown even on 6 inch wafer.

New Direction I

Room: Kohala 1
Session Chair: Yoshihiko Imanaka, Fujitsu Laboratories Ltd.

3:45 PM

(PACRIM-S20-006-2017) Giant Photovoltaic Effect of Ferroelectric Domain Walls in $BiFeO_3$ and $BaTiO_3$ (Invited)

Y. Noguchi*[1]; R. Inoue[2]; Y. Kitanaka[1]; M. Miyayama[1]

1. The University of Tokyo, Department of Applied Chemistry, Japan
2. Nihon University, School of Medicine, Japan

The photovoltaic (PV) effect in polar materials offers great potential for light-energy conversion that generates a voltage beyond the bandgap limit of present semiconductor-based solar cells. Ferroelectrics have received renewed attention because of the ability to deliver a high voltage in the presence of ferroelastic domain walls (DWs). In recent years, there has been considerable debate over the impact of the DWs on the PV effects, owing to lack of information on the bulk PV tensor of host ferroelectrics. In this study, we provide the first direct evidence of an unusually large PV response induced by ferroelastic DWs — termed 'DW'-PV effect. The precise estimation of the bulk PV tensor in single crystals of barium titanate enables us to quantify the giant PV effect driven by non-180-deg DWs. We show that the DW-PV effect arises from an effective electric field consisting of a potential step and a local PV component in the non-180-deg DW region. This work offers a starting point for further investigation into the DW-PV effect of alternative systems and opens a reliable route for enhancing the PV properties in ferroelectrics based on the engineering of domain structures in either bulk or thin-film form.

4:15 PM

(PACRIM-S20-007-2017) High pressure synthesis of a cubic perovskite $Sr_{1-x}Ba_xCoO_3$ showing giant magnetovolume effect (Invited)

S. Ishiwata*[1]

1. University of Tokyo and JST PRESTO, Japan

Perovskite oxides with unusually high valence 3d transition metal ions such as Fe^{4+} and Co^{4+} have been of great interest because of the unique magnetism inherent to the strong p-d hybridization. This is exemplified by the nontrivial ferromagnetism in Rh-doped $SrFeO_3$ and room-temperature ferromagnetism in $SrCoO_3$. However, search for novel functions in these oxides has been hampered by the difficulty in growing single crystals. In this talk, after the brief review on the unusually high valence perovskite oxides, we show our recent studies on novel perovskite $Sr_{1-x}Ba_xCoO_3$ prepared by high-pressure and chemical oxidation technique. By magnetization measurements on single-crystalline samples, we established the phase diagram, where a novel helimagnetic phase appears at x above 0.35. To discuss this result from the viewpoint of the lattice change, we applied pressure on the heilmagnetic compound and found the transition to the ferromagnetic state within 1 GPa. This novel pressure effect can be regarded as a giant magnetovolume effect. Based on the transport measurements and first-principles calculations, the results will be discussed in terms of the competing magnetic order in the Co^{4+}-O lattice.

4:45 PM

(PACRIM-S20-009-2017) Synchrotron high-energy x-ray study of formation and transformation of crystalline materials in complex sample environments

Y. Ren*[1]

1. Argonne National Lab, X-ray Science Division, USA

The availability of high-brilliance high-energy x-rays generated at the APS has significantly advanced the field of materials research, especially for in-situ/operando studies of applied materials in realistic conditions. In this talk, we will briefly introduce synchrotron high-energy x-ray diffraction techniques. We will emphasize the uniqueness and importance of synchrotron high-energy x-rays in structural characterization of crystalline materials under various conditions. Technical details and methodologies and scientific research opportunities with synchrotron high-energy x-rays will be discussed, including real-time monitoring material formation during synthesis, phase transition induced by temperature, pressure, electric and magnetic fields and other external stimuli. We will also present some recent results on the in-situ study of piezoelectric/ferroelectric crystals and ceramics and other crystalline materials in complex sample environments.

PACRIM Symposium 25: Ceramics for Next Generation Nuclear Energy

Hierarchical and Porous Materials for Waste Form Applications

Room: Kona 1
Session Chairs: Krista Carlson, University of Utah; Jake Amoroso, Savannah River National Laboratory

1:15 PM

(PACRIM-S25-001-2017) Multi-Scale Modeling for Hierarchical Waste Form Materials (Invited)

T. M. Besmann*[1]; M. Noordhoek[1]; C. Henager[2]; S. Hu[2]; Y. Li[2]; S. R. Phillpot[3]

1. University of South Carolina, Nuclear Engineering, USA
2. Pacific Northwest National Lab, USA
3. University of Florida, USA

Under a new DOE Energy Frontier Research Center, the Center for Hierarchical Waste Form Materials, novel hierarchical structures are being developed as potential precursors to nuclear waste form systems. To aid in design and to understand behavior these structures are being modeled across scales using existing and developmental approaches. Density functional theory calculations are being used to analyze the thermodynamics of systems such as nanoparticle uranium-gold alloy formation. Understanding the process of alloying includes characterizing the kinetics of uranium diffusion in gold and gold diffusion in uranium. The thermochemical representations of complex forms such as salt inclusion phases are being developed using topological and volume-based approaches. Based on the thermodynamic and kinetic properties from atomistic simulations and thermodynamic calculations, mesoscale phase-field models of nanoparticles and other forms are being developed and applied to determine phase stability and microstructure evolution pathways. This work was supported as part of the Center for Hierarchical Waste Form Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-SC0016574.

1:45 PM

(PACRIM-S25-002-2017) Real Time Evaluation for Nuclear Waste Forms Using In Situ Synchrotron Methods at National Synchrotron Light Source (NSLS) II (Invited)

S. K. Gill*[1]

1. Brookhaven National Laboratory, Nuclear Science and Technology, USA

Currently at Center for Hierarchical Waste Form Materials, Energy Frontier Research Center our focus is to combine experiment, characterization and modeling to develop hierarchical materials that effectively immobilize nuclear waste elements. Advanced synchrotron based characterization methods can play a pivotal role in development of hierarchical materials for waste immobilization and sequestration applications. The world-leading intensity the NSLS II at BNL, coupled with advanced sample chambers, presents an exceptional opportunity to understand the structural changes and chemical processes involved in the degradation of nuclear waste materials in extreme environments. Utilization of synchrotron-based X-ray diffraction for in-situ structural characterization of uranium based Salt Inclusion Materials (SIMs) to understand the role of salt precursors (halide and oxide) on the coordination structure of SIMs for nuclear waste form applications will be discussed. In addition combining high resolution synchrotron X-ray diffraction with DFT calculations to predict selective adsorption mechanism of inert gases in Ni-based Metal Organic Framework materials for the separation of environmentally hazardous gases from nuclear reprocessing applications will be discussed.

2:15 PM

(PACRIM-S25-003-2017) Hierarchical Waste Forms for the Immobilization of High-Level Waste Salt

K. Carlson*[1]; M. Simpson[1]; M. Wasnik[1]

1. University of Utah, Metallurgical Engineering, USA

Glass-bonded sodalite (GBS) is the baseline waste form for the immobilization of salt waste generated from electrorefining EBR-II spent fuel. However, this waste form is only capable of holding up to 7.5 mass% salt, equating to a metal loading of only 3.2 wt%. The resulting high waste processing and disposal costs for completion of the EBR-II spent fuel treatment project would discourage commercial use of electrochemical processing for closing the commercial nuclear fuel cycle. Since over half of the mass of this electrorefiner salt is chlorine in the form of non-radioactive chloride ions, we have devised a method for dechlorination to assist in waste volume reduction. Initial results have demonstrated that over 50% dechlorination was achieved via exchange of the metal ions into ultrastable H-Y (USHY) zeolite. As the dechlorinated zeolite will be in granular form, we have examined various binder glasses for immobilization. A low temperature-sintering process has been investigated as an alternative to high-temperature vitrification to minimize processing costs and fission product volatilization. In addition to increased processability, encapsulation of the zeolite also provides hierarchical protection against the release of fission products in a repository environment.

2:30 PM

(PACRIM-S25-004-2017) Salt-Inclusion Materials: A Potential Novel Hierarchical Wasteform

H. zur Loye*[1]; G. Morrison[1]

1. University of South Carolina, Chemistry and Biochemistry, USA

A practical working definition of a hierarchical structure is that of a structural motif contained within a larger structure or framework. Salt Inclusion Materials (SIMs) are a subset of a unique family of crystalline hierarchical structure types that consist of a more covalent metal oxide framework containing voids filled by an ionic salt lattice. SIMs are noteworthy because as a "stuffed" porous material, this type of hierarchical material is of fundamental interest in the development of new waste forms for nuclear waste storage. These materials are of the general formula $[A_mB_nX][(UO_2)_p(M_qO_r)_t]$ where $[(UO_2)_p(Si_qO_r)t]$ is the framework consisting of uranyl, UO_2^{2+}, and Si_qO_r units, where B_nX is the salt-inclusion and A are alkali or alkaline earth cations that are not part of the salt-inclusion. The presentation will focus on the synthesis, crystal growth, structures, and potential use of SIMs, including $[Cs_3F][(UO_2)(Si_4O_{10})]$, $[Cs_2Cs_5F][(UO_2)_2(Si_6O_{17})]$, $[Cs_9Cs_6Cl][(UO_2)_7(Si_6O_{17})_2(Si_4O_{12})]$, and $[Cs_2Cs_5F][(UO_2)_3(Si_2O_7)_2]$, with special emphasis on the overall crystal chemistry of these phases.

2:45 PM

(PACRIM-S25-005-2017) The effect of pore diameter in the arrangement of organic species grafted onto silica surfaces : application to solid phase extraction process

A. Grandjean*[1]; A. Charlot[1]; A. Leydier[1]; F. Cuer[2]

1. CEA, DTCD, France
2. CEA, DRCP, France

Mesoporous functionalized silica are particularly interesting in the development of solid phase extraction processes and the incorporation of heavy metal in a solid. The grafting of organic compounds into mesoporous silica materials allows to use them for the selective removal of heavy-metal from aqueous solution, by a solid phase extraction process. Here the effect of pore size on the post-grafting of silicas is studied, with a particular focus on the extraction of uranium from sulfuric media at low pH. The characterization of the solid during each synthesis step provides evidence that the structure of the pores influences the arrangement of the organic molecules

therein. Several types of experimental data show that there is a lower limit of around 4 nm below which the functionalization becomes heterogeneous because of the steric effect of the grafted molecules. In contrast, functionalization leads to the self-assembly of organic monolayers when the pores are between 5 and 20 nm in diameter, while a dense organic multilayer forms in larger pores. The uranium extraction capacity of these materials depends directly on the ability of the organic molecules to re-arrange themselves into the equatorial plane of the uranyl ions.

Aging and Degradation Mechanisms and Behavior of Nuclear Waste Form Materials

Room: Kona 1
Session Chairs: Ming Tang, Los Alamos National Lab;
Jake Amoroso, Savannah River National Laboratory

3:30 PM

(PACRIM-S25-006-2017) Long-Term Performance of Nuclear Waste Forms: Current Status and Future Perspective (Invited)

R. C. Ewing*[1]

1. Stanford University, Geological Sciences, USA

Over the past forty-years, there has been a considerable amount of research on nuclear waste forms of all types - glass, crystalline ceramics, composite ceramics and spent fuel, as well as a number of “novel” materials. I will briefly survey the progress that has been made in developing nuclear waste forms and in demonstrating their performance over the very extended periods that are characteristic of geologic disposal. One of the very unique aspects of waste form research is the need to develop a means of predicting materials behavior over hundreds of thousands of years. There are a number of approaches: experimental, computational and the use of natural systems that must converge in order to build confidence in these long-term predictions. More recently, there have been discussions of matching the waste form to the characteristics of the waste stream or of selecting waste forms whose durability is compatible with the geochemical and hydrologic conditions in the geologic repository. In both cases, the nuclear waste form brings added value to safety of the back-end of the nuclear fuel cycle.

4:00 PM

(PACRIM-S25-007-2017) Radionuclide Incorporation and Long Term Performance of Apatite Waste Form

J. Wang*[1]

1. Louisiana State University, USA

Iodine-129 is a volatile radionuclide formed as a product of nuclear fission. Due to its long half-life and high mobility in environment, it is imperative to develop suitable waste forms which are durable to retain I-129 in geological setting. Vanado-iodoapatite samples were synthesized using SPS method. The performance was evaluated with Accelerated Leach Test (ALT), a semi-dynamic leaching method, to investigate the iodine leaching behavior. The experiments were carried out in cap-sealed Teflon vessels at 90 ± 0.5 °C. Apatite samples ($Pb_{9.85}(VO_4)_6I_{1.7}$) were placed in deionized water. The leachates were collected and analyzed using ICP-MS. The results show that Pb and V were released stoichiometrically with a molar ratio Pb/V of 1.6, consistent with their stoichiometric ratio 9.8/6. However, the released iodine is significantly higher than its corresponding stoichiometric value (I/V) 1.7/6. In addition, at neutral pH with DI water, iodine leaching rate decreases with time, while at slightly acidic condition, the leaching rate becomes a constant. The estimated long-term leach rate of iodine is ~2 mg/m/day, significantly lower than a number of candidate iodine waste forms. The leaching behaviors show that the release of iodine is controlled by diffusion and dissolution processes. Our current study demonstrates the potential of vanado-iodoapatite as a waste form candidate to immobilize iodine-129.

4:15 PM

(PACRIM-S25-008-2017) Radiation Tolerance Study of Synthetic Hollandite-type Materials: $Ba_{1.0}Cs_{0.3}A_{2.3}Ti_{5.7}O_{16}$ (A = Cr, Fe, Al)

M. Tang*[1]; P. Tumurugoti[2]; B. Clark[2]; S. K. Sundaram[2]; J. Amoroso[3]; Y. Wang[1]; Y. Jiang[4]

1. Los Alamos National Lab, USA
2. Alfred University, USA
3. Savannah River National Lab, USA
4. University of New Mexico, USA

Hollandite structures have been widely studied as a promising host for the incorporation of radioactive Cs in crystalline ceramic waste forms. Crystal structure can be either monoclinic (rhombus), I2/m, or tetragonal (square), I4/m depending on the ratio of the average ionic radius of the A-site cations to that of the B-site cations. Radiation tolerance of synthetic hollandite-type compounds described generally as $Ba_{1.0}Cs_{0.3}A_{2.3}Ti_{5.7}O_{16}$ (A = Cr, Fe, Al) was evaluated by heavy ion (Kr) and light ion (He) irradiations. Single phase compounds possess tetragonal structure with space group I4/m. Ion irradiation damage effects were examined using grazing incidence X-ray diffraction (GIXRD) and transmission electron microscopy (TEM). GIXRD and TEM observations revealed that 600 keV Kr and 200 keV He ion irradiations could induce amorphization at room temperature, and a phase transformation from tetragonal to monoclinic was observed in He irradiated hollandites. The hollandite phase exhibited similar amorphization susceptibility under Kr ion irradiation when incorporated into a multiphase system. Temperature dependence of critical amorphization dose of single phase hollandite compounds was obtained by in situ 1 MeV Kr ion irradiation. The critical amorphization temperature Tc for hollandite was deduced by the experimentally determined critical amorphization fluence.

4:30 PM

(PACRIM-S25-009-2017) Vacancy enhanced recovery and phase segregation: The conflicting role of A-site deficiency in the radiation damage response of perovskite ceramics

S. M. Lawson*[1]; A. S. Gandy[1]; K. Whittle[2]; N. C. Hyatt[1]

1. University of Sheffield, Materials Science and Engineering, United Kingdom
2. University of Liverpool, School of Engineering, United Kingdom

The radiation damage response of the A-site deficient $Ca_{1-x}La_{2x/3}TiO_3$ perovskite solid-solution has been characterised as a model system for inert matrix nuclear fuels and actinide baring nuclear wasteforms. $Ca_{1-x}La_{2x/3}TiO_3$ samples were synthesised by solid-state synthesis, damage induced using 1 MeV Kr^+ and 5 MeV Au^+ ion irradiation, to fluences of $1x10^{15}$ ions cm^{-2} and $5x10^{14}$ ions cm^{-2}, respectively, and characterised using cross-sectional transmission electron microscopy (XTEM) and glancing-angle X-ray diffraction (GAXRD). XTEM analysis of Kr^+ irradiated $CaTiO_3$ indicates the formation of ‘crystallites’ among amorphous material, with a saturated volume swelling of 4.71% in $CaTiO_3$ calculated by GAXRD. Electron energy loss spectroscopy suggests this is the result of Ti(IV$\rightarrow$III) reduction. GAXRD and XTEM show full amorphisation in Kr^+ and Au^+ irradiated $Ca_{0.1}La_{0.6}TiO_3$, likely due to decreased tolerance for disorder through A-site vacancy ordering. $Ca_{0.8}La_{0.13}TiO_3$ remains highly crystalline by GAXRD and XTEM after Kr^+ and Au^+ irradiation, providing evidence of vacancy enhanced damage recovery for low La^{3+} baring phases. Furthermore, radiation induced phase segregation in $Ca_{0.8}La_{0.13}TiO_3$, $Ca_{0.5}La_{0.33}TiO_3$ and $Ca_{0.4}La_{0.4}TiO_3$ to the $CaTiO_3$/$Ca_{0.1}La_{0.6}TiO_3$ end members is observed by GAXRD through the advent of end-member native reflections.

4:45 PM

(PACRIM-S25-010-2017) Helium Behavior in Pyrochlore Type Nuclear Waste Form Materials

C. A. Taylor*[1]; M. K. Patel[2]; J. A. Aguiar[3]; X. Xu[4]; Y. Zhang[4]; M. L. Crespillo[2]; J. Wen[5]; H. Xue[2]; Y. Wang[6]; W. J. Weber[2]; K. Hattar[1]

1. Sandia National Laboratories, USA
2. University of Tennessee, USA
3. Idaho National Laboratory, USA
4. Oak Ridge National Laboratory, USA
5. Lanzhou University, China
6. Los Alamos National Laboratory, USA

Pyrochlores and other complex ceramics have been considered as potential candidates for long-term radionuclide immobilization because they offer higher chemical durability than vitreous waste forms. This work considers two pyrochlores: $Gd_2Ti_2O_7$, which amorphizes under irradiation at 0.2 dpa, and $Gd_2Zr_2O_7$, which undergoes a pyrochlore to defect-fluorite phase transformation under irradiation at 0.4 dpa. Ion beam irradiations were utilized as an accelerated aging method for simulating the long-term effects of alpha-decay in a waste form, including radiation damage and He accumulation. Transmission electron microscopy (TEM) was used to characterize He bubbles. Initial investigations indicated that bubbles greater than 1 nm in diameter would form after around 6 at.% He in $Gd_2Ti_2O_7$ and after around 4.6 at.% He in $Gd_2Zr_2O_7$. Bulk ion irradiations were found to produce an artificial bubble microstructure, not expected to occur in real waste, in $Gd_2Zr_2O_7$. He trapping was experimentally explored using thermal desorption spectroscopy and found to differ in both pyrochlores depending on the He implantation energy. The ex-situ characterization will be complimented with the results from in-situ ion irradiation TEM experiments that are currently in progress. In summary, this talk will provide an overview of He behavior expected in pyrochlores over waste form timescales.

5:00 PM

(PACRIM-S25-011-2017) The way forward in addressing the radiation damage in nuclear waste glass matrices

A. Mir*[1]; J. Hinks[1]; S. Donnelly[1]; S. Peuget[2]

1. University of Huddersfield, Electron Microscopy and materials Analysis, United Kingdom
2. CEA Marcoule, France

The self-irradiation damage in nuclear waste matrices has usually been simulated using actinide doping and external single-beam electron and ion irradiations. Despite being most realistic, it is impossible to discern the irradiation effects of individual projectiles on pristine and pre-damaged regions of the matrix from actinide doping studies due to a cumulative damage formation from different projectiles. Similarly, single-beam irradiations do not correctly simulate the actual multi-irradiation problem of the waste matrices. Recently, the focus has shifted to multi-beam sequential and simultaneous irradiation of simple and complex nuclear waste glasses. It has been shown that multi-particle irradiations when correctly employed can better simulate the actual irradiation problem. The research has also highlighted a significant difference in response of the surfaces and bulk of the material-thereby cautioning about the simple extrapolations of material response from surfaces to the bulk. Despite the progress made, a number of parameters for proper execution of the multi-beam irradiation experiments are poorly understood and unfortunately ignored. The aim of this presentation is to highlight the importance of the multi-beam irradiations and bring to light the often-ignored-fundamental-questions that are critical in moving forward to better understand the long-term response of the waste matrices

PACRIM Symposium 27: Ceramics for Enabling Environmental Protection: Clean Air and Water

Gas Filtration and Liquid Purification

Room: Queen's 6
Session Chair: Michael Lance, Oak Ridge National Lab

1:15 PM

(PACRIM-S27-001-2017) Decomposition of 2-naphthol in water by TiO_2 modified with MnO_x and CeO_y (Invited)

A. Nakajima*[1]; M. Shiohara[1]; D. Tanaka[1]; Y. Qi[1]; T. Isobe[1]; S. Matsushita[1]

1. Tokyo Institute of Technology, Materials Science and Engineering, Japan

MnO_x and CeO_y were modified onto TiO_2 (rutile) surface by chemisorption calcination cycle processing. The modification of MnO_x and CeO_y clusters provided decomposition activity on 2-naphthol in water in the dark. It was increased by visible light illumination. The decomposition activity in the dark was dependent on the reaction temperature. The synergy effect in the co-modification of these two clusters was inferred from the reaction constants. Although the activity in the dark decreased gradually through repeated use and resultant reduction of MnO_x and CeO_y clusters, it recovered by UV illumination and subsequent heating at 80°C in ambient air.

1:45 PM

(PACRIM-S27-002-2017) Cellular Supports for Catalytic Reactors: Zeolite Containing Hierarchical Composites as Catalysts (Invited)

W. Schwieger*[1]; A. Machoke[1]; T. Weißenberger[1]; A. Inayat[1]; H. Freund[1]

1. Friedrich-Alexander-University Erlangen-Neurnberg, Chemical Reaction Engineering, Germany

Structured monolithic reactors can be considered as a highly open porous system in which the surfaces can be utilized as carrier for active components useful as a catalyst in a desired reaction. Such a functionalization of the monolith surface, ceramic, glass or metallic based, with an additional porous material of a different pore size regime results in a hierarchically organized system. In this regard, the use of appropriate materials such as microporous zeolites allows for the development of a hierarchical organization of the porosity on either two (micro-/macro) or three (micro-/meso-/macro) different porosity levels. Thus, hierarchically zeolitic composites can benefit in their applications from both, the zeolitic function (e.g. separation, activity) and the function of the support. This contribution will focus on the trends and advances in the field of the preparation and properties of hierarchical zeolitic composites. Typical examples will be summarized on the basis of the literature and own results. A special focus will be on design methods to shorten the diffusion pathway in the zeolites and their resulting effect on their application properties Finally, we will demonstrate both the advantage of using hierarchical zeolites itself and the effect of supported zeolites on SiSiC-foams and periodic open cellular structures (POCS) in different catalytic reaction.

2:15 PM

(PACRIM-S27-003-2017) Porous Silicon Carbide Ceramics as Material for Diesel Particulate Filters (Invited)

J. Adler*[1]; U. Petasch[1]; H. Heymer[1]

1. Fraunhofer IKTS, Nonoxide Ceramics, Germany

Beside some unsuccessful trials with cordierite ceramics in the 1980s, the first commercially successful diesel particular filters (DPF) for cars were made of recrystallized silicon carbide (SiC) ceramics, introduced by Ibiden/Peugeot SA in 2000. Nowadays SiC ceramics have been state-of-the-art for applications in diesel particulate

filters, especially for cars but in light and heavy duty application, too. Silicon carbide ceramics with different particle bondings and microstructures are well known for very different industrial applications. Some of these materials are inherently porous, others were originally developed as fully dense materials. However, all of these materials can be adjusted to a structure with controlled pore size and pore volume for trapping diesel particulates. In detail, the vast majority of DPF is made of RSiC and Si bonded SiC, but in principle nearly every type of SiC ceramics has been tried, and in some cases established commercially, too. Starting with a short overview and comparison of materials for DPF, the presentation describes SiC-DPF materials in detail, explaining their special advantages and drawbacks regarding properties and manufacturing.

2:45 PM

(PACRIM-S27-004-2017) Synthesis of Hierarchically Porous Zeolite scaffolds by Freeze casting

H. Wang*[1]; H. Chang[1]; P. Chen[1]

1. National Tsing Hua University, Material Science and Engineering, Taiwan

Carbon capture has become a critical issue recently and absorbent for CO_2 like zeolite 13X is also attracting much attention. Aqueous suspension of zeolite 13X powder and inorganic binders is prepared as slurry. The hierarchically macro/micro porous structure is further created by freeze casting. These unidirectional channels give rise to higher permeability and enhance working capacity. The microstructure is observed by SEM and pore size is measured by mercury intrusion. Water vapor bath under 80°C contribute to crystalline water in bentonite to assist sintering. Sodium fluoride provides cations that serve as fluxing agent as well as lead to alkaline condition to maintain the colloidal stability. Proper thermal treatment ensures the stability of its mechanical property without destroying the specific crystal structure of zeolite. Gas adsorption properties are measured by thermogravimetric analysis (TGA) and column test. In summary, freeze casted zeolite scaffolds with hierarchically porous structure can improve volumetric efficiency and reduce cycle time.

3:00 PM

(PACRIM-S27-005-2017) Understanding the Interfacial Structure and Composition in Oxide-Supported Metal Catalysts for Low-Temperature CO Oxidation

R. Wang*[1]

1. The University of Alabama, Metallurgical and Materials Engineering, USA

The widely employed cerium based oxide three-way catalysts drastically reduce many of the critical pollutants (e.g., CO, NO_x, and hydrocarbons) in automotive traffic. The nearly unsurpassed performance of the cerium oxide redox system is, however, limited to rather high temperatures (>600ºC), which adversely effect the fuel efficiency of the engine-exhaust system. During cold start conditions, this is especially problematic and provides the primary impetus for the development of lower temperature catalysts. Surfaces play a crucial role for heterogeneous catalytic applications involving rare-earth oxides as the active species. The control of the crystal morphology presents itself as one of the major obstacles towards the development of more low-temperature active CeO_2 based catalysts. In this presentation, we will discuss our recent progress of shape/size controlled synthesis of CeO_2 and the interplay of metal catalyst and crystal facets of CeO_2, aiming at understanding atomic level interfacial structure and composition in active oxide-supported metals catalysts for low-temperature CO oxidation.

3:15 PM

(PACRIM-S27-006-2017) Optimization of cost-effective SiC based membrane for microfiltration applications

I. Song*[1]; S. Bukhari[2]; J. Ha[1]; J. Lee[1]

1. Korea Institute of Materials Science, Republic of Korea
2. Korea University of Science & Technology, Republic of Korea

Ceramic membranes can be applied under extreme operating conditions such as low pH, high pressure and high temperature. Especially, the inherent limitations of conventional polymer membranes can be overcome by adopting ceramic membranes simply to the existing water treatment systems. Moreover, there are a lot of potential applications of ceramic membranes such as distillation, adsorption and extraction in various industrial areas. Therefore, the ceramic membrane technology is not a mere ceramic processing technology, but a highly influential technology to the overall environment technology. In particular SiC has excellent mechanical properties and also has excellent properties related to membrane performance. However, high processing temperature increases cost of SiC products and thus limit's its use. In this study, oxidation bonding technique was used to fabricate cost-effective SiC microfiltration membrane at low temperature. The oxidation behavior at different thermal treatments was related with pore morphology and ultimately the membrane permeability. We have found that the membrane made by coating of oxidation bonded SiC layer over clay-bonded SiC support, sintered at 1000-1100ºC could make a defect-free microfiltration membrane with pure water permeability above 700 LMH per bar. The membrane has narrow pore size distribution with average pore size about 0.1 μm.

Novel Materials

Room: Queen's 6
Session Chair: Michael Lance, Oak Ridge National Lab

3:45 PM

(PACRIM-S27-007-2017) The Aqueous Corrosion Response of Ti(C,N)-Ni_3Al Cermets With Various Reaction-Formed Binder Contents (Invited)

Z. Memarrashidi[1]; K. P. Plucknett*[1]

1. Dalhousie University, Mechanical Engineering, Canada

In the current work the corrosion mechanisms of Ti(C,N) based cermets are analysed in a 3.5 wt.% NaCl aqueous solution. Cermets were prepared with 20 or 30 vol.% of in-situ reaction-formed Ni_3Al metal binder. The assessment of corrosion involved a variety of electrochemical measurements, including open circuit potential, potentiodynamic polarisation and cyclic polarisation, together with systematic analysis of the post-corrosion solution chemistries using inductively coupled plasma optical emission spectroscopy. The corrosion potential and current density were determined, following Tafel extrapolation, allowing estimation of the corrosion rates. It is demonstrated that the main corrosion mechanism for this type of cermet is mainly dissolution of the metallic phase during oxidation attack, and thus this response increases with the amount of binder in the cermet. It was also observed that addition of N content into the ceramic phase is beneficial to the corrosion characteristic of TiC based cermets, through significant refinement in the grain size of the hard phase.

4:15 PM

(PACRIM-S27-008-2017) Preparation and photocatalytic activity of Mo-doped Ti-HAp

N. Jiraborvornpongsa*[1]; T. Isobe[1]; S. Matsushita[1]; M. Wakamura[2]; A. Nakajima[1]

1. Tokyo Institute of Technology, Materials Science and Engineering, Japan
2. Fujitsu Laboratories Ltd., Environmental Technology Laboratory, Japan

To enhance photocatalytic activity under UV irradiation of titanium-doped hydroxyapatite (Ti-HAp), Ti-HAp powders were soaked with aqueous $CaMoO_4$ solution, follow by calcination at 500°C in ambient air for 1 h. This procedure was repeated several times. Then, UV-light photocatalytic activity of the doped powders was evaluated by the decomposition of gaseous 2-propanol (IPA). The crystal structure, light absorption and specific surface area of the doped powder were almost identical. The CO_2 generation rate of the doped powders was increased up to about 10 times compare with pure Ti-HAp. XPS results revealed that the Mo concentration was increased whereas the P concentration was decreased. From XRD pattern, the lattice volume of the doped powder was increased. These results indicated that MoO_4^{2-} was doped by substitution of PO_4^{3-} site in Ti-HAp structure that provided higher photocatalytic activity.

4:30 PM

(PACRIM-S27-009-2017) Highly Efficient, Visible-Light-Activated Photocatalysts with Post-illumination "Memory" Effect

Q. Li*[1]

1. Institute of Metal Research, Chinese Academy of Sciences, Shenyang National Laboratory for Materials Science, China

Highly efficient, visible-light-activated photocatalysts with post-illumination "memory" effect were recently developed in our work. This interesting post-illumination "memory" effect was firstly found by us on palladium oxide-modified, nitrogen-doped TiO_2 (TiON/PdO). Clear evidences of charge flow to/from PdO nanoparticles on the visible light photocatalytic TiON matrix were obtained under visible light illumination and after the illumination was shut off, respectively. The photoelectron flow to PdO nanoparticles enhanced photocatalytic disinfection efficiency under visible light illumination by the separation of electron and hole pair, while the discharging of PdO nanoparticles following the turn-off of the illumination created the interesting photocatalytic "memory" effect as demonstrated by its bacterial disinfection in dark. Further work demonstrated that the photocatalytic "memory" effect was not limited to noble metal modification. It may be possessed by any photocatalyst system, if in which photo-excited electrons could transfer from the light absorber component to the decoration component while the decoration component could trap and release them. Thus, the material cost could be largely reduced by removing noble metal components, beneficial for their potential applications.

4:45 PM

(PACRIM-S27-010-2017) 3D-macro-cellular SiC-based structures for ignition and combustion applications

N. Travitzky*[1]; P. Rambacher[2]; Z. Fu[1]; P. Greil[1]

1. University of Erlangen-Nuremberg, Materials Science, Germany
2. University of Applied Sciences Nuremberg, Department of Mechanical Engineering, Germany

A new electrically heated ignition element, which gets integrated in a three dimensional macro-cellular SiSiC reactor structure will be present. The fabrication of combined ignition and combustion reactors for flameless, very clean and stable burner applications requires innovative processing techniques and enhanced material systems. Three-dimensional printing (3DP) permits the production of regular reaction bonded silicon infiltrated silicon carbide (RB-SiSiC) structures with constant strut thickness. Due to high stability in a regular lattice and the controlled current flow paths, the ignition element could be directly integrated in a three dimensional macro-cellular SiC-based structures of combustion reactors. To get a controlled temperature distribution on the ignition element it was necessary to control the current density distribution in the three-dimensional macro-cellular reactor structure. The designed macro-cellular lattice structures with high porosity were shaped by indirect 3DP of a SiC powder mixed with a dextrin binder which also served as a carbon precursor. Pyrolysis of the stabilized printed parts at 1000 °C for 2 h in N_2 atmosphere led to the formation of the green 3D-macro-cellular structures with a strut porosity of ~52 %. Pressureless infiltration of silicon melt at 1500 °C in vacuum for 2 h driven by capillary suction finally resulted in dense struts of SiSiC structures.

5:00 PM

(PACRIM-S27-011-2017) Sorption of Cs^+ on Titania Nanotube Synthesized by Solution Method

T. Goto*[1]; S. Cho[1]; T. Sekino[1]

1. Osaka University, The Institute of Scientific and Industrial Research, Japan

The contamination to groundwater and soils of nuclear wastes from nuclear power plant is serious problem for environment fields. Many researchers has been attempted the purification of using various types of sorbent materials. Among them, hydrous titanium dioxide are expected as candidate of sorbents of radionuclides. In this study, we investigated the Cs^+ sorption capacity of titania nanotubes (TNTs), which was one-dimensional nanostructured material, as sorbent for environmental remediation of radionuclides. TNT was prepared based on the reference of solution method of Kasuga et al. For sorption test, aqueous Cs^+ solutions of 0.2-4.0 mM were prepared using cesium chloride (CsCl) without pH adjustment. TNT powders were shaken in CsCl solution with various concentration at 25°C up to 72 h. To compare the sorption density of Cs^+, chemical reagent of type X zeolite was also prepared in this test. From the results of sorption test, the sorption density of Cs^+ per gram of TNT was lower than that of zeolite. In contrast, comparing the sorption density per surface area of sorbents, the density of TNT was larger than that of zeolite. This results imply us that the Cs^+ was intercalated in layer structure of TNT crystal.

5:15 PM

(PACRIM-S27-012-2017) Synthesis of CeO_2 hollow microspheres with oxidase-like activity and its application in catalytic degradation of p-nitrophenol

H. Zhou[1]; K. Li[1]; C. Li*[1]

1. Zhengzhou University of Aeronautics, China

CeO_2 hollow microspheres were synthesized by a template-free hydrothermal method. X-ray diffraction(XRD), scanning electron microscopy(SEM), and nitrogen adsorption–desorption measurements were used to characterize the products. These CeO_2 hollow microspheres had been proved to possess oxidase-like activity in the oxidation of dyes, which can catalyze oxidation of the peroxidase substrate 3,3',5,5'-tetramethylbenzidine (TMB) by air to form a blue color in aqueous solution. The properties of the catalytic degradation of the organic pollutants p-nitrophenol by CeO_2 hollow microsphere material were studied. It was observed that the degradation efficiency of 15 $mg.L^{-1}$ p-nitrophenol was above 75% over CeO_2 dosage 40 mg at pH 4.8 in 4 hour.

5:30 PM

(PACRIM-S27-013-2017) Ion Conducting Solid Electrolytes for Energy Conversion, Synthesis and Grid Storage

S. Balagopal*[1]; F. Garzon[2]; C. Kreller[3]

1. Ceramatec, Inc., USA
2. University of New Mexico, USA
3. Los Alamos National Lab, USA

Electrochemical process to synthesize ammonia for massive energy storage. Ammonia is carbon-free, has a high energy density, >4kW/l,

which is easily stored in low cost tanks at the GW-hr level, and can be back converted to electricity using turbines or fuel cells at high efficiency. Key is use of innovative ion conducting solid-electrolyte which operates in the range of 200-300°C. The electrochemical production of this useful chemical opens the novel possibility of linking grid-scale energy storage with the chemical industry. This technology would enable massive energy storage in the form of liquid ammonia to use renewable energy resources by converting intermittent electricity into chemical fuel that is easily stored and back converted into electricity.

PACRIM Symposium 28: Advanced Materials and Technologies for Electrochemical Energy Storage Systems

Solid State Batteries

Room: Queen's 5
Session Chair: Palani Balaya, National University of Singapore

1:15 PM

(PACRIM-S28-001-2017) The Road to Solid State Batteries for Vehicular Applications (Invited)

M. Doeff*[1]

1. Lawrence Berkeley National Laboratory, Energy Storage and Distributed Resources, USA

Recent reports of explosions involving lithium-ion batteries in cell phones have heightened concerns about their safety. For this reason, the battery community is increasingly interested in developing all solid-state lithium batteries, particularly for vehicular applications. The performance requirements for such batteries are particularly stringent, particularly the need for high energy density and robust cycling. This talk will cover the challenges associated with designing these devices for vehicle applications, drawing upon the speaker's own research on ceramic electrolytes.

1:45 PM

(PACRIM-S28-002-2017) Interfacial Control of All Solid State Battery with Li Metal Anode, LLZAl Electrolyte and $LiMO_2$ Cathode (Invited)

K. Kanamura*[1]

1. Tokyo Metropolitan University, Graduate School of Urban Environmental Sciences, Japan

All solid state battery with Li metal anode, $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (LLZ-Al) and $LiCoO_2$ (LCO) or $LiNi_xMn_yCo_zO_2$ (LNMC) cathode was fabricated by using aero-sol deposition process. LLZ-Al pellet with 300 mm thickness was prepared by using standard ceramic process. Aero-sol deposition was carried out to prepare cathode layer of LCO or LNMC with Li_3BOO_3 additive. Li_3BO_3 improved the interface between cathode layer and LLZ-Al electrolyte. The electrochemical impedance spectroscopy and discharge and charge curves at constant current exhibited a reduction of interfacial resistance. In addition, the interface between Li metal and LLZ-Al was also modified to reduce the interfacial resistance. In this study, a gold interlayer was employed to form a good contact between Li metal and LLZ-Al electrolyte. The gold interlay was deposited on LLZ-Al pellet by DC-sputtering process. The thickness of the gold layer was 50 nm. Li metal was attached to the gold interlayer on LLZ-Al pellet and then heated at 150 °C to form LI-Au alloy. The alloy formation provided a good contact between Li metal and LLZ-Al pellet. In fact, the electrochemical impedance exhibited a low interfacial resistance between Li metal anode and LLZ-AL electrolyte. The discharge and charge curves also showed an excellent performance of the all solid state battery with the interfacial control.

2:15 PM

(PACRIM-S28-003-2017) High rate all-solid state sodium ion batteries (Invited)

S. Adams*[1]

1. National University of Singapore, Materials Science and Engineering, Singapore

All-solid-state Na-ion rechargeable batteries constitute promising high safety energy storage systems, where the solid electrolyte simplifies the fabrication and system integration and enhances shelf and cycle life of the batteries. Among the ceramic Na^+-ion conductors our computational screening suggests cubic Na_3PS_4 as a promising electrolyte. After systematically optimizing doping and processing of Na_3PS_4 a maximum total ionic conductivity of 2.5×10^{-4} S cm^{-1} is found for $Na_{3.1}Sn_{0.1}P_{0.9}S_4$ in line with our computational studies, Guided by our computational screening of rate performance in electrode materials, we utilize this Na^+-ion conductor to demonstrate a novel high rate performance all-solid-state sodium ion battery $Na_{2+2\delta}Fe_{2-\delta}(SO_4)_3$ | $Na_{3+x}M_xP_{1-x}S_4$ ($M = Ge^{4+}, Ti^{4+}, Sn^{4+}$) ($x = 0, 0.1$) | $Na_2Ti_3O_7$ based exclusively on earth-abundant safe materials. The initial room temperature capacity of these full cells matches its theoretical capacity (113 mAh per gram of $Na_{2+2\delta}Fe_{2-\delta}(SO_4)_3$) at low rates. At 2C the first discharge capacity at room temperature is still 83 $mAh.g^{-1}$ and at 80°C it rises to 109 $mAh.g^{-1}$ with 80% capacity retention over 100 cycles. All battery components remain (kinetically) stable between room temperature and 250°C with small volume changes (1-3%), so that it appears feasible to operate the battery over this entire temperature range.

2:45 PM

(PACRIM-S28-004-2017) Solid-state Lithium Batteries Rechargeable in "One" Second: Solid-electrolyte/Electrode Surperionic Conducting Interfaces (Invited)

H. Taro*[1]

1. Tokyo Institute of Technology, Japan

Solid-state Li batteries (LBs) are promising energy-storage devices owing to their high-energy densities with improved safety. Batteries capable of fast charging would revolutionize the usage of electronic devices, including mobile devices and electric cars. However, fast charging capability is hampered by the high resistance at the solid-electrolyte/electrode interfaces. In order to charge batteries in less than one second, it is crucial to reduce this specific interface resistance. Here, we show ultrafast charging/discharging properties in solid-state thin-film Li batteries using a 5V-class-cathode $Li(Ni_{0.5}Mn_{1.5})O_4$ epitaxial film. We fabricated thin-film LBs with electrolyte/electrode interface resistance below ~ 5 Ωcm^2, which is almost two orders of magnitude smaller than that in previous reports—even smaller than that observed in liquid-electrolyte-based Li-ion batteries. This low interface resistance enabled our batteries to charge/discharge in less than one second (70°C, half of the theoretical capacity). Surprisingly, the activation energy of the ionic conduction across electrolyte/electrode interface is found to be ~ 0.3 eV, which is comparable with Li superionic conductors. This result indicates that the Li conduction across the interface displays Li superionic-conducting state.

3:15 PM

(PACRIM-S28-005-2017) Materials Challenges to Develop Reliable "All-Solid-State" Batteries

L. Groleau[1]; M. Lachal[1]; M. Dolle*[1]

1. Université de Montreal, Chemistry, Canada

All solid state batteries have always been considered with a peculiar interest due to the advantages they offer, especially when safety and reliability issues are concerned. Since 1982 and the works of Hitachi Co, Ltd. Japan, thin film micro-batteries have been widely studied. However, their use remains limited to micro-electronic applications. In order to answer today's energy needs, bulk-type "all-solid-state" batteries would be of great interest since they offer higher energy densities than thin films. However, their development has been hindered by the difficulty to assemble laminated ceramics together as it is often very complicated to sinter sufficiently such compacts when compositions of each layer generally require different optimal sintering temperatures. Our approach was then to develop bulk-type all solid state batteries by means of the Spark Plasma Sintering (SPS) technique. Such a method turns out to be perfectly adapted to guarantee high quality contacts between materials in very short times. In this presentation, we will consider the choice of materials to develop such technology. The different steps to reach our goal will be detailed starting with the development of composite ceramic electrodes. Finally the electrochemical performances of half cells and full cells will be presented.

Solid Electrolytes + Supercapacitors

Room: Queen's 5
Session Chair: Mickael Dolle, Université de Montreal

3:45 PM

(PACRIM-S28-006-2017) Amorphous sulfide positive electrodes with high capacity in all-solid-state lithium batteries (Invited)

A. Hayashi*[1]; M. Tatsumisago[1]

1. Osaka Prefecture University, Department of Applied Chemistry, Japan

All-solid-state lithium batteries using nonflammable inorganic solid electrolytes meet the demand for large-sized rechargeable batteries with high safety and long cycle life. Sulfide solid electrolytes based on the system Li_2S-P_2S_5 have several advantages of high conductivity, wide electrochemical window, and appropriate mechanical properties suitable for forming close solid-solid interfaces with electrode active materials. Dense electrolyte pellets with about 90% relative density are prepared by only mold-pressing at room temperature without any sintering at high temperatures. Amorphous materials have a potential of an electrode active material because of their high capacity and good cyclability based on free volume in amorphous structure. Amorphous TiS3 has higher reversible capacity than crystalline one. Preparation of a positive electrode layer with higher active materials content is important for achieving large energy density in all-solid-state lithium batteries. An all-solid-state cell with the positive electrode using only a-TiS_3 active material without any carbon conductive additives and solid electrolytes exhibits a reversible capacity of over 550 mAh per gram of the positive electrode for 10 cycles. This paper reports electrochemical properties and structure analyses of several amorphous sulfide positive electrodes.

4:15 PM

(PACRIM-S28-007-2017) Defect Chemistry and Electrical Properties of Garnet-type $Li_7La_3Zr_2O_7$

M. Shirpour*[1]; X. Zhan[1]

1. University of Kentucky, Chemical and Materials Engineering, USA

Replacing the organic liquid electrolyte with a nonflammable solid electrolyte in lithium-ion batteries improves the safety, increases the volumetric and gravimetric energy densities, and potentially lowers the cost of the battery by increasing the battery life, decreasing the dead space in the battery pack, and simplifying the packaging. Garnet-type cubic $Li_7La_3Zr_2O_{12}$ (c-LLZO) has emerged as a promising candidate for solid electrolytes due to its high ionic conductivity, good chemical stability against lithium metal, and wide electrochemical stability window. Defect chemistry of this class of materials, yet less studied, is critical to the understandings of the ionic nature of conductivity and the electrode-electrolyte interfacial processes. In this presentation we will discuss the formation of ionic defects and defect pairs as well as their impact on the electrical properties of c-LLZO. The contribution of grain boundaries to the electrical conductivity of polycrystalline samples will also be presented.

4:30 PM

(PACRIM-S28-008-2017) Lithium diffusion in lithium garnet oxide $Li_5La_3Ta_2O_{12}$: A combined quasi-elastic neutron scattering and molecular dynamics study

W. Lai*[1]; M. Klenk[1]; S. Boeberitz[1]; N. Jalarvo[2]

1. Michigan State University, Chemical Engineering and Materials Science, USA
2. Oak Ridge National Lab, USA

Lithium garnet oxides are a class of materials that are very promising as solid electrolytes for lithium-ion batteries. Understanding their lithium diffusion mechanism is critical to materials performance improvement and design of new solid electrolytes. Compared with the nuclear magnetic resonance (NMR) technique, quasi-elastic neutron scattering (QENS) provides additional information on the local dynamics such as residence time and local jump length, due to its momentum transfer (Q) dependence. However, reports of QENS studies on lithium garnet oxides have been rare. In this talk, we will report our investigation of a model garnet material, i.e. Li5La3Ta2O12, using both QENS and molecular dynamics technqiues, in order to elucidate the local lithium diffusion mechanism. We extracted the half-width-half-maximum values of quasi-elastic peaks at different Q values and found they can be described by a jump-diffusion model based on the Singwi-Sjolander equation which assumes alternate oscillatory and directed motions. This is supported by the molecular dynamics simulation. The residence time has an Arrenhius temperature dependence varing from a few to hundreds of ps from 700 K to 500 K, while the average jump distance is less than 1A with negligle temperature dependence. Future work will be focused on the dopant effect.

4:45 PM

(PACRIM-S28-009-2017) Grain boundary atomic structures and lithium ionic conductivity in (La,Li)TiO_3 solid electrolyte

R. Ishikawa*[1]; S. Sasano[1]; T. Higashi[1]; T. Kimura[2]; Y. H. Ikuhara[2]; N. Shibata[1]; Y. Ikuhara[1]

1. University of Tokyo, Japan
2. Japan Fine Ceramics Center, Japan

Solid lithium ion electrolytes have recently paid more attentions for the development of all solid state Li ion battery, which has several advantages in electrochemical and thermal stability, and compact manufactures. One of good solid electrolyte candidates is $(Li_{3x}La_{2/3-x})TiO_3$, which is A-site deficient double perovskite structure. The LLTO single crystal (x~0.11) shows significantly high ionic conductivity of 10^{-3} S/cm, however, the conductivity in sintered bulk materials exhibit only 10^{-5} S/cm as a resultant of grain boundary resistance. In this study, we have investigated the relation between LLTO polycrystalline grain boundary structure and the local Li ion conductivity by using atomic-resolution scanning transmission electron microscopy combined with scanning probe microscopy. At first, we identified crystal orientation of grains by using EBSD and then measured Li ion conductivity at the same position by using SPM-ESM method. It was found that Li ion conductivity becomes higher at the [101] direction and lower at the [111] direction, which is consistent with the previous first-principles calculations. On the basis of our ESM measurement, Li ion conductivity generally becomes lower along the random grain boundaries, while symmetric grain boundary such as $\Sigma 5$ does not prevent the ion conductivity. This work was supported by the RISING II project of NEDO, Japan.

5:00 PM

(PACRIM-S28-010-2017) Ultrathin NiAl layered double hydroxide nanosheet arrays on carbon nanotube paper as advanced hybrid electrode for high performance hybrid capacitors

L. Zhang[2]; K. Hui[3]; K. Hui*[1]

1. University of Macau, Institute of Applied Physics and Materials Engineering, Macao
2. Pohang University of Science and Technology, Department of Chemistry, Republic of Korea
3. University of East Anglia, Faculty of Science, United Kingdom

Although metal oxide based supercapacitors offer higher energy density than that of electrical double-layer capacitors, their power density and rate capability are hindered by their low electrical conductivity. To effectively improve the power density and rate capability of metal oxide based supercapacitors, a hybrid supercapacitor (HSC) comprising of hierarchical ultrathin NiAl-layered double hydroxide (NiAl-LDH) nanosheet arrays on porous carbon nanotube paper (CNP-LDH) is developed with porous graphene nanosheets as the negative electrode. SEM image shows that hierarchical NiAl LDH nanosheet arrays are assembled by numerous ultrathin nanosheets with thickness of 10 nm. Remarkably, with an operating voltage of 1.6 V, the HSC possesses a high energy density of 50.0 Wh kg^{-1} at an average power density of 467 W kg^{-1}. Even at a fast discharging time of 3.9 s, a high energy density (23.3 Wh kg^{-1}) could also be retained at a power density of 21.5 kW kg^{-1}. Moreover, the HSC exhibits good cycling stability with a retention rate of 78% after 5000-cycle charge-discharge test at 5 A g^{-1}. The results inspire us to propose our high-performance CNP-LDH as a promising electrode for energy storage applications.

5:15 PM

(PACRIM-S28-011-2017) Graphene-encapsulated Carbon@ Nickel-Aluminum Layered Double Hydroxide Core–Shell Spheres Hybrid Structure for High Performance Supercapacitor

S. Wu[1]; K. Hui[2]; K. Hui*[3]

1. Pusan National University, School of Materials Science and Engineering, Republic of Korea
2. University of East Anglia, Faculty of Science, United Kingdom
3. Institute of Applied Physics and Materials Engineering, University of Macau, China

Achieving high energy density while retaining high power density is difficult in electrical double-layer capacitors and in pseudocapacitors considering the origin of different charge storage mechanisms. Rational structural design became an appealing strategy in circumventing these trade-offs between energy and power densities. A hybrid structure consists of chemically converted graphene-encapsulated carbon@nickel-aluminum layered double hydroxide core–shell spheres as spacers among graphene layers (G-CLS) used as an advanced electrode to achieve high energy density while retaining high power density for high-performance supercapacitors. The merits of the proposed architecture are as follows: (1) CLS act as spacers to avoid the close restacking of graphene; (2) highly conductive carbon sphere and graphene preserve the mechanical integrity and improve the electrical conductivity of LDHs hybrid. The G-CLS electrode exhibited high specific capacitance (1710.5 F g^{-1} at 1 A g^{-1}) under three-electrode tests. An ASC fabricated using the G-CLS as positive electrode and reduced graphite oxide as negative electrode operated at 1.4 V, and delivered a high energy density of 35.5 Wh kg^{-1} at a 670.7 W kg^{-1} power density with an excellent rate capability, as well as a robust long-term cycling stability of up to 10 000 cycles.

5:30 PM

(PACRIM-S28-012-2017) One-Dimensional Core/Shell $Ba_{0.9}Ca_{0.1}TiO_3$@TiO_2 Nanofibers for Enhancing the Energy Density of Polymer Nanocomposites

P. Zhongbin*[1]; J. Zhai[1]

1. Tongji University, School of Materials Science & Engineering, China

Electrostatic capacitors have been used for pulsed power applications that require large power density composing of moderate energy density and ultrafast charging/discharging speed in the order of a few milliseconds. In this article, the polymer composite films has been prepared by combing the one-dimensional $Ba_{0.9}Ca_{0.1}TiO_3$@TiO_2 nanofibers and the poly(vinylidene fluoride) (PVDF) polymeric matrices. The core-shell structure $Ba_{0.9}Ca_{0.1}TiO_3$@TiO_2 nanofibers have been synthesized via coaxial electrospinning. The dielectric constant, dielectric loss, breakdown strength and discharged energy density of the nanocomposites can be significantly improved by creating the TiO_2 shell layer of moderate dielectric constant on surfaces of $Ba_{0.9}Ca_{0.1}TiO_3$ nanofibers to form moderate interfacial area. The energy density was increased to 9.52 J cm^{-3} at 370 MV m^{-1} by small loading fillers, which was an enhancement of » 793% over the biaxially-oriented polypropylene (» 1.2 J cm^{-3} at 650 MV m^{-1}). This report will open up a conveniently and effectively way to development of practical application of the electrostatic capacitor by tuning surface of the fillers in polymer nanocomposites.

PACRIM Symposium 29: Advances in Polar, Magnetic and Semiconductor Materials: Extending Temperature Limits

High Temperature Applications and Materials

Room: Queen’s 4
Session Chairs: Paul Ohodnicki, National Energy Technology Laboratory; Michael Lanagan, Penn State University

1:15 PM

(PACRIM-S29-001-2017) High Temperature Power Electronics: Opportunities and Challenges (Invited)

S. Krishnamurthy*[1]

1. UTRC, USA

The emergence of wide band gap devices has pushed the boundaries of power converter operations. The devices enable the a power inverter to operate at switching frequencies and temperatures that are beyond the capability of standard silicon semiconductors. Operation at high temperature is attractive for a number of applications including oil and gas as well as aerospace power converters. The talk will present the opportunities in the aerospace industry for high temperature power electronics and the associated challenges wih respect to component availability and reliability.

1:45 PM

(PACRIM-S29-002-2017) Challenges of High Temperature Power Modules (Invited)

C. O’Neal*[1]

1. Wolfspeed, A Cree Company, Process Engineering, USA

High temperature presents many challenges for power electronics. Temperature puts stress on the materials and devices that make up a power module, from plastic housings, to dielectrics, to the required derating of semiconductors. The selection and testing of these materials becomes critical to long term reliability. These challenges are greatly amplified at temperatures exceeding 200 °C. Dielectric strength of polymers may be reduced, attachment material selections such as solder or epoxies become limited at these temperatures. In compact, high voltage power electronics preventing dielectric breakdown is critical, so dielectric potting materials that are temperature stable at temperatures are required. The thermally induced stresses at elevated reflow temperatures exceeding 300 °C are enough to warp metal baseplates, fracture ceramic power substrates, and cause delamination. New alternatives such as silver sintered attach materials are being evaluated and adopted into commercial power electronics. Silicon power semiconductors are largely limited to temperatures of 175 °C and have well understood switching characteristics. Silicon carbide semiconductors offer the ability to increase the device blocking voltage, lower the specific on-resistance over temperature, and increased switching speeds which reduces the size and demand of magnetics in the overall system. This presentation will explore how industry is tacking these challenges.

2:15 PM

(PACRIM-S29-003-2017) Development of dielectric material of multilayer ceramic capacitors for high temperature applications (Invited)

J. Ikeda*[1]

1. Murata Manufacturing Co., Ltd, Japan

Multilayer ceramic capacitors (MLCCs) with Ni electrode have been required to higher performance such as miniaturizing, larger capacitance and high heat-resistance. In order to meet above demands, the thickness of dielectric layer has been decreased and dielectric ceramics are necessary to have higher reliability compared with conventional materials used for MLCCs. It is well known that $(Ba,Ca)TiO_3$ based ceramics has higher reliability than that of $BaTiO_3$ based ceramics which conventionally used as dielectric materials for MLCCs. Furthermore, rare-earth oxide plays an important role in design of dielectric material for MLCCs. In this study, therefore, the influence of rare-earth oxides e.g., Gd, Dy, Y, and Er, in $(Ba,Ca)TiO_3$ based ceramics on the reliability and dielectric properties were investigated. We prepared MLCCs samples with $(Ba_{1-x}Ca_x)TiO_3$ based ceramics where x is from 0 to 0.16 with rare-earth oxides. The microstructure analyses were carried out by SEM and EDX in order to characterize the rare-earth ions. Y ions provided $(Ba,Ca)TiO_3$ ceramics with good temperature stability of capacitance and high reliability. Electric properties and reliability of the capacitors were attributed to solubility and distribution of rare-earth oxides. We will discuss the relationship between rare-earth oxides and Ca concentration of $(Ba,Ca)TiO_3$ based ceramics.

2:45 PM

(PACRIM-S29-004-2017) Experimental and Atomistic Modeling Studies of Advanced Materials for Radiation Environments (Invited)

G. R. Lumpkin*[1]

1. ANSTO, NFC Research, Australia

The development of materials for use in extreme environments, e.g., combinations of high temperature, pressure, radiation fields, and potentially corrosive surroundings, requires in-depth research, testing, and qualification prior to actual deployment. We have employed various approaches combining experimental work and atomistic modeling in order to understand the fundamental properties and radiation response of a range of materials being considered for use in the nuclear fuel cycle. Experimental work includes the synthesis and characterization of materials before and after irradiation using either thin films or bulk materials. A range of ions and energies are employed in order to investigate the response of the crystalline solid under differing conditions of fluence, temperature, and nuclear versus electronic stopping power. Several studies of oxide compounds are described here, including defect fluorite, pyrochlore, perovskite and other structure types. The results are discussed in terms of radiation tolerance as a function of ion fluence and temperature. In order to further assess the fundamental physics of radiation tolerance, several examples are described wherein atomistic simulations have been increasingly used to investigate the both the dynamics of particle-solid interactions and the energetics of defect formation and migration.

3:15 PM

(PACRIM-S29-005-2017) High Temperature Functional Oxide Enabled Sensors for Harsh Environment Applications

P. Ohodnicki*[1]

1. National Energy Technology Laboratory, USA

Optical and microwave based sensing platform shows a number of unique advantages for harsh environment sensing applications spanning power generation, aerospace, and manufacturing processes amongst others. To fully realize the potential for energy efficiency improvements and increased energy security achievable only through widespread deployment of the technology in commercially relevant applications, a number of key functional materials research and development challenges remain. This presentation will present recent results in the area of functional oxide enabled high teperature and harsh environment sensing technologies at the National Energy Technology Laboratory. In particular, a combination of experimental and theoretical results will be presented looking at perovskite based oxides and Au-nanoparticle integrated oxide sensors for high temperature sensing applications.

3:45 PM

(PACRIM-S29-006-2017) PbO-free piezoelectrics: Are we there yet? (Invited)

I. M. Reaney*[1]

1. University of Sheffield, Materials Science and Engineering, United Kingdom

Many PbO free materials have inferior performance to PZT across multiple metrics and are implausible substituents. However, a range of materials in the right application offer promise as potential replacements. $(Ba,Ca)TiO_3 - Ba(Zr,Ti)O_3$ has high piezoelectric activity ($d_{33} > 500$ pC/N) but low T_C. Despite the low T_C, there are low drive field, room temperature bimorph applications for which this material may substitute for soft PZTs. For room temperature sensors and actuators, $(Na_{1/2}Bi_{1/2})TiO_3$ (>0.4% strain at high field but hysteretic) and $(K,Na)NbO_3$ (KNN, $d_{33} > 300$ pC/N) are promising but they are not temperature stable above 100 ºC and cannot be used at high drive fields or for high temperature applications. Moreover, Life Cycle Analysis of KNN revealed environmental concerns over the mining and extraction of Nb_2O_5, Most recently, a KBT based electrostrictive material (0.16% strain) has been reported which shows promise for applications from 150 to 300 ºC which is temperature stable and fatigue resistant. Despite the appearance of promising candidates for specific applications, no single base of material meets all the necessary requirements to replace PZT. Switching from PZT to a 'mix and match' set of PbO free materials with higher in production cost, less abundant raw materials and divergent processing requirements is detrimental to the cost effectiveness and stability of the piezoelectric industry.

4:15 PM

(PACRIM-S29-007-2017) Processing and Base-Metal Integration of $Bi(M)O_3$-$BaTiO_3$ Dielectrics (Invited)

G. L. Brennecka*[1]; M. A. Beuerlein[1]; P. Lichty[2]; D. Cann[3]

1. Colorado School of Mines, USA
2. Pneumaticoat, Inc., USA
3. Oregon State University, Mechanical, Industrial, and Manufacturing Engineering, USA

A number of applications demand capacitors that can work at temperatures above 150C with higher capacitance, energy density, resistivity, and reliability at lower costs than currently-available options. Dielectrics based on $xBi(Zn_{0.5}Ti_{0.5})O_3 - (1-x)BaTiO_3$ and other members of the $xBi(M)O_3 - (1-x)BaTiO_3$ family (where M refers to a trivalent ion or trivalent-equivalent combination of ions) show very attractive properties for such operating conditions, including high permittivity values that are remarkably stable with both temperature and applied electric field as well as large resistivity values. Such dielectrics have been successfully cofired with precious metal electrodes in the past, but commercial use will remain low until they can be successfully cofired with low-cost base metal electrodes. Here we describe our efforts to use kinetics to assist with the thermodynamically-challenging integration of $Bi(M)O_3$-$BaTiO_3$ dielectrics with Cu electrodes. Understanding the processing science of these materials, particularly the complex interplay among defect chemistry, diffusion kinetics, and properties in commercially-relevant structures is crucial for fabrication of the desired low cost, high reliability capacitors.

4:45 PM

(PACRIM-S29-008-2017) Dielectric Nanocomposites for Energy Storage Application (Invited)

H. Wang*[1]; Q. Wang[1]

1. Xi'an Jiaotong University, State Key Laboratory for Mechanical Behavior of Materials, China

Dielectric capacitors for energy storage have advantages in fast charge-discharge capability and high power density but their energy densities are at least an order of magnitude lower than that of electrochemical devices, such as batteries and double-layer supercapacitors. Thus the dielectric materials with high energy densities are highly desirable and investigated to reduce the size and cost of electric power system. In this presentation, a brief review of the state of arts on the polymer-based nanocomposites for energy storage applications including our recent highlight works that exhibit excellent energy storage properties will be given. Spatial organization of polymer matrix and ceramic nanofillers into multilayer structured nanocomposites with the compositional tailoring effect have been systematically studied. A sandwich-structured polymer-based nanocomposite exhibiting a favorable energy density of 18.8 J cm^{-3} with the breakdown strength of 470 MV m-1, has been achieved by a novel macro-micro structure design on the composite structure as well as the fillers distribution. An extend study for high temperature applications at 150 °C and 200 MV m−1, results a sandwich-structured polymer nanocomposites outperforming the state-of-the-art polymer-based dielectrics in terms of energy density, power density, charge–discharge efficiency, and cyclability.

5:15 PM

(PACRIM-S29-009-2017) Piezoelectric Composites Based on the Flexoelectric Effect of Ferroelectric Ceramics

B. Chu*[1]

1. University of Science and Technology of China, Materials Science and Engineering, China

Flexoelectric piezoelectric composite materials (or piezoelectric metamaterials) can be designed by exploiting the flexoelectric effect of dielectric materials, an electromechanical coupling phenomenon under stain or electric field gradient. The flexoelectric effect and the resultant effective piezoelectric response of the composites can be sustained at a high temperature because the effect is not restricted by the crystal structure of the materials that are used to fabricate the composites. Because the magnitude of flexoelectric effect is correlated with the dielectric properties of materials, ferroelectric materials were often studied for the flexoelectric applications. In our study, the flexoelectric coefficients of several types of ferroelectric ceramics were measured. With these materials, flexoelectric piezoelectric composite materials were designed and fabricated. The composites exhibit excellent effective piezoelectric response which can be sustained above the Curie temperature of the ferroelectric ceramics. The mechanisms for the large piezoelectric response were also discussed.

PACRIM Symposium 31: Advances in Bioceramics: Biomineralization and Bioinspired Materials

Towards Smart Bioceramics

Room: Monarchy
Session Chair: Joanna McKittrick, UC San Diego

1:15 PM

(PACRIM-S31-001-2017) Bioinspired Functional Materials (Invited)

C. Zollfrank*[1]

1. Technical University Munich, TUM School of Life Sciences Weihenstephan, Germany

Bioinspired materials research is an extensively growing field in interdisciplinary materials science with large potential for generating novel functional materials. Biotemplating is a technique, which employs naturally occurring structured resources (plant tissue, insect scales, microorganisms, etc.) and processed materials (paper, cardboard, composites) as starting materials for the manufacturing of inorganic compounds. Owing to their structural diversity, natural materials can be used at various levels from the molecular scale up to complex three-dimensional parts. The replication of structural details of complex biological tissues over several levels of hierarchy down to the nanometer level is a major challenge. The presentation introduces the current knowledge about the replication of hierarchical biological materials into structural and functional inorganic materials with the special emphasis on wood and cellulose templates. It will be shown that hierarchical replication down to the nanoscale requires a careful pre-preparation of the biological template, followed by elaborate template infiltration via gas or liquid phases and their transformation into a solid material, and finally, the gentle removal of the template. A moisture sensitive silica actuator manufactured from a conifer pine cone will be demonstrated. Additionally, a novel approach to generate a random laser using biotemplated cellulosic material will also be presented.

1:45 PM

(PACRIM-S31-002-2017) Shape memory effect of natural materials and their potential applications (Invited)

W. Yang*[1]; H. Quan[1]; M. Meyers[1]

1. University of California, San Diego, USA

Shape memory materials, which can recover to its original shape after being deformed, have a wide range of applications. Nature designed many biological materials with shape memory effect for different purposes by applying simple and smart strategies. Investigation of the mechanisms behind those shape memory effects can provide us a source of inspiration and strategies for the smart materials' synthesis. Here we review eight natural materials with shape memory effect. Four of them are produced by animals including spider silk, bird feather, human hair, knobbed whelk egg case, and four of them are plant tissues, which are pine cones, wheat awns, luffa sponges and ice plant seed capsules. Based on different underlying mechanisms, they can recover to their original shapes with or without external stimuli, after being deformed or damaged. The shape memory effect of these plants enable the organisms to restore their structure or protect and release their seeds. The potential applications will be discussed according to the natural shape memory mechanisms.

2:15 PM

(PACRIM-S31-003-2017) Biomorphic transformation of natural structures: A new paradigm in bioceramics development

S. Sprio*[1]; A. Ruffini[1]; A. Ballardini[1]; M. Montesi[1]; S. Panseri[1]; A. Tampieri[1]

1. National Research Council of Italy, Institute of Science and Technology for Ceramics, Italy

The development of bioceramics with effective ability to regenerate critical size bone defects is still a major challenge, particularly when load-bearing bones have to be treated. In fact, effective bone regeneration can be reached only by using porous scaffolds with high compositional and structural mimicry of natural bone, that can uniquely trigger the exchange of cell-instructive information and activate bone regeneration. Hydroxyapatite is widely considered as the golden biomaterial for bone regeneration. However, biologic apatite has a composition and structure very far from the one obtainable by the classical ceramic process, where the sintering process destroys the bioactive chemical and structural features possessed by ion-substituted nano-apatites. The present work reports on a new synthesis approach based on the biomorphic transformation of natural structures into large bone scaffolds characterized by biomimetic composition, nanostructure and hierarchical organization at the multiscale. The biomorphic scaffolds exhibited enhanced mechanical properties and outstanding expression of genes relevant for the bone regenerative cascade. The nature-inspired synthesis approach here described can thus be considered a revolutionary concept in biomaterials synthesis, enabling the achievement of 3D scaffolds with unprecedented features, promising for regeneration of load-bearing bones.

2:30 PM

(PACRIM-S31-004-2017) Intrinsic and Extrinsic Control of Bioinspired Freeze Casting (Invited)

S. E. Naleway*[1]

1. University of Utah, Department of Mechanical Engineering, USA

Freeze casting is a bioinspired technique for the fabrication of tailored, porous ceramic materials. Mimetic of the growth of mammalian bone and other biomaterials where biopolymers template the deposit of biominerals to create complex composites, freeze casting employs a template of growing ice crystals to create a complex porous microstructure in any ceramic. I have proposed that this bioinspired technique can be controlled through either intrinsic (those that modify from within by altering the constituents) or extrinsic (those that apply external forces or templates) means. Through these classifications, I present novel examples of both intrinsic and extrinsic freeze cast, bioinspired structures with a focus on providing advanced control of the final material structure and properties. These new materials and techniques are proposed for structural, biomedical, and green material applications.

3:00 PM

(PACRIM-S31-005-2017) Synthesis of fish scale extracted hydroxyapatite and chitosan composite scaffolds by freeze casting for biomedical and environmental applications

B. Liaw*[1]; P. Chen[1]; W. Liu[1]; H. Chang[1]

1. National Tsing Hua University, Material Science and Engineering, Taiwan

Fish scales are typically considered as wastes in fishery industries yet important collagen and hydroxyapatite sources. In this study, hydroxyapatite minerals were extracted from scales of Tilapia fish (Oreochromis mossambicus) and utilized as raw materials for scaffolds synthesized by freeze casting technique. The hydroxyapatite extracted from scales has been confirmed by X-ray diffraction (XRD). Chitosan was further stirred with the hydroxyapatite to form scaffolds. The bio-mineral/polymer composites were crosslinked by different solvents. Microstructural features of scaffolds were characterized by SEM, revealing uniform laminar structures with 10-100 μm channels depending on cooling rates. The scaffolds present a great capability to remove heavy metal ions from waste water, which was quantified by Atomic Absorption Spectrometer (AAS). The adsorption capability was elevated and optimized by tuning the cooling rates and mineral/polymer ratios. Cell proliferation test was conducted by culturing human osteoblast cells within the scaffolds, and cell viability was evaluated by the MTS assay. Histological evaluation was carried out and results confirmed that the scaffolds were not cytotoxic. In summary, the fish scale-derived, hydroxyapatite/chitosan scaffolds have great potential to be applied in various fields.

3:15 PM

(PACRIM-S31-006-2017) Bioinspired self-shaping ceramics

H. Le Ferrand*[1]; F. L. Bargardi[1]; R. Libanori[1]; A. R. Studart[1]

1. ETH Zürich, Switzerland

Shaping ceramics into complex and intricate geometries using cost-effective processes still remains a challenge. Plant seed dispersal units have been an inspiration for hygroscopically responsive self-shaping composites. Indeed, seedpods' architectures consist of bilayers where the orientation of stiff cellulose fibres restricts the direction of the swelling of the surrounding matrix during hydration. Here we demonstrate that such self-shaping strategy can be implemented in ceramics by programming the material's microstructure to undergo local anisotropic shrinkage during heat treatment. The microstructural design is achieved by magnetically aligning functionalized alumina micron-platelets in a liquid ceramic suspension, and subsequently consolidating the system through an enzyme-catalyzed reaction. Bending, twisting and combination of both shapes could be successfully achieved in 95% dense alumina compacts, reaching radius of curvatures as large as 9 mm. Controlling the green-body geometrical dimensions, post-sintered curvatures and pitches of the ceramic can be predicted using established theoretical models, enabling the design of on-demand shapes. The simplicity and the universality of such a bottom-up shaping method makes it attractive for applications that would benefit from low-waste ceramic fabrication, temperature-resistant interlocking structures or unusual geometries not accessible using conventional top-down manufacturing.

Fundamental Aspects of Biomineralization - General Session

Room: Monarchy
Session Chairs: Stephan Wolf, Friedrich-Alexander-University Erlangen-Neurnberg; David Kisailus, UC Riverside

3:45 PM

(PACRIM-S31-007-2017) Analysis and control of preferential alignment of apatite crystals related to collagen fibers in various bones and in vitro bone-like tissues (Invited)

T. Nakano*[1]; T. Ishimoto[1]; A. Matsugaki[1]

1. Osaka University, Division of Materials and Manufacturing Science, Graduate School of Engineering, Japan

Bone tissue exhibits the specific oriented architecture dominantly composed of apatite crystallites and collagen fibers. Preferential orientation and degree of anisotropic apatite/collagen in bones strongly depend on the bone morphology, in vivo stress distribution, turnover, etc. The preferential alignment of apatite c-axis analyzed by μXRD, in particular, tends to arrange along the principal stress direction in the original bones, indicating the anisotropy of mechanical properties in bones. Recovery of anisotropic apatite/collagen alignment strongly depends on the portion and period of regeneration process, which is insufficient to reach the original level, while bone mineral density is almost improved to its original value. Moreover, apatite orientation rather than BMD is the dominant controlling factor to the stiffness of regenerated bone. The purpose in this study is to develop some strategies which can control the

preferential alignment of osteoblasts and the subsequent formation of normal anisotropic extracellular matrix composed of preferential arrangement of apatite and collagen. Finally, it is concluded that the appropriate anisotropic alignment of apatite/collagen with proper functions can be dominated by surface morphology and the chemical and/or physical environment in vivo and in vitro surrounding the constituent bone cells.

4:15 PM

(PACRIM-S31-008-2017) Structural and functional analyses of matrix proteins related to the formation of fibrous microstructure in the shell of Pinctada fucata (Invited)

K. Kubota[1]; T. Kogure[1]; S. Sakuda[1]; H. Nagasawa[1]; M. Suzuki*[1]

1. The University of Tokyo, Japan

The hinge ligament of bivalves is an important hard tissue that functions to open and close the shells. The ligament consists of fibrous aragonite crystals surrounded by dense organic matrices. Although a number of matrix proteins have been identified from various shell microstructures in previous works, ligament-specific matrix proteins have not yet been reported. In this study, in order to reveal the formation mechanism of the fibrous aragonite crystals in the ligament, we identified a novel, small acidic peptide, named ligament intra-crystalline peptide (LICP), from the aragonite crystals in the ligament of Pinctada fucata. LICP consists of 10 amino acid residues with N-terminal pyroglutamic acid. The result of cDNA cloning showed that the cDNA encodes another putative 10-residue peptide at the C-terminal end of LICP. LICP showed inhibitory activity on calcium carbonate precipitation. TEM and SEM observations of the aragonite crystals formed by the in vitro crystallization experiment showed that LICP inhibited growth of the aragonite crystals by stopping the elongation along the c-axis. The small aragonite crystals are aligned to make the thin long aragonite fiber. These results suggested that LICP has a role of regulating the formation of the aragonite crystals in the ligament.

4:45 PM

(PACRIM-S31-009-2017) Analysis of magnetite biomineralization in magnetotactic bacteria toward designed synthesis of magnetic nanomaterials (Invited)

T. Matsunaga*[1]; A. Arakaki[1]

1. Tokyo University of Agriculture and Technology, Japan

Living organisms produce inorganic nano-materials exhibiting unique structure and property. This bioprocess called biomineralization is an attractive strategy to develop future inorganic materials, although utilization of this process is still challenging. Magnetotactic bacteria synthesize nano-sized single crystalline magnetite (Fe_3O_4) within the cell. Various crystal morphologies observed in nature are species or strain dependent, which implies a high degree of biological control. During the molecular analyses of bacterial magnetites, we identified a group of proteins, termed Mms proteins, which plays a key role in crystal growth and morphological regulation of cubo-octahedral magnetite. In this talk, we present identification and functional analysis of Mms proteins. The morphology, size, and surface structure of the magnetite crystal in the bacteria are regulated by the cooperative action of Mms proteins on the crystal surface. Our results also suggest that the morphology, size and surface structure of magnetite crystals can be fine-tuned by controlling the expression of these proteins and that it is possible to design magnetic materials with desired morphological and magnetic characteristics. A new strategy for the production of magnetite crystals to use biological system will be introduced.

5:15 PM

(PACRIM-S31-010-2017) Nucleation, Phase Transformations and Structural Developments in the Damage-tolerant Teeth of a Giant Chiton

S. Herrera[1]; D. Restrepo Arango[2]; D. Ren[1]; M. Nemoto[3]; P. Zavattieri[2]; D. Kisailus*[1]

1. UC Riverside, Chemical and Environmental Engineering, USA
2. Purdue University, USA
3. Okayama University, Japan

Nature has evolved efficient strategies, exemplified in the crystallized tissues of numerous species, to synthesize materials that often exhibit exceptional mechanical properties. These biological systems demonstrate the ability to control nano- and microstructural features that significantly improve the mechanical performance of otherwise brittle materials. One such example is found in the heavily crystallized radular teeth of the chitons, a group of elongated mollusks that graze on hard substrates for algae. The radula, a toothed ribbon-like structure, which is used for this feeding are well known for their ability to efficiently erode the rocky surfaces on which they feed. The remarkable damage tolerance and abrasion resistance of these radular teeth were the inspiration for this investigation. Here, we investigate the development of these unique abrasion resistant and damage-tolerant crystallized structures using spectroscopic and microscopic characterization techniques to reveal nucleation, growth and phase transformation processes within the teeth. We are also synthesizing biomimetic structures to understand architectural features and organic-inorganic interactions that enhance abrasion resistance and damage tolerance.

5:30 PM

(PACRIM-S31-011-2017) Hierarchical Bone-like Materials via Biomimetic Processing

B. Wingender*[1]; P. Bradley[2]; J. Ruberti[2]; L. Gower[1]

1. University of Florida, Materials Science and Engineering, USA
2. Northeastern University, Bioengineering, USA

Clinical treatment of critical sized bone defects remains a challenge, particularly when the defect is located in a load-bearing bone. Tissue engineered constructs should promote the patient's natural healing process which will ultimately replace the synthetic scaffold with healthy, native tissue. These constructs should recapitulate the structure and function of native extracellular matrix (ECM), with matching mechanical properties and appropriate degradation behavior. The purpose of this study was to evaluate the affect of crosslinking on collagen matrices that were subsequently mineralized with calcium phosphate via the PILP process. Liquid crystal collagen (LCC) processing was used to generate highly organized, fibrillar collagen matrices with lamellar bone-like microstructure. The LCC matirces were mineralized via the PILP process which generates biomimetic, intrafibrillar nano-hydroxyapatite crystals to mimic bone's composite nanostructure. Composite scaffolds were characterized using electron microscopy and xray diffraction, UV-vis, and AFM.

Tuesday, May 23, 2017

GOMD Award Lectures

George W. Morey Award Lecture

Room: Kona 5

8:35 AM

(GOMD-PL-001-2017) The evolution of Chalcogenide glasses in Infrared Photonics – beyond invisible

K. Richardson*[1]

1. University of Central Florida, CREOL, USA

The prospect of low-cost, compact sensors that 'see and sense' has been a goal of technologists for decades. Previously only available in the defense realm, our ability to 'own the night' has transformed to a broad range of applications where the invisibility of infrared radiation, is no longer a foreign concept-rather it has become common place. Such innovations have been fueled by the miniaturization of electronic and optical components, and the availability of advanced materials which can be designed with diverse functionality and integrated into multi-material packages. The role that chalcogenide glass has played in the progress of such applications is discussed, including how the strategy to engineer optical function with manufacturabilty, has transformed the use of these glasses in diverse applications. Over the past decades efforts by the UCF team and our collaborators have focused on developing a toolbox of glass material chemistry options, processing methodologies and metrology tools that employ multi-component non-oxide chalcogenide glasses (ChGs). Basics of these versatile materials are discussed as well as key challenges that remain in optical material science that are being examined to create innovative solutions to further integrate these materials into bulk and planar applications for sensing, security and defense applications.

GOMD Symposium 1: Fundamentals of the Glassy State

Mechanical Properties of Amorphous Solids II

Room: Kona 4

Session Chair: Adama Tandia, Corning Incorporated

9:45 AM

(GOMD-S1-013-2017) Indentation Deformation and Cracking of Calcium Boroaluminosilicate Glasses (Invited)

T. M. Gross*[1]

1. Corning Incorporated, Physical Properties, USA

The deformation and cracking mechanisms of calcium boroaluminosilicate glasses were investigated using Vickers indentation. Factors that influence the indentation response include non-bridging oxygen content, packing density, and network connectivity. Resonant ultrasound spectroscopy is used to measure the elastic properties and the poisson's ratio is used to validate the calculated packing density trends. For glasses free of non-bridging oxygens, the crack resistance is shown to increase as tetrahedral silica is replaced with trigonal boron, despite an increase in packing density for this substitution. However, the crack resistance benefit of reduced packing density is evident for indentation measurements made on glasses with higher fictive temperatures. NMR analysis confirms minimal change in network connectivity with the fictive temperatures studied, so improved crack resistance with higher fictive temperature can be attributed to the decrease in packing density. The densification/shear deformation responses of the glasses were characterized by a variety of techniques including indentation cross-sectioning, pile-up measurements, micro-raman analysis, and polarized light microscopy.

10:15 AM

(GOMD-S1-014-2017) Hardness and Plastic Deformation Mechanisms in Calcium-Galliosilicate Glasses

S. Baker*[1]; L. Lamberson[2]; R. Youngman[2]; N. Wiles[1]

1. Cornell University, Materias Science and Engineering, USA
2. Corning Incorporated, USA

We have shown that the tectosilicate compositions of calcium-aluminosilicate and magnesium-aluminosilicate glasses exhibit a non-monotonic variation in hardness with increasing SiO_2 content. Hardness and indentation modulus both decrease as SiO_2 content increases, but above a certain SiO_2 concentration, hardness increases while indentation modulus continues to decrease. In the present work, we replacing Al with Ga (both acting as network formers) and find a similar non-monotonic variation in hardness, although the hardnesses at higher Ga contents are much lower and the minimum hardness occurs at a lower SiO_2 content. The modulus variation correlates well with density, but the origin of the hardness variations is not so obvious. Ga speciation in the glass was determined by NMR and used to apply topological constraint theory, but this does not describe the hardness variation. Instead, the variation is consistent with a change in plastic deformation mechanism from shear to densification. We describe the requirements for shear and densification deformation mechanisms in these glasses and compare the effects of Al and Ga content on them. Understanding these plastic deformation mechanisms is key to developing glasses that exhibit more desirable mechanical properties.

10:30 AM

(GOMD-S1-015-2017) Effect of Mg Replacement for Ca on Hardness of Aluminosilicate Glasses

L. Lamberson*[1]; S. P. Baker[2]; R. Youngman[3]

1. Corning Incorporated, Glass Research, USA
2. Cornell University, Materials Engineering, USA
3. Corning Incorporated, USA

In the glass making industry, aluminosilicate glasses are considered a highly important family of glasses due to their use in such products as car windshields, touch screens for cell phones, and tablets among others. However, little is understood about the plastic deformation mechanisms and what effects modifier ions such as Ca and Mg have on these mechanisms. In this paper the hardness and indentation modulus of a series of tectosilicate $MgO_{(x)}$-$Al_2O_{3(x)}$-$SiO_{2(1-2x)}$ (MAS) glasses determined using nanoindentation are compared with the composition, including aluminum speciation determined using ICP and NMR. The results are compared with previously reported data for tectosilicate $CaO_{(x)}$-$Al_2O_{3(x)}$-$SiO_{2(1-2x)}$ (CAS) glasses. It was found that the Mg atom in MAS glasses creates larger quantities of higher coordinated Al resulting in an increase in hardness over CAS glasses. The increase in indentation modulus of MAS glasses compared to CAS glasses was a result of an increase in constraints per volume for the MgO containing glasses. A transformation in hardness from shear to densification deformation was also observed in the MAS glasses just as it was previously in the CAS glasses.

10:45 AM

(GOMD-S1-016-2017) Indentation Crack Threshold and Hardness in Calcium Aluminosilicate Glasses

N. Wiles*[1]; S. P. Baker[1]

1. Cornell University, Materials Science, USA

Indentation hardness tests are commonly used to examine mechanical properties in silicate glasses, but the relationship between hardness and plastic deformation and fracture is not well known. At low loads, silicate glasses deform plastically without fracture in indentation. At some threshold load, cracks appear. We studied the crack threshold in calcium aluminosilicate glasses as a function of composition along the tectosilicate line (equal amounts of CaO and Al_2O_3) using Vickers microindentation. We defined the crack threshold to be the load at which two of the four indentation corners showed cracks. We find that not only the crack threshold but also the width of the crack fraction distribution—that is, the number of indentation corners showing cracks as a function of load—varies strongly with composition. We propose that the relationship between hardness and fracture around indentations is determined by plastic deformation. This work provides first steps towards understanding the relationship between hardness and failure modes, particularly fracture, in practical devices.

11:00 AM

(GOMD-S1-017-2017) Competing indentation deformation mechanisms in glass using different strengthening methods

J. Luo*[1]; P. J. Lezzi[1]; K. Vargheese[1]; A. Tandia[1]; J. Harris[1]; T. M. Gross[1]; J. C. Mauro[1]

1. Corning Incorporated, USA

Chemical strengthening via ion exchange, thermal tempering, and lamination are proven techniques for strengthening of oxide glasses. For each of these techniques, the strengthening mechanism is conventionally ascribed to the linear superposition of the compressive stress profile on the glass surface. However, in this work we use molecular dynamics simulations to reveal the underlying indentation deformation mechanism beyond the simple linear superposition of compressive and indentation stresses. In particular, the plastic zone can be dramatically different from the commonly assumed hemispherical shape, which leads to a completely different stress field and resulting crack system. We show that the indentation-induced fracture is controlled by two competing mechanisms: the compressive stress itself and a potential reduction in free volume that can increase the driving force for crack formation. Chemical strengthening via ion exchange tends to escalate the competition between these two effects, while thermal tempering tends to reduce it. The crack system also depends on the indenter geometry and the loading stage, i.e., loading vs. after unloading. It is observed that combining thermal tempering or high free volume content with ion exchange or lamination can impart a relatively high compressive stress and reduce the driving force for crack formation.

11:15 AM

(GOMD-S1-018-2017) The surface strength of thin display glass

A. L. Tremper*[1]; G. S. Glaesemann[1]

1. Corning Incorporated, Characterization Sciences, USA

Some commercial LCD glasses exhibit "normal" type damage mechanics behavior when examined using common Vickers diamond indentation methods. "Normal" behaving glasses demonstrate a greater propensity for forming strength limiting flaws when damaged in this fashion. Other display glasses exhibit "intermediate" type behavior and better resist median/radial crack initiation when indented with a Vickers indenter. This has led some to believe that "normal" behaving glasses will be generally less reliable. However, when subjected to similar display fabrication processes and handling events, the resulting strength distributions do not show the anticipated dependence on mechanical behavior assessed by Vickers indentation. This study used the tools of fractography, a novel strength testing method and damage replication to discover that display glass surfaces do not encounter damage events that are well-represented by classic diamond indentation understanding. The damage is best described as blunt frictive and sharp subthreshold scratches. The same discipline used to elucidate the nature of glass damage generated with a Vickers diamond over the past 40 years can be applied to the causes of these flaws as well.

11:30 AM

(GOMD-S1-019-2017) Sheet Glass Surface Relaxation Effect Understanding with Modeling and Experiment

Z. Zheng*[1]; T. M. Gross[1]; J. T. Westbrook[1]; P. J. Lezzi[1]; I. A. Nikulin[1]; D. Joshi[1]; R. Zhang[1]

1. Corning Incorporated, USA

Glass is found to have the surface relaxation phenomena, happening at a thin layer (<100μm) on the glass surface, enhanced by water diffusion, stress and temperature much lower than glass transition, even at room temperature (Tomozawa, RPI). As a result, noticeable permanent residual stress and deformation can be observed below strain point. In this study theoretical and numerical models have been developed based on the viscoelastic relaxation theory to characterize the surface relaxation effect and to understand the impact of environment parameters such as temperature and humidity. Experiment characterization is on-going to calibrate the model parameters and to verify the model results.

GOMD Symposium 3: Optical and Electronic Materials and Devices: Fundamentals and Applications

Rare Earth Doped Phosphors, Nanocrystals, and Glass-Ceramics

Room: Kona 3
Session Chair: Shibin Jiang, AdValue Photonics Inc

9:45 AM

(GOMD-S3-030-2017) Insight on moisture-induced degradation process of $Sr_xCa_{1-x}AlSiN_3$:Eu^{2+} red phosphors (Invited)

F. Yao[1]; Y. Zhuang*[1]; R. Xie[1]

1. Xiamen University, China

The chemical stability against moisture and heat during the term of service is a non-negligible factor for white-LED phosphors. However, litter attention has been put on how and why phosphors degrade in high-humidity and high-temperature environments until recent years. In this paper, we treated commercialized red phosphors $Sr_xCa_{1-x}AlSiN_3$:Eu^{2+} with different Sr/Ca ratio at extreme humidity conditions in order to accelerate the degradation process. Surprisingly, although the raw phosphors with different Sr/Ca ratio showed similar particle size, morphology and crystallinity, significate differences in photoluminescence intensity decrease, crystal phase transition, and particle morphology variation were found after the treatments. In other word, the phosphors with lower Sr/Ca ratio showed much better stability against moisture and heat. Comprehensive investigations including cathodoluminescence (CL) spectra, element analysis, and Rietveld refinement were performed to reveal the moisture-induced degradation process. The major reason for the stability was attributed to the bond lengths between Sr/Ca/Eu and N (coordination geometry of Sr/Ca/Eu) from the microstructure viewpoint.

10:15 AM

(GOMD-S3-031-2017) Europium doped oxynitride phosphate glasses as promising white phosphors

M. Cicconi[2]; A. Veber[2]; D. de Ligny[2]; J. Rocherullé*[1]; R. Lebullenger[1]; F. Tessier[1]; P. Bénard-Rocherullé[1]; X. Zhang[1]

1. University of Rennes, Chemical Sciences Institute, France
2. University Erlangen-Nürnberg, Materials Sciences and Engineering, Germany

In order to produce a new-generation of REE environmental friendly phosphors, we are developing a white phosphor emission from Eu-doped oxynitride phosphate glasses, with compositions compatible to the natural occurring REE-bearing minerals. Environmental friendly because, i) phosphate glasses require much lower synthesis temperatures with respect to silicate glasses, and ii) after the use of the device, REE could be reconcentrated by crystallization of phosphate phases, in order to recover REE. Eu-redox equilibrium in glasses depends strongly on temperature, species concentration, melt composition, polymerization and synthesis conditions. If phosphate glasses suffer from a low chemical durability, nitridation under ammonia is a suitable way to improve their chemical resistance. Because ammonia is both reducing and nitriding, the control of the O/N ratio is important for tuning the materials properties, especially when mixed oxidation states are present. Nitridation at 750°C allowed increasing glass transition temperatures and glass forming ability. Moreover, the N-treatment increased the amount of Eu^{2+} and a relevant broadening, as well as a slightly shift to higher wavelengths of Eu^{2+} emission band was observed. Being the first part of a larger project on the development of "green" Eu-based phosphors, this work also reports an attempt to investigate the crystallization behavior of these promising glasses.

10:30 AM

(GOMD-S3-032-2017) Oxyfluoride glass ceramic with LaF_3 nanocrystals doped with Eu^{2+} for white LED color conversion of 400 nm LED

H. Lee[1]; S. Lee[2]; Y. Choi[3]; W. Im[4]; W. Chung*[1]

1. Kongju National University, Division of Advanced Materials Engineering, Republic of Korea
2. Bass Ltd., Republic of Korea
3. Korea Aerospace University, Republic of Korea
4. Chonnam National University, Republic of Korea

Oxyfluoride glass ceramics with LaF_3 nanocrystal can provide high quantum efficiency of the doped rare earth ions due to low phonon energy of fluoride crystals. They also have high chemical and thermal stability of the oxide based glasses and thus can be a good candidate for inorganic color converting material for white LED. Among various rare earth ions, Eu^{2+}-ion is suitable for 400 nm LED color conversion and thus widely studied to make white emission. However, it was hard to achieve white LED due to low conversion efficiency of the glass ceramics. In this study, we fabricated Eu^{2+} co-doped oxyfluoride glasses based on SiO_2-Na_2O-Al_2O_3-LaF_3 and examined their color converting properties. Eu^{2+} emission was shifted from cyan to green when heat treated up to 750 °C for LaF_3 nanocrystal formation. When Mn^{2+} was co-doped to compensate red-emission, white LED with high color rendering index of 91 could be obtained via adjustment of MnO_2 concentration and thickness. Further shift of the emission peak and highly improved emission intensity of Eu^{2+} was also observed when the Eu^{2+} single-doped glass was further heat treated up to 800 °C. White LED could be also achieved and quantum yield of the glass was estimated. Formation of additional crystalline peak was responsible for the behavior.

10:45 AM

(GOMD-S3-033-2017) Trap depth and color variation of Ce_{3+}-Cr^{3+} co-doped $Gd_3(Al,Ga)_5O_{12}$ garnet persistent phosphors

S. Tanabe*[1]

1. Kyoto University, Japan

Persistent luminescent properties in Ce^{3+}-Cr^{3+} codoped Gd_3Al_{5-x} $GaxO_{12}$ garnet (GAGG:Ce-Cr) solidsolution have been investigated. The persistent luminescent color is shifted from orange to yellowish green with increasing Ga content because Ce^{3+}: 5d level splitting becomes much weaker. The depth of electron trap introduced by Cr odoping was estimated from the intense thermoluminescence glow peak by the initial rise method. The trap depth decreases from 0.56 eV to 0.29 eV with increasing Ga content. The shift can be explained by downshift of bottom of conduction band. From the persistent luminescence decay curve measurement after ceasing 450 nm blue illumination, the samples with x=2.5 exhibited the longest persistent luminescence for 405 min until the luminance becomes 2 mcd/m^2 in GAGG:Ce-Cr phosphors.

11:00 AM

(GOMD-S3-034-2017) Near-infrared long persistent luminescence of Er^{3+} in garnet for the third bio-imaging window

J. Xu*[1]; J. Ueda[1]; S. Tanabe[1]

1. Kyoto University, Graduate School of Human and Environmental Studies, Japan

By utilizing efficient persistent energy transfer from Ce^{3+} to Er^{3+}, we have successfully developed a novel garnet persistent phosphor of $Y_3Al_2Ga_3O_{12}$ doped with Er^{3+}, Ce^{3+}, Cr^{3+} ions (YAGG:Er-Ce-Cr) exhibiting long (>10 h) near-infrared (NIR) persistent luminescence (PersL) in the broad range from 1450 nm to 1670 nm due to the typical Er^{3+}:$^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition in garnet. The NIR PersL bands of Er^{3+} match well with the third bio-imaging window (NIR-III, approximately from 1500 nm to 1800 nm) and the response curve of InGaAs detectors. The photon emission rate (8.33×10^{17} cps/Sr/m^2) of the YAGG:Er-Ce-Cr persistent phosphor at 10 min after ceasing blue light illumination was over two times higher than that of the widely used $ZnGa_2O_4$:Cr^{3+} deep-red persistent phosphor (3.30×10^{17} cps/Sr/m^2). We also show the first PersL imaging by a commercial InGaAs camera monitoring Er^{3+} emission indicating that this material can be a promising candidate for in-vivo bio-imaging in the NIR-III window.

11:15 AM

(GOMD-S3-035-2017) Oriented $LiNbO_3$ nanocrystals photo-precipitation in Li_2O-Nb_2O_5-SiO_2 silicate glass by femtosecond laser direct writing

J. Cao[1]; M. Lancry*[1]; L. Mazerolles[2]; F. Brisset[1]; B. Poumellec[1]

1. University Paris Sud, France
2. Université Paris Est, France

We explore the femtosecond laser-induced modifications (i.e., morphology, crystallization, and nanostructure) in lithium niobium silicate glass at high-repetition-rate (1030nm, 300fs, 300 kHz) to get insight on the ultrafast laser-matter interaction according to pulse energy and writing configuration (laser polarization direction versus scanning one). The modifications can be classified into three regimes according to pulse energy: 1) at 0.3-0.4 μJ/pulse, one amorphous zone with a larger sensitivity to the chemical etching; 2) at 0.5-0.9 μJ/pulse, textured nanocrystals embedded in lamella-like amorphous phases whatever the laser polarization or scanning direction is; 3) at 1.0-2.2 μJ/pulse, crystallization dependent on the writing configuration. Remarkably, the orientation of the nanostructure can be controlled by laser polarization. The polar axis of the nanocrystal is distributed in the plane perpendicular to laser polarization direction. A mechanism based on the application of laser-induced torques on the nanocrystal electric dipole is proposed. In addition, this nanostructure is investigated in three-dimension by a combination of scanning electron microscope, electron backscatter diffraction, and transmission electron microscopy. This may have applications in fabricating non-linear optical devices based on second harmonic generation.

11:30 AM

(GOMD-S3-036-2017) A new class of nanocomposite glass for tunable optical functionality

R. Li*[1]

1. Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, China

Novel $AlPO_4$ nanocomposite glass, a new class of materials characterized by larger surface area and controlled pore sizes arranging from 2nm to 15 nm, has been developed by sol gel method by us recently. The incorporation of various photo-active species in nanoscale porous structure is currently attracting attention as new optical functionalities, which devotes particular effort to new optical materials for wide applications including solar cells, optical amplifiers, etc. In this scenario, three functional photo-active species, including laser dyes, and rare earth, have been separately incorporated in our AlPO4 mesoporous glass to achieve optical functionalities: 1) Different dipping methods are designed and controlled in our laboratory to explore luminescent nanocomposites-$AlPO_4$ mesoporous glassincorporated with PbS QDs, which enable the controlled luminescence with broad tunability or bimodal emission. Fig 1. Photoluminlescence for PbS-$AlPO_4$ composites 2) Different amount of rare earth Eu loaded mesoporous $AlPO_4$ glasses were prepared by simple dipping method. Controlled emission intensity showed obvious concentration and heated temperature dependences, signifying excellent fluorescence tailoring properties of blue and red emission;

GOMD Symposium 4: Glass Technology and Crosscutting Topics

Chalcogenide Materials for Memory Applications

Room: Waikoloa 3
Session Chair: David Drabold, Ohio University

9:45 AM

(GOMD-S4-001-2017) Atomistic modeling of resistance switching materials (Invited)

N. Onofrio*[1]

1. The Hong Kong Polytechnic University, Applied Physics, Hong Kong

Ionic diffusion in amorphous materials are key processes in a variety of emerging device operation for energy and electronic applications. For instance, electrochemical metallization (ECM) cells have the potential to replace Flash memories due to their low power consumption, fast operation, and scaling limits reaching nanometers. ECM cells consist of two metallic electrodes separated by an amorphous dielectric, and they can switch between high and low resistance states with the application of voltage, due to the formation and dissolution of a metallic filament. Although experimental studies are providing important insights regarding the fundamental physics of these devices, these techniques are not without limitations. Understanding the electrochemical dissolution, the migration and nucleation of metallic ions inside amorphous materials is key to accelerating the development of ECM cells into commercial products. Interestingly, the spatial and temporal scales involved make the problem amenable to molecular dynamics simulations, which can provide a full atomistic picture of ECM. We have recently developed the EChemDID method to describe the electrochemical driving force in molecular dynamics simulations, enabling atomistic simulations of switching at the nanoscale. In this talk, we will present EChemDID and discuss the atomic mechanism of filamentary switching, including examples based on simulations of Cu/a-SiO_2 cells.

10:10 AM

(GOMD-S4-002-2017) Heterostructures of chalcogenides and graphene for nonvolatile memory (Invited)

J. Akola*[1]; S. Kulju[1]; D. Prendergast[3]; R. O. Jones[2]

1. Tampere University of Technology, Materials and Molecular Modelling, Department of Physics, Finland
2. PGI-1, Forschungszentrum Juelich, Germany
3. Molecular Foundry, Lawrence Berkeley National Laboratory, USA

The remarkable ability of phase change materials (PCM) to switch between amorphous and crystalline states on a nanosecond time scale could provide new opportunities for graphene engineering. We have used density functional calculations to investigate the structures and electronic properties of heterostructures of thin amorphous and crystalline films of the PCM GeTe (16 Å thick) and $Ge_2Sb_2Te_5$ (20 Å) between graphene layers. The interaction between graphene and PCM is very weak, charge transfer is negligible, and the structures of the chalcogenide films differ little from those of bulk phases. A crystalline GeTe (111) layer induces a band gap opening of 80 meV at the Dirac point. This effect is absent for the amorphous film, but the Fermi energy shifts down along the Dirac cone by −60 meV. $Ge_2Sb_2Te_5$ shows similar features, although inherent disorder in the crystalline rocksalt structure reduces the contrast in band structure from that in the amorphous structure. These features originate in charge polarization within the crystalline films, which show electromechanical response (piezoelectricity) upon compression, and show that the electronic properties of graphene structures can be tuned by inducing ultra-fast structural transitions within the chalcogenide layers. Graphene can also be used to manipulate the structural state of the PCM layer and its electronic and optical properties.

10:35 AM

(GOMD-S4-003-2017) Novel computer memory based upon chalcogenide glasses (Invited)

M. Salinga*[1]

1. RWTH Aachen University, Germany

Information storage concepts employing resistive switching of chalcogenides have matured in recent years. The announcement of 3D-XPoint™ memory by Micron/Intel put a spotlight on a whole class of materials that has been studied since the 1960s. Chalcogenides can be switched reversibly between a highly-resistive and a highly-conductive state. A breakdown of the resistance occurs at threshold fields of 20 V/μm to 50 V/μm leading to a substantial increase of current which can induce crystallization through substantial Joule-heating. The time-scale on which stable crystallization can occur separates the so-called phase-change materials (PCM) from the ovonic-threshold switching materials (OTS). PCMs tend to form stable crystallites within a few nanoseconds, whereas OTS-materials prefer an amorphous atomic structure even at significantly elevated temperatures. However, both kinds of amorphous materials share a highly non-linear current-voltage characteristic. Despite intensive research, the origins of this non-linearity are still debated today. Here, the characteristic switching kinetics of this family of materials will be analyzed with a particular emphasis on implications for their employment in both next-generation computer memories and neuromorphic hardware.

11:00 AM

(GOMD-S4-004-2017) Density functional study of Ag/Ge/S and Ag/As/S alloys used in resistive RAM

J. Akola*[1]; R. O. Jones[2]

1. Tampere University of Technology, Materials and Molecular Modelling, Department of Physics, Finland
2. Forschungszentrum Juelich, PGI-1, Germany

Density functional/molecular dynamics simulations have been performed to determine structural and other properties of amorphous Ag/Ge/S and Ge/S alloys. In the former, the calculations have been combined with experimental data (x-ray and neutron diffraction, extended x-ray absorption fine structure). Ag/Ge/As alloys have high ionic conductivity and are among the most promising candidates for future memristor technology (conductive-bridging RAM). We find excellent agreement between the experimental results and large-scale (500 atoms) simulations in Ag/Ge/S, and we compare and contrast the structures of Ge/S and Ag/Ge/S. The calculated electronic structures, vibrational densities of states, ionic mobilities, and cavity distributions of the amorphous materials are discussed and compared with data on crystalline phases where available. The high mobility of Ag in solid state electrolyte applications is related to the presence of cavities and can occur via jumps to a neighbouring vacant site. We reflect our findings with our previous study on Ag/As/S and As/S alloys where a local modification of the covalent As-S network was observed upon Ag diffusion.

11:15 AM

(GOMD-S4-005-2017) Early-stage switching in chalcogenide-based Conductive-bridging Random Access Memory (CBRAM)

M. Sundararajan[1]; K. Prasai[1]; D. Drabold[1]; G. Chen*[1]

1. Ohio University, USA

The Conductive-bridging Random Access Memory (CBRAM) is a type of Resistive Random Access Memory (RRAM) that shows threshold switching in resistance under external disturbance. The CBRAM has advantages of high switching speed, low power consumption, excellent scalability and high endurance over the flash memory and is becoming a major player in the field of non-volatile memory. While a great deal of effort has been dedicated to commercializing the CBRAM technology, the atomistic mechanisms behind the fast switching of the amorphous chalcogenides remain elusive. The unsolved key question is related to the origin of the conductive filaments that are responsible for the switching. To tackle this problem, we synthesized Ag-doped Ge-Se thin films and CBRAM devices and study the kinetics of switching of the CBRAM devices using cyclic voltammetry. It was found that the early stage of switching was not related to formation of metallic filament. We prose a new atomistic model for the mechanism of switching which was supported by the results from our first-principle Molecular Dynamic simulations.

11:30 AM

(GOMD-S4-006-2017) Conductivity in CBRAM materials (Invited)

K. Prasai*[1]; G. Chen[1]; D. Drabold[1]

1. Ohio University, Physics and Astronomy, USA

Silver doped amorphous chalcogenides are being used to build memory elements because these elements show swift change in conductivity in response to a small external voltage. We have studied the atomistic origin of such conductivity using $(GeSe_3)_xAg_{100-x}$ as a canonical example. Using the recently developed method of gap sculpting, we show how a biased dynamics can be used to simulate conducting phase of this material. We study the models and point out the salient features of the conducting phase and draw the contrast with their insulating counterparts. We also point out the role of silver clusters/wires in conductivity by an explicit simulation of such structures within the glassy matrix.

Glass Corrosion I: Modeling

Room: Kona 2

Session Chairs: Stephane Gin, CEA; Aurélie Verney-Carron, LISA

9:45 AM

(GOMD-S4-007-2017) Glass Corrosion Models: Questions and Answers (that lead to more questions) (Invited)

J. Ryan*[1]

1. Pacific Northwest National Lab, USA

Glass corrosion, both in the short and long terms, has been the subject of research for years and the calculations that attempt to model the corrosion processes have taken many forms. Often, these models have relied on empirical fits to some extent in order to advance an operational form. It is largely agreed that radionuclide release from glass is due to the combined contributions of many mechanisms, including solution affinity, local solution changes due to secondary phase precipitation, non-dissolution reactions, solid state diffusion, altered chemistries due to pore tortuosity in alteration layers, and reactive transport. These processes and the interplay between them are so complex that existing models often either do not include their impacts or simplify them. This talk will compare the mechanistic processes inferred by selected models against recent evidence regarding those mechanisms. Areas where particular models excel and where they break down will be discussed. The talk will conclude with an examination of the implications of recent experimental results on glass rate models and where the opportunities and open questions lie in glass corrosion research.

10:15 AM

(GOMD-S4-008-2017) Nonlinear dynamics of aqueous dissolution of silicate glasses and its implications to glass waste form durability (Invited)

Y. Wang*[1]

1. Sandia National Laboratories, Nuclear Waste Disposal Research & Analysis, USA

Silicate materials have been used for numerous industrial, biomedical and environmental applications including nuclear waste disposal. The dissolution process has long been considered to be controlled by a leached surface layer in which cations in the silicate framework are gradually leached out and replaced by protons from the solution. This view has recently been challenged by observations of extremely sharp corrosion fronts and oscillatory zonings in altered rims of the materials, suggesting that corrosion of these materials may proceed directly through congruent dissolution followed by secondary mineral precipitation. The work presented here shows that complex silicate material dissolution behaviors can emerge from a simple positive feedback between dissolution-induced cation release and cation-enhanced dissolution kinetics. This self-accelerating mechanism enables a systematic prediction of the occurrence of sharp dissolution fronts (vs. leached surface layers), oscillatory dissolution behaviors and multiple stages of glass dissolution (in particular the alteration resumption at a late stage of a corrosion process). This work provides a new perspective for predicting long-term silicate weathering rates in actual geochemical systems and developing durable silicate materials for various engineering applications.

10:45 AM

(GOMD-S4-009-2017) Molecular modeling of nuclear waste glass and altered layers (Invited)

T. Ohkubo*[1]

1. Chiba University, Faculty of Engineering, Japan

A common complex feature of nuclear waste glasses originates from multi-components system, which forms various oxide bonds and stable ionic sites. We have developed our ab initio program in basis of DFT theory that specializes to efficiently deal with amorphous materials. On the computational cost, this program clearly shows superiority for non-periodic system. Therefore, ab initio molecular dynamics simulation with relatively large number of atoms and long simulation periods is now open for understanding of nuclear waste glass and melts. I would like to discuss structural properties of simplified nuclear glass and melts obtained from this approach. Surface layers formed by glass alteration play an important role for glass corrosion. In viewpoint of safety assessment regarding glass durability, a deep understanding of mass transports is required. I have tackled to make realistic drawing in molecular levels by molecular dynamics, which can reproduce transport parameters such as diffusion coefficients. Molecular models of the altered layer were built up by removing soluble elements and inserting water molecules in pristine alminoborosilicate glass, then energetically relaxed structure was obtained from molecular dynamics simulation. I would like to present the structure and water transport in this modeled layer.

11:15 AM

(GOMD-S4-010-2017) Density Functional Theory Modeling of Silicate Glass Dissolution

J. D. Kubicki*[1]; F. Tielens[2]; J. Boettger[3]

1. University of Texas at El Paso, Geological Sciences, USA
2. Sorbonne Université, France
3. Pennsylvania State University, Geosciences, USA

This work focuses on the atomic and electronic structure of silicate glass surfaces undergoing hydrolysis reactions that lead to dissolution. Corrosion of glasses is a critical process related to nuclear waste storage, ancient artifacts and weathering of naturally-occurring glasses, so understanding the molecular mechanisms behind glass corrosion is of broad interest. This study utilizes the surface model of amorphous silica published in Cimas et al. (J. Phys.: Condens. Matter 26 (2014) 244106). Because dissolution increases with acidic and basic pH as well as salt content in solution, the amorphous silica-water interface has been modeled with HCl, NaOH, and NaCl present. The effect of each of these solutes on the calculated activation energy barriers for hydrolysis of Si-O-Si, Si-O-Al and Si-O-B linkages has been investigated. In particular, we test the hypothesis of Kubicki et al. (J. Phys. Chem. C 2012, 116, 17479–17491) that intrasurface hydrogen-bonding can lead to H^+ transfer to bridging O atoms and hydrolysis of these key linkages. The model results are compared to experimental data on dissolution rates and activation energy barriers. In addition, the ^{29}Si and ^{27}Al NMR chemical shifts are calculated for comparison to observed values on dissolving glass surfaces.

11:30 AM

(GOMD-S4-011-2017) Structure of Multicomponent Glass Surfaces and Reactions with Water

S. H. Garofalini*[1]; M. Ha[1]; J. Urraca[1]

1. Rutgers Univ, USA

Simulations and analysis of the differences between bulk and surface structures and compositions of multicomponent aluminoborosilicate glasses and the effect of exposure to moisture will also be presented. Glasses containing Na, Ca, Si, Al, B, and O have been studied using multibody potentials that enable results consistent with NMR data for bulk glasses and show the changes occurring at the glass surface. Exposure to moisture for certain compositions shows the effect of the different surface compositions on hydroxylation, strengthening, and ion removal.

11:45 AM

(GOMD-S4-012-2017) Nanoscale stress-corrosion of silicate glass in aqueous solutions: Simulations and experiments

L. Criscenti*[1]; J. Rimsza[1]; R. Jones[2]; E. Matteo[3]

1. Sandia National Laboratories, Geochemistry, USA
2. Sandia National Laboratories, Mechanics of Materials, USA
3. Sandia National Laboratories, Nuclear Waste Disposal Research & Analysis, USA

Previous studies of silicate glass dissolution start by assuming interaction between a relatively flat glass surface in contact with aqueous solution. However, cracks may form in the glass that lead to more complex local glass-water interactions. Crack propagation in wet environments is the result of a combination of chemical reactions and mechanical stress. In ongoing research, molecular dynamics simulations and nanoscale experiments are being conducted in parallel to identify the coupled chemical-mechanical mechanisms that control crack propagation in silicates in the presence of water. In addition, the fracture toughness, a continuum-scale property, is calculated from the atomistic simulation results for comparison with experimental data. Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

GOMD Symposium 5: Professor Jacques Lucas Honorary Symposium

Fluoride?

Room: Kona 5
Session Chair: Xianghua Zhang, Université de Rennes 1

9:40 AM

(GOMD-S5-012-2017) Fluoride Glasses: History and prospects (Invited)

J. Adam*[1]

1. University Rennes - CNRS, France

Fluorozirconate glasses were discovered in the mid-70s at the University of Rennes. Rapidly, they became highly promising materials in photonics because of a broad transparency window from the UV to the mid-IR, up to 6-7 μm. Then, research activity expanded worldwide, not only to study the optical properties of these new materials, but also to investigate their original glass structure and thermo-mechanical properties. This paper reviews 40 years of research on fluoride glasses, essentially in terms of relations between glass compositions and infrared transmission, and of fluoride glass fiber manufacturing and properties, including fiber lasers and optical amplifiers.

10:00 AM

(GOMD-S5-013-2017) Nanoparticle Doping of Optical Fibers – Can Silica Behave like a Fluoride? (Invited)

J. Ballato*[1]; C. Kucera[1]; M. Vermillac[2]; W. Blanc[2]; H. Fneich[3]; A. Mehdi[3]; M. Cabié[4]; T. Neisius[4]; C. Baker[5]; J. Friebele[5]

1. Clemson University, USA
2. Université de Nice-Sophia Antipolis, France
3. Université de Montpellier, France
4. Aix-Marseille Université, France
5. US Naval Research Laboratory, USA

Rare earth doped silica optical fibers have become central tools in optical amplifier and high energy laser systems. However, while silica is known for its remarkable transparency and thermomechanical robustness, the fairly high energy of the Si-O bonds promote non-radiative relaxation from active dopants when compared to low phonon energy glasses, such as the fluorides. Further, while silica glass compositions can be tailored to enhance the spectroscopy of the rare earths, there are practical limits imposed by the CVD processes employed to make the silica glasses. In this work, a novel solution to these issues is addressed – the doping of silica optical fibers using rare-earth doped dielectric nanoparticles. By controlling the local molecular environment about the rare-earth, which is the most impactful from the perspective of both radiative and non-radiative relaxations, the spectroscopic properties of the rare earth emissions is enhanced in other-wise "conventional" telecommunications grade silica fiber. More specifically, to be discussed will be the doping of alkaline earth and lanthanum fluoride nanoparticles with a variety of rare earth ions and demonstration of controlled and enhanced energy transfer, radiative lifetimes, and broadened emission spectra. Additionally, fiber-draw-induced elongation and break-up of the particles inside the core of a silica-based optical fiber will also be noted.

10:20 AM

(GOMD-S5-014-2017) Spectroscopic study of Er^{3+} ions in fluorotellurite glass-ceramics

R. Balda*[1]; R. Morea[2]; J. Gonzalo[2]; J. Fernandez[1]

1. University of the Basque Country, Applied Physics, Spain
2. Laser Processing Group, Instituto de Optica, CSIC, Spain

Rare earth-doped transparent oxyfluoride glass-ceramics combine the good mechanical, thermal, and chemical properties of oxide glasses with the low phonon energy of fluoride crystals. This work reports the influence of the nanocrystallization process on the luminescence properties of Er^{3+} ions in transparent fluorotellurite glass-ceramics obtained by heat treatment of the precursor Er-doped glass. The comparison of the fluorescence properties of Er^{3+}-doped precursor glass and glass-ceramic confirms the successful incorporation of the rare-earth into the nanocrystals. The strong reduction of the Ω_2 Judd-Ofelt parameter and the intensity of the hypersensitive transition $^4I_{15/2}\rightarrow{}^2H_{11/2}$ in the heat treated sample indicate that Er^{3+} ions are in a crystalline environment. The $^4I_{13/2}$ decay in the glass-ceramic sample can be described by two single exponential functions which suggests that a fraction of Er^{3+} ions are forming nanocrystals while the rest remains in a glass environment. The presence of ErF_3 nanocrystals has a strong effect in the upconverted red emission from $^4F_{9/2}$ level. This emission increases significantly as compared with the green one in the glass-ceramic sample. The time evolution of the upconverted red emission suggests that energy transfer upconversion processes are responsible for the increase of this emission in the glass-ceramic sample.

Morey Lecture (2015)

Room: Kona 5
Session Chair: Steve Martin, Iowa State University

10:35 AM

(GOMD-S5-015-2017) Control of the metastable state of glasses (Invited)

J. Qiu*[1]

1. South China University of Technology, China

Materials science deals with relationships between composition, structure, property and performance of the materials. Glass is a special material featuring good homogeneity, variable composition, easy shaping and doping, owing to its meta-stable state and topological network structure. We have focused our research on the change and enhancement of the properties of glass by manipulation of the metastable nature of glasses. This strategy allows for precise control of the microstructure of glasses by using external fields e.g. light, temperature and pressure, and the development of novel and enhanced functionalities by controlling electronic band structure, defect state and nano- or microstructure of glass. In this talk, I will highlight our recent research developments on the design and control of the optical properties of glass through fast-cooling, crystallization and phase separation. We have demonstrated the realization of ultra-broadband near-infrared emission via control of valence state of Bi ion, ligand field around transition metal ions and energy transfer between two active ions for broadband optical amplification and tunable laser. I will also introduce our results on the printing of three-dimensional nano- or microstructures and multiple functions inside glasses by fs laser based on multiphoton absorption assisted control of excited state of dopants and nanostructures.

"X" Glasses

Room: Kona 5
Session Chair: Steve Martin, Iowa State University

11:15 AM

(GOMD-S5-016-2017) From TeX to Flex: The impact of Jacques Lucas on the next generation (and beyond) of ChG researchers (Invited)

K. Richardson*[1]

1. University of Central Florida, CREOL, USA

It has been more than 25 years since I made my first chalcogenide glass (ChG) and it would never have happened if it were not for Jacques Lucas and my advisor Bill LaCourse. The ability to compositionally tailor optical (and other) function in infrared glasses represented in the late 80's a marked change in the direction of amorphous chalcogenide materials that till that time was largely focused on crystals and applications in electronic and xerography applications. This presentation summarizes my perspective on how global ChG research has benefited from the strategy and innovative approach Jacques Lucas and the Univ. of Rennes team pioneered in the 1980's and since.

11:35 AM

(GOMD-S5-017-2017) The invention and development of the TeX glasses (Invited)

X. Zhang*[1]; H. Ma[1]; J. Lucas[1]

1. Université de Rennes I, France

The adventure of TeX Glasses started, about thirty years ago, with the examination of the crystalline structure of Te_3Cl_2, consisted in an infinite and distorted chain of tellurium. One tellurium over three is connected to two chlorines. As expected, this type of structure can easily lose its periodicity during the melt quenching, leading to a new family of glasses with excellent infrared transmission. That was the motivation in order to extend the transmission range of fluoride glasses which attracted, at that time, huge attention for its potential extremely low losses. Due to the relatively weak mechanical properties and chemical durability, the main interest of the TeX glasses is academic, as there are only few bi-atomic glasses which can also exist in crystalline form. Much effort has been necessaire to improve the properties of these glasses by introducing other elements. Techniques for purification and for shaping have also been developed. The process leading to commercial products will be presented.

PACRIM Third International Richard M. Fulrath Symposium on Discontinuous Progress for Ceramic Innovations

Fulrath Session I

Room: Queen's 6
Session Chairs: Takaaki Tsurumi, Tokyo Institute of Technology; Jon-Paul Maria, North Carolina State University

8:50 AM

(PACRIM-FUL-001-2017) Revising the Narrative of Ceramic and Ceramic –Polymer Composite Processing to a Fast, Sustainable Manufacturing Approach (Invited)

C. Randall*[1]; H. Guo[1]; J. Guo'[1]; S. Funahashi[1]; A. Baker[1]

1. Materials Research Institute, Penn State University, USA

For over 30,000 years, the general practice of sintering ceramics has involved a high temperature thermal treatment to drive the transport processes to densify the particles and minimize the surface energy of the material. Typical sintering temperatures consider 0.6 to 0.8 of the melting temperature (T_m) for many oxides; this means we sinter around 800 ºC to 1200 ºC for 2 to 10 hours. Here we introduce a broad body of systems that utilize a transient aqueous based liquid phase (1 to 10 wt%) that sinters under a uniaxial pressure, while being heated from room temperature to 250 ^{O}C, over a time period of 10 to 60 minutes. Given the massive drop in sintering temperature of the ceramic, this offers many new opportunities in material design, especially in composites. We will show three different types of polymer ceramic composites with high percentages of ceramic, 100% to 60%, with the thermoplastic polymers for dielectric applications, ionic electrolytes, and semiconducting composites. We will also show preliminary data with CSP with multilayer ceramics and printable electronics.

9:10 AM

(PACRIM-FUL-002-2017) Recent Topics in the Field of Ferroelectric Materials for BME-MLCCs (Invited)

T. Nomura*[1]; Y. Sasaki[1]; A. Nemoto[1]; Y. Akimoto[1]

1. Shoei Chemical Inc., Japan

The present paper focuses on the recent direction of materials technology for BME (Base Metal Electrode)-MLCCs (Multilayer Ceramic Capacitors). Recently, accelerating are miniaturization, high capacitance, and reduction of production cost of MLCCs, in order to meet the requirements of the electronics market. In order to maintain high capacitance values with smaller case sizes, the reduction in thickness and the multiplication of the dielectric layers have been advancing. Thinning dielectric layers, however, has a deleterious effect on the dielectric performance and it is considered getting closer to dimensional limit. Temperature stable MLCCs of high capacitance such as X7R, X7S, and/or X7T characteristics in EIA-STD have been employing $BaTiO_3$ based ferroelectric materials so far. In the case of $BaTiO_3$ based ferroelectrics, X8R characteristics may be a limit for temperature stable MLCCs, because Curie temperature of $BaTiO_3$ is around 120-130C. Under these circumstances, so many studies have been devoted to ferroelectric materials such as giant dielectric constant (K) materials, high Tc materials of high K, high withstanding voltage materials, and so on. In this paper, these challenges in the field of dielectric materials for MLCCs are reviewed, and a potential of filled tungsten-bronze-type ferroelectrics for high capacitance BME-MLCCs of X9R characteristics ($\Delta C/C_{25}$%±15%, -55~200C) will be proposed.

9:30 AM

(PACRIM-FUL-003-2017) Recent progress in multilayer ceramic devices (Invited)

H. Kishi*[1]

1. Taiyo Yuden Co., Ltd., R&D Laboratory, Japan

Progressive technological innovations in multilayer ceramic devices such as capacitors, inductors and piezoelectric actuators play a remarkably important role in downsizing and improving performances in a wide variety of electric equipments, especially in mobile electronic equipment such as smart phones and personal computers. The manufacturing technologies of multilayer ceramic capacitors (MLCC) with Ni electrode have progressed remarkably, and capacitive volumetric efficiency of Ni-MLCC has been increasing at the rate of two orders per decade. One of the key technologies for Ni-MLCC is decreasing the thickness of the dielectric active layers. The recent progress in material design and processing technology for realizing high-performance Ni-MLCC are reviewed. Multilayer chip inductors (MLCI) using Ni-Zn-Cu ferrite material have been also widely used due to their high magnetic permeability and high electrical resistivity. Recently, we have developed new type MLCI using Fe-based metal powders for smaller power inductors. We introduce the material design and the performance of newly developed power inductors with smaller case size. Also, we introduce recent some topics on piezoelectric devices and solid state battery using multilayer technology.

10:05 AM

(PACRIM-FUL-004-2017) Additive Manufacturing of Inorganic-Organic Hybrid Materials (Invited)

R. Narayan*[1]

1. NC State University, USA

We have shown that two photon polymerization of organically modified ceramic materials is able to create medical devices with smaller features than conventional microfabrication techniques. Organically modified ceramic materials exhibit exceptional chemical and thermal stability and as such are appropriate for use in either worn medical devices (e.g., microneedle devices) or medical implants (e.g., scaffolds for tissue engineering). Two photon polymerization involves the spatial and temporal overlap of photons to initiate chemical reactions that lead to photopolymerization and solidication within well-defined and highly-localized volumes. In this presentation, mechanical (e.g., fracture testing) and in vitro biological studies (e.g., 3-(4, 5-dimethylthiazol-2-yl)2,5-diphenyl tetrazolium bromide (MTT) assays) of organically modified ceramic materials that were processed using two photon polymerization will be described.

10:25 AM

(PACRIM-FUL-005-2017) Development of ceramic structure control method with DC and pulsed electric field

T. Nakayama*[1]; N. Matsutani[1]; H. Triet[1]; N. Son[1]; H. Suematsu[1]; T. Suzuki[1]; K. Niihara[1]

1. Nagaoka Univ of Tech, Japan

The main purpose of this study is a driving control of micro-structure by electric field. In particular, the drive control of the micro-structure in a non-aqueous solution to control from the outside by the electric field, are considering applications such as metering pump in the non-aqueous solution. In this study, we investigated the behavioral mechanisms of the inorganic material in non-aqueous solution when an electric field is applied. When a DC electric field is applied to the ZrO_2 balls in the polysiloxane solution, repetitive motion between the electrodes on an irregular interval was observed. In this repetitive motion, ZrO_2 balls is moved to the opposite polarity of the electrodes by the time elapsed from the beginning to the contact with the electrode. It has conducted a survey from the point of view of the electrochemical of non-aqueous solutions and electrophoresis for the mechanism of this repetitive motion.

10:45 AM

(PACRIM-FUL-006-2017) The Molten Core Fabrication of Novel Optical Fibers (Invited)

J. Ballato*[1]; P. Dragic[2]

1. Clemson University, USA
2. University of Illinois at Urbana-Champaign, Electrical and Computer Engineering, USA

The global ubiquity and near-instantaneous nature of information today is owed to the remarkable successes of glass optical fibers. As new applications have emerged where optical fibers are again the enabling technology, practitioners have largely leveraged the manufacturing methods employed in telecommunications. While such processes are mature and highly scaled, they permit only a limited range of glass compositions that do not necessarily meet the performance demands of these new applications. This talk will highlight advances in silica-based optical fibers fabricated using the innovative molten core approach which vastly expands the range of compositions that can be achieved. Particular attention will be paid to novel optical fibers that gain their performance from not-previously-employed core/clad interactions and exhibit properties of great value to next generation laser, communication, and imaging systems.

11:20 AM

(PACRIM-FUL-007-2017) Structure derived novel functions for future electronics (Invited)

A. Ando*[1]

1. Murata Mfg. Co., Japan

Structural designs are important to generate novel functions of electronic ceramics. A typical example of these structural designs is a multi-layered ceramic capacitor (MLCC). It has hierarchical structures, i.e. core - shell structure, grain - grain boundary structure, ceramic - electrode monolithic structure, and so on. Each structure should be designed to optimize the performance of the MLCC. Furthermore, in various electronic ceramic applications, such as piezoelectric devices, thermoelectric devices, structural designs have also played key roles to exhibit high performances. The structure derived novel functions of advanced ceramics will be discussed.

11:40 AM

(PACRIM-FUL-008-2017) Piezoelectric Films for Microelectromechanical Systems (Invited)

S. Trolier-McKinstry*[1]

1. Pennsylvania State University, Materials Science and Engineering, USA

Piezoelectric thin films are of increasing interest in low voltage microelectromechanical systems (MEMS) for sensing, actuation, and energy harvesting. They also serve as model systems to study fundamental behavior in piezoelectrics. The paper will discuss how materials are optimized for these applications, as well as examples of the use of piezoelectric films over a wide range of length scales. The key figures of merit for actuators and energy harvesting will be discussed, with emphasis on how to achieve these on practical substrates. For example, control of the domain structure of the ferroelectric material allows the energy harvesting figure of merit for the piezoelectric layer to be increased by factors of 4 – 10. Likewise, control of crystallographic orientation and substrate clamping enables large increases in the figure of merit for actuators. To illustrate the functionality of these films, examples of integration into MEMS structures will also be discussed, including adaptive optics for Xray telescopes, low frequency and non-resonant piezoelectric energy harvesting devices, and piezoelectronic transistors as a potential replacement for CMOS electronics.

PACRIM Symposium 02: Virtual Materials Design and Ceramic Genome

Modeling of Performances I

Room: Kohala 4
Session Chair: Masato Yoshiya, Osaka University

8:30 AM

(PACRIM-S2-011-2017) Strain and Excitation Effects on Defect Dynamics in Oxides (Invited)

Y. Zhang*[1]; J. Xi[2]; B. Petersen[2]; D. S. Aidhy[3]; B. Liu[4]; W. J. Weber[2]

1. Oak Ridge National Laboratory, USA
2. The University of Tennessee, USA
3. University of Wyoming, USA
4. Shanghai University, China

Extreme energy deposition and dissipation due to energetic particle irradiation are non-equilibrium thermodynamic processes. Understanding such processes at the level of electrons and atoms is fundamental to a wide range of research and applications. Among many important research topics, strain and excitation effects on defect dynamics are investigated in a few model oxides. In an effort to better understand experimental observations of charged defect annealing and enhanced grain growth at cryogenic temperatures in cubic ZrO_2, density functional theory has been used to investigate the stability and migration energies of neutral and charged oxygen vacancies and interstitials, as well as reveal insights on the role of charged defects on enhanced kinetics. To understand strain-induced phase and oxygen-vacancy stability, the effect of hetero-interfaces $CeO_2|ZrO_2$ and $ThO_2|ZrO_2$ interfaces are investigated. The tensile strain from interfacing of ZrO_2 with other larger lattice parameter crystals can lower oxygen vacancy formation energy. Modifying oxygen kinetics and dynamics near grain boundaries or interfaces provides a control to tune material functionality. Moreover, based on ab initio molecular dynamics, our studies on low energy recoil events have shown that the recoil events are partial-charge transfer assisted processes. This work was supported by the U.S. DOE, BES, MSED.

9:00 AM

(PACRIM-S2-012-2017) From ab initio simulations of point defects to material properties: Applications to silicon carbide (Invited)

G. Roma*[1]; T. Jourdan[1]; J. Crocombette[1]; F. Bruneval[1]

1. CEA, Université Paris-Saclay, DEN-Service de Recherches de Métallurgie Physique, France

Ab initio based evolution of defect populations using stochastic methods or rate theory has been developed since at least a decade and has provided the explanation of the evolution of material properties of irradiated materials. Its application concerns, however, mostly metals. Although applications to semiconductors or insulators exist, they overlook in most cases the variety of charge states of point defects. We present here an approach to overcome this limitation. As an example we discuss the evolution of defect populations in silicon carbide under specific non-equilibrium conditions, in particular under irradiation, and their consequences on some experimental signatures. First of all we compile a database of defect formation energies and energy barriers for migration and defect reactions in cubic silicon carbide, based on first principles calculations, discussing the limitations of standard approaches. Then we describe a way to take into account the role of charges in a homogeneous rate theory model. We then present some results of rate theory simulations for silicon carbide under or after electron irradiation. In particular, we show examples where the mutual influence of doping and kinetics in the material matters. Finally we present an example of coupling the rate theory model to the prediction of spectral signatures of irradiated materials.

9:30 AM

(PACRIM-S2-013-2017) Modeling the Morphology of Ion Tracks in Complex Oxides (Invited)

W. J. Weber*[1]; E. Zarkadoula[2]; R. Sachan[2]; D. S. Aidhy[3]; Y. Zhang[2]; C. Trautmann[4]

1. University of Tennessee, Materials Science & Engineering, USA
2. Oak Ridge National Lab, Materials Science & Technology, USA
3. University of Wyoming, Mechanical Engineering, USA
4. GSI Helmholtzzentrum für Schwerionenforschung GmbH, Germany

High angle annular dark field imaging, complemented with molecular dynamics simulations, are employed to characterize the formation, structure and properties of nanoscale ion tracks created by energetic ions in complex oxides. The atoms in the shell structure surrounding the amorphous core of the track in $Gd_2Ti_2O_7$ are disordered and have relatively larger cation-cation interspacing, suggesting the presence of tensile strain that can enhance oxygen ion conductivity in the shell structure. In Gd_2TiZrO_7, diametric variations in track diameters of up to 40% form along incremental track lengths, and molecular dynamics simulations suggest that the varations are due to the stoichastic variations in strain and the competition between Ti and Zr during track recrystallization. In $Yb_2Ti_2O_7$, amorphous ion tracks can be restructured to the defect fluorite structure by thermally annealing or with a nanoscale electron beam. The inelastic thermal spike model for insulators and molecular dynamic simulations have been used to investigate the effects of pre-existing damage on the energy dissipation and structural alterations in $SrTiO_3$ and $KTaO_3$ under ion irradiation. The results reveal a synergy between the pre-existing defects and the electronic energy loss. This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

Modeling of Performances II

Room: Kohala 4
Session Chair: Peter Kroll, UT Arlington

10:15 AM

(PACRIM-S2-014-2017) Material design for plasmonic and hot-carrier devices (Invited)

R. Sundararaman*[1]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA

Surface plasmon resonances of metallic nanostructures enable efficient light absorption at sub-wavelength length scales. Non-radiative decay of plasmon modes produce energetic electrons and holes in the material, which can potentially be utilized for photovoltaic or photochemical energy conversion with high efficiency, or for photodetection with high sensitivity. However, a fundamental challenge in utilizing plasmon-generated hot carriers remains that these carriers scatter against each other and phonons, losing energy rapidly prior to extraction. Delivering the promise of hot carrier devices requires a quantitative understanding of non-equilibrium carrier dynamics in nanostructures, and new materials with improved carrier lifetimes. We present a multi-scale framework for first-principles calculations of hot carrier excitation, transport and relaxation, critically accounting for the role of electronic structure and phonons. We demonstrate that in conventional plasmonic materials, the electronic structure characteristics that enable light absorption at small length scales also facilitate rapid thermalization of energetic carriers. We investigate whether this undesirable link can be severed in new classes of plasmonic materials such as nitrides, alloys and low-dimensional heterostructures, in order to retain efficient light absorption while minimizing carrier thermalization.

10:45 AM

(PACRIM-S2-015-2017) Atomic Structures and Chemical Bonding States across Slip Planes in Ionic Crystals (Invited)

K. Matsunaga*[1]

1. Nagoya University, Materials Science & Engineering, Japan

Ionic crystals such as metal oxides are generally difficult to undergo plastic deformation at low temperatures, and sometimes exhibit cleavage fracture. It is simply thought that such brittleness arises from the ionic nature of bonding. However, a number of exceptions were observed, which cannot be explained by the ionic bonding alone. In this study, some of ionically bonded crystals were focused, and physical origins of characteristic plastic deformation behavior were investigated by theoretical calculations. As an example, slip deformation behaviors in rock-salt structured sodium and silver chloride crystals were analyzed. Although these two systems are similar with each other, a primary slip system of sodium chloride at low temperatures is limited to {110}<110>, whereas silver chloride has several slip systems of {110}<110>, {111}<110> and {001}<110> to be activated. The present first-principles calculations showed that silver chloride has smaller potential barriers than sodium chloride due to the more covalent nature of bonding. Moreover, it was found that the slip system of {001}<110> can be activated only in AgCl. This is because occurrence of covalent-like bonds between cations across the slip plane, which cannot be expected in typical ionic crystals.

11:10 AM

(PACRIM-S2-016-2017) Properties of $RE_2Si_2O_7$ and Related Materials for Environmental Barrier Coatings (Invited)

M. Yoshiya*[1]; A. Ioki[1]; Y. Sumi[1]; T. Yokoi[1]

1. Osaka University, Department of Adaptive Machine Systems, Japan

$RE_2Si_2O_7$ and related materials have attracted attention for possible application for environmental barrier coatings of jet engines due to its excellent durability against highly corrosive gaseous species in jet engines, in addition to other essential properties such as mechanical properties or low thermal conductivity. Extensive experiments have been done to figure out the feasibility for the application with promising results. However, many phenomena observed during the experiments are not clarified yet, impeding the optimization of the environmental barrier coating systems. Another issue to be addressed is to sort out possible origins of fracture or spallation that determines life time of the environmental barrier coatings. In this study, first principles calculations based on density functional theory have been carried out to calculate theoretical values of properties that determine the life time of the coating by excluding the impact of microstructure and other defective structures that are present in reality, in order to obtain physical insight about the factors that determine those properties, and in turn, the life time of the coating systems.

11:35 AM

(PACRIM-S2-017-2017) A new ternary layered and damage-tolerance boride MoAlB: DFT insights and predictions (Invited)

Y. Bai[1]; X. Qi[1]; A. Duff[2]; N. Li[1]; F. Kong*[1]; X. He[1]; R. Wang[1]; W. E. Lee[3]

1. Harbin Institute of Technology, Center for Composite Materials and Structures, China
2. STFC Daresbury Laboratory, Hartree Centre, United Kingdom
3. Imperial College London, Department of Materials, United Kingdom

Density functional theory has been used to provide theoretical insights and predictions of crystal structure, electronic structure, lattice dynamics and elastic properties for a ternary nanolaminated and layered transition metal boride (MAB phase), MoAlB. The calculated atomic configuration matches well with experiment. The metal-like electronic structure contributes to the physical origin of the high electrical conductivity of MoAlB. Strong covalent bonding is present between the B atoms, as well as between the Mo and B atoms, and significantly the much weaker Al-Al bonds are consistent with the high fracture toughness and damage tolerance seen in MoAlB. With increasing pressure, the shrinkage is highest along the b axis, and lowest along the c axis. From the calculated second-order elastic constants, the bulk moduli B, shear moduli G, Young's moduli E and Poisson ratio μ are 207 GPa, 137 GPa, 336 GPa and 0.23, respectively. Significantly, the low G/B ratio of 0.66 due to the weak Al-Al bonds provides some evidence for the observed high damage tolerance, and demonstrates similarities in properties between MAB and MAX phases. Lattice dynamics were examined in detail, with 9 Raman-active modes and 6 infrared-active modes identified and analyzed in terms of their atomic motion and wavenumbers.

PACRIM Symposium 03: Novel, Green, and Strategic Processing and Manufacturing Technologies

Novel, Green, and Strategic Processing II

Room: King's 3
Session Chairs: Young-Wook Kim, University of Seoul; Wataru Sakamoto, Nagoya University; Toshihiro Ishikawa, Tokyo University of Science, Yamaguchi

8:30 AM

(PACRIM-S3-014-2017) Processing of complex shape ceramics by a hybrid technology (Invited)

F. J. Cambier*[1]; G. Martic[1]; X. Buttol[1]; E. Juste[1]; F. Petit[1]

1. Belgian Ceramic Resaerch Centre, R&D, Belgium

Various innovative methods allow to process complicated shape ceramic parts using computer numerical control (CNC). A lot of researches are today devoted to develop additive techniques, like stereo lithography, binder jet, etc. One of the main problems with such additive methods is (up to now) the relatively lower mechanical strength obtained for the dense materials when compared with classical shaping and sintering. At the industrial level, when near to net shape techniques like injection molding are not applicable (often for economic reasons) the subtractive milling of pre-sintered bodies using diamond tools is the most largely used. More recently, Laser machining of green blanks has been successfully developed, allowing rapid manufacturing of complex parts. A benchmarking of the proprietary Laser technique with diamond machining with a spindle has been carried out: precision (mismatch between what it is expected and the real measurement), reproducibility (local sintered densities through the sample, hardness, etc.). The results will be discussed in this presentation in terms of geometrical and dimensional tolerances and machining speed for various shapes. In the same way, classical milling of green blanks for rapid roughing combined in 2 steps with Laser machining allows to process very rapidly fine details of complex shape parts, without applying any mechanical stresses and therefore avoiding any risk of breakage

8:55 AM

(PACRIM-S3-015-2017) Theoretical and Experimental Analyses of Relationship between Processing and Thermal Conductivity of SiC with Oxide Additives (Invited)

Y. Hirata*[1]; H. Shirai[1]; R. Ando[1]; Y. Matsumoto[1]; T. Shimonosono[1]

1. Kagoshima University, Department of Chemistry, Biotechnology, and Chemical Engineering, Japan

This paper analyzes theoretically and experimentally the thermal conductivity of the SiC-oxide additive-pore system. In the developed 6 model structures, the thermal conductivity of an SiC compact (κ_b) with oxide was calculated as functions of the volume fractions of SiC, oxide additive and pores. The calculated κ_b decreases in the order of a continuous phase where the other two particulate phases are dispersed: SiC > oxide additive > pores. The measured κ_b values of SiC compacts hot-pressed with 4-50 mass% oxide additive (mixture of 33.3 mass% Al_2O_3-33.3 mass% Y_2O_3-33.3 mass% SiO_2) were well explained by the calculated κ_b in two types of oxide continuous phase models. The thermal conductivities for only SiC grains in SiC compacts hot-pressed with 4 mass% Al_2O_3, Y_2O_3, SiO_2, Al_2O_3-Y_2O_3, Y_2O_3-SiO_2 and Al_2O_3-Y_2O_3-SiO_2 at 1950°C were also estimated theoretically in the developed two model structures using the measured κ_b (oxide continuous phase model and SiC continuous phase model). Based on the calculated results, the following key factors are identified to achieve a high κ_b: (1) high sintered density, (2) a small amount of oxide additive with a high thermal conductivity, (3) no dissolution of foreign atoms from a liquid phase into SiC grains during solidification process.

9:20 AM

(PACRIM-S3-016-2017) A Review of Next Generation Green and Smart Manufacturing Technologies

S. Gupta*[1]

1. University of North Dakota, Mechanical Engineering, USA

In the presentation, we will present recent developments on the research and development of green technologies like green cements, "greening" of ceramic manufacturing, energy harvesting, and bioplastics. During part A, we will present recent results on the development of fly ash based cements. It is well known that the alkali activation of Fly Ash to produce cementitious materials is an important area of fundamental research. From environmental perspective, the use of alkali activators, for example NaOH, is an environmental concern as it is electrochemically generated with the concomitant production of harmful Cl_2 or HCl gas as by products. Recently, we proposed that it is possible to use activate Fly Ash to produce cementitious network by using low concentration of alkaline solutions (<0.05 M). In this presentation, we will present different results about the successful utilization of this novel technology for fabricating different novel composites by using both Class C and Class F fly ash from different sources. The fundamental chemistry responsible for the cementitious behavior of these novel structures will be discussed. In addition, detailed mechanical property studies, microstructure analysis, and phase analysis will be presented. During part B, we will present recent experimental results to optimize the manufacturing processes.

9:35 AM

(PACRIM-S3-017-2017) Ceramic Powder Processing: New Approaches for Glass Component Manufacturing

T. Moritz*[1]; J. Schilm[1]; A. Mueller-Koehn[1]; A. Mannschatz[1]; U. Scheithauer[1]; E. Schwarzer[1]

1. Fraunhofer IKTS, Processes/Components, Germany

Commonly, glass components are produced starting from a melt which limits the geometrical complexity, because sharp edges can only be attained by additional machining steps. For manufacturing of microstructured components photosensitive glasses are etched with fluoric acid – a dangerous and environmentally critical process. Pressing of glass powders is applied for relatively simply shaped parts only with subsequent sintering. The components show a certain amount of porosity and are mainly applied for filtering applications. Now, ceramic powder processing is applied to glass powders. In the presentation two suspension-based additive manufacturing methods, lithography-based ceramic manufacturing (LCM) and Thermoplastic 3D Printing (T3DP) such as Ceramic Injection Molding have been developed as novel shaping techniques for glass components starting from a glass powder instead of a melt. The advantages of the different methods for producing glass components in very complex geometry, with sharp edges or micro channels will be shown. Special variants like two-component glass powder injection molding for attaining multifunctional properties in glass products will be presented in different case studies. Furthermore, glass powder injection molding allows a large series production of components made of almost all kinds of glasses including pigments, ions or particles for attaining novel functional properties.

9:50 AM

(PACRIM-S3-018-2017) Multi-functional Si-C-N ceramics fabricated by 3D printing (Invited)

X. Yin*[1]

1. Northwestern Polytechical University, School of Materials Science, China

Si3N4 and SiC ceramics possess not only excellent mechanical properties but also attractive electromagnetic wave (EM) response characteristics, which make them promising materials in various applications relating to EM radiations. Owing to the tunable EM properties, the Si-C-N ceramics based on Si3N4 and SiC are attracting extensive interest in recent years. Si-C-N based materials and structure with EM properties ranging from transparent to shielding offer a high potential for light-weight, wide bandwidth, and multifunctional EM devices. Various processes have been developed to fabricate the above structural/functional ceramics. 3D printing combined with chemical vapor infiltration (CVI) or polymer derived ceramics (PDC) route not only have the potential to in-situ form the new type ceramics, but also make it possible to realize the ceramics-based hybrid structure at lower temperature. The key developments and future challenges in this field are summarized. The main issues regarding permittivity of high-temperature Si-C-N ceramics are discussed, with an emphasis on the EM transmission, shielding and absorption mechanisms that are responsible for EM properties.

10:20 AM

(PACRIM-S3-019-2017) Bioinspired materials templates by nature species (Invited)

D. Zhang*[1]

1. Shanghai Jiao Tong University, China

Biological materials naturally display an astonishing variety of sophisticated nanostructures that are difficult to obtain even with the most technologically advanced synthetic methodologies. Inspired from nature materials with hierarchical structures, many functional materials are developed based on the templating synthesis method. We will introduce the way to fabricate novel functional materials based on nature bio-structures with a great diversity of morphologies. We change their original components into our desired materials with original morphologies faithfully kept. Properties of the obtained materials are studied in details. Based on these results, we discuss the possibility of using these materials in photonic control, solar cells, electromagnetic shielding, energy harvesting, and gas sensitive devices, et al. In addition, the fabrication method could be applied to other nature substrate template and inorganic systems that could eventually lead to the production of optical, magnetic. or electric devices or components as building blocks for nanoelectronic, magnetic, or photonic integrated systems. These bioinspired functional materials with improved performance characteristics are becoming increasing important, which will have great values on the development on structural function materials in the near future.

10:45 AM

(PACRIM-S3-020-2017) Eco-friendly synthesis of Graphene using high pressure airless spray system

A. Khanna*[1]; K. S. Aneja[1]

1. Indian Institute of Technology Bombay, Metallurgical Engineering and Materials Science, India

Graphene appears to be a wonder material of the present decade. Its special properties such as electrical conductivity, electronic mobility, mechanical strength, optical properties have caught the attention of both the scientific as well as industrial community. One of the biggest bottlenecks of its widespread usage is its availability in large volumes. Hence any research which focuses on industrial scalable production of graphene is the need of the hour. Keeping this in mind, a novel high pressure eco-friendly approach has been developed to synthesize graphene. Highly crystalline graphite, used as a starting material, is dispersed in distilled water with the help of surfactants. This graphitic solution is passed through an airless spray system at a pressure of 2000-3000 psi. The nozzle of the spray gun creates a fan of the outgoing graphitic solution thereby atomising the graphite particles and forcing the individual sheets of graphene to separate out. These individual sheets of graphene can be then separated from the residual graphite by centrifugation. Studies have shown graphene yield of 15-20% from a starting material of graphite making this technique a high yield, cost effective and eco-friendly route for graphene production.

11:00 AM

(PACRIM-S3-021-2017) Bioprocess Inspired Synthesis of Electrode Materials on Genetically Modified Bacterial Surface for Lithium-ion Batteries

H. Xie*[1]; H. Ping[1]; J. j. Xie[1]; S. Xue[1]; M. Wang[1]; W. Wang[1]; H. Wang[1]; Z. Fu[1]

1. Wuhan University of Technology, China

In living organisms, biological processes are important and vital to the formation of elegant structures with unique functions and properties. Biomineralization is a typical biological process that is made up of many biochemical reactions for generating biominerals. Inspired by biomineralization processes, we developed a bacterial surface based technology for synthesizing energy storage materials. By incorporating functional domains of mineral proteins with intact bacterial cells through genetic manipulation, we constructed three confined mineralization environments on the bacterial surface for producing nanostructured electrode materials for lithium-ion batteries. By taking advantages of bacterial cells with functional domains of silaffin or silicatein-a on the surface, we synthesized nanostructured TiO_2 with excellent electrochemical performance. We proved that the synthesis process and resulted products are controllable by adjusting displayed proteins domains. By displaying glutamate tripeptide on cell surface, we synthesized hierarchical SnO_2 nanorods that were assembled by ultrasmall nanocrystals. These SnO_2 exhibited good lithium storage properties that are benefited from ultrasmall particles, carbon coating and mesoporous structure. These results demonstrate the potential applications of bioprocess inspired synthesis in producing functional materials.

11:15 AM

(PACRIM-S3-022-2017) Bioinspired facile synthesis of hierarchical Cu_2O nanoparticles as visible-light-driven photocatalysts

L. Lei*[1]; H. Xiao[1]; Z. Fu[1]

1. Wuhan University of Technology, China

Novel hierarchical Cu_2O nanostructures were synthesized with facile wet chemical process by using organic matrices as templates at room temperature. The as-prepared Cu_2O nanoparticles in the form of rods, hollow spheres and octohedras were obtained by changing the protein structure, hydroxyl functionality and oxidizing agent. A tentative mechanism was proposed for the formation of the nanoparticles with different morphologies in different protein addition. The absorption studies revealed that the Cu_2O nanoparticles with different morphologies exhibited tunable optical band gaps between 1.85 eV and 2.44 eV. The synthesized nanoparticles show a significant improvement in visible-light photocatalytic activity for both the degradation of organic pollutants and hydrogen production. Furthermore, self-assembly of 5 nm Cu_2O nanocrystallites affords a mesoporous 250 nm hollow spherical architecture with superior visible light photocatalytic performance that may be attributed to its unique hollow structure. The present work highlights its potential application as the selection of a organic matrix in producing advanced materials with optimized functional properties.

11:30 AM

(PACRIM-S3-023-2017) Natural organisms directed synthesis of ceramic materials

J. j. Xie*[1]; Z. Fu[1]

1. Wuhan University of Technology, China

In studying and mimicking the well-defined structures or unique functions of biominerals, scientists have succeeded in designing and synthesizing bio-inspired materials or bio-inspired functions. However, in most situations, a single protein or a combination of several proteins cannot be substituted for an entire natural organism since the evolution after many millions of years has kept the level of complexity and ingenuity in the living organisms out of chemists' hand. Herein, we propose and demonstrate, for the first time, a revolutionary bio-process inspired synthesis by taking advantages of natural living organisms as platforms for the deliberate synthesis of ceramic materials at ambient temperature. It gives a direct access to the desired material in a 'green' synthesis by implanting ceramic precursors into living mussels. A lot of interesting and valuable results have been obtained. For example, densification behavior of the SiO_2 sample was observed during the mineralization process, and hierarchically meso/macroporous nitrogen-doped TiO_2 with excellent visible-light photocatalytic activities was obtained directly in Cristaria plicata at ambient temperature, and macroscopic $CaCO_3$/Fe_2O_3 composite rods were formed by oriented growth of single-crystal $CaCO_3$ along implanted Fe_2O_3 nanocrystals. Our findings may inspire material production by novel synthetic techniques, especially under environmentally benign conditions.

PACRIM Symposium 07: Porous Ceramics: Innovative Processing and Advanced Applications

Ceramic Membranes

Room: King's 2
Session Chairs: Toru Wakihara, The University of Tokyo;
Andraz Kocjan, Jozef Stefan Institute

8:30 AM

(PACRIM-S7-012-2017) Tuning microporous ceramic membranes for gas separation or solvent nanofiltration (Invited)

L. Winnubst*[1]

1. University of Twente, Inorganic Membranes, Netherlands

Membranes, based on ceramic materials, are interesting because of their robustness and can therefore be applied under several demanding conditions, like H_2 recovery from syngas, 'sweetening' of natural gas (CO_2/CH_4 separation) or organic solvents recovery. Fabrication, microstructure and transport properties will be discussed of two types of membranes: (1) Solgel-derived ceramic membranes for gas separation. (2) Polymer-functionalized ceramic membranes for solvent nanofiltration. In order to obtain solgel-derived ceramic membranes with the desired separation properties in-depth knowledge is necessary on the whole fabrication process, from sol synthesis, via applying a gel-type coating on a porous support to temperature treatments in order to obtain a separation layer with the desired microstructure. Several aspects of this process will be discussed during the presentation. For organic solvent nanofiltration (OSN) state-of-the art polymeric or ceramic membranes do not always meet stability and/or selectivity demands at process-relevant conditions. We developed new types of OSN membranes by grafting small polymer chains into the pores of a 5 nm γ-alumina ceramic membrane. In this way the best of both was achieved, meaning the robustness of ceramic membranes and the selectivity of polymeric membranes.

9:00 AM

(PACRIM-S7-013-2017) Alternate Polymeric Precursor for Gas-selective Carbon Membrane (Invited)

X. Chen*[1]

1. Institute of Materials Research and Engineering, A*STAR, Polymer materials, Singapore

Carbon membranes are derived by heating polymer membranes in inert atmosphere, during which, the carbon backbones rearrange themselves with the release of volatile pendant groups. Such transformation creates a turbostatic carbon matrix, which offers gas selectivity capability and thermal stability, outperforming polymeric membranes. Thermosetting polymers, particularly polyimide-based, are preferred as the precursor to carbon membrane due to the ability to retain their structural integrity during pyrolysis; however, polyimide polymers remain costly. In this talk, I will introduce two new classes of materials that can be used as the polymeric precursors, namely, concluding polymers and glucose-based polymers. Particularly, fabrication pathways are designed to overcome the challenges of these new classes of materials, which includes poor solubility of polymer in solvent, low thermal stability, and thermal mismatch between the polymer and the support during pyrolysis. In both classes, we achieve gas-selectivity membranes with performances that exceed the Robeson Upper line based on existing membranes. In summary, the studies that will be discussed in this talk serve as a platform for discovery of new precursors for cheap, high-performing carbon membranes.

9:20 AM

(PACRIM-S7-014-2017) Properties of glass-bonded silicon carbide membrane supports

Y. Kim*[1]; H. Yeom[1]; S. Kim[1]; I. Song[2]

1. University of Seoul, Dept. of Materials Science & Engineering, Republic of Korea
2. Korea Institute of Materials Science, Republic of Korea

Porous SiC membrane supports were fabricated from SiC and glass frit at a temperature as low as 850ºC in air by a simple pressing and heat-treatment process. The effects of the initial SiC particle size and frit content on the porosity, flexural strength, and air permeation of the membrane supports were investigated. During heat-treatment, the glass frit transformed to a viscous glass phase, which acted as a bonding material between SiC particles and as a protecting layer for severe oxidation of SiC particles. The specific flow rate of the glass-bonded SiC membrane supports increased with increasing SiC particle size in the initial composition. This result indicates that the specific flow rate, in the porosity range of 37-46%, is primarily dependent on the pore size rather than the porosity. The strength retention of the glass-bonded SiC membrane supports was 71% and 60%, respectively, after 63 days of exposure in pH 3 and 11 solutions. Typical flexural strength, permeability, and specific flow rate of the porous SiC membrane supports fabricated using 65 μm SiC particles and 15 wt% glass frit were ~65 MPa, 1.04×10^{-12} m^2, and ~63 L/min/cm^2 at a Δp of 30 psi, respectively.

9:40 AM

(PACRIM-S7-015-2017) Porous recrystallized silicon carbide membranes for use in water filtration applications

A. Vincent[1]; L. Pierrot[1]; R. Neufert[2]; M. Moeller[2]; M. Faber[2]; M. Kuhn*[3]

1. Saint-Gobain, CREE, France
2. Saint-Gobain IndustrieKeramik Rödental GmbH, Germany
3. Northboro Research & Development Center, Saint-Gobain Innovative Materials, USA

The development of new porous materials with controlled microstructures is essential for the advancement of liquid purification technologies, especially for the filtration of liquids using ceramic membranes. Saint-Gobain High Performance Refractories is developing re-crystallized silicon carbide (R-SiC) dead-end and cross-flow filters with R-SiC membranes of various pore sizes, ranging from 30 μm to 250 nm. The re-crystallization process occurs at very high temperature through the sublimation of fine SiC particles that condensate at large SiC grain boundaries. The resulting membranes exhibit controlled pore sizes and a high open porous structure (over 40 %). The effect of pore size and filtration area on flux is studied by numerically simulating pressure gradients and flow patterns across the filter channels and membranes. The use of R-SiC filters for water filtration is presented in comparison to current technologies, such as sand filters for swimming pools. The honeycomb structure of the Saint-Gobain R-SiC filter with a surface area of 11 m^2 enables a very compact filtration system, and, coupled with the use of a 250 nm membrane, allows removal of all relevant species of bacteria from the water, resulting in significantly improved water quality.

High SSA Ceramics I

Room: King's 2

Session Chairs: Xinwei Chen, Institute of Materials Research and Engineering

10:15 AM

(PACRIM-S7-016-2017) Pioneering In Situ Recrystallization during Bead Milling: A Fastest Top-down Approach to Prepare Zeolite A Nanocrystals (Invited)

A. Chokkalingam[1]; T. Wakihara*[1]

1. The University of Tokyo, Japan

Zeolite nanocrystals have great potential in the fields of catalysis and separation, which are related to their particle size induced diffusional freedom. The bottom-up and top-down approaches are the two platforms available for the preparation of zeolite nanocrystals. A new in situ method that incorporates bead milling and recrystallization for the preparation of zeolite A nanocrystals under the top-down strategy is shown. A milling apparatus designed to work under high alkalinity and temperatures is used to perform the in situ recrystallization during milling. This one-pot process involves three concurrent functions, viz, miniaturization, amorphization and recrystallization. Tuning of zeolite A particle size is achieved by adjusting the milling period and temperature. X-ray diffraction, scanning electron microscopy and transmission electron microscopy results confirmed the particle size tuning of zeolite A nanocrystals relative to milling time and temperature. Being fastest of its kind, it takes just 30 minutes for the size reduction of Zeolite A from 3μm to 66 nm with uniform particle size distribution and high crystallinity. Especially, achieving this task in one-pot is a pioneering advancement in the field of zeolite nanocrystals.

10:45 AM

(PACRIM-S7-017-2017) High-performance γ-alumina porous green bodies with hierarchical heterogeneities (Invited)

A. Kocjan*[1]; T. Konegger[2]; A. Dakskobler[3]

1. Jozef Stefan Institute, Slovenia
2. Vienna University of Technology, Austria
3. VALL-CER d.o.o., Slovenia

High-performance γ-alumina porous green bodies with hierarchical heterogeneities were fabricated by consolidation of the AlN-powder-hydrolysis-derived mesoporous γ-alumina (MA) powder. The MA consists of nanocrystalline, yet micron-sized, hierarchically self-assembled, aggregated mesostructured lamellas with surface areas exceeding 220 m^2/g, also exhibiting a monomodal mesoporosity; whereas a single lamellae is presumably an iso-crystal composed of several nanometer-sized primary crystallites. In the present paper it will be shown that depending on the consolidation pressure it was possible to manipulate the pore size distribution from being bimodal, i.e., hierarchical heterogeneities – meso- versus macro-porosity, to being monomodal around the original narrowly distributed meso-pores within the MA precursor powder. Such MA porous green bodies, with no additional calcination or sintering step, exhibited high gas permeability in combination with high elasticity, flexural and compressive strengths, as a result of the homogeneous packing of the primary crystallites, also contributing to the lowered thermal conductivities. In this way we retained the intrinsic properties of the MA that can further influence the active materials in contact, aiming at an application related to catalysis, separation, filtration, sensing and thermal insulation.

11:15 AM

(PACRIM-S7-018-2017) Structural analysis of sodium-aluminosilicate precursors for the synthesis of aluminosilicate zeolites

H. Yamada*[1]; S. Sukenaga[2]; K. Ohara[3]; H. Shibata[2]; T. Okubo[1]; T. Wakihara[1]

1. The University of Tokyo, Chemical System Engineering, Japan
2. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan
3. Research & Utilization Division, Japan Synchrotron Radiation Research Institute (JASRI)/SPring-8, Japan

Zeolites are crystalline microporous aluminosilicate materials that have been widely used as catalysts, adsorbents, and ion-exchangers because of their unique features such as ordered microporous structures, solid acidities, high hydrothermal stabilities, and large ion-exchange capacities. However, structures of non-crystalline, sodium-aluminosilicate precursors for the synthesis of aluminosilicate zeolites have not yet been clarified enough because of the difficulty in analyzing their amorphous natures. Therefore, further analyses of zeolite precursors are needed for understanding and controlling zeolite crystallization process. In this study, the structural features of sodium-aluminosilicate precursors were investigated using a pair distribution function obtained from high-energy total X-ray scattering. By combining two simulations, Molecular Dyanmics (MD) and Reverse Monte Carlo (RMC), it was clarified that sodium-aluminosilicate precursor possesses highly-ordered Na environment and larger fraction of small-membered rings.

11:35 AM

(PACRIM-S7-019-2017) Controlling the Nanometer to Micrometer Scale Porosity of Metal Oxide Materials

R. Caruso*[1]

1. The University of Melbourne, Australia

The use of preformed templates, solvothermal approaches, electrospinning or self-assembly processes during synthesis allow the fabrication of materials with a range of pore sizes and outer morphologies. This structural control can influence the final properties of the material and hence its areas of application and effectiveness. Using such synthesis techniques, metal oxides can be crafted into beads, membranes or pellets containing an interconnected pore structure that can be ordered or disordered, monodisperse or hierarchical in size. The pore structure can be determined using electron microscopy and gas sorption techniques. These porous materials find application in, for example, photocatalysis, energy storage devices such as Li-based batteries and energy conversion devices such as solar cells where liquid diffusion through the material and highly accessible surfaces are important. This presentation will highlight the different synthesis techniques and characteristics of the materials produced, and how these properties can influence how well the material performs in these applications.

PACRIM Symposium 11: Engineering Ceramics: Processing and Characterizations

Mechanical Properties I

Room: King's 1

Session Chairs: Junichi Tatami, Yokohama National University; Pavol Sajgalik, Institute of Inorganic Chemistry, Slovak Academy of Sciences

8:30 AM

(PACRIM-S11-012-2017) Thermal Shock Resistance, Wear Behavior and Oxidation Resistance of Silicon Nitride Based Nano-Composites (Invited)

P. Sajgalik*[1]; M. Hnatko[1]; Z. Lences[1]; J. Dusza[2]; P. Tatarko[2]; A. Kovalčíková[2]; M. Kasiarova[2]

1. Institute of Inorganic Chemistry, Slovak Academy of Sciences, Ceramics Department, Slovakia
2. Institute of Materials Research, Slovak Academy of Sciences, Slovakia

Six different sintering aids (Lu_2O_3, Yb_2O_3, Y_2O_3, Sm_2O_3, Nd_2O_3 and La_2O_3) were used for the processing of dense Si_3N_4/SiC micro/nano composites. Thermal shock resistance: A critical temperature difference increased with an increasing ionic radius of RE^{3+} for both the composites and the monoliths. Wear behavior: The friction coefficient as well as the specific wear rate decreased with a decreasing ionic radius of rare-earth elements in both the monoliths and the composites. High bonding strength and the high fracture toughness are the reasons why the ceramics doped by Lu exhibited the best wear resistance. Oxidation resistance: Composites exhibited predominately parabolic oxidation behavior indicated diffusion as the rate limiting mechanism. Exception was only the Si_3N_4-SiC composite sintered with Lu_2O_3. In this case diffusion of cation has been strongly suppressed because of the beneficial effect of stable grain boundary phase and the presence of the SiC particles predominately located at the grain boundaries of Si_3N_4.

9:00 AM

(PACRIM-S11-013-2017) Bending strength and fracture toughness of Si_3N_4 ceramic surface in contact with molten aluminum measured using microcantilever beam specimens (Invited)

J. Tatami*[1]; S. Fujita[1]; T. Yahagi[2]; T. Takahashi[2]; M. Iijima[1]

1. Yokohama National University, Japan
2. Kanagawa Academy of Science and Technology, Japan

Although Si_3N_4 ceramics are utilized as structural components for Al-casting industry owing to excellent properties, they are occasionally broken after long-term use. In this study, degradation of the Si_3N_4 ceramic surface layer corroded by molten Al was evaluated by using microcantilever beam specimens, followed by fractography of the specimens. Microcantilever beam specimens to measure the bending strength and fracture toughness of the vicinity of the Si3N4 ceramic surface were fabricated by focused ion beam technique. Fracture test of the specimens was carried out by nanoindenter. Strength was calculated from the fracture load and the geometry of the specimen. The bending strength of the microcantilever beam specimens before and after contact with molten Al were 4.14 ± 0.65 and 2.40 ± 0.12 GPa, respectively. Fracture toughness of the corroded layer in Si_3N_4 ceramics was also degraded compared with that of the polished surface. As a result of fractography by SEM observation, it was shown that change in the grain boundary glassy phase resulted in the degradation of the strength and the fracture toughness.

9:30 AM

(PACRIM-S11-014-2017) c-axis oriented Si_3N_4 ceramics fabricated by preparing multilayered-graphene coated β-Si_3N_4 seeds and its orientation in a very low magnetic field

T. Takahashi*[1]; M. Sado[2]; N. Sugimoto[2]; J. Tatami[2]; M. Iijima[2]

1. Kanagawa Academy of Science and Technology, Japan
2. Yokohama National University, Japan

Molding in a magnetic field has been applied to prepare crystal-oriented ceramics. In this work, we fabricated c-axis oriented silicon nitride (Si_3N_4) ceramics by orientation of multilayered-graphene (MG) coated Si_3N_4 seeds in low and static magnetic field. SEM-EDS and AFM observation showed that the graphene particles were successfully coated on the Si_3N_4 seeds. The coated seeds were dispersed in the solvent with a dispersant by ultrasonication. It was confirmed that the c-axis of β-Si_3N_4 seeds coated MG oriented to the direction parallel to an applied magnetic field of 0.4 tesla, though uncoated seeds showed random orientation by applying the same magnetic field and in-plane orientation of c-axis of Si_3N_4 in 10 tesla. The reason for c-axis orientation at much lower magnetic field is that the MG has the large anisotropy of diamagnetic susceptibility. The green compacts prepared in various magnetic fields were fired at 1900°C for 6h in N_2 gas of 0.9MPa. As a result, c-axis oriented Si_3N_4 ceramics were successfully fabricated by molding using the MG coated Si_3N_4 seeds because the oriented seeds played a role of nuclei of grain growth. Thermal conductivities along parallel and normal directions to the applied static magnetic field were 96 and 65 $W\cdot(m\cdot K)^{-1}$, respectively.

9:45 AM

(PACRIM-S11-015-2017) Directional electrical transport in tough multifunctional layered ceramic/graphene composites

M. Belmonte*[1]; R. Cruz-Silva[2]; A. Morelos-Gómez[2]; M. Terrones[2]; P. Miranzo[1]; M. I. Osendi[1]

1. Institute of Ceramics and Glass, CSIC, Spain
2. Shinshu University, Faculty of Engineering, Japan

Layered ceramic structures arose in the 90's as a sensible way for enhancing the mechanical performance, as compared to monolithics or even composites, looking for applications in the fields of aerospace or bio-materials. A new approach consists in exploring the directional characteristics of layered materials, in particular regarding the electrical and thermal responses. We report, taking advantage of the high stiffness and outstanding electrical and thermal conductivities of graphene, the development of multilayered materials consisting of alternating silicon nitride ceramics (Si_3N_4) layers and graphene oxide (GO) films, which are in-situ reduced to multilayered graphene (rGO) during densification of the composite by spark plasma sintering. The resulting layered Si_3N_4/graphene system showed directional electrical transport with an increased electrical conductivity -up to 16 orders of magnitude- for the in-plane measurements. The thermal conductivity could proportionally be reduced increasing the number of rGO layers, which would be interesting for thermoelectric applications. In addition, the graphene layers impinged and deflected the cracks, thus enhancing the crack propagation resistance. This material could be used in the fabrication of impact resistance structures, electrostatic charge dissipation, electromagnetic interference shielding or thermoelectric devices.

Mechanical Properties II

Room: King's 1
Session Chairs: B V Manoj Kumar, IIT Roorkee; Jianfeng Yang, Xi'an Jiaotong University

10:15 AM

(PACRIM-S11-016-2017) Understanding tribology of ceramics and cermets in sliding wear contacts (Invited)

B. Kumar*[3]; S. Sharma[3]; B. Zugelj[2]; Y. Kim[1]; M. Kalin[2]

1. University of Seoul, Republic of Korea
2. University of Ljubljana, Slovenia
3. IIT Roorkee, India

Owing to the unique combination of superior mechanical and chemical properties, engineering ceramics and cermets are considered for several tribological applications. A thorough understanding on the influence of processing conditions, microstructure and mechanical characteristics as well as operating and environmental conditions on friction and wear is essential to estimate the potential of these advanced material systems. In the present talk, important observations from our recent studies on sliding wear behavior of hot pressed SiC-WC composites and spark plasma sintered TiCN-WC-Mo_2C-Ni-Co cermet are discussed. The friction and wear behavior are studied in unlubricated sliding conditions against commercially available SiC balls at different temperatures: ambient to elevated (500ºC), and loads: 6, 9 and 19 N for SiC-WC composites and 19, 42 and 115 N for the cermet. For both ceramic composites and cermet, wear increased with increase in load or temperature, whereas friction reduced with increase in load. Varieties of wear mechanisms including microcrack induced fracture, abrasion, adhesion, tribochemical layer removal are found for SiC-WC composites or TiCN-based cermets as function of material composition, sliding load and sliding test temperature. The friction and wear results obtained for ceramic composites and cermets are correlated with their respective microstructural and mechanical characteristics.

10:45 AM

(PACRIM-S11-017-2017) Fabrication and Properties of SiC ceramics with Low Content of Residual Si through Multi-Step Reaction Sintering Based on Compound Carbon Source (Invited)

J. Yang*[1]; N. Zhang[1]; P. Yin[1]; B. Wang[1]

1. Xi'an Jiaotong University, China

Excellent irradiation stability has been reported for SiC at wide temperature ranges and damage levels under neutron irradiation. Reaction sintering of the SiC ceramics has the advantages of low temperature and net shape production. But the high temperature performances of SiC were degraded by residual silicon. In the present paper, multi carbon source for the preparation of SiC ceramic material is proposed. With the carbon source with different reaction activity as raw material, SiC-carbon-silicon composite materials with controllable microstructure were firstly fabricated by reaction sintering, and then SiC ceramics with low residual silicon was obtained through diffusion reaction between carbon and silicon aroused by high temperature treatment. The graphitization degrees of carbon sources were determined by combining XRD and Raman spectra analyze. Silicon-carbon reaction activity of carbon source decreased as graphitization degree increased. The SiC ceramic materials of very low residual silicon and high density were fabricated by reaction sintering. The SiC materials show outstanding performance in strength of about 500MPa. Our works is of practical valuable for the enlarging application field of the materials, and provides a new idea for further research on ceramic materials.

11:15 AM

(PACRIM-S11-018-2017) Fabrication of textured B_4C ceramics by slip casting in a strong magnetic field and their mechanical and thermal properties

K. Yoshida*[1]; M. Fajar[1]; T. Yano[1]; T. Uchikoshi[2]; T. S. Suzuki[2]

1. Tokyo Institute of Technology, Japan
2. National Institute for Materials Science (NIMS), Japan

Boron carbide (B_4C) has been used as a neutron absorber material in fast reactor systems due to its high neutron absorption ability, thermal stability and low radioactivity after irradiation. During operation of fast reactors, B_4C pellets were fractured into pieces due to thermal stress and swelling, and absorber-cladding mechanical interaction (ACMI) was caused. Currently the lifetime of control rods is limited by ACMI, and high performance B_4C pellets for fast reactors have been strongly required. The authors have been attempting to develop high performance B_4C ceramics with excellent mechanical and thermal properties as a neutron absorber material in fast reactor systems to reduce the thermal stress and improve the thermal shock resistance. In this study, textured B_4C ceramics were fabricated by slip casting in a strong magnetic field (12 T), and their mechanical and thermal properties were evaluated.

11:30 AM

(PACRIM-S11-019-2017) Hot-Pressing B_4C Ceramics with Al as Sintering Aid

X. Li*[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Boron carbide (B_4C) ceramics were prepared by hot pressing method. 0-5 wt.% Al were added as sintering aids. Al can effectively boost the densification of B_4C ceramics. Microstructural characterization was carried to investigate the effect of the Al on the densification of B_4C ceramic. It was found that the presence of liquid phase during sintering improved the sinterability of B_4C ceramics. The diffusion of the Al into B_4C probably generated the free carbon, which probably also contributed to the densification. Relative density of the Al-addition ceramics is about 99%. With the Al addition increasing, flextural strength increases from 410 MPa to 462 MPa, while Vickers hardness slightly declines from 30.1 GPa to 29.1 GPa.

11:45 AM

(PACRIM-S11-020-2017) Mechanical Properties of Hot Pressed SHS Derived Ti_2AlN Active Precursor Powders

L. Chlubny*[1]; J. Lis[1]; P. Borowiak[1]; K. Chabior[1]; K. Zielenska[1]

1. AGH-University of Science and Technology, Poland

Ti_2AlN belongs to the interesting group of ternary nanolaminate materials called MAX phases. These compounds are characterised by unique set of properties situating them between metals and ceramics thanks to the heterodesmic chemical bonding and the nanolaminate structure. Ti_2AlN active precursor powders has been obtained by Self-propagating High-temperature Synthesis (SHS), which is one of the best methods of synthesizing fine active precursors powders of MAX phase materials. This method utilizes exothermal effect of the chemical reaction in adiabatic conditions and allows obtaining many compounds such as nitrides, carbides, composites, intermetallics, etc. at low energy consumption and with high efficiency and at relatively short time. Next, selected powders were hot-pressed at temperatures range from 1250 to 1400°C in order to obtain dense, polycrystalline product with high content of MAX phase and to establish optimal hot-pressing conditions. In this paper authors would like to present results of studies on mechanical properties of manufactured dense samples, such as Vickers hardness, bending strength, fracture toughness, etc.

PACRIM Symposium 17: Advanced Functional Ceramics and Critical Materials Perspective

Advanced Functional Ceramics and Critical Materials Perspective II

Room: Kohala 2
Session Chairs: Takaaki Tsurumi, Tokyo Institute of Technology; Kazuhiko Maeda, Tokyo Institute of Technology

9:00 AM

(PACRIM-S17-012-2017) Dielectric and ferroelectric characteristics of $Ba_4Pr_2Fe_2Nb_8O_{30}$ tungsten bronze ceramics

T. Gao*[1]; X. Zhu[1]; X. Chen[1]

1. Zhejiang University, School of Materials Science and Engineering, China

$Ba_4Pr_2Fe_2Nb_8O_{30}$ tungsten bronze ceramics have been prepared by a standard solid-state sintering method, and the electrical, dielectric and ferroelectric properties have been determined together with the structure. The valence fluctuation of Fe and Pr ions during annealing plays a crucial role in electrical, dielectric and ferroelectric properties in $Ba_4Pr_2Fe_2Nb_8O_{30}$ ceramics. The typical relaxor ferroelectric nature is generally indicated in the present ceramics, where the broaden dielectric constant and dielectric loss peaks with strong frequency dispersion feature are observed. The peak temperatures for both dielectric constant and dielectric loss are significantly increased together with the much stronger frequency dispersion by N_2-annealing, while the O_2-annealing result in the decreased peak temperatures and the suppressed frequency dispersion. These phenomena are closely related to the valence fluctuation of Fe and Pr ions. The hopping between Fe^{2+} and Fe^{3+} inside the grains causes the dielectric relaxation in as-sintered and N_2-annealed samples. The enhanced ferroelectricity near room temperature is attributed to the increased ion radius difference between A1 and A2 because of the "substitution" Pr^{4+} for Pr^{3+} after N_2-annealing.

9:15 AM

(PACRIM-S17-013-2017) Structure, dielectric, ferroelectric and magnetic properties of $Ba_4(Eu_xLa_{1-x})_2Fe_2Nb_8O_{30}$ ceramics

J. Hong*[1]; Y. Wu[1]; X. Chen[1]; X. Liu[1]

1. Zhejiang University, Laboratory of Dielectric Materials, School of Materials Science and Engineering, China

$Ba_4(Eu_xLa_{1-x})_2Fe_2Nb_8O_{30}$ (x=0, 0.3, 0.5, 0.7, 0.9, 0.95, 1) ceramics with tetragonal bronze structure are prepared by standard solid-state method. Structure, dielectric, ferroelectric and magnetic properties has been systematically studied for $Ba_4(Eu_xLa_{1-x})_2Fe_2Nb_8O_{30}$ (x=0, 0.3, 0.5, 0.7, 0.9, 0.95, 1) tungsten bronze ceramics. With the increase of x, $Ba_4(Eu_xLa_{1-x})_2Fe_2Nb_8O_{30}$ ceramics transform from paraelectric to ferroelectric. The ferroelectric behavior is associated with a commensurate octahedral tilting, which is caused by large A2-A1 ionic-radius difference. With the increasing x, the remanent magnetization increase obviously. It is confirmed that the radius difference between A2 and A1 cations plays a critical role on structure, dielectric and ferroelectric characteristics.

9:30 AM

(PACRIM-S17-014-2017) Processing of Reduction-Resistant Lead-Free (Ba,Ca)(Ti,Zr)O_3 Piezoceramics and their Grain Orientation Control (Invited)

W. Sakamoto*[1]

1. Nagoya University, Institute of Materials and Systems for Sustainability, Japan

Recently, development of piezoelectric materials which do not contain toxic elements is strongly required for the environmental issues. Therefore, lead-free piezoceramics have been intensively studied all over the world. On the other hand, to realize the high performance multilayer piezoelectric ceramic components with low cost, development of nonreducible piezoceramics is important. In this study, processing of reduction-resistant $BaTiO_3$-based ceramics as lead-free piezoelectric materials was investigated. Nonreducible (Ba,Ca)(Ti,Zr)O_3 ceramics were fabricated by appropriately controlling the amount of Mn doping. To enhance their electrical properties, (100),(001)-oriented (Ba,Ca)(Ti,Zr)O_3 ceramics were fabricated by controlling the grain growth process using platelike seed crystals. The ferroelectric and piezoelectric properties of the nonreducible $BaTiO_3$-based ceramics were improved as a result of fabricating grain-oriented samples. The reduction-resistant grain-oriented $BaTiO_3$-based ceramics developed in this study are expected to be promising candidates for lead-free piezoceramics for multilayer-type electronic component applications.

9:50 AM

(PACRIM-S17-015-2017) Mechanism of electro-optic effect in oxide ferroelectrics and relaxors (Invited)

T. Tsurumi*[1]; H. Takeda[1]; T. Hoshina[1]

1. Tokyo Institute of Technology, Japan

Miniaturized electro-optic (EO) modulators are regarded as a key device for realizing high speed optical networks in the future. EO-modulators fabricated on lithium niobate ($LiNbO_3$, LN) single crystals are currently used in optical communications. However, a material with higher EO-coefficient than that of LN crystal is required for miniaturizing EO-modulators because optical length decreases with the size of modulators. To understand the origin of EO-effect of ferroelectric relaxors, the relationship among the quadratic EO-coefficient, photo-elastic coefficient, and electron density was elucidated. The quadratic EO-coefficient was given by the product of the photo-elastic and electrostrictive coefficients. Materials consisting of heavy elements normally exhibit high refractive indices large photo-elastic effects, indicating that the photo-elastic coefficient increased with electron density of materials. The photo-elastic coefficient was calculated as a function of electron density of materials. The equations derived in this paper were experimentally confirmed using PLZT transparent ceramics. It was found that the origin of EO-effect in ferroelectric relaxors was the photo-elastic effect coupled with electric-field induced strain via. piezoelectric and elecrostrictive effect.

10:25 AM

(PACRIM-S17-016-2017) Atomic scale and in-situ electron microscopic analysis of ferroelectrics (Invited)

Y. Sato*[1]

1. Kyushu University, Dep. Mater. Sci. Eng., Japan

It is important to characterize the crystal structure and the microstructure such as domain structure in ferroelectrics, since various properties of ferroelectrics are closely related with them. Since transmission electron microscopy (TEM) and scanning TEM (STEM) is powerful tool to analyze material structure with high spatial resolution, we are studying microscopic structure of ferroelectrics using them. One of the examples is the atomic scale analysis of $BaTiO_3$ (BT) nano particle (NP). Whereas it is known that properties of BT NP often differs from those of bulk material, the reason is unclear though some reasons such as the size effect and surface effect are considered. In our study, atomic position has been identified with high precision in order to understand the atomistic structure near the surface. It was found that some Ba ions are displaced outward by greater than 20 pm at the surface. On the other hand, such large displacement was not observed for the Ti ions, which indicates that the ferroelectric order is not maintained at the surface. For the other example, our in-situ electrical biasing TEM analysis will be introduced. Since ferroelectrics is often subjected to external electric (E) field during the operation, it should be useful to understand the structure under E field. We have so far visualized the real-time response of nanodomain in morphotropic phase boundary $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$.

10:45 AM

(PACRIM-S17-017-2017) Use of Bayesian Inference in Characterization of Ceramic Materials: An Introduction and Applications in Ferroelectrics (Invited)

J. L. Jones*[1]; T. Iamsasri[2]; J. Guerrier[1]; C. Fancher[3]; J. Daniels[4]; A. Larsen[5]; A. G. Wilson[5]; B. J. Reich[5]; R. C. Smith[6]

1. North Carolina State University, Dept. of Materials Science & Engineering, USA
2. King Monkut's University of Technology North Bangkok, Thailand
3. Oak Ridge National Lab, Chemical and Engineering Materials Division, USA
4. UNSW Australia, School of Materials Science and Engineering, Australia
5. North Carolina State University, Statistics, USA
6. North Carolina State University, Mathematics, USA

Materials development remains limited by our ability to "see" and characterize newly synthesized materials. Over the past decades, great advancements have been seen in X-ray and neutron characterization instruments. However, the analysis of data from such instruments has progressed slowly, an example being the Rietveld method for refinement of crystallographic structures using least squares (1969). In this talk, I will introduce to the materials researcher the alternative statistical framework of Bayesian statistics and its application to analysis of diffraction data when employed in conjunction with a Markov Chain Monte Carlo (MCMC) algorithm. The talk will include a basic introduction and application to modeling single reflections, doublets from ferroelastic degenerate reflections, and the entire pattern (full profile). The parameters in the new models represent structure using probability distributions, treating solutions probabilistically with improved uncertainty quantification. For ferroelectrics, we demonstrate that these probability distributions can be readily propagated into new calculated parameters related to domain reorientation. The conventional least squares solutions and its confidence intervals will be compared/contrasted to the new approach and its credible intervals. The new approach offers more confident structure-property correlations.

11:05 AM

(PACRIM-S17-018-2017) Catalysis of perovskite-type oxide prepared by the decomposition of heteronuclear cyano complex (Invited)

H. Yahiro*[1]; S. Yamaguchi[1]

1. Ehime University, Japan

The specific surface area and homogeneousness are the important factors for achieving high catalytic activity of mixed metal oxide, depending on the preparation method. The thermal decomposition of cyano complex is a promising method (CN method) for preparation of homogeneous perovskite-type oxides with relatively high specific surface area because of the structural similarity between heteronuclear cyano complex and perovskite-type oxide. More recently, we have reported that the perovskite-type oxide with high crystallinity can be prepared at less than 300 °C by utilizing the exothermic reaction due to the oxidation of CN group. The perovskite-type oxides obtained by the title method were applied to the gas- and liquid-phase catalytic reactions. For example, $LaFeO_3$ and $SmFeO_3$ synthesized by CN method exhibited high catalytic activity for cyanosilylation proceeding on acid and base catalysts. In addition, the silver-supported perovskite-type oxide prepared by CN method was significantly active for the catalytic removal of particulate matter (PM) exhausted from diesel engine. Thus, the perovskite-type oxide prepared by CN method possesses high potential for some catalysis. In this presentation, the synthesis of perovskite-type oxides by CN method and their catalytic property will be outlined.

11:25 AM

(PACRIM-S17-019-2017) Water splitting using metal oxide photocatalysts (Invited)

K. Maeda*[1]

1. Tokyo Institute of Technology, Japan

Water splitting into H_2 and O_2 over a heterogeneous photocatalyst has attracted attention as a potential means of producing clean energy from renewable resources. In this presentation, some of new ideas and/or methodology to develop a photocatalyst that is capable of splitting pure water will be given. It is known that certain nanoparticulate metals or metal oxides on a semiconductor photocatalyst work as cocatalysts to promote water reduction and/or oxidation. In heterogeneous photocatalysis, the effect of cocatalyst size on the water-splitting performance had not been examined at sizes smaller than 1 nm due to the lack of an effective preparation method and a suitable photocatalyst. We have very recently demonstrated that metal nanoclusters (such as Pt) of <1 nm in size could be deposited on the interlayer nanospace of $KCa_2Nb_3O_{10}$ using the electrostatic attraction between a cationic metal complex and a negatively charged $Ca_2Nb_3O_{10}^-$ sheet, without the aid of any additional reagent. The material obtained exhibited 8 times greater photocatalytic activity for overall water splitting under band-gap irradiation than the previously reported analog using a RuO_2 promoter. This study highlighted the superior functionality of < 1 nm Pt nanoclusters for photocatalytic overall water splitting.

11:45 AM

(PACRIM-S17-020-2017) High mobility amorphous Zn-O-N thin films fabricated by pulsed laser deposition

T. Hasegawa*[1]; T. Yamazaki[1]; K. Shigematsu[2]; S. Nakao[2]; I. Harayama[4]; D. Sekiba[3]; Y. Hirose1[1]

1. University of Tokyo, Department of Chemistry, Japan
2. Kanagawa Academy of Science and Technology, Japan
3. University of Tsukuba, Tandem Accelerator Complex, Japan
4. University of Tsukuba, Graduate School of Pure and Applied Sciences, Japan

Amorphous Zn-O-N thin films with electron mobility of ~ 100 $cm^2V^{-1}s^{-1}$ are promising amorphous semiconducting oxide materials for flexible devices. Recently, it has been reported that the Zn-O-N thin films deposited by sputtering contained zinc oxide nanocrystals. Generally, sputtering deposition using high energy particles tends to induce the crystallization of zinc oxide or zinc nitride. Here, we employed pulsed laser deposition, in which less energetic particle beams are used, for growth of amorphous Zn-O-N on glass substrate. Nitrogen was supplied as activated radicals through an electron cyclotron resonance (ECR) plasma source. As a result, we found that the surface morphology of the obtained films was very sensitive to the nitrogen content controlled by the input current of the ECR source; the surface roughness was substantially decreased with increasing the nitrogen content. This implies that the incorporation of nitrogen suppresses the formation of the nanocrystals. The Zn-O-N film deposited under an optimal condition showed root mean square roughness less than 0.3 nm and high electron mobility exceeding 200 $cm^2V^{-1}s^{-1}$, which is almost twice of those previously reported.

PACRIM Symposium 19: Transparent Ceramic Materials and Devices

Transparent Ceramic Materials and Devices II

Room: Kohala 3
Session Chair: Do Kyung Kim, Korea Advanced Institute of Science and Engineering (KAIST)

8:30 AM

(PACRIM-S19-013-2017) Anisotropic solid-state single crystal growth in $Sr_5(PO_4)_3F$ (Invited)

Y. Liu*[1]; Y. Wu[1]

1. Alfred University, Materials Science, USA

Solid-state Single Crystal Growth (SSCG) has significant potential as an alternative approach to grow single crystals at low temperatures at much lower costs than traditional crystal growth processes. The major practical challenge in applying the process is the limited degree of solid-state crystal growth that occurs via boundary migration from the seed crystal into the polycrystalline matrix. A previous study of $Sr_5(PO_4)_3F$ (S-FAP) has demonstrated the ability to achieve seed crystal growth of up to 100μm with the help of an electric field. In this research, SSCG was performed in which different crystallographic planes of seed crystals were bonded to the polycrystals via sintering. Tremendous seed crystal growth of several hundred micrometers was observed in samples with certain planes such as the (321) bound to the polycrystal, whereas limited growth occurred with the hexagonal basal planes. The assimilation of grains as a result of seed crystal growth seems independent of normal grain growth in the ceramic. It was demonstrated that the influence of the specific crystallographic plane bound to the polycrystal is critical to crystal growth during the solid-state thermal treatment. This discovery may shed new light on further enhancement of the SSCG process as it applies to certain anisotropic crystals.

9:00 AM

(PACRIM-S19-014-2017) Transparent AlON Ceramics from Synthetic Submicron Powders by Pressureless Sintering (Invited)

Y. Shi*[1]; J. Lei[1]; J. Zhang[1]; J. Xie[1]; L. Zhang[1]

1. Shanghai University, Department of Electronics and Information Materials, China

The Synthesis of AlON ceramic powders were investigated by the novel wet chemical processings, followed by a carbothermal reduction and nitridation. The chemical compositions and thermal evolution behaviours of different precursor were studied in detail. After being calcined at 1700^0C for 4hrs, single-phased submicron polycrystalline AlON powder was synthesized with the media particle size of 0.62μm and specific surface area of $14.8m^2/g$ respectively. The pressureless sintering was employed to investigate the fabrication of transparent AlON ceramic under N_2 atmosphere. It was found that the best densification temperature was 1900^0C with sintering aid of $0.08wt\%Y_2O_3+0.02wt\%\ La_2O_3+0.2wt\%MgO$, the relative density of AlON ceramic could reach 99.5%. It was suggested that with the aids of the sintering additive, the exclusion of intragranular pores were greatly promoted, which was crucial to transparency of AlON ceramics. The optical linear transmittance attained to 80% (2mm thickness) in wavelength region of (1000-5000)nm. The bending strength and fracture toughness under room temperature attained (275±25)MPa and $(1.75\pm0.1)MPa.m^{1/2}$ respectively. The oxidation behaviour of AlON ceramics in air was explored by SEM observations and XRD analysis.

9:30 AM

(PACRIM-S19-015-2017) SPS of transparent Nd^{3+}:MgO ceramic using co-precipitated powders (Invited)

X. Chen*[1]; Y. Liu[1]; Y. Wu[1]

1. Alfred University, Kazuo Inamori School of Engineering, USA

Fully dense Nd^{3+}: MgO ceramics were consolidated by field and pressure assisted sintering (also known as Spark Plasma Sintering) at a relatively low temperature of ~1350°C using nanosized powders prepared by co-precipitation. The synthesized powders and consolidated ceramics were characterized by X-ray diffraction, scanning electron microscopy, and photoluminescence spectroscopy. The ceramics demonstrated high transparency of up to 50–80% in the >300 nm wavelength range. Results are presented with a major emphasis on potential laser applications, based on the unique thermal properties of the MgO host material.

10:15 AM

(PACRIM-S19-016-2017) Recent progress in transparent ceramics synthesized by full crystallization from glass

M. Allix*[1]; E. Véron[1]; C. Genevois[1]; F. Fayon[1]; S. Chenu[1]; G. Matzen[1]

1. CNRS (CEMHTI), France

Transparent ceramics are an emerging class of optical materials competing with single crystal technology for a broad range of applications. Ceramics offer several advantages, particularly in the fabrication of complex shapes and large-scale industrial production, and enable great and homogenous doping of optically active ions. However, up to date, only a limited number of cubic or nanocrystalline transparent polycrystalline ceramics requiring complex and expensive synthetic approaches has been reported. Our recent work shows the possibility to obtain new transparent ceramics by full and congruent crystallization from glass. This is demonstrated in the case of several new compositions, such as $BaAl_4O_7$, $Sr_3Al_2O_6$ and $Sr_3Ga_2O_6$, all showing high transparency in the visible and infra-red ranges. Lately, we have focused our work on large scale and highly transparent strontium aluminosilicate compositions. A crystallographic study coupled to NMR experiments and DFT calculations of the birefringence evidences the role of structural disorder (Al/Si substitution and presence of vacancies on strontium sites) to explain the optical isotropy observed in these hexagonal materials. These results propose an innovative concept, the addition of a controlled structural disorder within crystalline structures, in order to lower the birefringence and to elaborate new transparent ceramics.

10:30 AM

(PACRIM-S19-017-2017) Transparent polycrystalline spinel-type silicon nitride

N. Nishiyama*[1]; R. Ishikawa[2]; H. Ohfuji[3]; H. Marquardt[4]; T. Taniguchi[5]; B. Kim[5]; A. Masuno[6]; Y. Ikuhara[2]; F. Wakai[7]; T. Irifune[3]

1. Deutsches Elektronen-Synchrotron, Germany
2. The University of Tokyo, Institute of Engineering Innovation, Japan
3. Ehime University, Geodynamics Research Center, Japan
4. Universität Bayreuth, Bayerisches Geoinstitut, Germany
5. National Institute for Materials Sciences, Japan
6. Hirosaki University, Japan
7. Tokyo Institute of Technology, Japan

Transparent polycrystalline cubic silicon nitride (c-Si_3N_4) ceramics were synthesized at 15.6 GPa and 1800°C. c-Si_3N_4 is a high pressure polymorph with spinel structure stable at pressures above 13 GPa. The dimensions of the synthesized disks are 2 mm in diameter and 0.5 mm in thickness. Real in-line transmission (RIT) was measured at wavelength between 200 and 1600 nm. The RIT value of visible light reaches 38%. Atomic-resolution scanning transmission electron microscopy was performed to observe grain boundaries (GBs). We observed the presence of disordered/amorphous intergranular films (IGFs) with thickness less than 1 nm at GBs including multi-grain junctions. The thin IGFs may be related to the origin of the optical transparency of this polycrystalline material. We measured elastic moduli of this material by Brillouin spectroscopy. The determined parameters are: bulk modulus, 303 GPa; shear modulus, 248 GPa; Young's modulus, 584 GPa; Poisson's ratio, 0.179. Vickers indentation tests were performed at indentation loads between 0.196 and 19.6 N. The Vickers hardness determined at 9.8 N is 34.9 GPa. This material is categorized as one of the third hardest materials next to diamond and cubic boron nitride. The fracture toughness is determined to be 3.5 MPa m$^{0.5}$. This material is tougher than other transparent spinel ceramics.

10:45 AM

(PACRIM-S19-018-2017) Analysis on spinodal decomposition behavior and reflective spectra of Ca-Al-Si-O glass of Celadon glaze

Y. Chen*[1]; Y. Bai[1]; W. Wei[1]

1. National Taiwan University, Materials Science and Engineering, Taiwan

The main composition of the glazes in Ru-ware is a Ca-Al-Si-O based glass with a trace of Fe dopants as the color former. In this study, several Fe doped Ca-Al-Si-O glasses based on the composition of Ru-ware are systematically synthesized by a thermal melting method, and then coated on either kaolinite or anorthite substrates. Several techniques were taken to analyze the microstructures, compositions, crystal phases, and optical properties, such as the optical microscopy (OM), Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), visible optical spectrometer, etc. The results show that the glazes of Ru ware are consisted of bobbles, crystal precipitates, and glasses area. The crystal area is mainly the anorthite plates surrounded by Ca-Al-Si-O glass. The spinodal decomposition of the Ca-Al-Si-O glasses are found, and the morphologies of duel-phase glasses are either a spherical or a worm-like pattern. The visible reflective optical spectra show the peak wavelengths of the modern copies are different from that of Ru-ware. That maybe due to either the charge states of Fe (2+ and 3+) dopant, interference of scattering lights formed by different sized of anorthite grains, bobbles, or the spinodal patterns of the Ca-Al-Si-O glasses after sintering and long thermal treatment.

11:00 AM

(PACRIM-S19-019-2017) Microstructure, optical, and scintillation Properties of Ce:$Gd_2YAl_2Ga_3O_{12}$ Transparent Ceramics

B. Jiang[1]; L. Zhang[1]; S. Chen*[1]

1. Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Science, China

Inorganic scintillator materials are widely use in neutron detect, high energy particle physical experiments, new energy resource exploration and X-ray security, especially in medical imaging techniques. In this study, Cerium doped $Gd_2YGa_3Al_2O_{12}$ (GYGAG) ceramic with good performances have been fabricated by sintering in oxygen atmosphere and hot isostatically pressed (HIP). The microstructure, optical, scintillation characteristics of Ce:GYGAG ceramic were investigated. Transparent ceramic Ce:GYGAG ceramic achieves 78% transmittance in range from 500 to 800 nm. The photoluminescence emission of the Ce:GYGAG ceramic peaked at about 540 nm match well with the sensitivity of Si-based photodiodes. Radioluminescence intensity of the fast emission based on Ce^{3+} 5d→4f reaches up to 30 times that of BGO single crystal reference scintillator. The light yield within 0.75μs shaping time in Ce:GYGAG ceramic is about 23400Ph/MeV under the ^{137}Cs γ-ray irradiation. The result of using electron paramagnetic resonance indicate that there are Ce^{4+} ions in the oxygen-annealed Ce:GYGAG scintillator ceramics. The valence of Ce ions in the oxygen-annealed and hydrogen-annealed Ce:GYGAG scintillator ceramics was confirmed by X-ray photoelectron spectroscopy. Finally, the scintillator performance affected by the different of anneal atmospheres are discussed.

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

New Direction II

Room: Kohala 1
Session Chair: David Rogers, Nanovation

9:00 AM

(PACRIM-S20-010-2017) Crystal and electronic structures of $LaOBiS_2$ and $LaOInS_2$ (Invited)

A. Miura*[1]; Y. Mizuguchi[2]; C. Moriyoshi[3]; Y. Kuroiwa[3]; M. Higuchi[1]; K. Tadanaga[1]

1. Hokkaido University, Japan
2. Tokyo Metropolitan University, Japan
3. Hiroshima University, Japan

Oxysulfides have been intensively studied since coexistence of oxide and sulfide anions tend to adopt low-dimensional structures with anisotropic properties. Here, we show the crystallographic and electronic structures of $LaOBiS_2$ and $LaOInS_2$. Both structures consist of alternative stacking of distorted rocksalt-type M-S and PbO-type La-O layers. While two Bi-S layers are separated due to lone pair of Bi^{3+}, two In-S layers are strongly bonded. The In site splits into two sites, lowering the symmetry. Both the atomic displacement factors of Bi-S and In-S layers are abnormally high. The band gap of $LaOBiS_2$ and $LaOInS_2$ are estimated by optical absorption to be 1.0 eV and 2.6 eV, respectively. Bi6p and S3p orbitals compose the band gap of $LaOBiS_2$ while In 5s/5p and S3p form the gap of $LaOInS_2$.

9:30 AM

(PACRIM-S20-011-2017) Luminescent Lanthanide Coordination Compounds with Inorganic Lattice (Invited)

T. Nakanishi*[1]

1. Hokkaido University, Japan

Luminescent lanthanide coordination compounds get much attentions for their characteristic photo-physical properties. In this study, we present remarkable photo-functionalities of novel two lanthanide coordination compounds with inorganic lattice; 1) nona-nuclear lanthanide clusters composed of Ln-O inorganic blocks and light-harvest antenna ligands, and 2) Eu-activated tungsten polyoxometalate clusters (Eu-POM) with β-diketonate organic ligands. These inorganic coordination compounds are expected to open up a new field of advanced molecular materials.

10:15 AM

(PACRIM-S20-012-2017) Perovskite substrate crystals for strain engeneering (Invited)

D. Klimm[1]; C. Guguschev*[1]; M. Brützam[1]

1. Leibniz Institute for Crystal Growth, Germany

A significant number of double oxides with interesting ferroelectric, ferromagnetic, multiferroic, or simply electronic properties crystallizes in the perovskite structure; quite often the structure is orthorhombically distorted. If such substances are grown epitaxially on almost, but not completely, lattice-matched substrates, the Gibbs free energy of the layers is influenced by a contribution of elastic distortion at the interface. Rare earth scandates $REScO_3$ (RE = Pr ... Ho) proved to be especially well suited as substrates, because they are orthorhombic from their high melting points near or beyond 2000°C down to room temperature and exhibit almost square (110) lattice meshes with spacings around 4 Å, which is close to the lattice parameters of many relevant perovskite oxides. Haeni et al. [Nature 430 (2004) 758] could shift the Curie temperature for the transition of ferroelectric (low T) to the paraelectric (high T) phase of $SrTiO_3$ from almost absolute zero to room temperature by epitaxial growth

of 1% strained layers on $DyScO_3$ substrates. Depending on the epitaxial layer, the choice of appropriate substrates allows the adjustment of elastic strains stepwise, by the choice of proper RE ions. This talk will report how solid solutions of several perovskite mixed oxides can fill the gap between neighboring $REScO_3$, and can even extend the range of acessible substrate lattice parameters.

10:45 AM

(PACRIM-S20-013-2017) The Revolution of Metal Oxide Nanoparticles: From optical to biosensors (Invited)

E. Fortunato*[1]; A. Pimentel[1]; L. Santos[1]; A. Marques[1]; A. Gonçalves[1]; R. Martins[1]

1. FCT-UNL, Materials Science, Portugal

In this paper we refer the work performed within i3N/CENIMAT in the area of functional metal oxide nanoparticles to be used in a wide range of applications, from optical sensors to biosensors. In these work we will refer to the use of a very simple synthesis process based on the hydrothermal method to produce ZnO, WO3 and VO2 nanoparticles, that will be used in optical sensors, biosensors and as thermochromic materials, respectively. During the presentation real examples of applications will be given.

11:15 AM

(PACRIM-S20-014-2017) Synthesis and processing of nanocomposite ceramics for improved functionality of transparent materials

N. Ku*[1]; V. L. Blair[1]; Z. D. Fleischman[1]

1. U.S. Army Research Laboratory, USA

Transparent polycrystalline ceramics are used in various applications, such as laser hosts, infrared windows, and transparent armor. For such applications, superior optical, mechanical, and thermal properties of the material are needed, and the intrinsic properties of many traditional monolithic material systems are found lacking. Using nanocomposites in lieu of monolithic systems offer an engineering solution to this material problem. A challenge in using nanocomposites for transparent ceramics is the increased scattering due to the refractive index mismatch between the two materials, as well as the standard requirements of high purity and low porosity to achieve transparency in a bulk material. In this work, the synthesis and processing of an $Er:Y_2O_3$ and MgO nanocomposite for the use as a mid-infrared laser will be discussed. The advantage of adding MgO to the $Er:Y_2O_3$ lasing medium and creating a nanocomposite is the increase of the thermal conductivity, allowing for improved laser gain. Also to be investigated is a CaF_2 and ZnS system for use in IR transparent missile domes. The use of a composite system will increase strength due to reducing grain size of the product by grain pinning during sintering. For both systems, a wet chemical, precipitation route is used for synthesis. The subsequent challenges in processing to produce a sintered ceramic will also be discussed.

11:30 AM

(PACRIM-S20-015-2017) Transparent Ceramics with Tailored Composition (Invited)

Z. M. Seeley*[1]; I. Jones[2]; N. Cherepy[1]; S. A. Payne[1]

1. Lawrence Livermore National Lab, Chemical Sciences Division, USA
2. Lawrence Livermore National Lab, Physics, USA

Polycrystalline transparent ceramics offer advantages over single crystal or glass optical materials, including mechanical toughness and near-net shape manufacture. A unique opportunity that optical ceramics fabrication provides is the ability to form a tailored composition profile throughout the 3-dimensional bulk of the optic. Unlike most glass and single crystal optics, ceramics are fabricated from a solid preform and densified through a solid state sintering process. This process allows a preform with tailored composition, such as a doping gradient, to retain its compositional profile through to the final optic. To demonstrate this advantage of the ceramic processing, we are using the Direct Ink Write (DIW) additive manufacturing process to create preforms with tailored composition. The application of tailoring the laser ion dopant concentration gradient to match the pumping profile in gain media will improve the laser efficiency and stabilize the TEM00 mode. At the same time, we can also compensate for the change in refractive index by adding in an inert dopant thereby controlling the wavefront. We have successfully fabricated transparent ceramics with a Nd:YAG core and undoped YAG cladding by this method, and are working to improve the doping profile, aspect ratio, and optical scatter level. This work was performed under the auspices of the U.S. DOE by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

PACRIM Symposium 25: Ceramics for Next Generation Nuclear Energy

Properties and Performance of Nuclear Materials Under Extreme Conditions (i.e. High Radiation Dose, Elevated Temperature, Stress, Corrosive Environment, etc.)

Room: Kona 1

Session Chairs: Takashi Nozawa, National Institutes for Quantum and Radiological Science and Technology; Ming Tang, Los Alamos National Lab

8:30 AM

(PACRIM-S25-013-2017) Irradiation-tolerant Ceramics with Nanostructures: From Nanoporous ZrO_2, Multi-nanolayered W/ZrO_2 to Nano-laminated MAX Phase (Invited)

Y. Wang*[1]

1. Peking University, School of Physics, China

Several nanostructured materials, including nanocrystaline and nanoporous ZrO_2, multi-nanolayered W/ZrO_2 and nano-laminated metal ceramics MAX phase, were irradiated with heavy ions and He ions in a wide range of dpa. The irradiation tolerances of these nanostructured materials were investigated with TEM, XRD, Raman and nanoindentation, combined with ab initio and MD simulations. Generally, these nanostructured materials demonstrate a good character of damage resistance to irradiation. Especially, for MAX phases, we found that with formation of antisite defects and the rearrangement of C atoms, the original hcp structures are transformed into respective intermediated phases. Ti,Al-MAX phases cannot be amorphized and undergo an order to disorder structural phase transition at room temperature, forming a cation-disordered fcc structure. In contrast, Cr-based MAX phases are readily amorphized. Based on the irradiation results of numerous MAX phases and first-principles calculations, it was found that the bonding properties play an important role in the irradiation resistance to amorphization. Furthermore, Ti_3AlC_2 shows an excellent structural stability under ion irradiation at ~800 C, and the irradiation-induced defects are quite few even at very high doses, demonstrating a great potential for application in high temperature irradiation environment.

9:00 AM

(PACRIM-S25-014-2017) Exploring the Radiation Tolerance of Ceramic Nanoparticles via In-situ Ion Irradiation Transmission Electron Microscopy

K. Hattar*[1]; C. Barr[1]; B. Muntifering[1]; J. Kolar[1]; S. Pratt[1]; B. A. Hernandez-Sanchez[1]; T. J. Boyle[1]

1. Sandia National Laboratories, USA

To ultimately predict the properties and performance relationship of nuclear materials and radiation detector materials under extreme conditions, a fundamental understanding of the underlying displacement mechanisms is needed. Sandia National Laboratories has developed a unique tool, the In-situ Ion Irradiation Transmission Electron Microscope (I3TEM), to explore the radiation tolerance of materials with sub-nanometer resolution. This facility combines a high contrast TEM with two ion accelerators and 10 in-situ and tomography stages. The I3TEM was used to explore the radiation tolerance and develop a mechanisms of exposure of CeOx, through fuels removed from nuclear reactors. Additionally, potential discriminating radiation detectors were studied through a combination of electron microscopy and ion-beam induced luminescence characterization to determine the radiation stability and properties of PbWO3 and similar ceramic nanoparticles. In-situ observation of these systems permits understanding of the active mechanisms and the associated structural and property evolution.

9:15 AM

(PACRIM-S25-016-2017) Irradiation effects on metallic mitigation coatings for SiC cladding

C. Ang*[1]; C. Kemery[1]; J. Kiggans[1]; K. Terrani[1]; Y. Katoh[1]

1. Oak Ridge National Lab, Advanced Nuclear Materials, USA

Fuel cladding based on SiC_f-SiC composites faces critical challenges. Stress-induced microcracking may result from normal operations, which also includes radiolysis-assisted, aggravated hydrothermal corrosion. Barrier coatings based on Cr are investigated as a solution to these two issues. Coatings were developed by plasma spray, cathodic arc physical vapor deposition and electrolytic methods. A first-stage irradiation without coolant was conducted, and post-irradiation analysis compared properties before and after irradiation. Optical examination indicated behaviors associated with coating/substrate coefficient of thermal expansion and radiation swelling. Phase analysis, lattice parameter, crystallite size and microstrain analysis yielded new insights into coating materials behavior. Finally, destructive tests via ASTM D4541 were conducted to establish the extent of radiation resistance between the coating, bond coat and SiC substrate. The behavior under irradiation is crucial for evaluation and down-selection of in-pile coated specimens in the future.

9:30 AM

(PACRIM-S25-017-2017) Damage monitoring of silicon carbide and its composites by underwater acoustic emission waves

T. Nozawa*[1]; H. Tanigawa[1]

1. National Institutes for Quantum and Radiological Science and Technology, Japan

Silicon carbide (SiC) and its composites (SiC/SiC) are promising candidates of the accident tolerant fuel (ATF) cladding for the light water reactor and functional structure of the fusion blanket because of advantages such as superior radiation stability, chemical inertness, superior mechanical properties at elevated temperatures, etc. For the detailed design utilizing SiC materials, understanding fracture origin and crack propagation mechanism is essential not only in quality assurance but also in developing codes and standards specific to the composites. Accordingly, the acoustic emission (AE) method has been widely applied to characterize the failure process of various types of composite materials. However, due to the inherent anisotropy of the composites, there seem some difficulties in location determination by the AE sensors directly attached to the material. Besides, AE sensors cannot be directly placed nearby the components during operation. This study therefore aims to establish a new methodology to indirectly characterize the composite failure behavior using underwater AE waves. Preliminary evaluation was conducted by flexural tests in water for both SiC and SiC/SiC composites. This paper will discuss the first set of results about location determination and waveform analyses by FFT and wavelet to classify detailed failure types of the materials.

9:45 AM

(PACRIM-S25-018-2017) Behavior of interstitial helium in boron carbide: A first principles study

A. Schneider[1]; G. Roma*[1]; J. Crocombette[1]

1. CEA, Université Paris-Saclay, DEN-Service de Recherches de Métallurgie Physique, France

Boron carbide, a ceramic material known for its ultrahigh strength, is also used as a neutron absorber in nuclear power plants. As such it undergoes nuclear reactions producing non negligible quantities of helium. Although the kinetics of helium in boron carbide has been the subject of studies since the first usage of the material as a neutron absorber, the mechanisms leading to bubble formation and/or helium desorption are still largely unexplained. We present here a study of the stability and mobility of helium atoms in the lattice of boron carbide of stoichiometry B_4C, with the $B_{11}C$-CBC structure. Our results suggest first a temperature range where 2D diffusion, confined between two adjacent [111] planes, is taking place. At higher temperature we assist to the onset of 3D diffusion, with an activation barrier exceeding 2 eV. Although our results seem to provide a qualitative explanation of some experimental results, further work is in progress in order to assess the relevance of intrinsic defects assisted diffusion mechanisms, which could be important under irradiation.

10:15 AM

(PACRIM-S25-019-2017) Nanoscale Mechanical Behavior of Nuclear Materials

U. Carvajal Nuñez*[1]; E. Sooby Wood[1]; J. T. White[1]; N. Mara[1]; A. T. Nelson[1]

1. Los Alamos National Lab, USA

New fuel materials that offer greater resistance to cracking under the extreme environments encountered during nuclear reactor service would provide significant improvements to steady state. Options currently under investigation include 'nontraditional' nuclear fuels designated around high uranium density. These include uranium silicides, uranium borides, and composite fuel materials constructed of these and uranium nitride or uranium dioxide. Preliminary screening of the thermophysical and thermodynamic properties of these concepts has provided confidence in their soundness, but evaluation of their mechanical properties at relevant temperatures must be executed in order to support further study. Several research groups worldwide, have studied in some decades, the nanoindentation technique. The technique isexpected to be useful for measurement of the mechanical properties of local structure of various materials. By using the nanoscale properties, we can develop the advanced nuclear materials more effectively. However, are few attempts to apply the nanoindentation to evaluate the mechanical properties of the nuclear fuels and materials has been reported in the bibliography. Furthermore, no nanomechanical evaluation at room and a relevant temperatures of 'nonconventional' nuclear fuels, has been studied in the past. In this study, unique results are presented.

10:30 AM

(PACRIM-S25-020-2017) Safety Performance Evaluation of Silicon Carbide Ceramics for Accident Tolerance Fuel in Hydrothermal Exposure Condition

L. Kwang-Young*[2]; S. Lee[2]; Y. Kim[1]; W. Kim[3]

1. University of Seoul, Department of Materials Science and Engineering, Republic of Korea
2. KEPCO Nuclear Fuel, Materials Development Section, Republic of Korea
3. 3Korea-Atomic Energy Research Institute, Nuclear Materials Development Division, Republic of Korea

The recent events at the Fukushima Daiichi nuclear power plant in Japan highlighted the need for added safeguard, including fuels with enhanced accident tolerance that can delay or even prevent severe accidents. In this sense, the use of particle-based accident tolerant (PBAT) fuels is an alternative strategy for overcoming this issue by multiple silicon carbide (SiC) barriers such as SiC layer in TRISO and the dense SiC matrix. The performance on high temperature oxidation of PBAT fuel is one of important factors for plant safety of nuclear reactors. In this work, safety performance evaluation of SiC ceramics for accident tolerance fuel (ATF) in hydrothermal exposure condition was performed at ~1700 °C for ~25hr. PBAT fuel and monolithic SiC ceramics was fabricated by hot-pressing and normal sintering, respectively. After 25hr hydrothermal oxidation, some TRISO kernel in PBAT fuel were exposed and inner surface portion of PBAT fuel shows pore channel by permeated liquid phase through the grain boundary and junction. The high temperature oxidation resistance of SiC ceramics was dependent on the chemistry of the grain size, additive composition and the additive content. More importantly, suppression of liquid phase formation by reaction between SiO_2 and junction part is essential factor for oxidation resistance performance of SiC ceramics.

10:45 AM

(PACRIM-S25-021-2017) SiC-SiC CMCs for Nuclear Applications: Update on Progress of WG for Graphite & Composites in ASME BPV Code Section III, Division 5 High Temp Reactors

M. G. Jenkins*[1]; S. T. Gonczy[2]; Y. Katoh[3]

1. Bothell Engineering and Science Technologies, USA
2. Gateway Materials Technology, USA
3. Oak Ridge National Lab, USA

Future nuclear high-temperature reactors (HTRs) planned by US DOE will use SiC-SiC CMCs to enhance fuel performance and improve accident-yolerance because SiC-SiC CMCs are tolerant to irradiation and chemical environments. However, as nonconventional materials, SiC-SiC CMCs are of concern because the mission of the US Nuclear Regulatory Commission (NRC) is to license and regulate the nation's civilian use of byproduct, sources and special nuclear materials. NRC regulates nuclear reactors and new reactor design as well as reactor materials. NRC not only imploys, but is legally required to use, consensus codes and standards as an integral part of the regulatory process. In particular, the ASME Boiler and Pressure Vessel (BPV) Code Section III "Rules for Construction of Nuclear Components" is included in the NRC regulations. Division 5 HTR of Section III supports a working group on graphite and composites (e.g., SiC-SiC CMCs). Therefore, for SiC-SiC CMCs to be incorporated into nuclear reactors, they must be included in ASME BPV Code. This paper provides an update of progress on the portions of ASME BPV Code including design and qualification of SiC-SiC CMCs as well as several informational appendices on the testing, classification, composition, structure, manufacture, and properties of SiC-SiC CMCs for nuclear applications.

PACRIM Symposium 28: Advanced Materials and Technologies for Electrochemical Energy Storage Systems

Beyond Li-ion

Room: Queen's 5
Session Chair: Naoaki Yabuuchi, Tokyo Denki University

8:30 AM

(PACRIM-S28-013-2017) Sodium secondary batteries using bis(fluorosulfonyl)amide ionic liquids as electrolytes (Invited)

R. Hagiwara*[1]; T. Nohira[1]; K. Matsumoto[1]; K. Numata[2]; S. Sakai[2]; K. Nitta[2]

1. Kyoto University, Japan
2. Sumitomo Electric Industries, Ltd., Japan

A molten amide mixture, Na[FSA]-[C_3C_1pyrr][FSA] (C_3C_1pyrr = N-propyl-N-methylpyrrolidinium, FSA = bis(fluorosulfonyl)amide), was investigated as a potential electrolyte for sodium secondary batteries operating at intermediate temperatures (253-363 K). The cyclic voltammetry revealed that the electrochemical window of these salts is as wide as 5.2 V at 363 K, and electrochemical deposition/dissolution of sodium metal reversibly occurs at the cathode limit potential. Considering their non-volatility, non-flammability and inexpensiveness, the salt mixture is highly promising as a new class of electrolyte for sodium secondary batteries. The results of full cell tests will be described employing $NaCrO_2$ and hard carbon as positive and negative electrode materials, respectively. This study was partly supported by the Advanced Low Carbon Technology Research and Development Program (ALCA, No. 3428) of Japan Science and Technology Agency (JST), and the Elements Strategy for Catalysts and Batteries (ESICB) program of the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT).

9:00 AM

(PACRIM-S28-014-2017) Chances of Hückel-type salts based electrolytes for application in modern batteries (Invited)

M. Marcinek*[1]; A. Bitner[1]; T. Trzeciak[1]; P. Wieczorek[1]; M. A. Muñoz-Márquez[2]; B. Hamankiewicz[3]; L. Niedzicki[1]; W. Wieczorek[1]

1. Warsaw University of Technology, Chemistry, Poland
2. CIC EnergiGUNE, Spain
3. Univeristy of Warsaw, Poland

New electrode materials are designed and studied at many universities, but a lot of work needs to be done to implement new electrolytes in to the market. Our group is carrying out research on modern electrolytes based on imidazole salts. A concept of new lithium electrolytes and their sodium analogues as candidates for battery components is based on the idea of tailoring new salts. These salts can be applied in liquid as well as polymer systems. Salts are easy to obtain, and exhibit good conductivity in solution containing organic solvent (0.75M NaTDI (EC/DMC) – 11.9 mS/cm). Liquid electrolytes present also very good electrochemical stability versus sodium between 3.2 V – 4.5V. The lecture will be enriched by examples of application of newly designed electrolytes in preliminary cells with novel electrode materials and discussion on possible extension of its use in sodium or sulphur systems. Acknowledgements: The research leading to these results has received fundings from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement number 608502 (Sirbatt Project) and 865368 (EuroLion). Authors would like to acknowledge to Hanna Rajantie and Liam Bennett from Sirbatt Consortioum. Praca naukowa finansowana ze srodkow finansowych na nauke w latach 2013-2016 (Sirbatt) i 2011-2015 (EuroLiion) przyznanych na realizacje projektu miedzynarodowego wspolfinansowanego.

9:30 AM

(PACRIM-S28-015-2017) Mechanisms of Surface Reactions in Aqueous Sodium-Ion Batteries

M. Shirpour*[1]; X. Zhan[1]

1. University of Kentucky, Chemical and Materials Engineering, USA

Low cost energy storage systems are the key technologies for the fluctuating supply of electricity based on solar and wind power. Aqueous sodium-ion batteries offer multiple cost savings using less expensive electrode materials and much cheaper electrolyte solutions compared to the lithium-ion cells. They also have the extra advantage of being safer for (micro)grid applications. However, their poor overall performance and low electrode utilization (much of the electrode material ends up being electrochemically inactive) are the main barriers to implementing them in (micro)grid systems. In this presentation, we show that the poor performance of aqueous sodium-ion batteries is mainly associated with the reactions on the surface of NASICON-type phosphate anode materials. The surface reactions result in the formation of an electrically insulating layer on the surface, causing the failure of electrochemical performance and the precipitation of surface particles that block the pores and result in poor electrode utilization. These findings provide insight into new possibilities of improving the electrochemical performance of aqueous sodium-ion batteries by the design of protective layers that prevent the formation of insulating surface layers and insoluble precipitates.

Positive

Room: Queen’s 5
Session Chair: Marca Doeff, Lawrence Berkeley National Laboratory

10:15 AM

(PACRIM-S28-016-2017) Anion Redox Reaction for Rechargeable Li/Na Batteries (Invited)

N. Yabuuchi*[1]

1. Tokyo Denki University, Japan

The use of anion redox, especially oxide ions, is a crucial strategy to design and develop new electrode materials with high gravimetric/volumetric energy density for rechargeable lithium batteries. Reversible capacity of electrode materials is potentially further increased by the enrichment of lithium contents with less transition metals in the close-packed structure of oxide ions. Our group has reported that $Li_3Nb^{5+}O_4$ and $Li_4Mo^{6+}O_5$, which have higher lithium contents than that of Li_2MnO_3, are potentially utilized as host structures for a new series of high-capacity electrode materials. Recently, $Li_2Ti^{4+}O_3$ is also proposed as the host structure for high-capacity electrode materials with redox reaction of oxide ions. Mn^{3+}-substituted sample, $0.5Li_2TiO_3 – 0.5LiMnO_2$ ($Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$), delivers large reversible capacity of 300 mAh g^{-1}. Available energy density of $Li_{1.2-x}Ti_{0.4}Mn_{0.4}O_2$ exceeds 1 000 mWh g^{-1} as a positive electrode material. Moreover, charge compensation is realized by oxidation of oxide ions as evidenced by O K-edge X-ray absorption spectroscopy as a reversible process. From these results, we will further discuss the possibility of high-capacity positive electrode materials, which effectively use the solid-state redox of oxide ions for the charge compensation, for rechargeable Li/Na batteries.

10:45 AM

(PACRIM-S28-017-2017) Disordered Rock Salt type Structure as New Active Compound for High Energy Density Batteries (Invited)

V. Pralong*[1]; M. Freire[1]; E. Adamczyk[1]; E. Anger[1]

1. CNRS ENSICAEN, France

Due to their low weight, high energy densities and long cycle life, the battery scientific community is still trying to develop new high capacity cathodes materials in order to increase the energy density of storage devices. We found new electrode materials based on disordered rock salt type structure showing a capacity higher than 300 mAh/g. The nanostructured character of these materials will be discussed as well as the impact of the structure and composition. These results confirm the possibility to find materials showing 2 electrons per redox active centers leading to high energy density based on disordered 3D type structure.

11:15 AM

(PACRIM-S28-018-2017) Voltage Variation of Lithium Transition Metal Oxides Caused by the Migration of Cations (Invited)

Z. Chen*[1]; Y. Li[1]; Y. Qin[1]; Y. Ren[1]; K. Amine[1]

1. Argonne National Lab, USA

Major effort has been devoted to understanding the structure and the electrochemical benefit of lithium-rich transition metal oxides for high-energy density lithium-ion batteries because of their potentially high specific capacity of up to 250 mAh g^{-1} when the materials are electrochemically activated. It has been widely repeated that the excess lithium can be electrochemically activated at a potential above 4.5 V vs. Li^+/Li to deliver more reversible specific capacity, offering great opportunity for use of these lithium-rich transition metal oxides as high-capacity cathode materials. However, the structural instability of the material after electrochemical activation causes a continuous decrease in its working potential that hinders the commercial deployment of this class of high-capacity cathode materials. The migration mechanism of transition metal in the oxygen framework was investigated here to illustrate the voltage decay of lithium-rich transition metal oxides. For the first time, a voltage increase was observed during the cycling of a lithium manganese oxide spinel within a wide potential window. It was demonstrated that the voltage variation of these materials was caused by the continuous migration of transition metal ions, mostly Mn^{2+}, between the octahedral and tetrahedral sites, resulting in the ratio change between the spinel component and layered component.

11:45 AM

(PACRIM-S28-019-2017) In-depth investigation of process-structure-property relationship in the cathode materials of Li ion batteries

Q. Liu*[1]

1. Argonne National Lab, Advance Photon Source, USA

For lithium ion batteries (LIBs), the cathode materials are typically metal oxides or phosphates, which serve as the host for Li+ ion intercalation during discharge. Among the commonly-used cathode materials, V2O5 have been considered to be very promising cathode materials. However, the long-standing issues of low intrinsic electronic conductivity, slow lithium-ion diffusion and irreversible phase transitions on deep discharge prevent the high specific capacity/energy vanadium pentoxide from being used as the cathode material in practical battery applications. In this talk, our presentation will be centered on the study of V2O5 as the cathode materials for Li-ion batteries. Here we develop a method to incorporate graphene sheets into vanadium pentoxide nanoribbons via the sol–gel process. The resulting graphene-modified nanostructured vanadium pentoxide hybrids contain only 2 wt. % graphene, yet exhibits extraordinary electrochemical performance. Finally, the in-depth investigation of process-structure-property relationship in these hybrids-based Li-ion batteries has been studied using advanced in situ synchrotron techniques and existing tools.

PACRIM Symposium 29: Advances in Polar, Magnetic and Semiconductor Materials: Extending Temperature Limits

High Temperature Piezoelectrics

Room: Queen’s 4
Session Chairs: Andrew Bell, University of Leeds; Shujun Zhang, University of Wollongong

8:30 AM

(PACRIM-S29-010-2017) H-T Piezoelectric Devices Based on Modified $BiScO_3$-$PbTiO_3$ Ceramics (Invited)

J. Wu[1]; S. Dong*[1]

1. Peking University, Materials Science & Engineering, China

$(1-x)BiScO_3$-$xPbTiO_3$ (BS-PT) piezoelectric ceramics with the composition near MPB exhibiting high Curie temperature (T_c = 450°C) and comparable piezoelectric properties (d_{33}= 450 pC/N) have been widely investigated. From the perspective of the high Curie temperature Tc, BS-PT piezoelectric ceramics have potential as piezoelectric devices intended for applications in high-temperature circumstance. In this presentation, we will summary the progress in BS-PT based piezoelectric ceramics, including $(1-x)Bi(Sc_{3/4}In1/4)O_3$-$xPbTiO_3$ (BSI-PT) ($0.45<x<0.70$), Mn-modified$(1-x)BiScO_3–xPbTiO_3$(Mn-BSPT), $(0.98-x)Bi(Sc_{3/4}In_{1/4})O_3$-$xPbTiO_3$ -$0.02Pb(Zn_{1/3}Nb_{2/3})O_3$(BSI-PT-PZN),(0.95-x)

$BiScO_3$-x$PbTiO_3$-0.05$Pb(Cd_{1/3}Nb_{2/3})O_3$ (BS-PT-PCN), etc., and report the latest development of BS-PT based devices, including (i) H-T multilayer, shear-bending, and bimorph types of piezoelectric actuators, (ii) H-T linear motors operating L1-B2 double vibration modes, and orthogonal in-plane first bending mode (B1-B1 mode), respectively, (iii) H-T piezoelectric vibration energy harvesters operating d_{31} and d_{33} modes, respectively. Their H-T properties, steady performances, potential applications and future prospective will be discussed in detail. Our research results show that BS-PT based piezoelectric ceramics are promising materials for various H-T device applications.

9:00 AM

(PACRIM-S29-011-2017) A barbell-shaped high-temperature piezoelectric vibration energy harvester based on $BiScO_3$-$PbTiO_3$ ceramic

J. Wu*[1]

1. Peking University, China

In this paper, we report a barbell-shaped piezoelectric energy harvester (BSPEH) operating in d_{33} mode and aiming for mechanical vibration energy harvesting in high temperature (H-T) circumstance. BSPEH is composed of a ring-shaped multilayer piezo-stack, a tip mass, and an elastic shaft connecting them together. The piezo-stack is made of bismuth scandium lead titanate ($BiScO_3$-$PbTiO_3$) ceramic with a large piezoelectric coefficient d_{33} = 450 pC/N and a high Curie temperature point T_c around 450°C. Experimental results show that the BSPEH works effectively and steady in a wide temperature range from room temperature (R-T) till $T_c/2$. Furthermore, it is found that under a constant mechanical vibration excitation, the power output of the BSPEH at 200°C is even two times higher than that at R-T. The proposed harvester shows a great potential for applications as a self-power source of wire-less sensor system in H-T circumstance.

9:15 AM

(PACRIM-S29-012-2017) A high temperature piezoelectric platform for ultrasound transducers (Invited)

T. J. Stevenson[2]; A. J. Bell*[1]

1. University of Leeds, School of Chemical and Process Engineering, United Kingdom
2. Ionix Advanced Technologies Ltd, United Kingdom

Effective monitoring of asset integrity subject to corrosion and erosion in difficult and hazardous environments is a major problem in many industries. One solution is permanently installed ultrasonic monitoring equipment which can continuously provide information on the rate of corrosion or cracking, even in the most severe environments, to prevent the need for shutdown in existing plant. Current commercial offerings for ultrasonic condition monitoring transducers are limited by phase transitions, thermal expansion mismatch and low sensitivity from the piezoelectric active element as well as inefficiencies due to variability in acoustic coupling mechanisms. Recent advances in piezoelectric ceramic compositions at the University of Leeds have enabled the manufacture of materials with levels of transduction performance approaching that of PZT, but with operating temperatures almost 300°C higher. To exploit such piezoelectric performance requires a transducer design which is matched to the extreme conditions. Such designs are embodied in the HotSense® platform developed by Ionix Advanced Technologies. This presentation evaluates a permanently installed ultrasonic monitoring system based on the new materials and transducer designs. The system applicability for wall thickness monitoring in high temperature environments is demonstrated through experimental studies on nuclear steam pipes at temperatures up to 400 °C.

9:45 AM

(PACRIM-S29-013-2017) Ultrasonic Transducers for Harsh Environments

B. R. Tittmann*[1]; J. Daw[2]; B. Reinhardt[3]

1. Pennsylvania State University, Eng.Sc. & Mechanics, USA
2. Idaho National Laboratory, USA
3. Applied Research Laboratory, USA

Ultrasound offers measurements of parameters encountered in harsh environments such as steam generators, heat exchangers and nuclear reactors. But there is a lack of piezo-materials tolerant of high temperatures and irradiation. Pennsylvania State University was awarded an Advanced Test Reactor National Scientific User Facility (ATR NSUF) project to evaluate promising magnetostrictive and piezoelectric transducers in the Massachusetts Institute of Technology Research Reactor (MITR) for 18 months. The transducers experienced an integrated neutron fluence of about 8.68 E+20 n/cm^2 for n >1 MeV, temperatures over 420 °C, and a gamma fluence of 7.23 Gy/cm2. Three piezoelectrics were chosen with Aluminum Nitride (AlN), Zinc Oxide (ZnO), and Bismuth Titanate (BiTi) and two magnetostrictive transducers with Remendur and Galfenol as the active elements. Although most sensors performed well in this environment, it was not without some troubles. This is demonstrated and explained in the context of pulse-echo signals. Overall, this is the longest exposure experiment conducted to the researchers' knowledge on the chosen sensor materials and the first instrumented lead test for many of these materials, Thus, the potential usefulness of ultrasonic transducers in a nuclear reactor environment has been demonstrated. This opens the door to leave-in-place sensors for harsh environments.

10:15 AM

(PACRIM-S29-015-2017) High temperature piezoelectric sensing: Materials, devices and applications (Invited)

X. JIang*[1]

1. NC State, USA

High temperature sensors can be applied in engine, space, and power systems. Piezoelectric sensing is favorite because of its rapid response, low profile and simple signal conditioning. However, high temperature piezoelectric sensing has been challenged in many aspects including materials, device design and applications. In this paper, characterizations of several different types of high-temperature piezoelectric single crystals are presented, followed by piezoelectric sensing device demonstrations at temperatures > 1000 °C. Moreover, preliminary study on temperature dependence of flexoelectricity of some ferroelectric materials will be next presented, exploring the possibility of applying flexoelectric materials for high temperature sensing. Finally, discussions of existing challenges and future work for high-temperature piezoelectric sensing are presented.

10:45 AM

(PACRIM-S29-016-2017) High temperature piezoelectric crystals: Growth, properties and potential sensor applications (Invited)

F. Yu*[1]

1. Shandong University, State Key Laboratory of Crystal Materials, China

High temperature piezoelectric materials functional at harsh environment without failure are desired for structural health monitoring and/or nondestructive evaluation of the modern aerospace structures at elevated temperatures (>600°C). In addition, high temperature piezoelectric materials will also benefit the safety of electrical /nuclear power plants and energy storage facilities. Of all the researched high temperature piezoelectric materials, piezoelectric single crystals have stirred lots of interests. It is evident that the operational temperature range of the piezoelectric crystals based sensors is usually limited by the sensing capability of the piezoelectric crystals at harsh environment, the conductivity, mechanical attenuation, and variation of the piezoelectric properties with temperature etc. This report will discuss the single crystal growth and electro-elastic properties of different high temperature piezoelectric crystals, including langasite type crystals, melilite crystals, fresnoite crystals and oxyborate crystals, for potential sensor applications.

PACRIM Symposium 31: Advances in Bioceramics: Biomineralization and Bioinspired Materials

On Bone: Structural Aspects

Room: Monarchy
Session Chairs: Laurie Gower, University of Florida; Po-Yu Chen, National Tsing Hua University

8:30 AM

(PACRIM-S31-012-2017) Bone hierarchical structure and mechanics through 3D X-ray imaging techniques (Invited)

H. Birkedal*[1]

1. Aarhus University, Department of Chemistry & iNANO, Denmark

Bone is an anisotropic hierarchical composite material that is special amongst biominerals since it contains living cells, osteocytes, that acts as sensors of damage. The multi-length-scale structures of bone remain far from understood. We harness recent developments in X-ray science to shed new light on bone structure and mechanics. Bone has anisotropic mechanical properties. Its constituent mineral and collagen phases each carry a part of the applied load. However, it is not clear how a macroscopic load is distributed within bone. To address this problem we have developed in situ loading diffraction scattering computed tomography (DSCT). DSCT combines diffraction and scattering with tomography and allows reconstructing diffractograms from inside a specimen. In in situ loading DSCT, diffraction information is obtained under load allowing us to unravel how macroscopic mechanical load distributes across a bone noninvasively. Extending DSCT further, we study the orientation distribution of bone nanocrystals within bone in 3D and use it to show that minerals are oriented differently around blood vessels than in primary bone matrix in bovine cortical bone. Finally, nanotomography reveals that the osteocyte cellular network contains junctions, seen as voids in the bone matrix, where connections between several cells cross. This indicates that much remains to be learnt about how bone turnover is controlled.

9:00 AM

(PACRIM-S31-013-2017) Comparing structure, composition and properties of bio-inspired collagen/apatite systems with natural bone (Invited)

R. Kroeger*[1]; N. Reznikov[2]; K. Chatzipanagis[1]; M. Bilton[3]

1. University of York, United Kingdom
2. Imperial College, United Kingdom
3. Simon Frazer University, Canada

To replicate the properties of bone a number of key challenges have to be addressed regarding the chemical composition and the structural makeup and their impact on the mechanical properties. Important insights into the mineralization pathways, structure and mechanical properties were obtained by state-of-the-art transmission electron microscopy (TEM) and electron tomography, focused ion beam combined with scanning electron microscopy (FIB-SEM) and in situ Raman spectroscopy. Our studies focused on three key aspects of bone structure, mineralization and the correlation between composition and properties: - the ultrastructure of bone studied by scanning TEM tomography and FIB-SEM. This revealed an intricate nanoscale network of both the collagen and the apatite components with interlocking acicular mineral bundles. - possible pathways for the crystallisation via an amorphous calcium phosphate (ACP) precursor phase using citrate (constituting up to 5% of the organic phase in bone) as controlling additive. We find a a surface mediated mechanism for apatite formation from ACP. - the impact of collagen mineralization on the mechanical properties of collagen/apatite microfibers. Using in situ stress-strain measurements and in situ Raman we demonstrate that the mineral phase leads to a conformational change of the proline and hydroxyproline amino acids upon mechanical loading.

9:30 AM

(PACRIM-S31-014-2017) Enhancing mechanical properties of collagen through mineralization (Invited)

J. A. Elliott*[1]; P. J. Kiley[1]; K. Chatzipanagis[2]; R. Kroeger[2]

1. University of Cambridge, Department of Materials Science and Metallurgy, United Kingdom
2. University of York, Department of Physics, United Kingdom

Collagen is the principal load-bearing protein in both mineralized and unmineralized mammalian tissues. In tendon, where collagen is usually unmineralized, an interface is formed with the solvent (most commonly water, but other organic liquids and ionic solutions are also considered in this study) which significantly alters its tensile modulus. In bone, an organic-inorganic interface may also form via the crystallization of the hydroxyapatite mineral phase, which can result in an enormous increase in tensile modulus and stability. We present strain-realistic molecular dynamics simulations combined with thermodynamic integration to investigate the interfacial energy of collagen systems. Direct scaling of the interfacial energy reveals the importance of solvent-induced surface stress, which stabilizes the triple helix structure via a circumferential (not radial) contraction. Results are corroborated by small- and wide-angle X-ray scattering experiments, and the confining effect of solvent is attributed mainly to the entropy change of solvent ordering around the triple helix, which is strongly affected by the ionic strength of the solution. We also present Raman data demonstrating a novel mechanism for the effects of confinement by mineralization whereby the conformation of proline and hydroxyproline rings in collagen is altered, leading to greater stress transfer within the mineralized collagen structure.

Fundamental Apects of Biominerals II - Calcarous Systems

Room: Monarchy
Session Chairs: Laurie Gower, University of Florida; Hui-suk Yun, Korea Institute of Materials Science

10:15 AM

(PACRIM-S31-015-2017) Calcium Carbonate Formation Pathways and the Influence of Organic Templates (Invited)

M. Nielsen*[1]; J. Lee[1]; J. De Yoreo[2]; S. Aloni[3]; T. Willey[1]; C. Freeman[4]

1. Lawrence Livermore National Laboratory, USA
2. Pacific Northwest National Lab, USA
3. Lawrence Berkeley National Laboratory, USA
4. University of Sheffield, United Kingdom

Nucleation in the natural world often occurs at organic surfaces. During biomineralization, living organisms use macromolecular matrices to direct nucleation of a variety of inorganic materials by controlling the timing, polymorphism, morphology, and crystallographic orientation of mineral nuclei. In geochemical settings, mineral surfaces, which are often covered with organic layers or biofilms, surround the volume within which nucleation occurs. Despite the importance of nucleation phenomena in these natural settings, our understanding of the reaction dynamics and energetics of the process is limited. Issues such as the role of meta-stable precursors, polymorph selection during the initial stages of nucleation, the structural relationships between the organic matrix and the emerging nucleus, and the mechanisms by which the matrix controls crystallization are poorly understood. We address these issues through experimental and computational investigations into $CaCO_3$ nucleation with self-assembled monolayers of alkanethiols as simple models for organic matrices. We use fluid cell TEM to investigate $CaCO_3$ formation pathways at the nanoscale and complementary techniques to gain insight into the template's effect on crystallization. MD simulations of the template-crystal interface investigate differences in interfacial energies for closely related templates and results are compared to experiment.

10:45 AM

(PACRIM-S31-016-2017) Biomineralization of corals, sea urchins, and shells (Invited)

P. Gilbert*[1]

1. UW-Madison, Physics, USA

I will describe some of the formation mechanisms, termed biomineralization, of corals, mollusk shell nacre, and sea urchin spicules and spines. All these marine biominerals form via attachment of amorphous precursor particles, filling space and eventually crystallizing to aragonite or calcite, slightly disordered by occluded organics. Component maps display with colors the spatial distribution of the amorphous precursors in forming, fresh biominerals. Polarization-dependent Imaging Contrast (PIC)-maps display in color patterns of crystal orientations. PIC-maps also revealed that the physical structure of nacre correlates with the environmental temperature at the time of formation.

11:15 AM

(PACRIM-S31-017-2017) Hydrogels in Nature: Invertebrates use "jelly" to craft biominerals (Invited)

M. Pendola[1]; G. Jain[1]; A. Davidyants[1]; Y. Jung[1]; J. S. Evans*[1]

1. New York University, USA

It has been established that invertebrate organisms utilize silk-like proteins and polysaccharides to create hydrogel-environments for controlling the biomineralization process in the formation of shells and spines. Recently we have uncovered sets of proteins that contribute to this silk-gel phase. These proteins, which are residents within the nacre layer of the mollusk shell and the spines and spicules of sea urchins, self-assemble to form "smart" hydrogel particles that modify the surfaces and interiors of forming mineral crystals, organize mineral nanoparticles, and control the early events in nucleation. We will examine both systems in terms of what common and divergent features these proteins have, and how the scientific community can exploit these features to develop hydrogel systems for nanoparticle formation and organization.

11:45 AM

(PACRIM-S31-018-2017) Of amorphous phases and tilting crystals: A lesson in nonclassical crystallization from nature

S. E. Wolf*[1]

1. Friedrich-Alexander-University Erlangen-Neurnberg, Department of Materials Science and Engineering, Chair of Glass and Ceramics, Germany

Well-known for structural wealth on the macro- to the mesoscale, apparently all biominerals share a distinct nanogranular fine structure. This feature not only affects a remarkable number of properties of the bioceramic material, moreover, the nanogranularity seems to root in a common and nonclassical growth mode, as highlighted for bivalve nacre. This finding enables us to state a fundamental process-structure-property relationship in biominerals which may spark new design routes to biomimetic smart materials. We demonstrate further that ACC can form via different pathways and, under biomimetic conditions, form a dense and space-filling mineral body. Via a pseudomorphic transformation, organic additives can be incorporated giving rise to a nanoscale structure indiscernible from the biogenic counterpart. This allows tuning of the final mineral composition but also paves the way to a new field of crystal design. In a comparative case study, we show that the interplay between transforming mineral phase and organic inclusions give rise to crystal lattice twisting and tilting which can be ultimately employed as new means to generate gradient materials or to exert excellent control on the crystallographic texture of a material without the action of an actively templating scaffold.

GOMD Symposium 1: Fundamentals of the Glassy State

Mechanical Properties of Amorphous Solids III

Room: Kona 4

Session Chairs: Peter Lezzi, Corning Incorporated; Timothy Gross, Corning Incorporated

1:15 PM

(GOMD-S1-021-2017) Effect of water on mechanical strength of glasses (Invited)

M. Tomozawa*[1]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA

Water often has adverse effect on the strength of glasses. In general, a crack of glasses grows faster in wet atmosphere under a constant stress intensity; water in glass also increases a crack growth rate and reduces the mechanical strength of the glass. Yet, we found that glasses can be made stronger by water vapor, through the surface stress relaxation, when we hold the glasses under a high tensile stress. Thus, it appears that water has dual effects of both glass weakening and strengthening. Details of this dual roles of water will be considered so that we can make the most of this unique roles of water in the strength of glasses.

1:45 PM

(GOMD-S1-022-2017) An atomistic window into the mechanical failure of amorphous silica and silicate based systems

K. Muralidharan*[1]; K. Runge[1]

1. University of Arizona, Materials Science and Engineering, USA

Using robust multiscale paradigms that combine first principles methods with classical molecular dynamics simulations, brittle fracture of silica and alkali aluminosilicate (AAS) glasses are examined and characterized. Equally importantly, the role of water on the dynamics of brittle fracture is also examined and fundamental insight into the mechanisms that govern the hydrolytic weakening of these systems is obtained. In 'dry' silica glass, transformation from corner-sharing to edge-sharing silica tetrahedra occurs in regions of high stress, leading to compaction of the local structure and growth of nanoscale voids. Subsequently, the coalescence of the nanoscale voids leads to failure of silica glass. In the case of dry AAS glasses, stress induced diffusion of alkali ions leads to weakening of alumina tetrahedra, which subsequently destabilize, resulting in failure. In the presence of water, failure is enhanced due to concerted attack of water dimers on Si-O bonds in silica glass. However, in AAS glasses, fracture dynamics are primarily driven by the enhancement in alkali diffusion as a result of the interplay between the polarizing field arising due to the presence of water and the applied load.

2:00 PM

(GOMD-S1-023-2017) A physical rationale for subcritical crack growth in glasses

B. Poletto Rodrigues*[1]; L. Wondraczek[1]; C. Hühn[1]; M. Sierka[1]

1. Friedrich-Schiller-University Jena, Germany

We present a mechanistic analysis of the rate of subcritical fracture in glasses, covering crack extention in Regions I and III, where the fracture kinetics are determined by environmentally enhanced bond cleavage. Ab initio quantum chemical simulation is used for obtaining an accurate rationale of the energetics of cracking in the presence of molecular water. The model is tested against macroscopic data of bond cleavage activation energy, yielding remarkable agreement. As the macroscopic crack propagation rate is defined by the rate of consecutively successful events of molecular bond rupture, an adapted Boltzmann distribution is used to model the crack growth rate, where the system's volumetric strain energy is added to its thermal energy. The agreement of quantum chemical and experimental data suggests that during the fracture of silica, mechanical energy is dissipated alone through bond rupture, a result in line with the hypothesis of ideal brittleness of oxide glasses.

2:15 PM

(GOMD-S1-024-2017) Fracture toughness of amorphous silica in aqueous environments from atomistic scale molecular simulations

J. M. Rimsza*[1]; R. Jones[2]; L. Criscenti[1]

1. Sandia National Laboratories, Geochemistry, USA
2. Sandia National Laboratories, Mechanics of Materials, USA

Crack propagation rates in amorphous silica increase in wet or humid environments and it has been suggested that this increase is caused by reactions between water molecules and strained siloxane bonds located at the crack tip. Molecular dynamics simulations of fracture in amorphous silica were performed to identify the coupled chemical-mechanical mechanisms which control crack propagation in silicates in the presence of water. In the simulations, a bulk amorphous silica structure undergoes mode I fracture after the introduction of a slit crack. Water molecules are allowed to infiltrate the crack as the fracture opens. Classical and reactive force fields are used to examine the differences in fracture toughness due to (a) silica fracture in a vacuum, (b) silica fracture in unreactive water, and (c) silica fracture in a model system that allows for the hydroxylation of the fracture surfaces. Atomistic stress and energy data are upscaled using an Irving-Kirkwood method with a Lagrangian kernel estimator to calculate the J-integral around the crack tip and identify the fracture toughness. Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

2:30 PM

(GOMD-S1-025-2017) Environmentally assisted crack growth in quartz and amorphous silica

M. Wilson*[1]; K. T. Strong[2]; M. Chandross[1]

1. Sandia National Laboratories, Computational Materials and Data Science, USA
2. Sandia National Laboratories, Materials Mechanics and Tribology, USA

Silica glass is known to undergo undue mechanical fatigue in environments containing water, resulting in slow crack growth under load conditions. Referred to as stress corrosion, brittle failure of the material is accelerated due to the presence of water. This talk will discuss the failure mechanisms during stress corrosion, with a goal of understanding the role of water on crack growth. Molecular dynamics simulations are utilized to offer an atomistic-level representation wherein chemical processes can be explored. A reactive force field is employed, providing near-first-principles energetic bonding dynamics between atomic elements. Simulations results are compared to experiments for quartz and amorphous silica glass samples. Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

2:45 PM

(GOMD-S1-026-2017) Nanoscale mechanochemical wear of soda lime silica glass in humid air

H. He*[1]; J. Yu[1]; S. H. Kim[2]; L. Qian[3]; Y. Zhang[1]

1. Southwest University of Science and Technology, School of Manufacturing Science and Engineering, China
2. Pennsylvania State University, Materials Research Institute, USA
3. Southwest Jiaotong University, Tribology Research Institute, China

The applications of functional and engineering glasses depend on their surface mechanochemical properties. It is essential to understand the friction and wear of glass in various conditions. Previous investigations confirmed that wear of glasses could be significantly affected by the humidity and counter-surface at macro-scale, but mechanochemical wear of glass at nanoscale have not been considered. Using an environment-controlled atomic force microscope (AFM), nanoscale wear of soda lime silica (SLS) glass was studied under various reactive tips and reactive gas conditions. Experimental results shows that the nanoscale wear of SLS glass was very sensitive to the contact pressure, counter-surface chemistry, and humidity. On basis of these findings, three distinct wear regimes can be identified: mechanical wear, stress corrosion, and tribochemical wear. When mechanical effects dominated the nanowear behavior of SLS glass, hillock-like pattern can be produced at glass surface, and a very high contact pressure (>3.4 GPa) was needed to initiate substrate material removal. With the help of interfacial tribochemistry (stress corrosion, or tribochemical reactions), threshold stress for the surface material removal could be lowered to ~0.7 GPa in humid environments. These results may be useful to optimize tribological designs of functional and engineering glasses.

3:00 PM

(GOMD-S1-027-2017) Optimization of Strengthening by Surface Stress Relaxation

E. Aaldenberg*[1]; M. Tomozawa[1]

1. Rensselaer Polytechnic Institute, Materials Engineering, USA

Water diffusion into oxide glasses can cause relaxation of surface stresses below the glass transition temperature. This surface stress relaxation has been used to explain various phenomena in glass such as the fatigue limit and the degradation of ion-exchanged glass. Additionally, previous studies have shown surface stress relaxation to be a feasible method to strengthen silica and other oxide glass fibers. As a mechanism for strengthening, a thin glass sample is loaded to a sub-critical tensile stress and heat-treated. The stress in the near-surface region relaxes, and thus acquires a compressive stress when the applied load is released. The optimization of surface stress relaxation as a mechanism for strengthening glass was investigated.

3:15 PM

(GOMD-S1-028-2017) Fatigue of Mixed Alkali Glass (Invited)

J. H. Seaman*[1]; P. J. Lezzi[1]; T. M. Gross[1]

1. Corning Incorporated, USA

Glasses fail when a crack is loaded at the fracture toughness. However, the strength of glass is well known to be time-dependent in an atmosphere containing water or water vapor due to subcritical crack growth. The crack growth behavior is dependent on both the glass composition and the environment. In this research the slow crack growth behavior of alkali boro-alumino-silicate glass systems were investigated at ambient conditions where the alkali species was either Li^+, Na^+, or K^+. Further, the relative molar concentrations of the alkali species were varied to investigate the mixed-alkali effects on slow crack growth fatigue behavior. Slow crack growth was measured using the double cantilever beam (DCB) crack growth technique.

3:45 PM

(GOMD-S1-029-2017) Crack Resistant Alkali Aluminoborate Glasses (Invited)

M. M. Smedskjaer*[1]; K. Januchta[1]; R. Youngman[2]; A. Goel[3]; M. Bauchy[4]; S. Rzoska[5]; M. Bockowski[5]

1. Aalborg University, Department of Chemistry and Bioscience, Denmark
2. Corning Incorporated, USA
3. Rutgers University, USA
4. University of California - Los Angeles, USA
5. Institute of Physics Polish Academy of Sciences, Poland

Alkali aluminoborate glasses are found to exhibit favorable mechanical properties, especially high resistance to indentation cracking, due to their relatively low resistance to network compaction during sharp-contact loading. We study the origin of the high crack resistance by measuring changes in structure and mechanical properties in both peralkaline and peraluminous compositions with different alkali cations. The network densification mechanism during both indentation and hot compression involves an increase in the average coordination number of both boron and aluminum and a shortening of the sodium-oxygen bond length. The glasses most prone to network compaction exhibit the highest damage resistance, but surprisingly the crack resistance scales better with the relative density increase achieved by the hot compression treatment rather than with the extent of densification induced by indentation. As such, tuning the network structure may lead to the development of more damage resistant glasses.

4:15 PM

(GOMD-S1-030-2017) Structural origin of intrinsic ductility in binary aluminosilicate glasses

J. Luo[1]; K. Vargheese*[1]; A. Tandia[1]; J. Harris[1]; J. C. Mauro[1]

1. Corning Incorporated, USA

We evaluate the fracture mechanism in the binary aluminosilicate glasses using molecular dynamics simulations. The simulations using two independent force fields reveal that increasing the alumina content promotes shear and suppresses fracture, thereby increasing the intrinsic ductility of the glass, in agreement with experimental observations. In indentation simulations, it is directly demonstrated that the deformation mechanism shifts from densification to shear flow with the increase in alumina content. The origin of this intrinsic ductility is that the Al atoms are more amenable to plastic flow and can reduce the creation of lower coordinated weak spots during deformation.

4:30 PM

(GOMD-S1-031-2017) Topological engineering of high-modulus glasses

K. Philipps*[1]; K. Kölker[1]; R. Conradt[1]; C. Roos[1]

1. RWTH Aachen University, Institute of Mineral Engineering, Department of Materials and Process Technology – Glass and Composites, Germany

Strategic development of glass compositions requires the consideration of a great number of properties. On one hand the resulting product properties should meet the demands of the customer, on the other hand production parameters as liquidus temperature and viscosity curve as well as raw material costs and availability have to be taken into account. Young's modulus may serve as an example for tailor-made properties of reinforcement glass fibres. Targeted design of high-modulus glasses is needed to improve the composite performance. The present work will give an insight into the overall topological dependences of elastic moduli in silicate glasses. The constitutional approach to glass, which has been so far applied to thermochemical properties, is expanded to the elastic properties and further on to production parameters, e.g. the determination of liquidus temperature T^{liq}.

4:45 PM

(GOMD-S1-032-2017) Effects of thermal poling on glass elastic properties: A Molecular Dynamics Study

A. Tandia[1]; M. Reveil[3]; P. Clancy[3]; J. C. Mauro[2]; K. Vargheese[1]; S. Goyal*[1]; J. Luo[1]

1. Corning Incorporated, Modeling & Simulation, USA
2. Corning Incorporated, Glass Research, USA
3. Cornell University, Robert Frederick Smith School of Chemical and Biomolecular Engineering, USA

In this work, thermal poling of ternary oxide glasses including Borosilicates and Aluminosilicates was studied using Molecular Dynamics. For the glass compositions simulated, results show that thermal poling generally lowers the elastic moduli of oxide glasses. However, in Aluminum containing glasses, uncovered trends provide insights into how thermal poling could lead to an increase in elastic properties. Additionally, comparisons between the structure of those glasses before and after poling, as well as comparison with their binary as-melted counterparts of the same composition reveal that the changes in elastic properties can be attributed to changes in void size distributions within those glass networks. Overall, this study shows that thermal poling can effectively be used to alter the elastic properties of oxide glasses.

5:00 PM

(GOMD-S1-033-2017) Effect of water on wear of phosphate laser glass and BK7 glass

J. Ye[1]; J. Yu*[1]; H. He[1]

1. Southwest University of Science and Technology, China

Nd-doped phosphate laser glass and BK7 borosilicate glass are two important optical material used in high-peak-power solid-state laser systems. Understanding the effect of water on the wear of glass is helpful to understand the material removal in glass processing. Using a ball-on-flat tribometer, the friction and wear behaviors of phosphate laser glass and BK7 borosilicate glass were investigated by rubbing against Al_2O_3 ball in dry air and water to reveal the effect of water on the wear of the two glasses. In dry air, the wear of PL glass and BK7 glass shows a typical characteristic of mechanical wear. The damage of PL glass dominates by the formation of Hertzian crack, and the damage of BK7 glass dominates by exfoliation-in-chips. Water affects both the subsurface fracture and material removal for the two glasses. On the one hand, the subsurface fracture is suppressed greatly for both the PL glass and BK7 glass when they are rubbed in water. The low shear stress caused by water film at friction interface is considered as the main reason of weakened subsurface cracking for the two glasses. On the other hand, compared with dry air, water promotes the material removal of PL glass but reduces the material removal of BK7 glass. It suggests that the material removal of glass in water depends on the combined effect of the chemical stability of glass and the contribution of water related boundary lubrication.

Novel Modeling of Amorphous Materials

Room: Kona 3
Session Chair: Partha Biswas, The University of Southern Mississippi

1:15 PM

(GOMD-S1-034-2017) Materials modeling by design: A swarm-intelligence approach (Invited)

P. Biswas*[1]; D. Limbu[1]; D. Drabold[2]

1. The University of Southern Mississippi, Physics and Astronomy, USA
2. Ohio University, USA

In recent years there has been a rapid development of optimization techniques based on modeling simple behavior of individuals and the local interaction with the environment in an effort to study complex problems that appear in the context of optimization problems. Swarm intelligence is an example of such a method, which is based upon the concept of bounded rationality and the collective behavior of decision-making approach to solve difficult global optimization (GO) problems. Originally proposed by Eberhart and Kennedy, to simulate the social behavior of a population, a variant of this approach is now known as the particle-swarm optimization (PSO) and has been used recently to solve a number of difficult GO problems. In this talk, we discuss applications of swarm intelligence to disordered complex materials. In materials modeling, one often confronts a difficult optimization problem: a certain set of experimental observations ('data') needs to be satisfied by a proposed solution ('a model'), subject to the optimization of total 'energy' or a cost function defined by structural and experimental information. We demonstrate that the PSO can be employed efficiently to address structural modeling of disordered materials with an emphasis on a-Si, a-SiO2, amorphous graphene, and Fe and Ni clusters. A comparison with the results from traditional simulation methods and experimental data is presented.

1:45 PM

(GOMD-S1-035-2017) Predicting Structural Relaxation in a Glass-to-Metal Seal Connector: How Does Long-Term Storage Affect Performance?

B. Elisberg*[1]; J. Christensen[1]; D. Anderson[1]

1. Sandia National Laboratories, USA

Glass-to-metal seal (GTMS) connectors are used in a variety of applications to feed electrical conductors through boundaries of hermetically sealed electronic packages. GTMS connectors may be subjected to extreme temperature, pressure, and/or mechanical shock and must remain hermetic during operation, but might sit on a shelf for years before being fielded. Engineers need to know what happens to the glass during that time and if aging can influence the performance of the seal. Material models have recently been calibrated to predict the history dependent behavior of materials common to a GTMS. Those models were used to predict the evolving state of stress in a multi-conductor GTMS connector as it undergoes a complex history involving manufacturing, long term storage, and post-manufacturing thermal cycling. To validate predictions, thermal testing was performed on hardware to examine seal performance after varying amounts of post-manufactured "shelf time" at room temperature before thermal cycling. Complex history predictions, experimental observations, and modeling intricacies will be discussed. Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

2:00 PM

(GOMD-S1-036-2017) Force Enhanced Atomic Refinement: A new paradigm for modeling amorphous materials

D. Drabold*[1]; A. Pandey[1]; P. Biswas[2]

1. Ohio University, Dept. of Physics and Astronomy, USA
2. University of Southern Mississippi, Physics and Astronomy, USA

The general and practical inversion of diffraction data–producing a computer model correctly representing the material explored–is an important unsolved problem for disordered materials. Such modeling should proceed by using our full knowledge base, both from experiment and theory. In this paper, we describe a robust method to jointly exploit the power of ab initio atomistic simulation along with the information carried by diffraction data. The method is applied to two very different systems: amorphous silicon and two compositions of a solid electrolyte memory material silver-doped $GeSe_3$. The technique is easy to implement, is faster and yields results much improved over conventional simulation methods for the materials explored. By direct calculation, we show that the method works for both poor and excellent glass forming materials. It offers a means to add a priori information in first-principles modeling of materials, and represents a significant step toward the computational design of non-crystalline materials using accurate interatomic interactions and experimental information.

2:15 PM

(GOMD-S1-037-2017) Modeling of phase separation in binary silicate glasses

H. Inoue*[1]

1. The University of Tokyo, Institute of Industrial Science, Japan

In an attempt to understand the liquid-liquid phase separation in the Li_2O-SiO_2, Na_2O-SiO_2 and K_2O-SiO_2 systems, the structural models were calculated using the classical molecular dynamics simulations. It is known that the smaller the alkali metal ion is, the wider the phase separation region is. The phase separation regions of Li_2O-SiO_2, Na_2O-SiO_2 and K_2O-SiO_2 systems spread to 30, 25 and 18 mol% of alkali metal oxide contents, respectively. The potential parameters of Born-Mayer type, which was optimized based on the diffraction experiments, were used in the simulations. The oxygen coordination number around an alkali metal ion was increased with an increase of the ionic radius of alkali metal ion in the structural models. The number of non-bridging oxygen was determined by the content of alkali metal oxide. The non-bridging oxygen were coordinated by the same number of alkali metal ions in the structural models at the boundary of the liquid-liquid separation. Deviation from the phase separation means the stability of the uniform structure. As the non-bridging oxygen is stabilized by the alkali metal ions, it was found that the number of coordinated alkali metal ions around the non-bridging oxygen is the most important factor.

2:30 PM

(GOMD-S1-038-2017) Ab-initio modeling of vibrational spectra of silicate glasses and decomposition into principal structural components

D. A. Kilymis[1]; B. Hehlen*[1]; S. Peuget[2]; J. Delaye[2]; S. Ispas[1]

1. University of Montpellier, Physics, France
2. CEA Marcoule, France

Density functional theory is used to calculate the vibrational properties of pure silica and sodo-silicate glasses with 20, 25, and 33 mol% of Na_2O. The infrared and Raman spectra are calculated and the full responses are decomposed into principal structural components (PSC). Those are for example the SiO_4^{n-}-tetrahedra with n non-bridging oxygens defining the Q_n-species at the origin of the structured feature at high frequency, and the Si-O-Si bridges leading the broad Raman R-band at intermediate frequencies. Our results confirm that Si-O-Si bending in bridges with large angle vibrate preferentially at lower frequencies than those with low angle. In addition, the spectral response of the Q_2-species is bimodal and overlaps with that of the Q_3, while the Q_4 response covers almost all of the spectral range of the Q_n-band. The ab-initio individual spectral responses of the PSC are used to reconstruct the experimental Raman responses. Contrary to the commonly used multi-Gaussian decomposition, this approach provides unambiguous band-assignments and hence a more accurate way to probe the structural and chemical properties of glasses from their spectroscopic signature.

2:45 PM

(GOMD-S1-039-2017) Machine Learning for Glass Properties Prediction: Effects of data quality and model choice

A. Tandia*[1]

1. Corning Incorporated, Modeling & Simulation, USA

With the advent of sophisticated algorithms for machine learning and the existence of dormant glass properties data, it makes more and more sense to use data-driven modeling to reduce the temporal cycle and financial burden embedded in the design of commercial glass compositions. Glass properties hold different levels of non-linearity and complexity, hence different machine learning algorithms should be considered in their modeling. We have generated synthetic glass properties data for a four-oxide component system with different levels of non-linearity and compared blind prediction accuracy of different models such as linear, Neural Networks, Gaussian Process and Symbolic Regression. We have built these models with clustered and non-clustered data from a restricted area of the composition space and tested their prediction accuracy in different areas of the composition space. Our study demonstrate the huge impact of data characteristics such as quality, clustering status, and also the choice of the machine learning algorithm on the accuracy of the predicted properties when models are used for interpolation or extrapolation. We demonstrate the capability of Machine Learning to successfully help gain clear insight in the design of industrial glass compositions with targeted properties.

3:00 PM

(GOMD-S1-040-2017) "Qualimetry" of Viscosity-Temperature Curve: "Best Equation" – For What?

A. Priven*[1]

1. Corning Korea, Republic of Korea

Quantitative description of the viscosity-temperature curve remains a subject of discussions for nearly a century, starting from the famous papers of Vogel, Fulcher and Tamman in 1920's. Many equations (both theoretical and empirical) describing the temperature dependence of viscosity for glass-forming substances were suggested since then, and the discussion about the best choice among them is still continuing. In this discussion, however, an important question seems to be overlooked: "best" – for what? In other words, what are the "customer's" requirements to this "product"? Such "marketing" approach, being a little bit conventional when applied to science, highlights the problem of diversity of the use of mentioned equations. Being a key property for glass science and technology, viscosity is used with different purposes, which makes specific demands to the viscosity-temperature equation. The keyword here is "prediction": what is to be predicted, from what source data, for what type of compositions, and with which accuracy? In the presentation, different situations will be considered, such as interpolation and extrapolation, development of composition-dependent viscosity models, calculation of structural relaxation, etc. Author considers that clear understanding of practical needs would help the further discussion to avoid scholasticism and bring new value to the glass science and industry.

3:15 PM

(GOMD-S1-041-2017) Multi-composition EPSR modelling of chalcogenide glasses

E. Nilsson*[1]; J. Towey[1]; E. Barney[1]

1. Department of Mechanical, Materials and Manufacturing Engineering, United Kingdom

Mid infra-red (mid-IR) spectroscopy opens possibilities towards identification of molecules via their specific absorbans in this range. This technique is impaired by the lack of commercially available mid-IR optics, but glasses made from chalcogenide elements (S, Se, Te) are exhibiting promising characteristics. These glasses can be synthesised over a large compositional range, giving rise to a possibility of optimising the glass properties. A desired route to design new materials would be to use computer modelling to predict a materials physical properties. Similarly to reverse Monte Carlo (RMC), empirical potential structure refinement (EPSR) is designed to reconstruct an atomistic model from experimental data. However unlike RMC, EPSR uses empirical interatomic potentials to generate models that predict diffraction data and, with a good understanding of structure property relationships, use the models to predict key functional properties. In this work neutron and x-ray diffraction data has been used to determine potentials for two glass systems, As-Se-S and Sb-Ge-Se. However, inconsistencies in the pair-potentials between compositions occur if each sample is modelled individually. Hence, multi-composition EPSR has been developed to provide a set of pair potentials for all compositions simultaneously. Modelling results from will be shown and the predictive ability of the pair potentials will be demonstrated.

3:45 PM

(GOMD-S1-042-2017) Modeling the Atomic Structure of Calcium Aluminosilicate Glasses Using an Iterative Simulation-Experiment Methodology

K. Gong[1]; C. White*[1]

1. Princeton University, Civil and Environmental Engineering, USA

Ground granulated blast-furnace slag (GGBS), an industrial by-product of steel-manufacturing, is incorporated in alkali-activated materials (AAMs) as a glassy aluminosilicate source, which, when mixed with an alkaline activator, produces a binder material with similar properties to Portland cement paste and a lower CO_2 footprint. Despite the widespread interest on the use of GGBS in different cementitious systems, the atomic structure of GGBS is still not fully understood due to the amorphous nature of this calcium aluminosilicate. In this study, we aim to uncover the detailed atomic structure of a GGBS by using an iterative methodology alternating between density functional theory (DFT) calculations and pair distribution function (PDF) analysis. In this methodology, the DFT calculations are used to maintain chemical feasibility of the atomic structure, while the experimentally-driven refinements allow for exploration of the potential energy landscape. Through this iterative process, a final structure is obtained that is not only thermodynamically favorable but also in agreement with experiment data. The iterative methodology outlined here is expected to be readily transferrable to other amorphous material systems where detailed atomic structures are currently not available.

4:00 PM

(GOMD-S1-043-2017) The role of Ga^{3+} in oxide glass network structures studied by solid state nuclear magnetic resonance

J. Ren*[1]

1. Shanghai Institute of Optics and Fine Mechanics of the Chinese Academy of Sciences, China

Gallium–based glasses have import potential in nonlinear optics and fluorescent materials. In this presentation we will show precise analysis of the short and middle structure of gallium- based glasses with the composition of $GaPO_4$-SiO_2 and Ga_2O_3-$NaPO_3$ by some new SSNMR approaches. Local structure of gallium and glass formers, the connectivity between gallium and glass formers, and the connectivity between glass formers are resolved by the comprehensive application of advanced SSNMR techniques such as refocused INADEQUATE, REDOR, J-resolved, DQ-DRENAR, WURST SSNMR and so on. In $GaPO_4$-SiO_2 glass system, four-coordinate Gallium Ga(IV) dominates in its three kinds of coordination polyhedrons. Ga(IV) together with P^{5+} forms SiO_2-type $GaPO_4$ amorphous clusters, while Ga(V) and Ga(VI) work as glass modifiers to connect $GaPO_4$ and SiO_2 clusters. In Ga_2O_3-$NaPO_3$ glass system, with the increment of Ga_2O_3 content, Ga^{3+} role changes from glass modifier to glass former. On the base of precise analysis of the glass structures and the local environment of Ga^{3+}, the glass structure evolution models are proposed. And the intermediate role of Ga^{3+} in the glass network is discovered.

4:15 PM

(GOMD-S1-044-2017) Segregation of Network Modifiers in Borosilicate Glasses: Insights from a New Transferable Potential

M. Wang[1]; M. M. Smedskjaer[2]; J. C. Mauro[3]; G. Sant[1]; M. Bauchy*[1]

1. University of California, Los Angeles, Civil and Environmental Engineering Department, USA
2. Aalborg University, Denmark
3. Corning Incorporated, USA

The existence of network modifying (alkali or alkaline-earth) atoms' segregation or clustering inside silicate glasses remains controversial. Such heterogeneity could play a crucial role in controlling mascroscopic properties, including crystallization propensity, fracture, or dissolution. Here, based on molecular dynamics simulations, we report the existence of such clustering in borosilicate glasses. First, a novel inter-atomic potential was developed for modified borosilicate glasses. This new potential is found to offer an excellent transferability, as, with constant parameters, it correctly predicts the coordination number of boron atoms and the density of the glass over a wide range of Si/B ratios, from silicate to borate glasses. Predicted structure factors are also found to be in good agreement with available experimental data. Second, the simulated structures are analyzed to assess the heterogeneity of the distribution of Ca and Na atoms inside a series of borosilicate glasses. We observe a strong propensity for network modifier clustering, both for Ca and Na atoms. In turn, boron atoms are shown to enhance the homogeneity of the network. The origin of this trend is discussed.

4:30 PM

(GOMD-S1-045-2017) Realistic inversion of diffraction data for amorphous solids: An application

B. Bhattarai*[1]; A. Pandey[1]; P. Biswas[2]; D. Drabold[1]

1. Ohio University, Department of Physics and Astronomy, USA
2. The University of Southern Mississippi, Department of Physics and Astronomy, USA

In this talk, we discuss applications of the newly developed method FEAR "Force Enhanced Atomic Refinement" (http://www.nature.com/articles/srep33731) to create computer models of amorphous solids. The logic underlying our calculation is to estimate the structure of an amorphous solid using experimental data and chemical information included in a non-biased way, starting from random coordinates. In this talk, we will be discussing the applications of the method FEAR in different systems (a-Phosphorus, a-Carbon, etc.) and their comparison with the available experimental and theoretical results. The models obtained are in close agreement with experiment with a suitable minimum energy according to density functional calculations. The method is more efficient and accurate than conventional melt quench methods. Notably, FEAR based models have given an accurate description of the atomic vibrations in different solids, which tend to be a particularly challenging test.

4:45 PM

(GOMD-S1-046-2017) Enhancing MD simulations with minimal knowledge of electronic gap

K. Prasai*[1]; P. Biswas[2]; D. Drabold[1]

1. Ohio University, Physics and Astronomy, USA
2. The University of Southern Mississippi, Department of Physics and Astronomy, USA

A priori knowledge of structural information has long been used to model amorphous materials. Electronic structure information can similarly be helpful to arrive at models that represent the materials more faithfully. Here, we show how a minimal knowledge of electronic gap can be used to bias the MD simulations to arrive at better models. We show that such biased dynamics can produce models that exhibit better agreement with experiments structurally as well as electronically. We present here the examples of amorphous a-Si, a-C and a-$GeSe_2$.

5:00 PM

(GOMD-S1-047-2017) Improved Description of the Structure of Silicate Glasses through Reactive Molecular Dynamics Simulations

Y. Yu*[1]; B. Wang[1]; G. Sant[1]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA

Reactive potentials are becoming increasingly popular as they are expected to bridge the gap between ab initio and classical molecular dynamics. However, their applicability and potential benefits to model multicomponent glassy materials are yet to be assessed. Here, we simulate silica and a series of sodium silicate glasses using the ReaxFF potential, and compare the predicted structures to those obtained by a classical potential. In both cases, ReaxFF is found to offer an improved description of the atomic structure, both at the short- and medium-range. In particular, owing to its bond order form that dynamically adjusts potential energies according to the local atomic environment, ReaxFF reproduces the effect of modifiers on the Si–O network, a demonstration of its good transferability to various compositions. Overall, ReaxFF provides a promising alternative to classical and ab initio methods for simulating the complex structure of multi-component silicate glasses. In addition, it paves the way for an improved understanding of silicates' surface reactivity.

GOMD Symposium 2: Glasses in Healthcare: Fundamentals and Applications

Structural Basis of Bioactive Glass Design

Room: Waikoloa 3
Session Chairs: Akash Akash, Glidewell Dental; Qiang Fu, Corning Incorporated

1:15 PM

(GOMD-S2-011-2017) Formation and Structure of Calcium Phosphate Invert Glasses (Invited)

T. Kasuga*[1]; H. Maeda[1]; T. Tamura[2]; A. Obata[1]; S. Lee[3]; T. Nakano[3]

1. Nagoya Institute of Technology, Division of Advanced Ceramics, Japan
2. Nagoya Institute of Technology, Division of Applied Physics, Japan
3. Osaka University, Division of Materials & Manufacturing Science, Japan

Calcium-phosphate-based glasses are believed to have high potential for use as biomaterials. However, there are almost no reports on their bioactivity, since most of them concerned easily-soluble metaphosphate glasses. Our group has reported some of calcium phosphate glasses with the composition of high Ca/P ratio, containing small amounts of TiO_2, Nb_2O_5 and/or MgO. The glasses, consisting of ortho- and pyro-phosphate groups, are called "phosphate invert glasses (PIGs)". The additives play important roles in their glass formation and ion-release control. The present work discusses the effect of the additives on their structures and properties. Incorporation of TiO_2/Nb_2O_5 and MgO in the PIGs formed P-O-Ti/Nb and P-O-Mg bonds, resulting in the improvement of glass-forming ability. The P-O-Ti/Nb bond was considered to improve the chemical durability of the PIGs, since bonding strength of P-O-Ti/Nb bond is stronger than that of P-O-P bond. The P-O-Mg bond, however, degraded the chemical durability of the PIGs: the bond weakens the glass network structure and induces hydrolysis. The ion-release from the PIGs can be controlled by the amount of P-O-Ti/Nb and P-O-Mg bonds in the PIGs. Ions released from the PIGs might work effectively for enhancing cell adhesion, proliferation, differentiation and calcification.

1:45 PM

(GOMD-S2-012-2017) Designing polymers as organic source for synthesis of silicate hybrids: Lessons learned and future perspectives (Invited)

A. L. Macon*[1]; Y. Goto[1]; L. Connell[2]; J. Chung[2]; J. Jones[2]; A. Obata[1]; T. Kasuga[1]

1. Nagoya Institute of Technology, Japan
2. Imperial College, United Kingdom

Designing materials with suitable and tuneable mechanical properties for the in situ regeneration of hard tissues is a real challenge, if all the other requirements that need to be fulfilled by synthetic bone-grafts are taken into account. The bottom-design of sol-gel derived class II hybrids, where organic and inorganic networks are covalently and molecularly interpenetrated, represents a promising biomimetic approach. Polymers can be synthesised with built-in alkoxysilane moieties using advanced polymerisation techniques offering a wide range of polymeric compositions and structures. This diversity adds another degree of complexity towards determining the full potential class II hybrids due to the influence of the polymer chemistry on the structure and resulting properties of the biomaterials. However, polymer can be classified into different families from which model study can be derived. Here, we aimed to evaluate the impact of using superhydrophilic and high cross-linking density polymers on the structure and properties of silicate hybrids using poly(2-hydroxyethyl methacrylate) and poly(3-methoxysilylpropyl methacrylate) as polymer models.

2:15 PM

(GOMD-S2-013-2017) A rigorous approach for studying the dissolution behavior of bioactive glasses

N. Stone-Weiss*[1]; R. Youngman[2]; N. J. Smith[2]; A. Goel[1]

1. Rutgers University, Materials Science and Engineering, USA
2. Corning Incorporated, Science and Technology Division, USA

The concept of designing third–generation bioactive glasses for tissue engineering is based on the principle of activating a synchronized sequence of genes at the cellular level by the ionic dissolution products of glasses. The chemical degradation of a glass is governed by several factors including its chemical composition, molecular structure, thermal history, surface area-to-volume ratio, etc. While there is considerable literature published on chemical dissolution behavior and apatite-forming ability of potentially bioactive glasses, most of the literature in this domain lacks consistency and reproducibility of results. A recent round-robin study by Macon et al. emphasizes adoption of a uniform experimental procedure to study the chemical dissolution behavior and in vitro evaluation of bioactive glasses. However, there are several scientific lacunae that need to be filled before we can obtain a holistic understanding of chemical dissolution behavior of these glasses. In this presentation, we will present an overview of the experimental challenges or choices that need to be carefully navigated in order to unearth the mechanisms governing the chemical dissolution behavior of bioactive glasses, and propose a rigorous methodology to study their mechanism of chemical degradation and ion release using a borosilicate based model glass system.

2:30 PM

(GOMD-S2-014-2017) In Vitro Dissolution Behavior of Scaffolds Sintered from Bioactive Glass S53P4

L. Aalto-Setälä*[1]; P. Uppstu[1]; O. Karlström[1]; N. Lindfors[2]; L. Hupa[1]

1. Åbo Akademi University, Finland
2. Helsinki University, Finland

Bioactive glass S53P4 granules (grain size 300-500um) were sintered into porous scaffolds at 720C. The scaffolds were characterized and their dissolution in simulated body fluid (SBF) was studied. During sintering the particles softened and formed a neck between each others, and they formed a partly crystalline layer (thickness 60-80um). The particle cores stayed amorphous. The in vitro dissolution was studied using a dynamic set-up, where fresh SBF flows through the sample. Concentrations of the ions dissolving from the glass were analyzed using ICP-OES from solution samples collected at certain time intervals throughout the run time. Amorphous S53P4 particles of the same size were used as a reference. After different immersion times (1-14 days), cross-sections of the scaffolds were analysed using SEM. The partly-crystallized layer caused scaffolds to dissolve differently from glass granules. First, the glassy phase of the partly crystalline layer is leached out. Second, the non-crystallized core of the S53P4 granules dissolves away, leaving only porous, crystalline shells. Finally, the alkalis from the crystalline layer leach away, leaving crystalline shells consisting only of silica. These results will be used in the interpretation of the reported in vivo studies of scaffolds and granules of S53P4.

2:45 PM

(GOMD-S2-015-2017) 3D printed bioactive glass and its behaviour in vivo

X. Shi*[1]; A. Nommeots-Nomm[2]; N. M. Todd[3]; A. Devlin-Mullin[3]; P. D. Lee[4]; C. A. Mitchell[3]; J. Jones[1]

1. Imperial College, Materials, United Kingdom
2. Tampere University of Technology, Finland
3. Ulster University, United Kingdom
4. The University of Manchester, United Kingdom

Porous melt-derived bioactive ICIE16 (49.46% SiO_2, 36.27% CaO, 6.6% Na_2O, 1.07% P_2O_5 and 6.6% K_2O, in mol%) glass scaffolds developed by Wu et al. showed rapid hydroxyapatite (HA) formation after 3 days immersion in simulated body fluid, which is a sign of high bioactivity. In this study, the three-dimensional ICIE16 porous scaffolds fabricated by a 3D printing technique. Here we report their ability for in vivo bone regeneration in a 3 mm rat condyle femur head defect model. Micro computed tomography (μCT), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX), and transmission electron microscopy (TEM) have been used to quantify the interconnect size of scaffold and the bone ingrowth rate. The bonding mechanism between bone and the glass has also been discovered by determining changes in the chemical composition and crystalline structure of the bioactive glass and new bone growth. The 3D printed scaffold showed uniform interconnected macropores (~125 μm), suitable porosity (~45.5%) and enhanced compressive strength (18.3 ± 2.2 MPa). After 12 weeks, outer regions of glass struts completely dissolved and a thick calcium-phosphate rich layer formed to replace the glass. The core part of the struts partially dissolved, and network modifier ions were released. New bone ingrowth into the scaffold was found within the region of interest and the amount was higher than the defect only control samples.

3:00 PM

(GOMD-S2-016-2017) Evaluating the adhesion of bioactive glasses onto titanium alloy substrates under mode I loading condition

A. Matinmanesh*[1]; O. Rodriguez[1]; M. Towler[1]; P. Zalzal[2]; E. H. Schemitsch[3]; M. Papini[1]

1. Ryerson University, Mechanical and Industrial Engineering, Canada
2. Oakville Trafalgar Memorial Hospital, Canada
3. St. Michael's Hospital, Canada

In the current paper, a fracture mechanics testing method is postulated to evaluate the adhesion of bioactive glasses onto Ti6Al4V substrates. Using this method, the glass/metal adhesion can be quantified in terms of a measured critical strain energy release rate (G_{IC}). This goal was achieved by developing bi-layer double cantilever beam (DCB) test specimens. The developed technique was used to measure the coating/substrate adhesion for different glass coating thicknesses and was found to generate repeatable and consistent measures of G_{IC} for the tested systems. It was shown that by

increasing the coating thickness from 90 to 390 μm, the measured G_{IC} of the system decreased significantly from 6.2 to 2.5 J/m^2. The effect of residual stresses on the adhesion was also studied. Such residual stresses are created in the glass/metal system due to the high temperatures that involve in the enameling process. It was found that by increasing the coating thickness from 90 to 390 μm, the residual stresses in the coating also increased from 6.8 to 17.9 MPa, thus reducing the adhesion of thicker coatings. Finally, the T-stress values for coatings with different thicknesses were calculated in order to quantify the directional stability of the propagating crack. It was shown that the crack in thicker coatings destabilized and tended to kink rather than travel in a straight line.

3:15 PM

(GOMD-S2-017-2017) Effect of dense strontium containing sol-gel derived bioactive glass nanoparticles (Sr-BGNPs) on human mesenchymal stem cells (hMSCs)

P. Naruphontjirakul*[1]; L. Siwei[1]; A. E. Porter[1]; J. Jones[1]

1. Imperial College London, Materials, United Kingdom

Monodispersed dense sol-gel derived bioactive glass nanoparticles containing strontium (Sr) with an amorphous spherical form 80-100 nm in diameter were developed using a modified Stöber process to stimulate osteogenic response of hMSCs in vitro. Sr-BGNPs have no toxic to hMSCs identified even up to the concentration of 250 μg. ml^{-1}. Following three weeks of culture in both basal and osteoinductive conditions, Sr-BGNPs and their dissolution ions stimulated ALP activity and calcium deposition in the extracellular matrix of hMSCs. Markers associated with osteogenic differentiation including Col1a1, Osteopontin and Osteocalcin were expressed (IHC staining). The synergic effects on osteogenic differentiation markers of hMSCs were significantly presented, as shown in up-regulate gene expression (RT-PCR). Following 24-h incubation of hMSCs with Sr-BGNPs, uptaken particles had internalised in the vesicles form bordered by a cell membrane and released Sr and Ca from silica networks during degradation process inside the vesicle (TEM). Sr and Ca were remained in the partially degraded particles (EDS-TEM). Fluorescent images confirmed that Sr-BGNPs internalized inside hMSCs (Confocal microscope). Taken together, Sr-BGNPs have promising potential for bone regeneration because they are able to internalise and release therapeutic cations inside the cells.

Glasses for Dental or Soft Tissue Applications

Room: Waikoloa 3

Session Chairs: Chengtie Wu, Shanghai Institute of Ceramics, Chinese Academy of Sciences

3:45 PM

(GOMD-S2-018-2017) Crystallization and densification behavior in lithium silicate glass ceramics (Invited)

P. Bhargava*[1]

1. IIT Bombay, Metallurgical Engineering and Materials Science, India

A synergistic relation has existed between the ceramic processing technology and the needs of materials with specific for structural and aesthetic requirements for dental applications. A number of different ceramic materials are currently in use in the oral cavity but there exists scope for improvement. Lithium silicate glass ceramics have proven to be an important class of materials for dental prostheses due their excellent mechanical properties, aesthetic characteristics. While a significant amount of literature exists on lithium silicate ceramics, work is continuing in this area to understand better the crystallization behavior and to further improve their mechanical properties. The present study is directed towards the same. Powder raw materials were mixed and melted at 1430 °C and then quenched into water to get a clean glass. This glass powder made pellet is then crystallized at different temperatures (as per DTA) to get glass ceramic. The nucleating agent is added into pulverized glass powder prior to powder consolidation, sintering and compared with glass ceramics prepared with in-situ formed nucleating agent. The impact of amount of lithium in the material beyond the stoichiometric on the phase content, crystal morphology, aspect ratio, densification and mechanical properties was examined. The externally added nucleating agent appeared to result in superior material characteristics.

4:15 PM

(GOMD-S2-019-2017) Dental Materials: Trends and Challenges (Invited)

A. Akash*[1]

1. Glidewell Dental, USA

Glass-Ceramics (like Lithium Silicate / Lithium Disilicate) have become a popular choice for direct and indirect dental restorations due to their higher esthetics and are metal-free restorations. Historical trends suggest an increasing acceptance of glass-ceramic based dental restorations in the last decade. Survival rates have improved over time with new innovations in composition and microstructure. Different factors have to be considered while designing a glass-ceramic material for use as a lab-based product versus a chair-side (CAD/CAM milled) product. New innovations in glass-ceramic have lead to a new possibility of a glass-ceramic being pressed over metal which is a significant improvement over still highly popular conventional porcelain fused to metal (PFM) restorations. However, new innovations in ceramics, particularly dental zirconia, offer superior combination of strength and esthetics, are now beginning to threaten the popularity of glass-ceramic dental materials for use in esthetic dental applications.

4:45 PM

(GOMD-S2-020-2017) 3D bioactive glasses with antibacterial ability for wound healing

A. Obata*[1]; Q. Ju[1]; E. G. Norris[2]; A. L. Macon[1]; G. Poologasundarampillai[3]; J. Jones[2]; T. Kasuga[1]

1. Nagoya Institute of Technology, Japan
2. Imperial College London, United Kingdom
3. The University of Manchester, United Kingdom

Sol-gel bioactive glasses, 70S(30-x)CxAg (70 mol% SiO_2, (30-x) mol% CaO and x mol% Ag_2O (x=0, 1, 2)), with a 3D cotton-wool like structure were developed with electrospinning for wound healing. A mixture of the sol of the glasses and poly(vinyl butyral) (PVB) were electrospun with controlling humidity in the spinning system to produce 3D structured fibres and then sintered at 600 – 800 °C in air. A 3D structured fibres with about 300 nm in diameters were successfully prepared for all of the glass compositions. The size of silver nanoparticles formed in the resulting fibres was found to increase with increasing the sintering temperature from results of XRD and TEM. XPS results demonstrated that most of the silver in the fibres possessed metallic state. Wollastonite was predominantly present in the fibres after sintering at 800 °C. Antibacterial activity of the samples was evaluated against E. Coli and S. aureus. after 24 h cultivation. The Ag-doped glass fibres inhibited the growth of the bacteria, whereas non-doped one, 70S30C, possessed no influence on the growth.

GOMD Symposium 4: Glass Technology and Crosscutting Topics

Glass Corrosion II: Testing and Characterization

Room: Kona 2
Session Chairs: Joseph Ryan, Pacific Northwest National Lab;
S. Sundaram, Alfred University

1:15 PM

(GOMD-S4-013-2017) Structure and Chemical Durability of Lead Crystal Glass (Invited)

F. Angeli*[1]; P. Jollivet[1]; T. Charpentier[1]; M. Fournier[1]; S. Gin[1]

1. CEA, France

The approach based on the relations between glass composition, glass structure and alteration layer structure, has often been successfully applied to assessing the chemical durability of nuclear waste glasses. This methodology can be used to get more insight into the behavior of potentially hazardous elements present in manufactured products used in daily life, such as lead crystal containing beverages. An illustration is given through crystal glasses leached in acetic acid solution, with or without silica saturation, at various stages of reaction. Multinuclear solid-state NMR was used to probe the local structure of pristine and altered lead crystal glasses. Inserted into the vitreous structure between the network formers as Si-O-Pb bonds, the behavior of Pb is closely related to the structural configuration it adopts, as much in the pristine glass as in the alteration layer. Homogeneously dispersed in commercial glasses within the silicate network, mixed with alkalis near NBOs, Pb is released following a diffusion-controlled dissolution. The preferential release of alkalis is followed by an in situ repolymerization of the silicate network. Pb is only depleted in the outermost part of the alteration layer. In the rest of the layer, it stays mainly surrounded by Si in a stable structural configuration, similar to that of the pristine glass. These data enabled parameters to be set for a predictive lead leaching model.

1:45 PM

(GOMD-S4-014-2017) Chemical durability of UK vitrified high level waste in Si-saturated solutions

M. T. Harrison*[1]

1. National Nuclear Laboratory, WM&D, United Kingdom

In the UK, the Waste Vitrification Plant (WVP) at Sellafield converts the high level liquid waste (HLLW) from the reprocessing of spent nuclear fuel into a glass wasteform suitable for long term storage and disposal. After the completion of reprocessing operations, the HLLW storage tanks will be emptied and washed out to remove any accumulated solids. These solids are expected to contain high concentrations of molybdenum. Hence, a new glass formulation has been developed specifically for immobilisation of these waste streams. This 'Ca/Zn' glass allows for significantly higher waste loadings by the formation of $CaMoO_4$ crystals when the Mo content exceeds its solubility limit in the glass. The product quality of the new Ca/Zn glass is currently undergoing validation, which includes measuring the chemical durability to demonstrate its suitability for long-term storage and disposal. Previous powder-based leach tests have indicated a very slow approach to the low residual dissolution rate regime in contrast to other HLW glasses. Hence, this study investigated the leaching of Ca/Zn glasses in Si-saturated solutions at high surface area to volume ratios (~2,000 m^{-1}) in order to probe the long-term dissolution rate. The alteration layers on the Ca/Zn glasses were also studied via SEM and FIB using a monolithic sample leached in the same high S/V and Si-saturated conditions as the powder.

2:00 PM

(GOMD-S4-015-2017) Silicate glass stability under various pH conditions

S. Gin*[1]

1. CEA, DTCD, France

The role of pH on glass corrosion remains a subject of debate and there is not yet a general model able to take into account for the coupled mechanisms controlling the glass dissolution rate in a large range of pH. We first investigate the behavior of ISG and basaltic glass at fixed pHs to better understand the role of surface layers and the effect of glass composition. We then study the effect of dissolved silica on ISG glass dissolution between pH 3 and 10.5 and show a minimum of alteration near pH 9.5. The greater alteration of the glass out of this domain can be explained by a direct effect of ion exchange in acidic conditions with no formation of passivating layers and the disruption of the amorphous passivating layers by secondary phases such as zeolites under basic pH conditions. The nature and the properties of the passivating layers formed in basic pH need to be investigated. These layers are likely formed by a mechanism of dissolution/precipitation whereas they are formed by in situ reorganization of the silicate network between pH 7 and ~9.5.

2:15 PM

(GOMD-S4-016-2017) Contribution of the different glass alteration mechanims as a function of glass composition and experimental conditions

A. Verney-Carron*[1]; L. Sessegolo[1]; M. Saheb[1]; P. Ausset[1]; R. Losno[2]; D. Mangin[3]; N. Valle[4]

1. LISA, France
2. IPGP, France
3. University de Lorraine, France
4. LIST, Luxembourg

In order to assess glass durability, it is necessary to understand its alteration mechanisms, such as interdiffusion, dissolution, condensation or precipitation reactions. However, the respective contribution of each process to the global alteration is dependent on glass composition and experimental conditions. In this study, we present alteration experiments of a historic Si-K-Ca glass that have been performed using a flow-through device, at 30°C, at pH of 8 and 9 and with a solution doped in ^{29}Si to discriminate between the silicon from glass (mainly ^{28}Si) and from solution. Isotopic analyses were carried out by SIMS and HR-ICP-MS. The results demonstrate that the alteration layer is not a glass skeleton as it is reorganized by hydrolysis and precipitation reactions. The comparaison of these results with those obtained from nuclear glass experiments shows that the general mechanisms are similar but that glass composition and solution pH can favor or inhibit the role of interdiffusion. The diffusion coefficient of mobile species of the highly depolymerized historic glass is higher by several orders of magnitude than nuclear glass. Moreover, alkaline pH will improve dissolution and limit interdiffusion. These parameters have thus to be considered to explain discrepancies between different glass alteration mechanisms proposed in the literature.

2:30 PM

(GOMD-S4-017-2017) Dissolution behavior of neodymium-containing aluminoborate glasses

M. Kim*[2]; C. Lee[1]; N. C. Hyatt[2]; J. Heo[1]

1. Pohang University of Science and Technology(POSTECH), Material Science and Engineering, Republic of Korea
2. The University of Sheffield, Materials Science and Engineering, United Kingdom

Nd-containing aluminoborate glasses were fabricated to immobilize radioactive rare-earth(RE) elements from pyro-processing. The composition(mol%) of the aluminoborate glasses prepared was $20CaO\text{-}15Al_2O_3\text{-}45B_2O_3\text{-}20Nd_2O_3$. Aluminoborate glasses are known

for lower chemical durability compared to borosilicate glasses since gel formation in borosilicate glass can retard glass dissolution. The released concentrations of Nd in the borosilicate glasses are also very low since Nd can incorporated into gel layer during dissolution. However, even though gel formation in any borate glass has not reported until now, released concentration of Nd from our aluminoborate glasses were below the limit of detection of inductively ICP-AES(<0.1ppm) based on our previous experiments. Here, the structural role of Nd during dissolution is questionable. Nd ions are presented in the glasses as a modifier. Therefore, we expect that Nd may be dissolved together when boron, the main glass former, is dissolved into solution and Nd secondary phases precipitated on the glass surface, accounting for the low dissolved concentration of Nd. To understand the dissolution mechanism of these glasses, and the particular role of Nd, we performed 140 days dissolution test using powder speicmens of aluminoborate glasses, and determined the released concentrations of all components using ICP-AES and the surface alteration of leached powders using XRD and SEM.

2:45 PM

(GOMD-S4-018-2017) Sensitivity Analysis of Transition State Theory Kinetic Rate Law Parameters as Applied to Nuclear Waste Glasses

J. Neeway*[1]; J. Ryan[1]; B. Parruzot[1]; M. Asmussen[1]; P. Rieke[1]

1. Pacific Northwest National Lab, USA

The initial dissolution rate of silcate waste glasses in dilute conditions depends principally on temperature, pH, and glass composition. The effect of pH and temperature on the rate of glass dissolution can be quantified and implemented into an affinity-based rate law based on Transition State Theory (TST). In dilute conditions, the TST rate equation contains an intrinsic rate constant term, k_0, a pH power law coefficient, h, and an activation energy, E_a. However, it is not possible to know a priori the value of k_0, h, E_a from a given glass composition. Therefore, for every new glass composition, tests must be conducted to quantify these parameters. In this presentation, we provide forward rate parameters for a set of simulant nuclear waste glasses and discuss a set of statistical analyses that was performed on experimental data that provides uncertainties in the parameters and quantifies the degree of correlation between them. In general, the TST equation can fit experimental data from a number of different glass compositions in dilute conditions. However, the high degree of correlation between rate law parameters may suggest that there is a missing term from the TST equation. We discuss implications for this correlation and suggest how this method of analysis can be extended to attempt to calculate a set of rate law parameters based solely on glass composition.

3:00 PM

(GOMD-S4-019-2017) Evaluation of a novel leaching assessment for nuclear waste glasses

C. L. Thorpe[1]; R. J. Hand[1]; N. C. Hyatt[1]; A. A. Kruger[3]; D. A. Kosson[4]; B. Riley[2]; C. L. Corkhill*[1]

1. University of Sheffield, Materials Science and Engineering, United Kingdom
2. Pacific Northwest National Lab, USA
3. US Department of Energy, Office of River Protection, USA
4. Vanderbilt University, USA

At the Hanford site, USA, low activity tank wastes will be immobilised by vitrification to create 150-350,000m^3 of Immobilised Low Activity Waste (ILAW). ILAW is destined for disposal in a shallow subsurface Integrated Disposal Facility where conditions are expected to differ from of a deep geological disposal facility for high level waste. Project GLAD (Glass Leaching Assessment for Disposability) investigates newly developed leaching technologies for assessing the durability of ILAW glasses. Four new methodologies developed by the U.S. Environmental Protection Agency for application to the accelerated ageing of ILAW glass are compared to established tests accepted for evaluation of waste glasses, including PCT and MCC-1 protocols. The GLAD project studies the process of glass dissolution as a function of temperature, pH, groundwater composition and flow rate. Three candidate glasses, LAW A44, ORP LB2 and LAW A23 were analysed by US EPA leaching methods ‘1313’ and ‘1315’ in both deionised water and synthetic groundwater and results were compared to those obtained by standard PCT-B and MCC-1 tests. The advantages and limitations of each test are discussed and their reproducibility is assessed by comparing results across multiple laboratories. Funding for this work was provided by William F. Hamel, Jr., of the U.S. DoE Office of River Protection Waste Treatment & Immobilization Plant Project.

3:15 PM

(GOMD-S4-020-2017) Role of modifier identity and network structure in corrosion of aluminosilicate glasses

N. J. Smith*[1]; R. Schaut[1]; E. Bakowska[1]

1. Corning Incorporated, USA

In attempts to fundamentally understand and develop predictive models for the glass-composition dependence of chemical durability, we have been experimentally evaluating the dissolution response of a variety of simplified glasses in commercially-relevant aqueous media, under conditions far from saturation. In this presentation, we contrast extraction and dissolution behaviors of ternary sodium aluminosilicate and calcium aluminosilicate glasses in media from acidic to basic pH, and particularly as a function of wide variations in network structure. Included is a comparison of altered surface layers, as well as a discussion of experimental considerations.

3:45 PM

(GOMD-S4-021-2017) Structure – dissolution relationship of a ZnO/CaO-modified base glass for high level waste

A. J. Fisher*[1]; C. L. Corkhill[1]; R. J. Hand[1]; L. J. Gardner[1]; N. C. Hyatt[1]

1. The University of Sheffield, Material Science and Engineering, United Kingdom

The UK is currently in the process of adopting a modified base glass, containing ZnO and CaO, for vitrification of high level waste at a ratio of 40:60 Zn:Ca in the nominal Magnox Waste (MW) formulation. Previous studies have given an insight to how Zn may influence glass dissolution, however the dual role of Zn and Ca remains poorly constrained. This investigation studies a series of simplified base glasses with different ZnO/CaO ratios, with the aim of understanding how the varying ratios influence the structure of the glass and how this relates to the long-term durability. Structural analysis using MAS-NMR has been utilised to determine the relative influence of Zn and Ca on the borosilicate glass network. Static batch dissolution experiments (PCT-B and MCC-1) give insight to the dissolution rates and alteration layers formed for the various ZnO/CaO ratios. From these studies, an optimized base glass formulation has been derived. The durability of a simulant MW-loaded version of this glass is compared with the currently applied formulation.

4:00 PM

(GOMD-S4-022-2017) Topological Model of the Dissolution Kinetics of Silicate Glasses

M. Wang[1]; I. Pignatelli[1]; T. Oey[1]; M. M. Smedskjaer[2]; J. C. Mauro[3]; G. Sant*[1]; M. Bauchy[1]

1. University of California, Los Angeles, USA
2. Aalborg University, Denmark
3. Corning Incorporated, USA

Understanding and predicting the dissolution rate of silicate glasses is of primary importance for various applications, including bioactive glasses and borosilicate wasteforms. However, the mechanism of silicates’ dissolution – and its rate-limiting step – remains poorly understood. In particular, present models linking the composition and structure of silicate glasses to their dissolution rate in a given solvent have remained largely empirical thus far. Here, based on vertical scanning interferometry (VSI), we study the dissolution of a family of borosilicate glasses under several values of pH. In addition, we parametrized a new transferable inter-atomic potential to assess the structure of these glasses from molecular dynamics (MD) simulations. From a detailed analysis of the simulated structures, we demonstrate that the kinetics of the dissolution is controlled by the topology of the atomic network. Finally, we propose a new topological model of the dissolution, which is shown to offer realistic predictions of the activation energy of dissolution for a wide selection range of silicate glasses and crystals.

4:15 PM

(GOMD-S4-023-2017) A review of experiments with the International Simple Glass

T. Kaspar*[1]; J. Ryan[1]

1. Pacific Northwest National Lab, USA

Vitrification has the potential to immobilize radionuclides to limit their release into the biosphere over long periods, often covering many thousands of years. Robust models based on a scientific and mechanistic understanding of the processes responsible for glass degradation and radionuclide release are desired for the calculation of the long-term behavior of glass waste forms. The glass corrosion community recognized the usefulness of analyzing a simple but representative glass composition, the six-component International Simple Glass (ISG). Here we present many of the results to date on ISG, compiled from more than 15 institutions. Physical characterization of the unaltered glass has included measurements of composition density, viscosity, and the glass transition temperature, as well as mechanical, optical, and electronic properties. Aqueous alteration experiments in both static and flow-through configurations have been undertaken to characterize the rate and mechanism of corrosion of ISG. Post-corrosion solution analysis has been complemented by various microscopy (SEM, TEM, EFTEM), spectroscopy (FTIR, EDS, Raman, XPS, NMR, ellipsometry), and spectrometry (ToF-SIMS, NRA) characterization techniques. This multi-pronged approach utilizing the state-of-the-art, multi-scale experimental and theoretical tools available to the collaborators will lead to fundamental insights into the corrosion behavior of the glass.

4:30 PM

(GOMD-S4-024-2017) Dissolution Kinetics of the International Simple Glass (ISG) in Brine Solutions at 90ºC

J. P. Icenhower*[1]; Y. Xiong[1]; L. Kirkes[1]; J. Dean[1]; C. Marrs[1]; J. Knox[1]

1. Sandia National Laboratories, Repository Performance, USA

Rock salt displays excellent physical characteristics, such as low permeability, high heat conduction, and self-sealing, which makes its use as a natural repository material for nuclear waste attractive. Several countries, including the U.S., are considering disposing high level nuclear waste glass in salt, but questions regarding how brine might intrude the repository and interact with vitreous waste forms remain. Although previous investigators have examined this question, consistent dissolution rate data for glass are lacking; both rate enhancement and inhibition have been reported for glass in NaCl-bearing solutions. We conducted flow-through dissolution experiments on both monoliths and powders of ISG at 90ºC, pH(25ºC) = 9 over an ionic strength (IS) interval (up to 4.0 m NaCl). Both monolith (15 x 15 x 4 mm) and powder experiments were conducted at the same flow-rate to surface area (q/S) ratio. Dissolution rates for monoliths and powders were the same within experimental uncertainty. Compared to rates in NaCl-free solutions, dissolution rates in 0.5 m NaCl solutions were 3x to 10x faster. With increasing IS, rates decreased linearly as a function of $(a_{H2O})^2$, in accordance with kinetic theory for SiO_2 dissolution. These data indicate that dissolution of borosilicate glass in NaCl solutions is governed by rupture of Si—O bonds.

4:45 PM

(GOMD-S4-025-2017) Dependence of pH on Alteration Layer Formation for International Simple Glass

J. Reiser*[1]; J. Ryan[2]; N. Wall[1]

1. Washington State University, Chemistry, USA
2. Pacific Northwest National Lab, Energy and Environment Directorate, USA

Alteration mechanisms need to be understood to predict the durability of nuclear waste glass, particularly alteration layer formation mechanisms. Several crucial characteristics of alteration layers need to be defined to advance mechanistic understanding, including thickness, composition, pore structure, and morphology. In this study, International Simple Glass (ISG) was altered in static aqueous solutions at various initial pH values (3, 5, 7, 9, 11 at room temperature) for 7 days at 90°C. A low glass surface area to solution volume ratio (20 m^{-1}) was used to quickly create a large alteration layer for simple analysis. Scanning electron microscopy demonstrated that alteration layers were thicker at extremely low and extremely high pH values, indicating higher glass alteration. Electron X-ray dispersion spectroscopy showed increasing Ca and Al concentration in alteration layers with increasing pH. Small angle X-ray scattering analysis and positron annihilation spectroscopy were performed to analyze the pore structures of alteration layers. Results and their implications will be presented.

GOMD Symposium 5: Professor Jacques Lucas Honorary Symposium

IR Materials I

Room: Kona 5
Session Chair: Jean-Luc Adam, University Rennes - CNRS

1:15 PM

(GOMD-S5-018-2017) Structure and Dynamics of Fast Ion Conducting Chalcogenide Glasses: A 30 Year Quest for Faster and Better (Invited)

S. W. Martin*[1]

1. Iowa State University, Materials Science & Engineering, USA

Ion conducting glasses have been known for more than 100 years. Being predominanlty alkali oxide silicate glasses, these glasses are better characterized as “dielectric” glasses with an ion conductivity that only becomes measureable above room temperature and often near their respecitive glass transition temperatures of ~500 ºC. These glasses have been mostly scientific curosities to help guide and understand the fundamental mechanisms of ion conduction in disordeded solid electrolytes. Recently, the author and others have shown that taking a small step down the period table to non-xode chalcogenide glasses has enabled the development of glasses with orders of magnitude higher ion conductivities. Li^+ conductivities as high as 10 mS/cm at 25 C have been achieved in these sulfide glasses and as such these glasses are now routinely termed fast ion conducting glasses. Such glasses are now being used as solid electrolytes in new types of all solid state batteries. In this talk, the author will summarize his more than 30 year exploration of these glasses and summarize the field with an eye towards showing the enormous progress that has been made in increasing the ionic conductivity of these glasses and to showing how they are now being used to assemble new all solid state batteries that are safer and have higher energy densities than conventional liquid electrolyte batteries.

1:35 PM

(GOMD-S5-019-2017) The effect of silver on the structural and optical properties of thin films in the system $Ag_x(As_{40}S_{60})_{100-x}$

M. Nalin*[1]; M. Resende[1]; S. Santagnelli[1]; A. Douaud[2]; S. Messaddeq[2]; M. El-Amraoui[2]; Y. Messaddeq[2]

1. Institute of Chemistry - UNESP, General and Inorganic Chemistry, Brazil
2. Laval University, COPL, Canada

The co-thermal evaporation method allows extending the vitreous domain of chalcogenide materials when they are prepared as films. Accordingly, new chalcogenide glassy domains belonging to Ag-As-S system were explored: $Ag_x(As_{40}S_{60})_{100-x}$ (x = 0, 15, 25, 50 at %) was prepared varying the evaporation rates of glassy $As_{40}S_{60}$ and metallic Ag. The structural and optical changes due to presence of silver were studied by means of Raman, UV-Vis and M-Lines spectroscopy. The chemical compositions of the films was determined using EDX while the morphology was analyzed using an AFM. The results show that addition of silver decreases the bandgap while the refractive index increases. Vibrational study suggests that addition of Ag induced breaking of the sulfur bonds and favours the remaining S create Ag–S–Ag bridging bonds to form AgS_3 pyramids. The photosensitivity of the chalcogenides films was evaluated by irradiating with a laser (λ= 457 nm). The films optical transmittances were used to evaluate their refractive index and absorption coefficient before and after irradiation through the software PARAV. The irradiation process resulted in photoexpansion and photodarkening phenomenona on the films. A direct laser writing of relief diffraction gratings were recorded on the films surface using two methods: a phase mask and a Lloyd mirror set-up.

1:50 PM

(GOMD-S5-020-2017) Optimizing properties in chalcogenides glasses: From simple structural models to rigidity guided molecular simulations (Invited)

M. Micoulaut*[1]

1. UPMC, France

Optimizing properties in glasses and disorderd materials has been always the driving force for new basic research, and this has been the case for the introduction of basic concepts such as topological degrees of freedom, mean-field rigidity, and elastic phase transitions strongly affected by the inherent out-off equilibrium nature of the glassy state. Here, we will present the most recent developments and applications of Rigidity Theory in chalcogenide glasses, a class of materials on which Professor Jacques Lucas has been working during several decades. While the framework of rigidity and topological constraint counting has been extensively used in glass science in the past, its potentially wide applicability has remained difficult because of some inherent limitations of the theory. Here, we review promising methods that have been recently introduced, and which allow to overcome such limitations, and to extend these methods to address effects that have been observed recently such as isostatic windows, structural defects, and the coexistence of well-defined atomic geometries. During the course of the conference, we will also review the ongoing effort and the limitations of the actual simulation activity on chalcogenides.

2:10 PM

(GOMD-S5-021-2017) Compositional dependence of Ag-photodoping behaviors in bulk sulfide chloride glasses

K. Kadono*[1]; K. Hosoya[2]; Y. Tokuda[3]; A. Okada[1]; T. Wakasugi[1]

1. Kyoto Institute of Technology, Faculty of Materials Science and Engineering, Japan
2. Kyoto Institute of Technology, Graduate School of Science and Technology, Japan
3. Shiga University, Faculty of Education, Japan

Photodoping is one of the most interesting phenomena among the photoinduced effects for chalcogenide glasses. Photodoping in chalcogenide glasses have been conventionally investigated for thin films prepared by sputtering method, etc. In that case, however, a number of defects present in the films possibly affect the photodoping behaviors. This makes difficult to analyze the compositional dependences of the photodoping because both effects from the difference in the compositions and defects can be hardly separated. Then, we investigated the compositional dependences of the Ag-photodoping behaviors for bulk sulfide glasses based on GeS_2-Sb_2S_3, Ga_2S_3-Sb_2S_3, and Ga_2S_3-GeS_2 systems, which were prepared by the melting-quenching method. Excess amount of sulfur and/or CsCl were incorporated into the glasses. Photodoping most easily occurred for the GeS_2-Sb_2S_3 based glasses and became difficult in the order of Ga_2S_3-Sb_2S_3 and Ga_2S_3-GeS_2. Incorporation of excess sulfur into these glasses enhanced the photodoping while the incorporation of CsCl had an opposite effect. The effects of the compositions on the photodoping behaviors was discussed using the doping mechanism based on the photo-induced redox reaction between the glasses and silver accompanying Ag^+ migration into the glasses.

2:25 PM

(GOMD-S5-022-2017) From the chemistry of chalcogenide glasses to the creation of the SelenOptics company (Invited)

J. Troles*[1]; A. Chardon[3]; L. Brilland[2]

1. University of Rennes 1, France
2. SelenOptics, France
3. Photonics Bretagne, France

Compared to oxide based glasses, vitreous materials composed of chalcogen elements (S, Se, Te) show large transparency windows in the infrared. Indeed, chalcogenide glasses can be transparent from the visible up to 12-20 μm, depending on their compositions. In addition, chalcogenide glasses contain large polarisable atoms and external lone electron pairs which induce exceptional non-linear properties. Consequently, the non-linear properties can be 100 or 1000 times as high as the non-linearity of silica. In addition, an original way to obtain single-mode fibers is to design microstructured optical fibers (MOFs). These fibers present unique optical properties thanks to the high degree of freedom in the design of their geometrical structure. This paper will present the interest and the development of chalcogenide MOFs that can permit to create in 2015 the SelenOptics company. Several applications of the chalcogenide MOFs, such as, endlessly singlemode transmission, Mid-IR supercontinuum generation and Mid-IR spectroscopy will be presented.

2:45 PM

(GOMD-S5-023-2017) Fabrication and Characterization of High-resolution Chalcogenide Imaging Fiber Bundles

B. Zhang[1]; Z. Yang*[1]; C. Zhai[1]; S. Qi[1]; H. Ren[1]; Y. Yu[2]; B. Luther-Davies[2]

1. Jiangsu Normal University, China
2. Australian National University, Australia

Ordered fiber bundles (FBs) operating in the mid-infrared spectral region are desirable for the collection and delivery of thermal images in extreme (e.g. under nuclear irradiation) or unfavorable environments (e.g. stray electromagnetic fields, in restricted spaces, etc.). In this work, a series of chalcogenide FBs suitable for transmitting images in the 2-6 μm and 3-11 μm spectral ranges are fabricated and characterized. A modified fabrication method, which combines an extrusion and a stack-and-draw techniques, is demonstrated for fabricating chalcogenide FBs with a high resolution and a large active area (or filling factor). The fabricated FBs show a resolution of >20 lp/mm, an active area of > 54%, and a crosstalk of < 3%. Fine thermal images of hot and room-temperature objects are delivered through the FBs.

IR Materials II

Room: Kona 5
Session Chair: Setsuhisa Tanabe, Kyoto University

3:15 PM

(GOMD-S5-024-2017) Recent development of materials for IR applications (Invited)

L. Zhang*[1]; X. Jiang[1]; X. Yuan[1]; X. Mao[1]

1. Shanghai Intitute of Optics and Fine Mechanics, CAS, China

Infrared windows and optics are widely used in low temperature imaging, night vision, ranging and surveying, remote sensing applications and free space optical communication. The windows of IR-sensors on missiles and aircraft often become the key point of failure for systems because of their interaction with the harsh environment. These windows must provide maximum transmission of signal with negligible absorption, withstanding the thermal shock, electromagnetic interference (EMI), radar latent, and abrasion from raindrops and sand particles. Large numbers of programs require windows with sizes larger than 500 mm diameter, which puts additional limitations on the available materials. It's still a great challenge to fabricate the IR- transparent materials with high-properties and large size. In this talk, the recent progress to face the above challenge was demonstrated and reviewed, especially which were done in our group. The prospect of the infrared materials toward cutting-edge applications was also discussed in this talk.

3:35 PM

(GOMD-S5-025-2017) Development of chalcogenide glass fibers for mid-infrared sensing (Invited)

B. Bureau*[1]; C. Boussard-Pledel[1]; V. Nazabal[1]; J. Lucas[1]

1. University of Rennes 1, Institute of Chemical Sciences, France

Chalcogenide glasses are fascinating materials which combine large transparencies in the mid-infrared with thermo-mechanical properties making them easy to shape into different kind of devices. During the past twenty years, a specific research group, originally founded by the Professor Jacques Lucas, works on the development of innovative optical fibers made from selenide glasses. The most exciting application for these fibers relies on their large optical window extending in the mid-infrared giving access to molecular fundamental vibrational modes shifted far in the IR. Such fibers have been tested in varied frameworks with different final users, for examples in biology with INSERM, medical diagnosis with the Public City Hospital in Rennes, for CO_2 detection to strike against the global warming or for the Darwin mission of the European Space Agency (ESA). The talk will be devoted to the description of these achievements which has led to the founding of the DIAFIR company. A focus will be proposed on the new pure-telluride glasses which enable to expand the spectral working window further in the mid-IR until 20 μm.

3:55 PM

(GOMD-S5-026-2017) Highly Dispersive Ge-Ga-Sb-S Glasses for Long-Wavelength Infrared Lens Applications

J. Lee*[1]; J. Yi[1]; W. Lee[1]; J. Choi[2]; Y. Choi[1]

1. Korea Aerospace University, Republic of Korea
2. KOPTI, Republic of Korea

Ternary Ge-Sb-S glass is one of the prototypical chalcogenide glasses, which exhibits quite a good thermal stability. If we want to employ this glass as a lens capable of transmitting the long-wavelength infrared (LWIR) range, i.e., 8 ~ 12 μm, not only its refractive index but also its infrared transmission edge needs to be engineered. In particular, unlike the Ge-Sb-Se glasses which exhibits a low-dispersion characteristic over the LWIR range, this sulfide glass would become highly dispersive. In this regard, we have aimed to optimize the glass compositions by introducing the fourth element. Several candidate elements were inspected in terms of optical, thermal and mechanical properties. Then, gallium turned out to be most effective, and therefore Ge-Ga-Sb-S glass was mainly analyzed in this study. Refractive index dispersion of this quaternary glass was elucidated, and it was verified that a doublet lens configuration consisting of low-dispersion Ge-Sb-Se glass and high-dispersion Ge-Ga-Sb-S glass is effective in minimizing the optical aberrations.

4:10 PM

(GOMD-S5-027-2017) Linking optical and structural propertes of glasses (Invited)

G. Calas*[1]; L. Galoisy[1]; L. Cormier[1]; G. Lelong[1]

1. University P&M Curie, Paris, Mineralogy, France

Since the discovery of glass making, the coloration caused by transition elements has always been one of the most attractive properties of glasses. Still now, transition metal ions constitute the most important source of glass coloring agents. Coloration varies, for a given transition element, as a function of chemical and physical parameters such as glass composition or melting/fining conditions. At the same time, the electronic transitions responsible for light selective absorption and glass coloration provide unique information about the local structure and chemical bonding of glasses. This presentation aims to review optical absorption data at the light of complementary information provided by a broad range of experimental and numerical structural approaches, providing a unique harvest of results: unusual coordination numbers as 5-fold coordination, site distribution, medium-range organization, heterogeneous spatial distribution… Some characteristics are inherited from melt dynamics and may show a significant modification as a function of temperature. As transition elements can be connected to the various structural subsets of glasses, they are useful color indicators of the complex structure of these materials. Vice versa, using a better knowledge of the structural behavior of transition elements, the variation of colors may be rationalized as a function of glass composition and melting conditions.

4:30 PM

(GOMD-S5-028-2017) Why are obsidians black?

L. Galoisy*[1]; G. Calas[1]; M. Chassé[1]

1. UPMC, IMPMC, France

Speciation of iron in obsidians from various localities has been determined using X-ray Absorption spectroscopy, Optical Absorption Spectroscopy and Transmission Electron microscopy. Optical absorption spectra were measured from 10K to 1073K. XANES measurements show variable Fe^{2+}/Fe^{3+} ratio depending on formation conditions and provenance of the obsidian. Optical absorption spectra show a spectacular temperature-induced evolution. This is interpreted as arising from the coexistence of distinct absorption processes due to different Fe-speciations. Isolated Fe^{2+} is located in a regular octahedral site, a local environment unknown in silicate glasses, whereas isolated Fe^{3+} is found in both tetrahedral and octahedral coordinations, in the structure of the glassy matrix. The presence of iron intervalence charge-transfers processes is evidenced through the temperature dependence of the intensity of associated bands. The specific coordination of Fe^{2+} together with the charge-transfer bands are related to the existence of iron oxide clusters (< 5nm), in the glass evidenced using TEM. These clusters (amorphous or crystalline), show a specific arrangement around iron in the glass and may be precursors of crystalline nanophases of iron oxide (titano-magnetite, magnetite or maghemite). The high temperature measurements show an evolution of the structure around iron in these glasses compatible with a re-dissolution of the Fe-clusters in the glassy matrix.

4:45 PM

(GOMD-S5-029-2017) Chalcogenide Glasses for Phononic Devices (Invited)

P. Lucas*[1]; P. Deymier[1]; N. Boechler[2]

1. University of Arizona, USA
2. University of Washington, USA

Control of acoustic signals is key for many telecommunication technologies such as surface acoustic wave filters in cell phones. The ability to tune the propagation of acoustic phonons in materials is therefore highly desirable. In particular light-induced control of phonon transport would permit the realization of novel phenomena such as loss-less transport of acoustic waves or opto-accoustic devices like tunable phononic filters. Chalcogenide glasses are ideal candidates for this application due to their high photosensitivity and the resulting photo-elastic effect which permit to optically tune the phonon propagation characteristics in the glass. Here we use the transient grating method to perform true direct measurements of photo-elastic processes in Ge-Se glasses. Large changes in elastic constant are observed upon irradiation and the compositional dependence of this process is investigated. The potential of these effects is discussed in terms of phononic device applications

PACRIM Third International Richard M. Fulrath Symposium on Discontinuous Progress for Ceramic Innovations

Fulrath Session II

Room: Queen's 6
Session Chairs: Roger Narayan, NC State University; Ken-ichi Kakimoto, Nagoya Institute of Technology

1:15 PM

(PACRIM-FUL-009-2017) Piezoelectric Enhancement of Bismuth based Piezoelectric Ceramics by Nanodomain Engineering (Invited)

S. Wada*[1]

1. University of Yamanashi, Material Science and Technology, Japan

Recently, the BT-Bi($Mg_{1/2}Ti_{1/2}$)O_3 (BT-BMT) were reported as relaxor ferroelectrics with high T_{max} over 250 C. It is possible to control domain configurations by solid solution system between the above relaxors and normal ferroelectric such as $BiFeO_3$ (BF) with high T_c of 830 C. In this study, the BT-BMT-BF system ceramics were prepared using a conventional solid–state reaction and their crystal structure and electrical properties were investigated. TEM observation revealed that BT-BMT had no domain configuration while BF-rich ceramics had normal rhombohedral domain configurations. Moreover, the ceramic with the intermediate composition between relaxor and BF had nanodomain configuration with domain sizes less than 50 nm. Finally, their strain vs. electric-field behaviors were measured, and for the ceramics with nanodomain configuration, the strain curve with hysteresis was clearly observed and the apparent d_{33}^* (=S_{max}/E_{max}) from the slope was over 850 pC/N.

1:35 PM

(PACRIM-FUL-010-2017) Technical Challenges in Lead-free Alkali Niobate Piezoceramics (Invited)

K. Kakimoto*[1]

1. Nagoya Institute of Technology, Frontier Research Institute for Materials Science, Japan

Piezoelectric materials generate a voltage when subjected to mechanical strain and can deform when exposed to a voltage. This electromechanical behavior makes them useful in many applications including sensors, actuators, transducers, electric appliances, automobiles and medical devices. The study of lead-free materials is motivated by the growing demand for materials that are benign to the environment and human health, and we have taken on the technical challenge of developing lead-free alkali niobate piezoelectrics that match the performance and stability of existing lead-based materials. The niobates have excellent piezoelectric properties and also a higher maximum operating temperature, which makes them stable in practical applications. Our group is also working on novel applications of their niobate piezoelectric technology, such as vibration harvesters for energy generation. The idea of using the electromechanical coupling of piezoelectric materials to harvest vibrational energy has become increasingly attractive for simple, stand-alone energy harvesting, which could allow batteries to be replaced with miniature piezoelectric power systems.

1:55 PM

(PACRIM-FUL-011-2017) Donor doped cadmium oxide: A gateway material for mid-infrared plasmonics (Invited)

J. Maria*[1]; K. Kelley[1]; E. Runnerstrom[1]; E. Sachet[1]; C. T. Shelton[1]; J. Ihlefeld[2]

1. North Carolina State University, Materials Science and Engineering, USA
2. Sandia National Laboratories, USA

The widespread interest in plasmonic technologies surrounds a wealth of emergent optoelectronic applications, such as plasmon lasers, transistors, sensors, and information storage. While materials for UV-VIS and near infrared wavelengths applications have been found, the mid-infrared range remains a formidable challenge to address: only a few known systems can achieve sub-wavelength optical confinement with low loss. Here, we undertake this challenge. We will present data for several doping series that collectively demonstrate an extreme peak of electron mobility in donor-doped CdO that is achieved through "defect equilibrium engineering". In so doing, we create a tunable plasmon host that satisfies the demanding criteria for mid-infrared spectrum plasmonics, and overcomes the losses seen in conventional plasmonic materials like Ag and Au. The substitutional lattice strain induced by Dy-doping is sufficiently small, allowing mobility values around 500 cm^2/V s for carrier densities above 10^{20}/ cm^3. CdO:Dy resembles the ideal "lossless metal", a potentially new material for exploring integrated mid-IR plasmonic applications. Similar trends will be shown for Y, Sn, Ce, and In, as well as doping on the anion lattice with F. We will show how dopant control and high mobility regulate interaction with IR light and ebable one to create tunable sub-wavelength absorber.

2:30 PM

(PACRIM-FUL-012-2017) Aliovalent substitution of $BaTi_2O_5$ (Invited)

T. Goto*[1]

1. IMR Tohoku University, Japan

$BaTi_2O_5$ (BT_2) is a non-lead ferroelectric compound with a high Curie temperature (T_c) of 748 K. We have succeeded to prepare relatively large BT_2 single crystal by using heat-reservoir in a floating zone (FZ) method, and found a significant ionic conduction of BT_2 in the b-direction as well. The ionic conduction of BT_2 would be caused of oxygen vacancy associated with Ti^{3+}, which is also observed in $BaTiO_3$ (BT). Ba^{2+} and Ti^{4+} were substituted by K^+ and Mg^{2+}, Al^{3+}, Fe^{3+}, respectively. The lower valence substitution has caused an increase in dielectric loss and decrease of T_c. The K^+ substitution has yielded a significant increase in electrical conductivity, and 1 to 5 at% K^+ substitution increased electrical conductivity two orders of magnitude greater than that of pristine BT_2. The lower valence element substitution has caused the increase of Ti^{3+} and oxygen vacancy formation. With increasing the higher valence element substitution, the permittivity at room temperature increased and the T_c decreased. With increasing the higher valence element substitution, the electrical conductivity decreased below 0.1 at%Nb^{5+} and La^{3+}, while it increased over 0.2 at%Nb^{5+} and La^{3+}. The remanent polarization of 0.2 at%Nb^{5+} and 0.4 at%La^{3+} substituted BT_2 exhibited 2.3 and 6.4 times higher than that of pristine BT_2, respectively.

2:50 PM

(PACRIM-FUL-013-2017) 3D printing of bioceramics in bone disorders: Understanding the science and clinical significance (Invited)

S. Bose*[1]

1. Washington State University, School of Mechanical and Materials Engineering, USA

Additive manufacturing (AM) or 3D printing technology enables us to make devices with controlled geometry / architecture and chemistry depending on clinical needs. There are an estimated one million bone grafting procedures performed annually in the U.S. and a few million worldwide to repair fractures, craniomaxillofacial defects, bone defects, tumors, as well as hip and knee replacements due to the aging population, increase in musculoskeletal disorders and sports related injuries. Sometimes patients with special anatomical needs or defect complexity, patient matched devices are necessary. 3D printed resorbable calcium phosphate (CaP) ceramics show significant promise towards bone tissue engineering and surface modified metallic load bearing hip knee devices. Dopant chemistry plays a vital role in controlling their mechanical strength, degradation kinetics, as well as biological properties. 3D interconnected channels provide pathways for micronutrients, improved tissue – material interactions, osteogenesis and angiogenesis with these 3D printed scaffolds. Multi material incorporation also help improve mechanical and biological properties of these multifunctional devices. The presentation will include recent scientific and technological advances as well as challenges towards developing next generation biomedical devices using 3D printing for bone disorders

3:10 PM

(PACRIM-FUL-014-2017) Transparent and Luminescent SiAlON bulk ceramics for high power LED (Invited)

J. Tatami*[1]; T. Takahashi[2]; M. Iijima[1]

1. Yokohama National University, Japan
2. Kanagawa Academy of Science and Technology, Japan

One of the typical systems of the current white LEDs is composed of blue or UV LEDs and ceramic phosphor particles which were dispersed in a resin. One of the problems to be solved in high power application is the thermal degradation of the resin because the operation temperature increases as applied power. In this study, we prepared the transparent and luminescent SiAlON ceramics by controlling powder processing. As a result, the developed Ce doped Y-α SiAlON ceramics showed over 60% transparency at 600 nm in wavelength and blue or blue-green emission excited by UV light. The maximum excitation and emission were obtained at 370 and 480 nm, respectively. Transparent Eu doped Ca-α SiAlON ceramics was also developed, of which emission was yellow color by blue light excitation. The wavelength of excitation and emission and quantum efficiency of the Ca-α SiAlON ceramics is almost the same as that of the powders reported in the previous study. Eu^{2+}doped $CaAlSiN_3$ ceramics developed by spark plasma sintering technique showed high relative density. SEM observation showed that the grain size was less than 1 μm and there was no pore. The emission and excitation peaks of photoluminescence were about 471 and 633 nm, respectively, which is almost the same as the previous study. Furthermore, luminescence of red color was confirmed by radiation of the UV or blue light behind the sample.

4:00 PM

(PACRIM-FUL-015-2017) High-Energy Electron Beam Lithography of Ceramic Nanowires for Breath-Gas Sensors (Invited)

P. Gouma*[1]

1. University of Texas, Arlington, MSE, USA

Ceramic oxides have long been used as gas-sensitive elements in resistive gas sensors. The latter are inexpensive sensor technologies that find applications from environmental monitoring to breath-based diagnostics. The author's prior research on ceramic-based biosensors for olfactory systems (which was recognized by a Fulrath award) has shown that selective gas sensors may be developed utilizing different polymorphs of binary metal oxides. Such probes may become asthma monitors, when NO is selectively sensed, or diabetes monitors when acetone is detected, for example. To meet the need for highly selective and sensitive detection of gaseous biomarkers in breath, single crystal nanowires are the desired sensing elements. A novel process of forming single crystal nanowires of WO3 by means of high-energy electron beam lithography is described in this work. The instantaneous growth of single crystal nanowires of the monoclinic polymorph from sol-gel-based nanoparticle precursor is discussed. The nanowire growth occurs by an electron-beam induced massive phase transformation. The nanowires thus obtained may be used to develop highly-sensitive sensors that are needed for cancer detection breath-diagnostics.

4:20 PM

(PACRIM-FUL-016-2017) THz dielectric spectra and lattice dynamics of perovskite oxides (Invited)

T. Hoshina*[1]; H. Takeda[1]; T. Tsurumi[1]

1. Tokyo Institute of Technology, School of Materials and Chemical Technology, Japan

Intrinsic dielectric properties of high-permittivity materials such as perovskite oxides are predominantly determined by the ionic polarizations related to the lattice vibrations (phonon). Therefore, it is necessary to measure the complex dielectric permittivity as a function of frequency in THz region to understand the origin of the intrinsic dielectric property. In this presentation, we will introduce THz dielectric spectra of perovskite oxides measured by a far-infrared ellipsometer and discuss the lattice dynamics. We uniquely developed an ellipsometric system based on a Fourier transform far-infrared spectrometer for determining THz dielectric functions of high-permittivity materials directly. At first, we measured the complex permittivity of $SrTiO_3$ at 0.75–21 THz to verify the effectiveness for the measurement of ionic polarizations. All optical phonon modes of $SrTiO_3$ were clearly observed, and the dielectric function agreed with a damped harmonic oscillator model. On the other hand, the THz dielectric spectrum of $BaTiO_3$ could not be represented by a harmonic oscillator model, which suggested anharmonicity of ferroelectric phonon mode. Based on an eight-site order-disorder model, molecular dynamics calculation was performed and analyzed the THz dielectric spectrum of $BaTiO_3$. It was found that the order-disorder mode coupled with the Slater mode greatly contributes the high permittivity of $BaTiO_3$.

4:40 PM

(PACRIM-FUL-017-2017) The photochemical properties of polar surface domains on non-polar surfaces (Invited)

G. Rohrer*[1]; P. Salvador[1]

1. Carnegie Mellon University, USA

Polar semiconductors have recently received significant attention because their internal fields separate photogenerated electron-hole pairs and reduce recombination. On surfaces with polar domains, electrons are attracted to positively terminated domains where they promote reduction reactions and holes are attracted to negatively charged domains where they promote oxidation. We have found that polar domains can be created on the surfaces of non-polar materials, including $BiVO_4$, WO_3, and $SrTiO_3$. In the cases of WO_3 and $BiVO_4$, polarity arises from the flexoelectric effect. On $SrTiO_3$, polarity arises from polar terminations on different terraces. For $SrTiO_3$, it is possible to control the fraction of the surface terminated by positive or negative charges by annealing the surfaces in environments with an excess or deficit of strontium. In this talk, we will describe photochemical reactions on the surfaces of materials with polar domains and discuss opportunities to exploit polar domains in materials where they are not expected on the basis of the known bulk properties.

5:00 PM

(PACRIM-FUL-018-2017) Grain Boundary Atomic Structures, Vacancies and Dopants of Oxide Ceramics (Invited)

Y. Ikuhara*[1]

1. University of Tokyo, JFCC, Tohoku University, Japan

Properties of electronic materials are strongly dependent on the grain boundaries (GBs) which have different atomic structures due to the disorder in the periodicity. The grain boundary structures are also influenced by dopants and vacancies segregated at GBs, providing various functional properties. In order to control GB structures to improve the properties, we need to understand the relationships between GB characters, atomic structures and chemistry. For this purpose, well-defined GBs structures of various oxides such as ZnO and CeO_2 with and without dopants, which are systematically fabricated by the bicrystal techniques, are used as the model samples, and the behavior of the GB structure reconstruction due to the vacancies and dopants are quantitatively investigated by combining aberration-corrected STEM, EELS mapping and first principles calculations.

PACRIM Symposium 02: Virtual Materials Design and Ceramic Genome

Modeling of Functional Materials I

Room: Kohala 4
Session Chair: William Weber, University of Tennessee

1:15 PM

(PACRIM-S2-018-2017) Thematic Simulation Platform for Nano Materials Design (Invited)

K. Lee*[1]

1. Korea Institute of Science and Technology, Republic of Korea

Molecular level simulation is driving a new paradigm of materials research. Increased predicting power of the ab initio calculation combined with molecular dynamics approach can now guide the experimental research. Furthermore, combined with WEB 2.0 technology, web-based materials design platform has been drawn much attention to reduce the entrance barrier for non-theoretical researchers to utilize the massive computation tools for the design of materials. These platforms are supposed to be combined with the materials big-data to discover new materials of novel properties and optimize the materials processes. I will introduce recently developed web-based platforms to design materials using the process and property simulation methods. We have built the thematic platforms that mimics the procedure of the experimental works in the nano-fab of real space as closely as possible. In the virtual fab for nano materials design (http://nano.vfab.org), sample preparation room, processing room and analysis rooms are provided with the simulation modules for major processes such as annealing, etching, oxidation, deposition and implantations and for major analysis tools like 'simuloscope', AFM/STM and IV measurement equipment. Virtual Fab for Li ion battery materials (http://battery.vfab.org) is composed of Anode Design Lab, SEI Simulation Lab, Cathode Design Lab, Electrolyte Design Lab and Full cell simulation module.

1:35 PM

(PACRIM-S2-019-2017) Carbon-based Nanomaterials in Energy Applications manipulated by Atomic Functionalization (Invited)

T. Liao*[1]

1. Queensland University of Technology, School of Chemistry, Physics and Mechanical Engineering, Australia

The salient electronic and catalytic properties of novel atomic functionalized carbon-based nanomaterials pave the way to design high-performance devices for energy harvesting, conversion and storage. In this presentation, a strong facilitating effect of heteroatom doping and welding of flat graphene nanoribbons has been illustrated by DFT calculations, which includes charge carrier adsorption and transfer in an aqueous environment, induced half-metallic properties, and stimulating effect on the splitting reaction of H_2O/H_2S molecules. The calculated results not only confirm the possibility of manipulating the performance of carbon-based electrochemical devices in energy application through atomic functionalization but, more importantly, the idea of heteroatom doping and welding of foldable two-dimensional systems may develop into a versatile design strategy that can be extended to BN, MoS_2, TiO_2, and other two-dimensional (2D) nanosheets.

1:55 PM

(PACRIM-S2-020-2017) Structural study of metal oxide nanoparticle structure on functional nanowire gas sensor devices (Invited)

S. Steinhauer[2]; J. Vernieres[2]; J. Zhao[1]; Z. Wang[3]; F. Djurabekova*[1]; K. Nordlund[1]; P. Grammatikopoulos[2]; M. Sowwan[2]

1. University of Helsinki, Department of Physics, Finland
2. Okinawa Institute of Science and Technology (OIST) Graduate University, Nanoparticles by Design Unit, Japan
3. Xi'an Jiaotong University, China

Metal oxide nanowire gas sensors decorated with catalytic nanoparticles have attracted considerable interest due to favorable physico-chemical properties and excellent device performance. However, the interplay between atomic-scale structure, chemical activity and electrical properties of the employed nanomaterials remains largely unexplored. We demonstrate different in situ and ex situ approaches for studying catalytic nanoparticles supported on metal oxide nanowires by environmental transmission electron microscopy (TEM). By combination of TEM imaging and performing the density functional theory calculations of different structural defects and migration paths of oxygen atoms in CuO-Pd interface, we study morphological changes of CuO nanowire-supported Pd nanoparticles due to oxidative treatments, revealing the decisive influence of the interface on nanoparticle oxidation. Eventually, the results are correlated with gas sensing properties and new prospects related to in situ TEM of functional metal oxide nanodevices are discussed.

2:15 PM

(PACRIM-S2-021-2017) Spin-orbit coupling effects in 5d metal oxide superlattices from DFT calculations (Invited)

H. Xu*[1]; J. Liu[2]

1. The University of Tennessee, Department of Materials Science and Engineering, USA
2. The University of Tennessee, Department of Physics & Astronomy, USA

Energy conversion between the electric and magnetic domains requires mutual couplings of the charge and spin degrees of freedom. In this study, the effects of spin-orbit coupling on interfaces are investigated in oxide superlattices consisting of irradiates and other transitional metal oxides using density functional theory in combination with empirical corrections (DFT+U). Specifically, we examine the electronic and magnetic structure of these systems and evaluate the magnetization change under an applied electric field. These calculations provide an estimation of the magnetoelectric coupling, allowing prescreen and identification of superlattices with potential enhanced coupling effects. This study is in close synergy with experimental efforts of synthesizing these oxide superlattices using laser molecular beam epitaxy and characterizing them using various techniques.

2:35 PM

(PACRIM-S2-022-2017) High-Throughput Design of Two-Dimensional Electron Gas Systems Based on Perovskite Oxide Heterostructures (Invited)

K. Yang*[1]

1. University of California San Diego, Department of NanoEngineering, USA

The perovskite-based oxide heterointerfaces between two wide-band-gap insulators such as $LaAlO_3$ and $SrTiO_3$ are attracting increasing interests because of their novel electronic properties such as the two-dimensional electron gas (2DEG) at the interface that have potential applications in the next-generation nanoelectronic devices. In this talk, we show that a group of combinatorial descriptors such as the polar character, lattice mismatch, band gap, and the band alignment between the perovskite-oxide-based band insulators and the $SrTiO_3$ substrate, can be introduced to realize a high-throughput (HT) design of SrTiO3-based 2DEG systems using perovskite-oxide-oriented quantum materials database. By using these combinatorial descriptors, we have carried out a HT screening of all the polar perovskite compounds, uncovering 42 compounds of potential interests. Our approach, by defining materials descriptors solely based on the bulk materials properties, and by relying on the perovskite-oriented quantum materials repository, opens new avenues for the discovery of perovskite-oxide-based functional interface materials in a HT fashion.

2:55 PM

(PACRIM-S2-023-2017) Theoretical investigation of defect interaction in $SrTiO_3$ (Invited)

B. Liu*[1]; Y. Gao[1]

1. Shanghai University, China

In perovskite $SrTiO_3$, intrinsic defects are closely related to its various properties, which are thought to be the origin of its wide application, such as insulating layers in dynamic random-access memories, ferroelectric thin-film structures, high-Tc superconductor substrates, gate oxides and for the immobilization of nuclear waste. In this work, the density functional theory calculations are performed to study the combining of point defects and the point defect – grain boundary interaction. The dependence of defect stability on the chemical potential is clarified. Furthermore, we find that oxygen vacancies segregate towards the GB, preferring to reside within the next nearest neighbor layer. The migration barriers of oxygen vacancies diffusing to the first nearest-neighbor layer of the GB are low, while those away from this layer are very high. The segregation and trapping of the oxygen vacancies in the first nearest-neighbor layer of the GB are attributed to the large local distortions, which can now accommodate the preferred six-fold coordination of Ti. These results suggest that the electronic, transport, and capacitive properties of $SrTiO_3$ can be engineered through the control of defect structure.

3:15 PM

(PACRIM-S2-024-2017) Investigation of ferromagnetism of Al-doped 6H-SiC and theoretical calculation

Y. Huang*[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

SiC with d^0 ferromagnetism is thought to be one of the most important materials in the spintronics field, and it received widespread attention at home and abroad. In this paper, Al:SiC magnetic powder was fabricated by high temperature calcination method with Ar gas protecting. XRD results showed that the obtained powder was in 6H-SiC phase, and Al was proposed to enter into the 6H-SiC crystalline. Raman results showed that Ar gas play a crucial role in impeding the decomposing of SiC at high temperature. With the protection of Ar gas, it kept round shape after calcination about 2200ºC. The obtained powder showed magnificent magnetic hysteresis loop, large coercive force. Its saturation magnetic moment reached 0.07emu/g. With the rise of calcination temperature, the magnetism of the powder changed from diamagnetism to ferromagnetism. When the calcination temperature rise to 2200ºC or more, it would change back to diamagnetism. By first principles calculation, the origin of its ferromagnetism was studied, and its spin situation in the space was mapped. The results showed that the combination of Al and Vacancy lead to a local magnetic moment of $1.0\mu_B$, and magnetic coupling is steady at c axis direction. It is found that the p electron of Carbon is the origin of the net spin.

Modeling of Functional Materials II

Room: Kohala 4
Session Chair: Kwang-Ryeol Lee, Korea Institute of Science and Technology

3:45 PM

(PACRIM-S2-025-2017) Porous graphene-like 2D membranes as lithium ion battery anode materials (Invited)

M. Hankel*[1]; D. J. Searles[1]

1. The University of Queensland, Australia

Carbon structures have been extensively studies over recent decades as energy storage materials. One of the industry applications is as the anode of lithium (Li) ion batteries. The lithium ion battery (LIB) is one of the essential technologies required for the development of portable electronics. Graphite, a layered material consisting of sp^2 bonded carbon sheets is currently the predominant anode material offering a theoretical capacity of LiC_6 with Li inserted between the layers. To achieve higher storage capacity novel anode materials, such as carbon allotropes or carbon nitrides or graphene composites that can surpass the capacity of graphite are widely being pursued. We investigate the Li storage capacity of novel porous graphene-like 2D membranes. These include porous graphitic carbon nitrides, g-C_3N_4, g-CN and hC_2N, and 2D carbon only membranes, graphenylene and biphenylene and siligraphene, SiC_3 and SiC_7. Density functional theory (DFT) calculations are employed to obtain the maximum Li loading of such membranes for single layer and bilayer or bulk. We also, in some cases, calculate diffusion barriers for the Li to hop from one site to another via transition state theory to determine the mobility of the Li atoms within the material. In addition to this we also present the charge transfer from the Li to the membrane.

4:10 PM

(PACRIM-S2-026-2017) Understanding the Chemical Bonds in Thermoelectric Materials (Invited)

J. Yang*[1]

1. Shanghai University, Materials Genome Institute, China

Understanding the chemical bonds in materials are crucial for rationalizing the property variations, and predicting new phases. For thermoelectrics, chemical bonds have subtle influences on the microscopies, including the electronic structures and phonon spectra, which determine the electrical and thermal transport. In this talk, two recent works on thermoelectric materials have been summarized, focusing on the relations between transport properties and chemical bonds. In the filled CoSb3, we found a type of negative polarized guest-host interactions, i.e., electronegative fillers together with the positively charged host. This is in contrast with the long believing that the fillers in CoSb3 should be strong electropositive metallic ions. Some electronegative fillers form polarized covalent bonds with the neighboring Sb atoms, resulting in abnormal temperature dependence of lattice thermal conductivities and enhanced thermoelectric figure of merits. For α-MgAgSb, we found the unique Mg-Ag-Sb multicenter bonding, originating from the lattice distortion of this compound. The multicenter bonding not only causes a low-lying optic phonon due to the collective vibration, but also opens up the band gap. Both of these are beneficial to the superior thermoelectric efficiency of α-MgAgSb. Nowotny-Juza compounds, where α-MgAgSb belongs, are proposed for thermoelectric applications due to the similar chemical bondings.

4:35 PM

(PACRIM-S2-027-2017) Computer Simulation of the Effects of Disorder on Li Diffusion in Ceramics (Invited)

R. Devanathan*[1]

1. Pacific Northwest National Lab, USA

In this presentation, we will highlight the role of disorder—either deliberately introduced during processing or sustained as a consequence of operating in an extreme environment—on the transport of species in ceramics. We performed molecular dynamics simulations to understand the role of atomic-level defects and defect clusters on Li diffusion in lithium aluminate (g-$LiAlO_2$). This material has applications in lithium polymer batteries, where enhanced Li transport is desirable, and tritium production using a nuclear reactor, where Li migration may have undesirable effects. We introduced displacement damage and found that g -$LiAlO_2$ at 573 K was rapidly disordered at a dose between 0.1 and 0.2 displacements per atom after which it became fully amorphous. The collapse of the ordering of the AlO_4 tetrahedra during the disordering process induced phase separation into Al-O rich and Li rich regions. Regions of lower density occurred within the disordered structure leading to significant enhancement of Li diffusion. We will present the observed structural and compositional disorder in the context of experimental observations and discuss the implications for limiting or enhancing the diffusion of species in ceramic materials, and for the design of novel energy storage materials.

4:55 PM

(PACRIM-S2-028-2017) Hydrogen-transfer-mediated electrochemical reactions to increase storage capacity in Li-ion and Na-ion Batteries (Invited)

J. Liu*[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Developing cumulative cationic and anionic redox chemistry offers a transformative approach to increase energy storage capacity in Li-ion batteries and active sites of catalysts. Realizing reversible anionic redox reactions in Li-ion battery materials remains to be a large challenge even after a long-time effort. First-principles calculations were used to explore hydrogen-transfer mediated electrochemical reactions to increase energy densities and improve reversibility of Li-ion and Na-ion batteries. In this talk, we present that an open-framework Iron-fluoride L-ion battery could operate with hydrogen-transfer-mediated cumulative cationic (Fe^{3+}-->Fe^{2+}) and anionic (O^{-}-->O^{2-}) redox reactions to reach a highly stable and reversible electrochemical process. In addition, carbonyl-based organic salts as Na-ion battery materials were discussed to elucidate hydrogen-transfer-mediated electrochemical reaction mechanism. Our calculation results were compared with experimental characterization in electrochemical performance. The present study opens a new avenue to develop high-capacity electrode with the hydrogen-transfer-mediated cumulative redox reactions and elucidate anionic redox chemistry.

5:15 PM

(PACRIM-S2-029-2017) Reactive interatomic potentials for metal oxides

K. Nordlund*[1]; J. Byggmästar[1]; F. Djurabekova[1]

1. University of Helsinki, Finland

Modelling of nonequilibrium materials processes on the atomic level requires reactive interatomic potentials, i.e. ones that allow simulation of bond formation and breaking. A good potential should be able to describe not only the equilibrium structure, but also metastable structures, defects, and surfaces. Moreover, to enable simulations of phase transitions, a potential for compounds should ideally be able to describe also the pure elements well. We have shown that Tersoff-like potentials can at least in principle fulfil all these requirements. In this talk, we will present the development of Tersoff-like potentials in general, and in particular for the metal oxides ZnO and FeO, and give examples of their application to nonequilibrium processes such as radiation effects and nanowire elongation.

PACRIM Symposium 03: Novel, Green, and Strategic Processing and Manufacturing Technologies

Novel, Green, and Strategic Processing III

Room: King's 3

Session Chairs: Zhengyi Fu, Wuhan University of Technology; Yoshihiro Hirata, Kagoshima University

1:15 PM

(PACRIM-S3-025-2017) Processing and Manufacturing Technologies of Complex Ceramic Materials using Rapid High-Energy Phenomena (Invited)

J. Lis*[1]; D. Kata[1]; L. Chlubny[1]; A. Tajdus[2]; T. Slomka[3]

1. AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Poland
2. AGH University of Science and Technology, Faculty of Mining and Geoengineering, Poland
3. AGH University of Science and Technology, Faculty of Geology, Geophysics and Enviromental Protection, Poland

A progress in ceramic materials prepared by different rapid high-energy phenomena (RHEP) processes is discussed. Specifically, two approaches are shown: Combustion Synthesis – it's also called Self-Propagating High-Temperature Synthesis (SHS), and Laser Manufacturing (LM). Both technologies are based on the use of high-energy sources for synthesis or local consolidation of powders. The physicochemical processes e.g. melting, reaction route and sintering occurred as the result of rapid temperature rising have untypical features and give possibility to prepared new compounds. The combined effects of rapid heating and cooling bring non-equilibrium conditions for synthesis and thus different forms of covalently bonded solid-solution, MAX phases or nanocomposites can be prepared. Analysis of these conditions related to chemical energy (SHS) and laser energy (LM) sources leads to conclusion that both processes have a lot in common. The review of different complex ceramics prepared directly by SHS or LM is presented. The Si-C-N, AlN-SiC, Ti-Si-C-N as well as Inconel-WC systems are explored in details. Due to the use of external energy sources, low energy consumption by the local course of reaction, SHS and LM technologies are potentially energy efficient. It is concluded, that the generally RHEP techniques may be considered as perspective approach for materials engineering.

1:40 PM

(PACRIM-S3-026-2017) Preparation of Mg Submicrometer Particles Prepared by Pulsed Wire Discharge (Invited)

H. Suematsu*[1]; K. Tanaka[1]; N. Hieu[1]; T. Suzuki[2]; T. Nakayama[1]; K. Niihara[2]

1. Nagaoka University of Technology, Extreme Energy-Density Research Institute, Japan
2. Nagaoka University of Technology, Department of Nuclear System Safety Engineering, Japan

Particles of Mg draw interests of researchres for their potential in hydrogen storage products and onboard emergency heat sources. However, the smallest commercially available Mg powder has an average grain size of 45 μm. Recently, pulsed wire discharge (PWD), which is an physical evaporation method, has been developed and organic matter coated metal nanosized powders of Cu, Ti and Zr have been successfully prepared in organic fume/vapor. In this study, preparation of Mg particles were attempted by PWD. A Mg wire with a diameter of 0.3mm and a length of 32mm was placed between electrodes, which were connected to a 10μF capacitor charge at 5kV through a gap switch. The wire and electrodes were placed in a chamber filled with Ar mixed with mineral oil fume/vapor at ambient pressure. Then, the gap switch was closed and a large current went through the wire to evaporate. The evaporated Mg was cooled quickly by Ar-mineral oil fume/vapor to form particles, which were collected on a membrane filter by evacuation. The powder X-ray diffraction pattern for the prepared powder showed that all peaks corresponded to those of Mg. In transmission electron microscopy and selected area diffraction analysis, the powder consisted of submicron Mg particles covered with MgO fine grains with size of ~10nm. From these results, it was concluded that submicron Mg particles were successfully prepared by PWD.

2:05 PM

(PACRIM-S3-027-2017) Fabrication of Silica Glass from Mesoporous Powder by SPS

L. Wang*[1]; W. Jiang[1]

1. Donghua University, China

Silica glasses containing noble metal nanoparticles are of great interest due to the surface plasmon resonances of these nanoparticles which behave as optically functional phases. These composite materials are expected to be exploited in photonic devices. Despite the prospects of application, the traditional fabrication methods impair homogenously nucleation of nanoparticales resulting in an obstacle to control the size and dispersion of nanoparticles dopnant. Here, a new versatile processing strategy based on solid-state sintering is reported for preparation such bulk transparent glass composite. Mesoporous silica SBA-15 powders encapsulating Au, Ag and Pt nanoparticles are prepared via host-guest synthesis method and then dynamically consolidated to form a bulk transparent specimen by Spark Plasma Sintering(SPS). The whole sintering process takes place under much lower temperature (1020°C) and within very short times (10min) than traditional melting-quenching method.

2:20 PM

(PACRIM-S3-028-2017) Optimization of Spark-Plasma-Sintering (SPS) Processing for Attaining Transparent $MgAl_2O_4$ Spinel

K. Morita*[1]; B. Kim[1]; H. Yoshida[1]; K. Hiraga[1]; Y. Sakka[1]

1. National Institute for Materials Science (NIMS), Japan

Spark-plasma-sintering (SPS) technique is a powerful sintering tool and has widely been utilized to consolidate various types of materials. The benefit of the SPS technique is heating rates higher than 50°C/min, and hence, can save the total processing time. It is reported, however, that the SPS processed oxides such as Al_2O_3, ZrO_2 and spinel exhibit discoloration. Such a discoloration is known to be remarkable than the HIP/HP processed oxides and affect the optical properties. The discoloration in spinel can be explained by the combination of carbon contaminations and lattice defects, which are introduced in the spinel matrix depending on the SPS conditions. The carbon contamination would cause serious problems for the SPS processed materials, especially for oxide ceramics. In the presentation, therefore, we will discuss i) the effects of temperature and loading schedule on the carbon contamination, ii) a possible carbon contamination mechanism during the SPS processing and iii) a effective SPS processing to suppress the carbon contamination. In addition, iv) the carbon contamination will be discussed in other oxide ceramics such as alumina (a-Al_2O_3) and 3mol%-Y_2O_3-stabilized tetragonal zirconia polycrystal (3Y-TZP) as well.

2:35 PM

(PACRIM-S3-029-2017) Ultra-fast densification of boron carbide by flash spark plasma sintering

Z. Fan*[1]; B. Niu[1]; J. Zhang[1]; W. Wang[1]; Z. Fu[1]

1. Wuhan University of Technology, China

We present a simple method of sintering ceramic powders in 1 min at low temperature and low pressure. Nearly fully dense (99.2%) B_4C with limited grain growth was prepared at 1931 °C with an applied pressure of 15.3MPa. Comparison of our method to a simple SHS/QP process reproducing the same aggregate thermodynamic conditions shows that our process yields significantly higher and faster densification. We attribute this outcome to the particular spatial and temporal variations of Joule heating within the material. A short sintering time and plastic deformation lead to limited grain coarsening. The novel method (FSPS) combines flash sintering and electric field assisted sintering. Over previous reports of flash sintering, our method requires both less energy and less processing time for an improved outcome. Neither preheating of the sample, which is energetically costly, nor the fabrication of a pre-sintered sample, which is temporally costly, is required to initiate the flash sintering. In addition, the Joule heating inspired by the pulsed current is highly localized to the particle interfaces, yielding efficient coalescence with limited energy input. In future work, we will apply this process to prepare other conductive and semiconducting ceramics.

2:50 PM

(PACRIM-S3-030-2017) Microwave sintering of nuclear ceramics: Development of a specific microwave setup and sintering tests on UO_2 pellets

J. Croquesel*[1]; S. Pillon[1]; F. Valdivieso[2]; S. Saunier[2]

1. CEA, DTEC/SECA/LFC, France
2. Ecole des Mines de Saint Etienne, France

Microwave sintering is a promising technique to bring innovative microstructures, while reducing temperature, processing time and energy consumption. This process could be used to improve nuclear ceramics sintering efficiency, reduce economic costs and to potentially improve fuels features. This paper describes the development of an instrumented and automated microwave setup qualified on fuel surrogates which allows reproducible and reliable comparison of microwave nuclear fuels experiments with those in conventional sintering. Finite elements modeling were used to design the setup and a hybrid heating technique with a specific sintering cell in a multimode furnace has been chosen to obtain uniform and controlled heating of the specimens under Ar/4%-H_2. This original setup is used first to perform sintering tests on UO_2 pellets and then on MOX fuels. The sintering results (densification behavior and microstructural evolution) will be compared with conventional sintering experiments under the same thermal conditions (sintering rate and temperature) and for higher heating rates. The results will be used to evaluate the feasibility and the advantages of the microwave sintering of nuclear ceramics and also to identify possible microwave effects on densification and sintering temperature and to look at the future development of an industrial furnace.

3:05 PM

(PACRIM-S3-031-2017) Investigation on thermal effects during the preparation of carbide by microwave heating

R. Zhang*[1]; B. Song[2]; B. Fan[2]; X. Guo[1]

1. Zhengzhou University of Aeronautics, Henan Key Laboratory of Aeronautical Material and Application Technology, China
2. Zhengzhou University, College of Material Science and Engineering, China

β-SiC crystals were synthesized by microwave sintering with coal mineral particles as raw materials, and microwave sintering was conducted in a microwave chamber with TE666 resonant mode. Heating rates were controlled by input microwave power and heating behavior during the microwave sintering was also investigated. XRD, SEM, Raman, TEM techniques were carried out to characterize β-SiC powders. It was found that different particle size of coal mineral particles showed different heating effect, leading to different growth mechanisms of powders, it might be an unique feature of microwave sintering method. Particular SiC crystals dominated for small coal mineral particles, which could be attributed to thermal effect of microwave plasma. While SiC whiskers or fibers dominated for large coal mineral particles, which was corresponded to thermal effect of microwave coupling. Coupling thermal effect prevailed for low heating rate which was prone to form particular SiC crystals. Whereas, higher heating rate enhanced microwave plasma and primarily resulted in SiC whiskers or fibers.

3:35 PM

(PACRIM-S3-032-2017) New concept aiming for high performance SiC-polycrystalline fiber (Invited)

T. Ishikawa*[1]; H. Oda[2]

1. Tokyo University of Science, Yamaguchi, Applied Chemistry, Japan
2. Ube Industries, Ltd., Japan

SiC-polycrystalline fiber (Tyranno SA, Ube Industries, Ltd.) shows very high heat-resistance and excellent mechanical properties up to very high temperatures. However, further increase in the strength is required. Up to now, we have already clarified the relationship between the strength and the defect-size of the SiC-polycrystalline fiber. The defects are formed during the conversion process from the raw material (amorphous Si-Al-C-O fiber) into SiC-polycrystalline fiber. In this conversion process, a degradation of the Si-Al-C-O fiber and a subsequent sintering of the degraded fiber proceed as well, accompanied by a release of CO gas and compositional changes, to obtain the dense SiC-polycrystalline fiber. Since these changes proceed in each filament, the strict control should be needed to minimize residual defects on the surface and in the inside of each filament for achieving the higher strength. In this paper, a new concept for reducing the residual defects will appear.

4:00 PM

(PACRIM-S3-033-2017) Controlling factors for creating dense SiC-polycrystalline fiber

R. Usukawa*[1]; H. Oda[2]; T. Ishikawa[1]

1. Tokyo University of Science, Yamaguchi, Applied Chemistry, Japan
2. Ube Industries, Ltd., Inorganic Products Development Center, Japan

Tyranno SA fiber (SiC polycrystalline fiber, Ube Industries Ltd.) shows excellent heat-resistance up to 2000°C with relatively high mechanical strength. Tyranno SA is synthesized by a conversion process from an amorphous Si-Al-C-O fiber into SiC-polycrystalline fiber. In this conversion process, a degradation reaction of the amorphous Si-Al-C-O fiber and the subsequent sintering of the degraded fiber proceed. The degradation reaction is sensitively affected by the following factors: (a) Partial pressure of SiO-gas, (b) Partial pressure of CO-gas, (c) Heating rate and degradation temperature, (d) Argon gas flow. Accordingly, to obtain the desirable crystalline structure, we have to strictly control the reaction conditions during the conversion process. In this paper, lots of changes, which occur during the degradation reaction of the amorphous Si-Al-C-O fiber and the subsequent sintering of the degraded fiber, will be described in detail, and also a new idea for obtaining the denser structure will appear.

4:15 PM

(PACRIM-S3-034-2017) Pressure-Assisted Sintering of Sulfide-Based Infrared Optical Ceramics (Invited)

Y. Wu*[1]; Y. Li[1]

1. Alfred University, Kazuo Inamori School of Engineering, USA

Due to their favorable optical performances in the infrared (IR) wavelength region, zinc sulfide (ZnS) and calcium lanthanum sulfide ($CaLa_2S_4$) are both suitable candidates for IR-transparent optical ceramics. In the present study, ZnS, $CaLa_2S_4$ and ZnS-$CaLa_2S_4$ IR optical ceramics were fabricated via pressure-assisted sintering techniques, including hot pressing and field assisted sintering. Microstructural characterization was performed to investigate the influence of different processing parameters on the grain size and morphology of these sulfide-based ceramics. The densification behavior and grain growth kinetics associated with different consolidation routes in both the pure ZnS and composite ceramics are discussed in order to shed new light on the consolidation mechanisms of sulfide-based ceramics.

4:40 PM

(PACRIM-S3-035-2017) Microstructure and mechanical properties of B_4C--TiB_2--SiC composites fabricated by reactive hot pressing from the B_4C–TiC–Si as raw materials

W. Wang*[1]; Z. Fu[1]; H. Wang[1]

1. Wuhan University of Technology, China

High-performance B_4C--TiB_2--SiC composites were fabricated with a new reaction system of B_4C–TiC–Si by reactive hot pressing. The chemical reaction processing, microstructure evolution and mechanical properties of composites were studied. The results show that The chemical reaction processing was controlled by the diffusion of boron atoms and hindered by the accumulated product layer of TiB_2 and C. The melting Si can offer another diffusion path for boron atoms, thereby promoting the reaction process. The Vickers hardness, flexural strength, and fracture toughness of the fabricated B_4C--TiB_2--SiC composites respectively reached 34--36 GPa, 650-700MPa, and 6-7MPa $m^{1/2}$. Both the intergranular fracture resulting from mismatch in thermal expansion coefficient between TiB_2 and SiC and the transgranular fracture resulting from the network structure of TiB_2 can enhance the fracture toughness of the TiB_2–SiC composite.

4:55 PM

(PACRIM-S3-036-2017) A Novel BN-MAS System Composite Ceramics with Greatly Improved Mechanical Properties Prepared by Low Temperature Hot-pressing

J. Zhang*[1]; Z. Yang[2]; Y. Xu[1]

1. Beijing Institute of Space Long March Vehicle, China
2. Institute for Advanced Ceramics, School of Materials Science and Engineering, Harbin Institute of Technology, China

A novel composite ceramics with excellent mechanical properties were fabricated by means of low temperature hot-pressing using hexagonal boron nitride (h-BN) and magnesium aluminum silicate (MAS) as raw materials. The influences of starting MAS content on the microstructural evolution and mechanical properties of the composites were investigated. The results indicate that the effective enhancement of relative density of composites has been achieved, which shows that MAS is an effective liquid-phase sintering aid during the hot-pressing. MAS also can improve the structural ordering of h-BN flakes. On the other hand, h-BN exhibits significant inhibiting effect on the crystallization of α-Cordierite. Furthermore, h-BN flakes with layered structure can play a role in strengthening the MAS matrix. So h-BN and MAS are considered to be co-enhanced by each other, resulting in better sintering ability and mechanical properties of composite ceramics are better than that of both h-BN and MAS. Composite ceramics incorporated with 50 wt.% MAS exhibits the highest bending strength and fracture toughness of 213 ± 25 MPa and 2.49 ± 0.35 MPa.m$^{1/2}$, respectively.

PACRIM Symposium 07: Porous Ceramics: Innovative Processing and Advanced Applications

High SSA Ceramics II

Room: King's 2
Session Chairs: Ulrich Vogt, Empa, Swiss Federal Laboratories for Materials Science and Technology; Jingyang Wang, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences

1:15 PM

(PACRIM-S7-020-2017) Micro-Meso Porous Alkali Bonded Ceramics (Invited)

V. Medri*[1]; E. Papa[1]; M. Mazzocchi[1]; E. Landi[1]; S. Amari[2]; J. Manaud[3]; A. Vaccari[4]

1. National Research Council of Italy, ISTEC, Italy
2. Chimie ParisTech, École Nationale Supérieure de Chimie de Paris, France
3. University of Limoges, Faculty of Sciences and Technologies of Limoges, France
4. University of Bologna, "Toso Montanari" Department of Industrial Chemistry, Italy

Alkali bonded ceramics are synthetic and amorphous alkali aluminosilicates, currently known as geopolymers. They are chemically consolidated in alkali aqueous solutions under mild thermal treatment (<100°C). At the atomic scale, SiO_4 and AlO_4 tetrahedra form Si–O–Al–O rings of various sizes in the network and endow the geopolymer matrix with ion exchange properties. The microstructure of metakaolin-based geopolymer is intrinsically meso-porous since it consists of nano-particulates, separated by pores, whose dimension can be tailored by varying the Si/Al/H_2O ratios, the alkali cation or the synthesis condition. Since alkali bonded ceramics can be regarded as the amorphous counterpart of zeolites, their application can be potentially extended in the chemical sector of molecular sieves. In this research, alkali bonded ceramics pure or added with zeolite were synthetized and characterized in term of chemico-physical properties and microstructure to optimize the process. The materials have been also tested in term of CO_2 up take, just to highlight one of the possible functional properties.

1:45 PM

(PACRIM-S7-021-2017) Capacitive properties of carbon spheres with hierarchical pore structure synthesized by hydrothermal carbonization and alkaline activation (Invited)

M. Inada*[1]; K. Hayashi[1]; J. Hojo[1]

1. Kyushu University, Japan

Electric double layer capacitor (EDLC) is attracting attention as an energy storage system. The control of pore structure in carbon electrode is important for enhancement of capacitive property. We have synthesized carbon spheres by hydrothermal carbonization of glucose and subsequent alkaline activation. The capacitive property of the carbon spheres was enhanced with an increase in meso-pore volume by alkaline activation. The hierarchical pore structure was fabricated in carbon spheres by the control of synthetic conditions, which leads to high capacitance even at high current density.

2:15 PM

(PACRIM-S7-022-2017) Designed M@SiCN ceramics for various catalytic applications (Invited)

G. Motz*[1]; R. Kempe[2]

1. University of Bayreuth, Ceramic Materials Engineering, Germany
2. University of Bayreuth, Inorganic Chemistry II, Germany

Main applications for preceramic polymers (precursors) are ceramic fibres, matrices and coatings. Especially ceramics derived from SiCN precursor have been investigated due to very interesting properties like high temperature and oxidation stability, corrosion resistance and long term durability. A further extension of the property profile like improved electrical and thermal conductivity or special catalytic activity can be expected by the introduction of different metals in the ceramic material. Usually metal-ceramic composites are produced by using porous ceramics, ceramic particles or ceramic fibers in combination with a molten metal. However, this leads to a relatively coarse microstructure. To provide for a homogeneous distribution of the metals a general molecular approach basing on simple reactions of metal (e.g. Cu, Fe, Au, Pt) complexes and polysilazanes was developed. However for using of the resulting M@SiCN ceramics as robust catalysts, an increase of the specific surface area is necessary, that most of the metal nano particles are accessible. This is possible by using e.g. defined polystyrene or polyethylene particles as both template and sacrificial filler but also by formation of polyolefine-silazane block copolymers. Subsequent pyrolysis leads to catalytic active ceramics with tailored porosity. The SiCN matrix stabilizes the metal particles and allows the use of the material as very robust catalysts.

2:45 PM

(PACRIM-S7-023-2017) Mesoporous Ceramics through Precursor Chemistry: From Design of 3D SiC, Si_3N_4 and SiCN-based Structures to Catalytic Application (Invited)

A. Lale[1]; U. B. Demirci[2]; S. Bernard*[1]

1. CNRS, France
2. University Montpellier, France

PEM fuel cell-based systems are attractive alternatives to current energy conversion technologies due to their potential to directly convert hydrogen into electrical energy. However, one of the most critical issues is the hydrogen source: it is produced from natural gas which means evolution of CO_2. Liquid-phase hydrogen carriers are more attractive alternatives but the conditions to generate hydrogen from these compounds are usually severe. For that purpose, we develop a template-assisted precursor chemistry to design carbide, carbonitride and nitride materials including monolithic ceramics and nanocomposites structures with tailored mesoporosity for the growth of platinum nanoparticles. The resulting materials are used for the catalytic generation of hydrogen from sodium borohydride in water. We report the preparation of silicon carbide and silicon carbonitride as well as silicon nitride and its titanium nitride/silicon nitride nanocomposite counterpart as mesoporous monoliths. Our main results concerning structural, textural and functionalization of these materials are reported. Their performance is discussed. Results show that nitrides are promising nanocatalysts in pursuit of practical implantation of boron- and/or nitrogen-based hydrides as a hydrogen source for fuel cells.

3:05 PM

(PACRIM-S7-024-2017) Topochemical conversions of Mn oxide nanosheets to tunnel structures: Control over 2-D and 3-D nanostructuring

T. Hey[1]; P. Metz[1]; S. T. Misture*[1]

1. Alfred University, MSE, USA

Nanosheets derived from bulk layered oxides are promising for use as supercapacitor and battery electrodes, as well as for catalysis and sorption applications. In an effort to design low-density solids with hierarchical porosity, we chemomechanically exfoliate crystalline powders to form nanosheet suspensions that can be flocculated through the addition of acids and salts. Homogeneous flocculation or gelation of the nanosheets yields thin-walled macroporous solids with surface areas exceeding ~200 square meters per gram. Intersheet ion exchange with mono-, di- and trivalent cations is possible, and controlled cation introduction with subsequent optimized heat treatments yields novel 3-D tunnel-structure (cryptomelane) MxMnO2 nanostructures. We demonstrate the use of 6 different intercalation cations and show that low levels of alkali are most useful to nucleate the topochemical conversions from layer to tunnel structures, with complete conversion possible. The structural reaction mechanism was determined using high energy X-ray scattering pair distribution function analysis.

Novel Engineering Applications of Porous Ceramics I

Room: King's 2

Session Chairs: Samuel Bernard, CNRS; Valentina Medri, National Research Council of Italy

3:45 PM

(PACRIM-S7-025-2017) Innovative Engineering Applications for Reticulated Cellular Ceramics (Invited)

U. F. Vogt*[1]; B. Fumey[1]; G. Plesch[2]; A. Fernandez[3]; A. Bonk[1]; P. Dimopoulos[4]; A. Steinfeld[5]

1. Empa, Swiss Federal Laboratories for Materials Science and Technology, Materials for Energy Conversion, Switzerland
2. Comenius University, Department of Inorganic Chemistry, Slovakia
3. Instituto de Ciencia de Materiales de Sevilla, Advanced Laboratory for the NANO-analysis of Novel FUNCtional Materials, Spain
4. Empa, Swiss Federal Laboratories for Materials Science and Technology, Automotive Powertrain Technologies Laboratory, Switzerland
5. ETH, Renewable Energy Carriers, Switzerland

Reticulated macro-porous ceramic foams are highly porous with 75–90% porosity, a open three-dimensional network structure and are well established for filters, catalyst supports and many other applications. Ceramic foams of different compositions like Al_2O_3, ZrO_2, SiC etc. can be prepared by the well established Schwartzwalder replica method. The pore size can vary from 10 to 100 ppi, corresponding to pore diameters between 4500 and 500 µm. To improve the mechanical stability, pre-sintered foams can be re-impregnated with ceramic slurry to fill up the hollow struts, followed by a second sintering cycle. The presentation will give an overview on developments for numerous applications. In Thermo-Photo-Voltaics (TPV), foams are used to convert radiation into electricity by using commercial silicon photocells, applied to Yb_2O_3 based foam ceramics at 1800 K. The purification of water from organic pollutants by a photocatalytic process could be verified by a TiO_2 thick film coated Al_2O_3 foam substrate. For hydrogen based cooking and room heating a novel catalytic diffusion burner based on highly porous Pt coated SiC ceramics could be realised. The Pt catalyst was demonstrated to be highly active even below room temperature. H_2 and CO (Syngas) can be synthesized from H_2O and CO_2 by a solar-thermochemical driven RedOx reaction on CeO_2 ceramics. Detailed results of the different applications will be presented.

4:15 PM

(PACRIM-S7-026-2017) Application of porous carbon material for heat shield of re-entry capsule (Invited)

Y. Kubota*[1]; R. Inoue[2]; Y. Kogo[2]; T. Aoki[1]; Y. Ishida[1]; T. Ogasawara[3]

1. Japan Aerospace Exploration Agency, Structures and Advanced Composite Research Unit, Japan
2. Tokyo University of Science, Department of Materials Science and Technology, Japan
3. Tokyo University of Agriculture and Technology, Departmenta of Mechanical System Engineering, Japan

Porous carbon materials have had a great potential in the aerospace field because of low density and good thermal properties. We focused on these properties so as to develop a new ablator. An ablator is a heat shield material applied for a thermal protection system of re-entry capsule, and protects the inside of capsule from re-entry severe environments by its chemical and physical consumption. An ablator is basically fabricated by infiltrating a resin to a preform. A lightweight ablator, which means the ablator having lower density than 0.5 g/cm^3, uses a preform consisted of carbon fibers bound by a little pyrolyzed carbon. Although the carbon-fiber-based-preform shows enough low density and good thermal insulation property, the ablator using this perform shows high surface recession. This recession imposes a limitation of re-entry conditions of a capsule. Our motivation was to develop a lightweight ablator showing high recession resistance. The new lightweight ablator was fabricated from a porous carbon having three-dimensional network and open cell structure. Their performance was evaluated by using an arc wind tunnel. Microstructural observations revealed that the three-dimensional network structure of the ablator was maintained after the heating tests. Consequently, the recession resistance was better than those of existing ablators fabricated from carbon fiber based preform.

4:45 PM

(PACRIM-S7-027-2017) Optimal nanostability of super thermal insulation materials (Invited)

J. Wang*[1]

1. Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, High-performance Ceramics Division, China

The critical challenge of current nanoscale oxide super thermal insulation materials, such as SiO_2 and Al_2O_3 nano-particle aggregates and their composites, is the trade-off between extremely low thermal conductivity and unsatisfied thermal stability (nanostability typically below 1100 °C). It is crucial important to modify current materials and further discover novel candidates which could balance the two key properties. This presentation shows progresses on optimal thermal stability of modified Al_2O_3 nano-paticle aggregate; and in addition, new thermal insulation candidates, such as nano-Si_3N_4 and nano-SiC, which originally have very high lattice thermal conductivity. Especially, porous nano-SiC exhibits good thermal stability up to 1500 °C and very low thermal conductivity as well. The interesting properties originate from an integration of the superior thermal stability of SiC and multiple phonon-scattering mechanisms in nano-scale. This work provides a novel idea to approach ultra-low thermal conductivity through morphology engineering on structural ceramics with excellent thermal stability, regardless their high intrinsic lattice thermal conductivities.

5:05 PM

(PACRIM-S7-028-2017) Fabrication and characterization of HA/BT piezoelectric biocomposites with aligned porous structures

K. Zhou*[1]; F. Xue[1]; D. Zhang[1]

1. Central South University, State Key Laboratory of Powder Metallurgy, China

In order to mimic the piezoelectric properties of the collagen in bone and explore a novel way to improve the self-healing ability of the bone, a piezoelectric phase BaTiO3 is incorporated into the HA ceramics matrix. In addition, unidirectionally oriented lamellar porous scaffolds was obtained via an ice-templating method, which can overcome the drawbacks of dense bioceramics and isotropic porous scaffolds in the applications of bone repair and replacement, i.e. low efficiency, weak mechanical strength and poor biomimetic functionality. By exploring the control mechanism of the microstructures, designing the suspension's constituents, investigating the rheological properties and precisely controlling the freezing conditions, the scaffolds with controllable microstructures and improved mechanical strength can be obtained. The effects of contents and grain sizes of both phases on the sintering behavior, mechanical and piezoelectric properties of the HA/BaTiO3 composites are investigated. The project will define the feasibility and establish the theoretical foundation in preparing aligned porous piezo-active composites with good biocompatibility, excellent mechanical and piezoelectric properties, which are significant to broaden the clinical applications of porous bioceramics.

PACRIM Symposium 11: Engineering Ceramics: Processing and Characterizations

Thermal Properties

Room: King's 1
Session Chairs: You Zhou, National Institute of Advanced Industrial Science and Technology (AIST); Young-Wook Kim, University of Seoul

1:15 PM

(PACRIM-S11-021-2017) High Thermal Conductivity Silicon Nitride Substrates for Power Device Application (Invited)

Y. Zhou*[1]; H. Hyuga[1]; H. Miyazaki[1]; D. Kusano[2]; K. Hirao[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan
2. Japan Fine Ceramics Co. Ltd., Japan

Silicon nitride ceramics were prepared by a sintering of reaction-bonded silicon nitride (SRBSN) process using a high purity silicon powder as the starting material. The ceramics possessed higher thermal conductivity than the silicon nitride ceramics prepared by the conventional gas pressure sintering of silicon nitride powder. The improvement of thermal conductivity was attributed to the lower content of oxygen impurity dissolved in the lattice of Si_3N_4 grains. In addition to high thermal conductivity, the SRBSN ceramics had superior fracture toughness property. Thermal fatigue tests of active metal brazing substrates made of the SRBSN plates were carried out between -40 and 250 °C, and the results showed degradation of flexural strength of the SRBSN plates was very limited even after being treated for 1000 thermal cycles. SRBSN ceramics with both high thermal conductivity and good mechanical properties should be promising substrate materials for the next generation of high-power electronic devices. This work was supported by Council for Science, Technology and Innovation(CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "Next-generation power electronics/Consistent R&D of next-generation SiC power electronics" (funding agency: NEDO).

1:45 PM

(PACRIM-S11-022-2017) Factors Affecting Thermal Conductivity of Silicon Carbide Ceramics (Invited)

Y. Kim*[1]; S. Jang[1]; T. Cho[1]

1. University of Seoul, Dept. of Materials Science & Engineering, Republic of Korea

Silicon carbide is an important structural material due to its excellent thermal conductivity, wear resistance, corrosion resistance, and mechanical properties. Various industrial applications of SiC ceramics such as substrate materials for semiconductor devices, heaters, heater plates, focus rings, and dummy wafers for semiconductor processing, capsule materials for nuclear fuel, gas seal rings in compressor pump, take advantage of its excellent thermal conductivity as well as its other properties. However, there was no systematic research on the factors affecting thermal conductivity of liquid-phase sintered SiC (LPS-SiC) ceramics. The purpose of this research is to investigate the effects of oxygen impurity, phase transformation, and grain growth on thermal conductivity of LPS-SiC ceramics. The effect of sintering atmosphere on the thermal conductivity of SiC ceramics was also investigated. Major conclusions are as follows: (1) the thermal conductivity of LPS-SiC ceramics increased with an increase in grain size of SiC grains if there is no $\beta \rightarrow \alpha$ phase transformation of SiC; (2) the occurrence of the $\beta \rightarrow \alpha$ phase transformation of SiC decreased thermal conductivity; and (3) oxygen-doping in SiC lattice was detrimental in improving thermal conductivity of LPS-SiC ceramics.

2:15 PM

(PACRIM-S11-023-2017) Influence of Silicon Powder Characteristics on Microstructure and Thermal Conductivity of GPSed Reaction Bonded Silicon Nitride

J. Ko*[1]; M. Kim[1]; H. Kim[1]; J. Kim[1]; Y. Park[1]

1. KIMS (Korea Institute of Materials Science), Republic of Korea

Recently, the value of Reaction Bonded Silicon Nitride (RBSN) ceramics is estimated again due to many advantages such as low cost fabrication, small shrinkage during nitridation and post sintering. In this study, the influence of raw powder characteristics on microstructure and thermal conductivity of Gas Pressure Sintered Reaction Bonded Silicon Nitride (GPSed RBSN) mixed with sintering additive was investigated. Si powders from different source were prepared with different particle size and oxygen content. The nitridation of Si compacts and post sintering by GPS were carried out at given temperatures. The microstructure of the GPSed RBSN samples is composed of large elongated grains and small grain matrix. The high thermal conductivity of GPSed RBSN can be attributed to its relatively small amount of grain boundary phase during post sintering. It is understood that the choice of raw Si powder for RBSN should be carefully made since the nitridation rate, final microstructures and mechanical properties.

2:30 PM

(PACRIM-S11-024-2017) Mechanical and Thermal Properties of Pressureless Sintered Silicon Nitride Containing β-Si_3N_4 Seeds

H. Yeom*[1]; Y. Kim[1]

1. Functional Ceramics Laboratory, Department of Materials Science and Engineering, Republic of Korea

When a small amount of β-Si_3N_4 seed particles is added during the preparation of Si_3N_4 ceramics, a bimodal microstructure is obtained by pressureless sintering at 1780°C. The effects of β-Si_3N_4 seed content on microstructure, mechanical, and thermal properties of the pressureless sintered Si_3N_4 ceramics were investigated. The microstructure, flexural strength, fracture toughness, hardness, and thermal conductivity values of the Si_3N_4 ceramics with β-Si_3N_4 seeds and 8 wt% sintering additives will be presented and compared with those without β-Si_3N_4 seeds. The relationship between microstructure and thermal conductivity will be discussed in this presentation.

Typical flexural strength and fracture toughness values of pressureless sintered Si_3N_4 ceramics without seeds were ~900 MPa and ~8 MPa $m^{1/2}$, respectively.

2:45 PM

(PACRIM-S11-025-2017) Theoretical and Experimental Analyses of Young's Modulus and Thermal Expansion Coefficient of the Alumina-Mullite System

Y. Hirata[1]; S. Itoh[1]; T. Shimonosono[1]; S. Sameshima*[1]

1. Kagoshima University, Department of Chemistry, Biotechnology, and Chemical Engineering, Japan

Young's moduli (E) and thermal expansion coefficients (TECs) of the alumina–mullite–pore system (96.4%–99.5% relative density) were measured for a wide mullite fraction range from 0 to 100 vol%. Both E and TEC values decreased at high mullite fractions. These properties were theoretically analyzed with four proposed model structures that were constructed by three-phase systems of mullite (or alumina) continuous phase 2–pore dispersed phase 1–alumina (or mullite) dispersed phase 3. The ratios of E(theoretical)/E(experimental) and TEC(theoretical)/TEC(experimental) were very close to unity, depending on the mullite fraction. That is, the measured E and TEC values are closely related to the change in the composite microstructure as a function of mullite fraction.

3:00 PM

(PACRIM-S11-026-2017) Influence of iron on crystallization behavior and thermal stability of the insulating materials - porous calcium silicates

S. Haastrup*[1]; D. Yu[1]; Y. Yue[1]

1. Aalborg University, Chemistry and Bioscience, Denmark

The properties of porous calcium silicate for high temperature insulation are strongly influenced by impurities. In this work we determine the influence of Fe^{3+} on the crystallization behavior and thermal stability of hydrothermally derived calcium silicate. We synthesize porous calcium silicate with Ca/Si molar ratio of 1, to which Fe_2O_3 is added with Fe/Si molar ratios of 0.1, 0.5, 0.7, 1.0, and 1.3%. Structure and morphology of the porous calcium silicate, with different iron concentrations, are investigated using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). FTIR measurements reveal a pronounced decrease in the number of Q^3 sites in the calcium silicate with an increase of Fe^{3+}, and thereby lower the crystal fraction of xonotlite ($Ca_6Si_6O_{17}(OH)_2$) phase, and increase the crystal fractions of tobermorite($Ca_5Si_6O_{16}(OH)_2 \bullet 4H_2O$) and calcite ($CaCO_3$) phases, as confirmed by XRD analysis. The thermal stability and compressive strength of the calcium silicates are seriously influenced by the changes of their crystal structure. Linear shrinkage of the reference sample is 1.3% at 1050°C, whereas the sample with Fe/Si =1.0% does by 30.4%. In conclusion, the presence of Fe^{3+} modifies the crystal structure of porous calcium silicates, leading to a significant shrinkage in these materials.

3:15 PM

(PACRIM-S11-027-2017) Development of mold slag for controlling heat transfer by scattering behavior of iron particles in $CaO\text{-}SiO_2\text{-}B_2O_3$ glasses

D. Yoon*[1]; J. Cho[2]; S. Kim[1]

1. Pohang University of Science and Technology(POSTECH), Materials Science and Engineering, Republic of Korea
2. Pohang University of Science and Technology(POSTECH), Graduate Institute of Ferrous Technology, Republic of Korea

To alleviate surface defects on the slab in continuous casting of steel, it is urgently required to moderate heat flux across mold slag film between mold and strand. Many researchers suggested that increasing crystallization of slag could decrease heat flux by larger interfacial thermal resistance and low transmittance of radiation. However, high basicity mold slag might cause different type of defects such as streak mark or sticker breakout by poor lubrication. This study focuses on regulating heat transfer through mold slag layer with scattering effects by using micro-sized iron particles onto borosilicate glasses. The heat flux of designed glass system has been investigated by infrared emitter technique (IET). Also, the extinction coefficient was measured for glassy slag film using a UV and FT-IR spectrometer. For verifying scattering effects of iron particles on extinction coefficient, the number density and size of particles have been examined by scanning electron microscope (SEM). The scattering coefficient was calculated by Mie scattering theory. It was confirmed that Mie scattering coefficient is reproduced about 1,600-3,300m^{-1} comparing with experimental value of 1,700-3,700m^{-1}. Therefore, scattering behaviors of particles in mold slag could control heat transfer across glassy slag film without any detrimental effects on friction in casting process.

Applications and Nanotechnology

Room: King's 1
Session Chairs: Abhaya Bakshi, Morgan Advanced Materials;
Hagen Klemm, FhG IKTS Dresden

3:45 PM

(PACRIM-S11-028-2017) Improvement of hydrothermal corrosion resistance of SiC fibers for CVI-SiC/SiC composites (Invited)

S. Suyama*[1]; M. Ukai[1]; M. Uchihashi[1]; K. Kakiuchi[1]; H. Heki[1]

1. Toshiba Corporation, Japan

Recently, SiC/SiC composites have become one of the candidates for structural materials used in accident tolerant fuel systems. We have started optimizing the design of SiC/SiC composites for use in hydrothermal environments. In this study, candidate SiC fibers for CVI-SiC/SiC composites were examined in pure water at operating conditions such as 300°C and 8 MPa and 16 MPa to determine the optimal SiC fibers for preventing or minimizing hydrothermal corrosion of CVI-SiC/SiC composites. Uncoated SiC fibers were degraded by hydrothermal corrosion in 300°C water from a very early stage. It was found that dissolved oxygen in the water accelerated corrosion. To protect the SiC fiber from hydrothermal corrosion, a dense carbon coating on the entire surface of the SiC fiber was found to be necessary.

4:15 PM

(PACRIM-S11-029-2017) High dielectric strength ceramic for power tubes (Invited)

A. K. Bakshi*[1]; M. Habermann[1]; C. Lee[1]

1. Morgan Advanced Materials, USA

Alumina ceramics are widely used in high power vacuum tubes, which can be found in X-Rays, lasers, SEMs, microwaves, etc. Many of these devices are progressively operating at higher voltages with smaller designs. This requires the alumina to have high dielectric strength to prevent voltage breakdown during operation. They also require mechanisms to dissipate secondary electrons and charge accumulation on the outer surface to avoid arcing. In many applications, where AC current is used to power the system, the ceramic needs to have lower loss tangent to prevent overheating. In this article, we will discuss the influence of ceramic microstructure, surface morphology, and grain boundary chemistry on the electrical properties of alumina power tubes.

4:45 PM

(PACRIM-S11-030-2017) TiO_2 photocatalytic nanofilms: After design, what are the issues to consider towards their successful application in the building sector?

E. I. Cedillo-González*[1]; C. Mugoni[2]; C. Siligardi[2]

1. Universidad Autonoma de Nuevo Leon, Facultad de Ciencias Quimicas, Mexico
2. Università degli Studi di Modena e Reggio Emilia, Dipartimento di Ingegneria "Enzo Ferrari", Italy

Since the discover of the photo-splitting of H_2O in a TiO_2 anode photochemical cell in 1972, the field of photocatalysis has constantly grown. The BCC AVM069B report states that the total market for photocatalyst products is forecast to grow in the next 5 years and is estimated to be valued ≈ $2.9 billion by 2020. TiO_2 is the most studied photocatalyst and TiO_2 nanofilms are used to develop self-cleaning building materials. Despite of the excellent performance, their application in this sector is still limited due to practical issues. This work was focused in some of them: poor film-substrate adhesion; deactivation; weathering and influence of atmospheric variables in the photocatalytic performance. Some issues were successfully investigated by the Design of Experiments approach. Experiments were conducted by using 3 nanofilms (nanoparticulated, dense and mesoporous) in different conditions (as-prepared, chemical treated, at different climatic conditions). Adhesion was increased by varying the roughness of the substrates, and chemical treatments avoided deactivation. All films show good photocatalytic performance that strongly depends of the environment of exposition. It was concluded that all the studied TiO_2 nanofilms are efficient and they can be successfully used in the building sector in function of the environment of exposition.

5:00 PM

(PACRIM-S11-031-2017) An ancient nanotechnology in ceramic and its application in today

F. Wang*[1]; P. Shi[1]

1. Shaanxi University of Science & Technology, China

The chemical compositions and microstructures of the Jun ware, Ru ware and Yaozhou ware were investigated in this work. And the complicated separation structures, such as lamellar, aggregate, interconnected, discrete droplet, droplet around the interconnected and droplet aggregate were found. The formation mechanism of separation structures and the types of structural colors were analyzed and verfied by the archaeological experimental method. Based on these studies, the ceramic glazes derived from industrial slag were prepared. The results indicated that in ancient separative-phase glazes, most of them conformed to the structural color of photonic crystal rather than the mentioned opalescence blue. While in the white ware or other wares, due to the low refractive indices difference and few separation structures, the structural color was very light, which could be clearly strengthened through double heating treatment. In addition, if the glaze contained some coloring elements and impurity elements, which were always detected in the microphase, causing the difference of refractive indices increased. Meanwhile, due to the increased colorant concentration in the microphase, like the crystal flower, spots and stripes patterns etc. appeared in the glaze, or the monochrome glaze with high color saturation was obtained. By using this technique, some kinds of art glazes were prepared with industrial slag.

5:15 PM

(PACRIM-S11-032-2017) Doped $BaTiO_3$ 1D-nanostructures prepared by template-mediated colloidal chemistry

A. Ianculescu*[1]; C. A. Stanciu[1]; B. Vasile[1]; R. Trusca[1]; M. Cernea[2]; L. Trupina[2]; A. Nicoara[1]

1. Politehnica University Bucharest, Romania
2. National Institute of Materials Physics, Romania

In the present study, the preparation by template-mediated colloidal chemistry, as well as the characteristics of Ce^{3+}-doped $BaTiO_3$ nanotubes and nanowires with the nominal formula $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ were described. Porous polycarbonate membranes with channels diameter of 100 nm and 200 nm, respectively, were used as templates. The precursor sol was deposited on both membranes by spin coating. The uncalcined nanotubes obtained by using as template the membrane with channels diameter of 100nm show an average outer diameter of about 86nm and an average wall thickness of 9nm, while, the uncalcined nanoshell tubes obtained by using the membrane with channels diameter of 200nm show an average outer diameter and wall thickness of 186nm and 12nm. Crystalline Ce-doped $BaTiO_3$ nanoshell tubes obtained after thermal treatment in air, at 700°C/1h, exhibit a mean outer diameter of 157nm, higher porosity and larger grains consisting of larger crystallites than the nanotubes with a mean outer diameter of 77nm, which show grain size and crystallites smaller. Uniform, uncalcined wires with diameter of about 81nm were produced by the same method. After calcination in similar conditions the amorphous 1D-structures were converted into crystalline nanowires. PFM investigations indicated ferroelectric and piezoelectric characteristics for all the $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ nanotubes/nanowires prepared in this study.

5:30 PM

(PACRIM-S11-033-2017) Preparation and characterization of copper silica-based nanocomposites

M. Dulski*[1]; J. Peszke[1]; A. Nowak[1]; K. Balin[1]; S. Sulowicz[1]; Z. Piotrowska-Seget[1]; B. Nowak[1]; A. Mrozek-Wilczkiewicz[1]; K. Malarz[1]; M. Wojtyniak[1]; J. Szade[1]

1. University of Silesia, Poland

The metal ions in nano-size form arouse great curiosity from many years but their application has certain limitations due to potentially easy leaching and aggregating in the environment. This process can be stopped by combination of nanoparticles in inorganic matrix preserving cytotoxic features and realising gradually into the environment for long time at relatively low metal concentration. We choosed for investigations copper nanostructures which in bulk or agglomerated form is extremely troublesome to the environment. We prepared copper nanoparticles and combined them with silica matrix. In addition, hydrophilic and hydrophobic SiO_2 applied. Such systems investigated using physicochemical methods (XRD, Raman, SEM+EDX, XPS, TEM) and biological studies (microorganism, fibroblast) for non- and thermal treated conditions to check stability of systems and determine their features. Preliminary studies indicated mono-dispersed metallic ions in the matrix with size of Cu nanoparticles ~12 nm for hydrophobic and ~4 nm for hydrophilic system. Structural data showed amorphous silica (RT) and crystalline phase above 900oC. XPS showed metallic copper while Raman spectroscopy presence of Cu_2O and CuO. During the heating above 900oC observed lack of copper ions in the matrix. Biological tests highlighted the inhibition growth of bacteria and fungi whereas fibroblast data lack of impact for the human cells, in general.

5:45 PM

(PACRIM-S11-034-2017) Correlations between processing routes, microstructure developments and properties of bulk polycrystalline 'ceramic alloys' and nanocomposites

A. Mukhopadhyay*[1]; L. Gurnani[1]; M. K. Satam[1]

1. Indian Institute of Technology (IIT) Bombay, Metallurgical Engineering and Materials Science, India

Despite ceramic nanocomposites possessing improved mechanical/tribological properties compared to corresponding monoliths and composites having coarser microstructure, processing challenges associated with handling/dispersion of nanosized particles/fibers and requirements of advanced sintering techniques (usually with inert/reducing atmosphere) have severely hindered their commercial take-up. Additionally, nanocomposites developed via physical mixing of starting powders, followed by sintering, lead to the presence of deleterious/coarse second phase fibers/particles, primarily at the matrix grain boundaries. Against these backdrops, recent developments of bulk polycrystalline 'ceramic alloys', via facile solid-state precipitation route (in air), resulting in achieving 'near-ideal' microstructures characterized by uniformly dispersed nanosized inter/intragranular coherent second phase particles, will be presented. Following this, successful development of carbon nanotube (MWCNT) reinforced bulk polycrystalline ceramics, with the reinforcing MWCNTs present uniformly within the sintered matrix grains (i.e., intragranular reinforcements), as achieved for the first time using an innovative processing route (sans ball-milling) will be discussed. Such microstructure-type led to improvements in wear resistance; as possibly not achieved before.

PACRIM Symposium 17: Advanced Functional Ceramics and Critical Materials Perspective

Advanced Functional Ceramics and Critical Materials Perspective_3

Room: Kohala 2

Session Chairs: Junichi Hojo, Kyushu University; Yamato Hayashi, Tohoku University; Kenji Toda, Niigat University

1:15 PM

(PACRIM-S17-021-2017) Fabrication and electromagnetic property of Fe/SiC hybrid fiber (Invited)

Y. Zhang*[1]; Y. Hou[1]; Q. Chen[1]

1. Northwestern Polytechical University, Materials Science, China

Fe/SiC hybrid fibers with different iron content were fabricated by electrospinning and high temperature pyrolysis. The hybrid fiber shows a muti-scale structure with nanoscale amorphous nanowire grown on the surface of microscale Fe/SiC fiber when pyrolyzed at 1300 ºC. The doping of iron element dramatically enhances the crystallization degree of the SiC and eliminates the existence of free carbon, which closely infect the EM parameters (permittivity and permeability) of the hybrid fiber. The hybrid fiber shows a typical soft magnetic properties with coercivity around 30 Oe and saturation magnetization between 12.2 to 45.8 emu/g. The minimum reflection loss of the hybrid fiber reaches -41.86 dB at the frequency of 6.4 GHz. The hybrid fiber prepared in this paper presents good microwave absorbing property in a relatively low frequency between 2-8 GHz compared with SiC fiber. The hybrid fiber could also realize frequency selective absorbing by manipulating the doping content of iron.

1:35 PM

(PACRIM-S17-022-2017) Fabrication and Application of Ag Nanowire Flexible Transparent Conductive films by Organic Precursor Painting Reduction Method (Invited)

Y. Hayashi*[1]

1. Tohoku University, Appl. Chem, Japan

Ag nanowire transparent conductive film, which is prepared by depositing Ag nanowires onto a substrate, shows both high optical transparency and high electrical conductivity. Ag nanowire flexible transparent conductive film coated onto flexible polymer substrate shows good bending tolerance, it can be used in flexible devices, such as flexible display, lighting equipment, and so on. In general, it is necessary to apply Ag nanowires to complicated high temperature and high pressure annealing process to make connections among wires when transparent conductive film is prepared. Consequently, the overall process requires high cost and emits much waste. To improve these problems, a new method, painting and subsequent reduction of organic precursor, is proposed in this study. In this method, needle-shaped organic precursor is used as a self-template, and then Ag nanowire is simply obtained by reducing them to metallic Ag with retaining their needle-shaped morphology. By optimizing synthetic and reducing conditions of the precursor, preparation of highly transparent and conductive Ag nanowire flexible transparent conductive film could be expected easily. This method can synthesize silver nanowires and fabricate the transparent conductive film simultaneously, in low cost and high throughput.

1:55 PM

(PACRIM-S17-023-2017) Thermal Conductivity and Electromagnetic Property of Dual-functional Sheet Composed of Ceramic Coated Fe-alloy Powders and Silicone Polymer

H. Choi*[1]; K. Lee[2]; S. Suh[1]

1. SungKyunKwan University, Material Science and Engineering, Republic of Korea
2. Nopion Corporation, R&D Center, Republic of Korea

As electronic devices become thinner and multi-functional, heat dissipation and EMI (Electro Magnetic Interference) related problems became more serious for device functionality. So, the higher performance materials to solve the thermal and EMI problems simultaneously are strongly requested in image transferring devices and high power wireless telecommunication systems in particular. Dual-functional sheets which have EMI absorbing and thermal conducting property have been reported before. But, because these materials are generally containing Fe based metal alloy powders, these materials have low dielectric breakdown voltage. And also low thermal conductivity of these sheets, 1.0~1.5 W/mK, is not enough for commercial use. We solved these problems with designing core-shell structured powders and sophisticated powder blending technology based on Horsfield's packing model. Al_2O_3 powders of 0.2 μm size (D_{50}) were coated on Fe-Cr, Fe-Si powders of 50 μm and 10 μm by high speed super mixer, repectively. By tape casting process after blending core-shell structured powders and silicone polymer, dual-functional sheets which have thermal conductivity of 3.1 W/mK and dielectric breakdown voltage of 3 kV could be achieved with power loss of 34% at 1 GHz. These properties are sufficient for commercialization in the high power electronic applications.

2:10 PM

(PACRIM-S17-024-2017) Observation of Abnormal Ionic Diffusion for the water assisted room temperature solid state reaction under 400 K

K. Toda*[1]; S. Kim[1]; K. Uematsu[1]; M. Sato[1]

1. Niigata University, Japan

Ionic-diffusion in ionic crystal is very slow at room temperature. Therefore, the solid-state reaction method requires a high temperature to synthesize the ceramic materials with a single-phase form. The synthesis at a high temperature leads to increase in the processing cost and irregular particle morphology of the obtained powders. In contrast, we have recently proposed the water assisted solid state reaction (WASSR) method. Using the WASSR method, many ceramics can be synthesized under 400 K just by mixing of the raw materials. The addition of water is significantly important to proceed the reaction between the raw materials and water act as a reaction accelerator. The water phase formed on the surfaces of the raw material powder generated the nanocrystallites at the contact points between raw material particles. Consequently, we can successfully synthesized many nano-sized ceramic materials, such as YVO_4, $SrMoO_4$, $BaTiO_3$, and $NaEuMo_2O_8$. In this study, we present the characteristic and availability of our proposed WASSR technique on an industrial application for ceramic materials synthesis processing.

2:25 PM

(PACRIM-S17-025-2017) Structural and Magnetic Properties of Polymorphic Nickel Titanate Nanofibers

S. K. Balakrishnamurthy*[1]; V. C. Gudla[2]; R. Ambat[2]; S. K. Kalpathy[3]; S. Anandhan[1]

1. National Institute of Technology Karnataka, Metallurgical and Materials Engineering, India
2. Technical University of Denmark, Produktionstorvet, Mechanical Engineering, Denmark
3. Indian Institute of Technology Madras, Metallurgical and Materials Engineering, India

Nickel titanate (NTO) ceramic nanofibers were synthesized from pyrolysis of sol-gel assisted precursor electrospun nanofibers at three different temperatures, i.e. 773, 973, and 1173 K. X-ray diffraction pattern revealed the presence of both ilmenite and defective spinel polymorphs of NTO. The percentage of spinel polymorph of NTO decreased from 44 to 37% approximately with the increase in pyrolysis temperature. In this study, an attempt has been made to analyze the effect of defective spinel NTO (space group Fd-3m) on the magnetic, optical and structural properties of the composite nanofibers exhibiting polymorphism. The anisotropic distribution of the spinel NTO along the nanofibers was analyzed using surface enhanced Raman imaging technique to study the evolution of defective NTO nanofibers. Electron energy loss spectroscopy and x-ray photoelectron spectroscopy were used to confirm and understand the formation of Ni-rich spinel NTO.

2:40 PM

(PACRIM-S17-026-2017) Various Factors on Dye-Sensitized Solar Cells of Mesoporous Titania-Based Electrodes by Sol-Gel Processes (Invited)

J. Hojo*[1]; M. Inada[1]

1. Kyushu University, Faculty of Engineering, Japan

Dye-sensitized solar cells have received an attention because of high photoenergy conversion, facile preparation and low cost. Titania electrodes have been typically used. The photoelectrode requires large surface area for dye adsorption, high crystallinity for electron transfer and large pore for electrolyte diffusion. We have synthesized mesoporous titania microspheres by sol-gel method, and the effects of hydrothermal treatment, silica addition and calcination were investigated. Mesoporous microspheres of anatase nanoparticles were synthesized by hydrolysis of titanium butoxide. Titania aggregates were formed by hydrothermal treatment of microspheres, leading to increase in crystallite size, pore size and photovoltaic efficiency, but the surface area decreased. Mesoporous titania-silica composites were prepared by hydrolysis of titanium oxychloride and silicon ethoxide. Rutile phase formed without silica addition, whereas anatase phase was stabilized by silica addition, crystallite size decreased and surface area increased, leading to increase in photovoltaic efficiency. However, the cell efficiency decreased at large silica contents. Titania-silica composites were calcined to improve the crystallinity, but the cell efficiency decreased owing to decreased surface area by particle growth. The optimal electrode structure will be totally discussed.

3:00 PM

(PACRIM-S17-027-2017) Microstructural Design and Dielectric Properties of Conductor/Insulator Nanocomposite Materials (Invited)

S. Ueno*[1]; Y. Hattori[1]; H. Kakiuchi[1]; S. Wada[1]

1. University of Yamanashi, Japan

A development of high-dielectric-constant ceramics has been required for miniaturization of electronic devices and applications to energy storage, and conductor/insulator nanocomposite is one of the candidates for such capacitor materials. We focus on the boundary layer (BL) microstructure which commonly consist of conductor grains and insulated thin grain-boundary layers and exhibit high dielectric constant. First, metal/insulator nanocomposite ceramics, Ti/$BaTiO_3$, were successfully prepared by the hydrothermal process (below 300 °C) from nanostructure-controlled Ti (core)-$BaTiO_3$ (shell) particles to avoid oxidization of basic metals. The resultant Ti/$BaTiO_3$ composites exhibited the high dielectric constant over 10000, and their dielectric properties depend largely on the thickness of $BaTiO_3$ boundary (shell) layers. However, as the dielectric breakdown strength is still lower for practical applications. It can be improved by the nanostructure modification, but one of the critical reasons is a grain boundary between the $BaTiO_3$ nanoparticles in the shell which is possible to provide electric paths. Thus, we employed conductive perovskite oxides, $LaNiO_3$ and $SrRuO_3$ enclosed by crystal facets, as core materials and tried to fabricate conductor/insulator perovskite composite ceramics with epitaxial boundary layers by the wet chemical approach using the sol-gel route.

3:35 PM

(PACRIM-S17-028-2017) Preparation and characterization of textured $0.99(K_{0.5}Na_{0.5})_{0.95}Li_{0.05}Nb_{0.93}Sb_{0.07}O_3$-$0.01CaZrO_3$ ceramics by templated grain growth

B. Liu*[1]

1. Tongji University, School of Materials Science and Engineering, China

In this study, <00l>-textured $0.99(K_{0.5}Na_{0.5})_{0.95}Li_{0.05}Nb_{0.93}Sb_{0.07}O_3$-$0.01CaZrO_3$ [abbreviated as 0.99KNLNS-0.01CZ] lead-free ceramics are prepared by template grain growth (TGG) method using 3 mol% $NaNbO_3$ template and sintered by two-step sintering method with different soaking time. Through the analysis of X-ray patterns, all textured samples with high Lotgering factor (> 0.8) are orthorhombic-tetragonal phase. Large piezoelectric constant d_{33} (~ 300-310 pC/N) are obtained in the textured samples with 12 h heat preservation which is almost twice as increase compared with the random one, and field-induced strain (d_{33}^* ~ 440 pm/V) with good temperature stability of the textured ceramic with 6 h soaking time is larger than the random one (~ 297.5 pm/V). These results show that TGG is a very effective way to fabricate high oriented ceramics and improve the electrical properties.

3:50 PM

(PACRIM-S17-029-2017) Catalytic Combustion-type Carbon Monoxide Gas Sensor Applying Platinum-loaded Oxide Ion Conducting Solids (Invited)

N. Imanaka*[1]

1. Osaka University, Applied Chemistry, Japan

One of the great demerits in the case for conventional catalytic combustion-type CO gas sensors (such as Pt loaded Al_2O_3 or Pd loaded Al_2O_3) is that they need relatively high operating temperatures higher than 400 degree C for the complete CO gas oxidation. Because other gases such as methane and volatile organic compounds (VOCs) also burn at such elevated temperatures, this type of sensors lacks in selectivity. Recently, we have succeeded in developing new type of catalytic combustion-type gas sensor showing appreciably low-temperature operable characterstics by using 10 wt% Pt loaded $Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}$ composite as the catalyst and they sucessfully demonstrated their operation at 70 degree C, which is more than 300 degree C below compared with the above introduced conventional ones. Furthermore, by the combination of the superior thermoelectric material of aluminum nitride (AlN)) ceramics powder as an intermediate layer with the Pt loaded $Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}$ composite, a novel catalytic combustion-type CO gas sensor was realized, with an superior sensing performance that drastically accelerated the senser response at the operating temperature of 70 degree C.

4:10 PM

(PACRIM-S17-030-2017) Liquid gigahertz viscosity sensors using shear mode c-axis tilted ScAlN piezoelectric thin films

Y. Yamakawa*[1]; R. Karasawa[1]; T. Mori[2]; K. Sano[1]; M. Suzuki[1]; T. Yanagitani[3]

1. Waseda University, Japan
2. Nagoya Institute of Technology, Japan
3. Waseda University, JST PRESTO, Japan

In the ultrasonic viscosity sensors, shear wave excitation is required because the usual longitudinal wave energy leaks into the liquid. We have recently reported new large shear wave piezoelectricity in the c-axis tilted ScAlN films. The quasi-shear mode electromechanical coupling k'_{15} of the ScAlN reaches maximum at c-axis tilted angle of around 30°, which is approximately 320 % as much as the maximum k'_{15} of pure AlN. In this study, by using the 60° oblique angle sputtering grown, we fabricated the resonator type viscosity sensor consisting of the c-axis tilted ScAlN film (7000 nm) on AT-cut quartz crystal plate (0.5 mm). The extremely temperature stable thick AT-cut quartz plate enables robust measurement against the external temperature change. The resonant frequency of the sensor decreases due to the increase of the viscous penetration depth between the liquid and the resonator interface. Then the change of liquid viscosity can be determined by this frequency shift. We observed strong shear wave excitation by using a network analyzer in the air. When reverse side of the sensor was immersed in the glycerine solution, resonant frequency decreased with increasing the glycerine concentration. This experimental frequency shift show good agreement with the theoritical prediction by equivalent circuit model.

4:25 PM

(PACRIM-S17-031-2017) Divalent Cation Conducting Solid Electrolytes with NASICON-type Structure (Invited)

S. Tamura*[1]; N. Imanaka[1]

1. Osaka University, Japan

Today, we use a large number of lithium ion batteries in our lives due to their high energy density and compactness. However, lithium is one of the rare metals whose reserve in earth is relatively few, we have to start developing the next-generation batteries. Divalent ions such as magnesium and calcium ions are expected to be alternatives for lithium ion, and the research on divalent cation conductors is increasing. In order to develop the practically applicable divalent cation conductors, we have to strictly design the constituents and crystal structure. However, since the reports on divalent cation conducting solids are still few compared with monovalent cation conductors, new findings on divalent cation conduction in solid lattice are greatly requested. Recently, we have succeeded in developing various kinds of divalent cation (Mg, Ca, Zn) conductors by selecting the three dimensional NASICON-type structure. Among them, $(Mg_{0.1}Hf_{0.9})_{4/3.8}Nb(PO_4)_3$ solid showed the highest ion conductivity, and its value was greatly higher than that of previously reported Mg^{2+} ion conducting solids.

PACRIM Symposium 19: Transparent Ceramic Materials and Devices

Transparent Ceramic Materials and Devices III

Room: Kohala 3
Session Chair: Yiquan Wu, Alfred University

1:15 PM

(PACRIM-S19-020-2017) Photoluminescent MgAlON Spinel Transparent Ceramics Doped by Rare Earth and Transition Metal Cations (Invited)

H. Wang*[1]; X. Liu[1]; B. Chen[1]; B. Tu[1]; W. Wang[1]; Z. Fu[1]

1. Wuhan University of Technology, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, China

Due to their outstanding optical transparency and mechanical properties, transparent ceramics with spinel structure have been regarded as one of the most important material groups for both optical and mechanical applications. Moreover, dual coordinate sites and changeable composition make spinel ceramics feasible to accommodate a variety of functional metallic cations. In this regard, additional functions, such as novel photoluminescence, could be introduced into spinel transparent ceramics through elaborately controlling composition and processing. In this work, functionalized MgAlON spinel transparent ceramics were developed by doping with different rare earth (RE) and transition metal (TM) cations. The optical and mechanical properties as well as microstructure of doped transparent ceramics were investigated. It is shown that high transparency and photoluminescence could be simultaneously realized in doped- MgAlON transparent ceramics. Compared to the TM-doped MgAlON, which TM cations were solved in MgAlON spinel lattice, the existence of grain boundary in MgAlON transparent ceramics is crucial for the accommodation of RE cations with large radii.

1:45 PM

(PACRIM-S19-021-2017) Low-Temperature Spark Plasma Sintering of Transparent Ceramics by Using SiC Molding Set (Invited)

B. Kim*[1]

1. National Institute for Materials Science, Field-Assisted Sintering Group, Japan

Hydroxyapatite (HAP) and alumina ceramics were sintered at low temperatures by using the SiC molding set during spark plasma sintering (SPS). Transparent ceramics were obtained at 800 C and 1000 C for HAP and alumina, respectively. The SiC is electrically conductive, so that the molding set was directly heated from the room temperature without external heating. Compared to the conventional graphite molding set, the voltage level during heating was higher due to the lower electrical conductivity. The SiC molding set lowered the sintering temperatures for the transparent ceramics by about 150 C. For transparent HAP, The in-line transmission is 82 % at a wavelength of 600 nm. The high transmission is a result of fine and dense microstructures. The light scattering behavior is examined and discussed with a theory of Rayleigh scattering. The relationship between the scattering coefficient and the wavelength indicates that the scattering was caused by nano-sized pores rather than by grains. For transparent alumina, the transmission is considerably affected by the heating rate. At a heating rate of 50 C/min, the transmission of the alumina decreases due to the accelerated grain growth. In this study, the effects of the SiC molding set were examined on the densification temperature, transmission, voltage level and grain growth.

2:15 PM

(PACRIM-S19-022-2017) Optical damage performance of conductive transparent indiun tin oxide and gallium nitride: Spatial, temporal, and lifetime modeling

S. Elhadj*[1]; J. Yoo[1]; R. Negres[1]; M. Marlon[1]; J. Adams[1]; N. Shen[1]; I. Bass[1]; D. Cross[1]; J. Bude[1]

1. LLNL, Targets System Optics Technology- Condensed Matter and Materials Division, USA

The optical damage performance of electrically conductive Gallium Nitride (GaN) and Indium Tin Oxide (ITO) films is addressed using large area, high power laser beam exposures at 1064 nm sub-bandgap wavelength. Analysis of the laser damage process assumes that onset of damage (threshold) is determined by absorption and heating of a nanoscale region of a characteristic size reaching a critical temperature. This model is used to rationalize semi-quantitatively the pulse width scaling of the damage threshold from picosecond to nanosecond timescales, along with the pulse width dependence of the damage threshold probability derived by fitting large beam damage density data. Multi-shot exposures were used to address lifetime performance degradation described by an empirical expression based on the single exposure damage model. A damage threshold degradation of at least 50% was observed for both materials. Overall, the GaN films tested had 5-10x higher optical damage thresholds than the ITO films tested for comparable transmission and electrical conductivity. The route to optically robust, large aperture transparent electrodes and power optoelectronics may thus involve use of next generation widegap semiconductors such as GaN.

2:30 PM

(PACRIM-S19-023-2017) Transparent Sialon Ceramics

S. Lee*[1]

1. Sun Moon University, Materials Engineering, Republic of Korea

The transparent sialon ceramics have been prepared by hot press sintering technique at various temperatures and pressure. The transmittance was measured by a UV-Vis spectroscopy in order to make window application. Also rare earth elements were doped to get a very intense infrared to visual frequency upconversion and near infrared frequency downconversion photoluminescence. The quadratic dependence of upconversion intensity on the excitation power indicates that the upconversion process is governed by two photo absorption process. The highest phonon energy was found to be 855 $^{cm^{-1}}$. Excellent up and down conversion emission properties together with moderately low phonon energy of the sialon ceramics make the material potential candidate for multifunctional application.

2:45 PM

(PACRIM-S19-024-2017) Fabrication of Textured ZnO Transparent Ceramic by Slip Casting in High Magnetic Field and Spark Plasma Sintering

D. Lin*[1]; L. Fan[1]; J. Xie[1]; L. Zhang[1]; Y. Shi[1]

1. Shanghai University, Department of Electronics and Information Materials, China

Anisotropic grains in ZnO ceramics cause considerable light scattering in the grain boundaries due to its hexagonal crystal structure. The influence of refractive-index difference can be minimized by making the predominant orientation of the grains coincided with the direction of the optic axis. Textured transparent ZnO ceramic was achieved by exposing slip casting under 9T magnetic field followed with a densification by spark plasma sintering at 850°C for 10min. X-ray diffraction and electron back-scattered diffraction indicated that the grains have been successfully orientated in the ZnO ceramic. Compared with non-textured SPS ZnO ceramic sample, the in-line optical transmittance of textured ZnO transparent ceramic was improved more than 15% in the visible(400-700 nm) range due to the increasing of the orientation factor to 23.7% calculated from XRD characteristics.

3:00 PM

(PACRIM-S19-025-2017) Processing of photoluminescent transparent polycrystalline alumina doped by rare earth elements

K. Maca*[1]; K. Drdlikova[1]; D. Drdlik[1]; R. Klement[2]; D. Galusek[2]

1. Brno University of Technology, Czech Republic
2. Joint Glass Centre of the IIC SAS, TnU AD, and FChFT STU, Slovakia

Fully dense polycrystalline alumina with sub-micrometre grain size exhibits optical transparency in both the infrared and visible region with significant potential for a wide range of applications, e.g. transparent armors, visible-infrared windows, and envelopes for energy saving light sources. Addition of complementary functional property, such as photoluminescence, enhances the application potential of this material. In this work we report on the processing of such material by combination of wet shaping, pressure-less pre-sintering and hot isostatic pressing. The optimization of all processing steps is needed to obtain the final product with desired combination of high transparency and luminescence. Special attention was paid to homogeneous distribution of dopants (Er, Eu) during shaping and pre-sintering. The final product was characterized in terms of real in-line transmission, measurement of photoluminescence spectra in visible and NIR spectral region, and also by hardness measurement. The combination of superior optical (RIT > 50%), luminescent and mechanical (Vickers hardness > 25 GPa) properties makes this material a promising candidate for high-tech applications.

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

Piezo/Ferro

Room: Kohala 1

Session Chair: Christo Guguschev, Leibniz Institute for Crystal Growth

1:45 PM

(PACRIM-S20-016-2017) Strontium and tantalum based ferroelectric perovskite oxide materials

F. Marlec[1]; C. Le Paven*[1]; F. Cheviré[2]; L. Le Gendre[1]; R. Benzerga[1]; B. Guiffard[3]; T. Dufay[3]; F. Tessier[2]; A. Sharaiha[1]

1. University of Rennes 1, Institute of Electronics and Telecommunications of Rennes (IETR), France
2. University of Rennes 1, Institut des Sciences Chimiques de Rennes, France
3. University of Nantes, Institute of Electronic and Telecommunications of Rennes, France

The present study concerns the achievement of layered-type perovskite ferroelectric materials with a Curie temperature tailored to be at ambient temperature. This was achieved by combining two ferroelectrics ($Sr_2Ta_2O_7$ (STO), T_C = -107°C, and $La_2Ti_2O_7$ (LTO), T_C = 1461°C) in a $(Sr_2Ta_2O_7)_{1-x}(La_2Ti_2O_7)_x$ solid solution, with x = 0.00-0.05. Compounds were first synthesized as powders using a high-temperature solid-state reaction route starting from stoichiometric amounts of $SrCO_3$, Ta_2O_5, La_2O_3 and TiO_2. Dense ceramics were then obtained by sintering pellets at 1400°C for 3h. X-ray diffraction analysis confirmed the elaboration of phase pure compounds and Rietveld crystal structure refinement pointed out a linear variation of the lattice parameters within the studied solid solution domain. At 1 kHz and ambient temperature, dielectric measurements show permittivities in the 50-350 range. Characterization as function of temperature evidenced the presence of a permittivity maximum, with a corresponding maximum temperature (T_M) increasing as the LTO concentration increases.

Polarization measurements (@10Hz, 40kV/cm) pointed out ferroelectric hysteresis for x concentrations in the 0.0165 – 0.03 range. Results are consistent with the formation of new ferroelectric materials with T_C close to ambient temperature. Work is still in progress to synthesize these compounds as thin films by magnetron reactive rf sputtering.

2:00 PM

(PACRIM-S20-017-2017) Polarity inverted PZT/$PbTiO_3$ ferroelectric epitaxial film for frequency switchable resonator filters

T. Shimizu*[1]; T. Mori[2]; M. Suzuki[1]; T. Yanagitani[4]; K. Wasa[3]

1. Waseda University, Advanced Science and Engineering, Japan
2. Nagoya Institute of Technology, Engineering, Japan
3. Yokohama City University, Japan
4. Waseda University, JST PRESTO, Japan

Piezoelectric film bulk acoustic resonator (FBAR) filters have attracted attention as frequency filters for mobile communications. The frequency switchable filters are suitable for selecting the vacant frequency bands. Usual polarity unidirectional single layer resonator excites fundamental mode whereas polarity inverted double layer resonator excites second mode. In general, the coercive electric field of $PbTiO_3$ is higher than that of PZT. $PbTiO_3$ and PZT also have high electromechanical coupling coefficient kt, which means that they have high ultrasonic conversion efficiency. In this study, we considered that polarity inverted structure is easily obtained by applying the intermediate coercive electric field of PZT and $PbTiO_3$ to epitaxial film. First, $PbTiO_3$ epitaxial films were grown on La-$SrTiO_3$ by a sputtering. Next, PZT epitaxial films were grown on the $PbTiO_3$ films. Ultrasonic conversion loss was measured by a network analyzer with the bias voltage -36 V to 36 V. During the application of -36 V, the two-layered resonator excites 1st mode at 0.55 GHz. On the other hand, during the application of +36 V, the resonator excites 2nd mode at 1.63 GHz. These results show polarity inversion by voltage application. The polarity inverted PZT/$PbTiO_3$ epitaxial film is expected as the frequency switchable resonator filters in the future.

2:15 PM

(PACRIM-S20-018-2017) Piezoelectric pressure wave sensor for health care application

K. Kobayashi[1]; T. Ishiguro[1]; Y. Doshida[1]; T. Gotoh[1]; H. Kishi*[1]

1. Taiyo Yuden Co., Ltd., R&D Laboratory, Japan

In the areas of medical and health care, many devices have increasingly become electronified and automated, and high-precision sensors are required. Piezoelectric sensor can detect many kind of tiny vibration with ultra low frequency, such as coming from human blood vessels. Thus, we developed integrated sensor module constructed from the PZT based piezoelectric sensor, instrument amp, A/D converter, and so on. The module size was small with 13x13x3mm, can be applied as wearable device. We successfully detect pulse wave of blood vessels precisely, and confirmed piezoelectric sensors enable continuous output of very clear acceleration plethysmogram waveforms. We present some features of developed piezoelectric pressure wave sensor compared with conventional pulse oximeter type sensor. Furthermore, from high precision pulse wave analysis, we demonstrate that vascular age or mental activity can be estimate. For further improvement of analysis performance, study on the influence of the piezoelectric materials on sensing properties is still necessary. Some results of the effect of various piezoelectric materials, such as PZT based ceramics, lead-free piezoelectric ceramics and PMN-PT single crystal on sensing properties will be presented.

2:30 PM

(PACRIM-S20-019-2017) Growth of Lead-Free Piezoelectric Single Crystals by Solid State Single Crystal Growth

J. G. Fisher*[1]; E. Uwiragiye[1]; H. Sun[1]; U. Farooq[1]; S. Moon[1]; J. Lee[1]; H. Han[2]; H. Kim[2]; W. Jo[2]

1. Chonnam National University, Materials Science and Engineering, Republic of Korea
2. Ulsan National Institute of Science and Technology, Materials Science and Engineering, Republic of Korea

Ceramics based on $(K_{0.5}Na_{0.5})NbO_3$ and $(Na_{0.5}Bi_{0.5})TiO_3$ are receiving extensive study as lead-free replacements for $Pb(Zr,Ti)O_3$ piezoceramics. Ceramics with properties approaching those of $Pb(Zr,Ti)O_3$ are now being developed. The piezoelectrical properties can be improved further by using single crystals; however, single crystal growth usually requires expensive Pt crucibles and specialized equipment. In this work, the growth of single crystals of $(0.97\text{-}x)K_{0.48}Na_{0.52}NbO_3\text{-}Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}ZrO_3\text{-}x(Bi_{0.5}Na_{0.5})TiO_3$ and $0.96(Na_{0.5}Bi_{0.5})TiO_3\text{-}0.04CaTiO_3$ using the solid state single crystal growth technique is described. This technique uses conventional ceramic processing equipment and is suitable for growth of single crystals of complex composition. Ceramic powders are prepared by the mixed oxide method. Seed crystals of $KTaO_3$ and $SrTiO_3$ are buried in the powders and pressed into pellets. The pellets are sintered and single crystals of the ceramic powder composition grow onto the seed crystals. The microstructure of the single crystals is examined using scanning electron microscopy. Chemical composition is examined using energy dispersive spectroscopy and electron probe microanalysis. The structure of the single crystals is studied using micro-Raman scattering. The dielectric, ferroelectric and piezoelectric properties are also measured.

2:45 PM

(PACRIM-S20-020-2017) Growth of Ca-doped $0.8(Na_{0.5}Bi_{0.5})TiO_3\text{-}0.2\ SrTiO_3$ Single Crystals by Solid State Crystal Growth

P. G. LE*[1]; J. G. Fisher[1]

1. Chonnam National University, Materials Science and Engineering, Republic of Korea

Lead-free ceramics based on $(Na_{0.5}B_{0.5})TiO_3$ (NBT) are well-known as promising candidates for actuator applications because of an extraordinarily large strain generated by a field-induced phase transition [1]. Many modified NBT solid solutions such as NBT-$BaTiO_3$, NBT-$SrTiO_3$, NBT-$CaTiO_3$, NBT-$(K_{0.5}B_{0.5})TiO_3$, etc. were synthesized to improve the piezoelectric properties. The $(1\text{-}x)(Na_{0.5}Bi_{0.5})TiO_3\text{-}xSrTiO_3$ system exhibits a morphotropic phase boundary at x = 0.2-0.3, leading to higher values of converse piezoelectric constant d^*_{33} [2, 3]. The piezoelectric properties can be improved by producing single crystals of ceramic materials [4]. In this work, $0.8NBT\text{-}0.2(Sr_{1-x}Ca_x)TiO_3$ single crystals have been grown for the first time by the solid state crystal growth technique. $0.8NBT\text{-}0.2(Sr_{1-x}Ca_x)TiO_3$ powder with x = 0, 0.01, 0.02, 0.03, 0.04 was synthesized by solid state reaction. $SrTiO_3$ [001]-oriented seed single crystals were buried, pressed into pellets, and then sintered at 1200°C for 1, 3, 10, 20 h. The grain size and single crystal growth distance as a function of Ca concentration were investigated in detail. Matrix grain growth in the $0.8NBT\text{-}0.2(Sr_{1-x}Ca_x)TiO_3$ samples was suppressed compared to that of $0.8NBT\text{-}0.2SrTiO_3$ powder when sintering for a long time, therefore enhancing the driving force for single crystal growth, especially at x = 0.03.

3:00 PM

(PACRIM-S20-021-2017) Electrical resistivity and piezoelectricity of $Ca_3TaGa_{3-x}Al_xSi_2O_{14}$ single crystals as a function of oxygen partial pressure and Al content

X. Fu*[1]; V. Garcia[1]; Y. Kitanaka[2]; Y. Noguchi[2]; M. Miyayama[2]; K. Shimamura[1]; N. Ohashi[1]

1. National Institute for Materials Science, Japan
2. The University of Tokyo, Japan

Piezoelectric langasite $Ca_3TaGa_{3-x}Al_xSi_2O_{14}$ (CTGAS) single crystals are attracting much attention for high temperature sensor applications. However, the growth of CTGAS with high Al concentration has been reported to be difficult. In this work, CTGAS (x=0~3) single crystals are successfully grown by Czochralski method. The temperature dependence of resistivity and piezoelectric properties are systematically investigated for the first time as a function of the Al content and the oxygen partial pressure during growth. The growth of CTGAS under various oxygen partial pressures indicated that, although the piezoelectric properties were invariant, the resistivity was remarkably higher the lower the oxygen partial pressure. On the other hand, Al-free CTGS exhibits the lowest values for the d_{11} and the resistivity. By the gradual substitution of Ga by Al, both parameters tend to enhance continuously, reaching the highest values for the fully substituted CTAS. In conclusion, high resistive CTAS is the most promising single crystal among the langasite family for high temperature piezoelectric applications. This work has been partially supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Element Strategy Initiative to Form Core Center of Japan.

3:15 PM

(PACRIM-S20-022-2017) Growth and Physical Properties of Multiferroic $LuFeO_3$ and $YbFeO_3$ Thin Films

R. C. Rai*[1]

1. SUNY Buffalo State College, Physics, USA

We present structural, optical, and magnetic properties of multiferroic $RFeO_3$ (R = Lu and Yb) thin films, deposited on single crystal sapphire and YSZ substrates by an RF magnetron sputtering system. Growth temperature and annealing are found to be critical to stabilize hexagonal $RFeO_3$ thin films. Based on the X-ray diffraction data, annealing above 950 °C has been found to change the crystal structure of $RFeO_3$ from a metastable hexagonal to an orthorhombic structure. Optical spectroscopy in the 0.5-6.5 eV range has been used to study the optical and electronic excitations of the $RFeO_3$ thin films. The electronic excitations, dominated by Fe d to d on-site as well as O 2p to Fe 3d, R 6s, and R 5d charge-transfer, for hexagonal and orthorhombic $RFeO_3$ thin films are distinctly different, consistent with the excitations expected from the FeO_5 and FeO_6 building blocks for hexagonal and orthorhombic $RFeO_3$, respectively. Further, the optical spectra exhibit strong temperature dependence, indicating evidence for a structural distortion at the magnetic transition temperature. We'll also discuss the magnetization data of $RFeO_3$ thin films. Acknowledgement: National Science Foundation (DMR-1406766)

Optical Material I

Room: Kohala 1

Session Chair: Luisa Bausa, Universidad Autonoma de Madrid

3:45 PM

(PACRIM-S20-023-2017) The origin of coloration and its effect on the physical properties of $CaGdAlO_4$ crystal (Invited)

X. Tao*[1]

1. Shandong University, State Key Lab of Crystal Materials, China

CaGdAlO4 (CGA) is a promising laser host crystal. So far, remarkable achievements have been made by Yb3+ doped CGA crystals in the output of ultrafast laser due to its broad spectra and good thermal conductivity. However, CGA single crystals grown under oxygen-containing atmosphere presented inconsistent brown coloration. The origin of coloration was studied by the density functional theory, and the simulated results show the oxygen defects and absorption matched well with the experimental results. The brown coloration of CGA is due to the interstitial oxygen atoms. The fundamental properties of CGA crystals with different colour, including crystal density, hardness, thermal and optical properties, were systematically investigated and compared when taking into account of the effect of color center inside. The colourless CGA was grown under inert gas atmosphere and exhibits a wide transparency range of 227-7140 nm. The maximum phonon energy was determined to be as low as 618 cm^{-1}. The colourless CGA host crystal with disordered structure, good thermal conductivity, low maximum phonon energy and wide transparency is promising for ultrafast ultraviolet and visible laser applications.

4:15 PM

(PACRIM-S20-024-2017) Crystal Semiconductor Core Optical Fibers (Invited)

J. Ballato*[1]

1. Clemson University, USA

Rapid advances in semiconductor-based photonics have generated intense interest in the eventual integration of electronics and optics. The extension from a planar waveguide platform to an optical fiber one would be a significant progression to this emerging field. This talk will review a new class of optical fibers: crystalline semiconductor core optical fibers fabricated using conventional fiber draw techniques. Specifically, the fabrication and properties of unary and binary semiconductor core fibers will be discussed in detail as will methods employed for their continued optimization. Such highly crystalline semiconductor core optical fiber have significant potential for Raman fiber devices, mid- and long-wave infrared sensing and power delivery, and terahertz guided wave structures.

4:45 PM

(PACRIM-S20-025-2017) Characterization of Yb-doped $CaYAlO_4$ single crystal for ultrafast lasers (Invited)

T. Ogawa*[1]; A. Eilanlou[1]; M. Higuchi[2]; S. Wada[1]; K. Midorikawa[1]

1. RIKEN, Japan
2. Hokkaido University, Japan

Nonlinear optical process using by the ultrshort pulse lasers is of importance in the field of quantum electronic, ultrafast optics and so on. We are developing the attosecond lasers by using high harmonic generation based on the ultrashort pulse lasers. In order to generate high harmonics, efficient and high intensity fs lasers are required. Laser crystals doped Yb as an active ion is much attention as a laser medium for direct-LD-pumped ultrashort pulse lasers. Absorption and fluorescence properties are depending on host crystal. Therefore, various Yb-doped crystals are investigated to obtain suitable performances. Yb-doped $CaYAlO_4$ crystal is known as one of the candidates for the ultrashort pulse lasers since this crystal has broad fluorescence near 1μm. In this work, we successfully grew the Yb:$CaYAlO_4$ crystals by using the FZ method. 1at.% and 4at.% Yb-doped crystals were obtained. Absorption cross section of 3×10^{-20} cm^2 was observed at 979 nm with a 1at.% Yb-doped crystal. This crystal shows an extremely broad fluorescence band with a high emission cross-section from 1000nm to 1100nm at room temperature. $CaYAlO_4$ is expected as a superior host crystal for ultrafast lasers. Also, we demonstrated lasing experiment using 1at.% Yb-doped crystal. Excellent laser performance was demonstrated. A maximum slope efficiency reached 36%. Stark effect of the ground state will be discussed in the presentation.

5:15 PM

(PACRIM-S20-026-2017) Crystal growth and Terahertz time-domain spectroscopy of $Sm_xR_{1-x}FeO_3$ (R-Tb,Er)orthoferrites

A. Wu*[1]; X. Zhao[1]; B. Wang[1]; L. Su[1]; Z. Jin[2]; G. Ma[2]

1. Shanghai Institute of Ceramics, CAS, China
2. Shanghai University, China

In this research, $Sm_xTb_{1-x}FeO_3$ and $Sm_{0.4}Er_{0.6}FeO_3$ single crystals were selected as the media for studying. The crystals were grown by optical floating zone method, using the high purity oxide as the starting materials. Terahertz time-domain spectroscopy (THz-TDS) was used to study the ferromagnetic mode and antiferromagnetic mode of $Sm_{0.5}Tb_{0.5}FeO_3$ and $Sm_{0.4}Er_{0.6}FeO_3$ which excited by THz pulse. The resonant amplitude and frequency of antiferromagnetic mode were significantly changed in the spin reorientation transition temperature range, which demonstrates that the antiferromagnetic mode can be directly and non-thermally excited. The room temperature terahertz time-domain spectroscopies of $Sm_{0.4}Er_{0.6}FeO_3$ demonstrate that the antiferromagnetic mode and ferromagnetic mode can be excited when the magnetic field of THz pulse were parallel and vertical to magnetic vector of rare earth orthoferrites, respectively. Our measurement demonstrates that the terahertz time-domain spectroscopy is a sensitive mean to explore the spin reorientation transition in rare earth orthoferrites

PACRIM Symposium 25: Ceramics for Next Generation Nuclear Energy

Accident Tolerant Cladding and Fuel Materials for Nuclear Energy

Room: Kona 1
Session Chair: Andrew Nelson, Los Alamos National Lab

1:15 PM

(PACRIM-S25-022-2017) Advanced Nuclear Fuels by Field Assisted Sintering Technology: Accident Tolerance and Fuel Performance Modeling (Invited)

J. Lian*[1]

1. Rensselaer Polytechnic Institute, USA

The advanced ceramic fuel development program is exploring revolutionary ceramic fuels with enhanced high thermal conductivity, oxidation resistance, high temperature mechanical properties, and thus improved accident tolerance. The US NEAMS program is developing science-based next generation fuel performance modeling, and critical experimental data are needed to validate phase field-based MARMOT models, particularly on effective thermal transport and fracture behavior. In this talk, recent advancements of using spark plasma sintering (SPS) in fabricating advanced fuels and engineering fuel matrix with tailored properties will be highlighted. The sintering fuels by SPS include monolithic UO2 with well-controlled microstructure, grain size and porosity across multiple length scales from nano-metered to micron-sizes, and the impact of the microstructure on the fuel properties is discussed within the context of the MARMOT predictions. Composite UO2 fuels are also fabricated in which heterogeneous secondary phases are used as the additives to improve thermal conductivity and mechanical properties.

1:45 PM

(PACRIM-S25-023-2017) Field assisted sintering of UO_2

E. Kardoulaki*[1]; A. Raftery[1]; J. Valdez[1]; D. Byler[1]; K. Mcclellan[1]

1. Los Alamos National Laboratory, Materials Science and Technology Division, USA

Our work focuses on flash sintering (FS) for the development of a novel fabrication route for accident tolerant fuel (ATF) composites. FS requires the application of an electric field and current across a sample to sinter powders at reduced times and temperatures relative to conventional sintering. The conditions during FS, therefore, enable a viable fabrication route for ATF composites that cannot be fabricated conventionally due to reactions between composite constituents. UO_2, as the main constituent for several candidate ATF composites, was selected for studying the mechanisms governing FS. In this work we define the parameters that govern the characteristic behavior of current runaway associated with Joule heating and the increase of electrical conductivity in UO_2 during FS. FS is induced by a critical field at a critical onset time, parameters shown to be dependent on temperature and O/M. FS of UO_{2+x} has been demonstrated at a lower critical field compared to $UO_{2.00}$. Additionally, high density pellets (~ 92%TD) were fabricated using FS on $UO_{2.16}$ at 600 °C; much lower than temperatures encountered in conventional sintering. Despite the fact that high density pellets are produced using FS, we are still unable to precisely control their resulting density and microstructure. Therefore, recent work has concentrated on systematic studies of FS of UO_2 in an effort to identify the parameters that control grain growth and defect formation.

2:00 PM

(PACRIM-S25-024-2017) Development of high density fissile composite nuclear fuels

A. T. Nelson*[1]; J. T. White[1]; K. Mcclellan[1]

1. Los Alamos National Lab, Materials Science and Technology, USA

Development of nuclear fuel forms that provide an increased uranium density relative to reference uranium dioxide (UO_2) is attractive when uranium enrichment is fixed. This advantage can be used to either offset neutronic penalties incurred by non-zirconium cladding or be leveraged to increase power output or cycle length. The high-density fissile composite concept was conceived as a means to address the need to prioritize uranium density while developing nuclear fuels for commercial reactors. Design of composites containing a high-density uranium compound as well as secondary (or ternary) uranium compounds provides the opportunity to meet or exceed the neutronic performance of UO_2 while simultaneously offering performance advantages. The two properties of primary interest are thermal conductivity and fracture toughness relative to UO_2. Augmentations to both properties can be realized through deployment of fissile composite designs, but it is equally important to ensure that the proposed fuel forms do not suffer penalties in other critical areas (e.g. oxidation behavior, corrosion resistance, operating margin). Composite fuel design methodology, performance objectives, and ongoing analysis of both constituent phases and composites emphasizing UN and U-Si composites are discussed concluding with a description of ongoing irradiation testing.

2:15 PM

(PACRIM-S25-025-2017) Al additions to U_3Si_2 to increase oxidation resistance

E. Sooby Wood*[1]; J. T. White[1]; A. T. Nelson[1]

1. Los Alamos National Lab, Materials Science and Technology, USA

Uranium silicide intermetallic compounds are currently under investigation by the DOE-NE Advanced Fuels Campaign as candidate accident tolerant nuclear fuel concepts. While some compounds in this system offer benefits compared to reference UO_2, they have been shown to display poor oxidation resistance and pellet cracking. It is hypothesized that introducing an additional compositional degree of freedom by exploring U-Si-X ternary systems may provide the means to design a candidate nuclear fuel which optimizes the benefits of each binary. Presented are the delayed onset of breakaway oxidation of U_3Si_2 caused by incorporating Al into the fuel form. Various U-Si-Al compositions have been synthesized and oxidized in both air and steam; these data are presented. Analysis of the effect of these additions to the fuel forms oxidation resistance is also presented.

2:30 PM

(PACRIM-S25-026-2017) Mechanical Degradation of SiC_f/SiC Composite after Hydrothermal Corrosion and Thermal Shock

D. Kim*[1]; H. Lee[1]; J. Park[1]; W. Kim[1]

1. Korea Atomic Energy Research Institute, Nuclear Materials Development Division, Republic of Korea

A SiC_f/SiC composite is a candidate material for accident-tolerant fuel cladding of light water reactors. During normal operation, it is exposed to high-temperature, pressurized coolant water, which can lead to the hydrothermal corrosion. It can also suffer from the thermal shock during the design basis accident because the emergency core cooling systems automatically supply the reactor core with the emergency cooling water when the peak temperature of the fuel clad reaches to 1204ºC. In this study, several kinds of multi-layered SiC composites were fabricated by a chemical-vapor process. The hydrothermal corrosion and thermal shock tests were carried out to evaluate the degradation of mechanical strength of multi-layered SiC composite. The results showed that the strength of multi-layered SiC composite tubes was significantly reduced by hydrothermal corrosion at 360ºC, 20 MPa water because of the dissolution of a SiC matrix phase. On the other hand, the mechanical strength of composites was slightly reduced by water-quenching from 1200ºC to room temperature, depending on the existence of interphase and a buffer monolithic SiC layer.

2:45 PM

(PACRIM-S25-027-2017) $Zr_{n+1}AlC_n$ and $Zr_{n+1}SiC_n$ MAX phases for future fission environments: Challenges and limitations

E. Zapata-Solvas*[1]; N. Ni[2]; W. E. Lee[1]

1. Imperial College London, Centre for Nuclear Engineering. Dpt. of Materials, United Kingdom
2. Imperial College London, Centre for Advanced Structural Ceramics. Dept. of Materials, United Kingdom

After Fukushima's nuclear disaster there has been a growing interest in introducing new safety concepts for future fission reactors. One approach is to develop Accident Tolerant Fuels (ATF) that can withstand the harsh environment within a fission reactor for at least 10 hours in a Loss-of-Coolant-Accident (LOCA). MAX phases are potential candidates for use in ATF as cladding. The system that has been targeted is $Zr_{n+1}AlC_n$. Zr offers compatibility with the zircaloy cladding, Al offers resistance to corrosion and oxidation, while C limits nuclear transmutation. In addition, $ZrSi_2$ has been recently proposed as another candidate for ATF, which suggests that $Zr_{n+1}SiC_n$ MAX phases could be potentially used in ATF. However, there are some concerns about corrosion resistance due to the presence of Si and SiO_2 solubility under normal pressurized water reactor (PWR) operating conditions as well as accident scenarios. This work examines stabilization of $Zr_{n+1}AlC_n$ MAX phases by partial substitutions in the quaternary systems $(Zr,M^*)_{n+1}AC_n$ and $Zr_{n+1}(A, A^*)C_n$ where A = Al, Si. Synthesis and sintering of MAX phases will be discussed as well as oxidation resistance, corrosion resistance in PWR conditions and thermal properties.

Advancements in Modelling Materials for Nuclear Applications

Room: Kona 1
Session Chair: Andrew Nelson, Los Alamos National Lab

3:30 PM

(PACRIM-S25-029-2017) Nuclear Fuel Modelling and Perspectives on Canadian Efforts in Fuel Development (Invited)

M. H. Piro*[1]

1. University of Ontario Institute of Technology, Faculty of Energy Systems and Nuclear Sciences, Canada

Significant progress has been made in recent years in developing a new generation of nuclear fuel models, simulations and codes with the overall goal of enhancing predictive capabilities of nuclear fuel behaviour to improve performance and safety. Computational efforts span the entire multi-scale multi-physics spectrum, ranging from atomistic electronic structure and classical inter-atomic potential calculations, to meso-scale simulations of micro-structural evolution, to continuum scale thermo-mechanical simulations of fuel performance. These computational activities support performance and safety analyses for industry while also providing guidance to various experimental research programs. For instance, the aforementioned computational research has supported Canadian efforts in the development and testing of non-conventional fuels, including thoria-urania, thoria-plutonia and urania-plutonia fuels. Advanced fuel cycle development activities at the Canadian Nuclear Laboratories include fuel fabrication, fuel performance assessments, safety related testing, materials behaviour, etc. This presentation will give an overview of recent advances in nuclear fuel modelling and simulation activities in addition to providing some perspectives on efforts in nuclear fuel development in Canada.

4:00 PM

(PACRIM-S25-030-2017) Combining Simulation and Experiments to Accelerate Reactor Fuel Development

M. R. Tonks*[1]

1. Pennsylvania State University, Mechanical and Nuclear Engineering, USA

The future of nuclear reactor fuel is likely to look very different than the past. Currently, all commercial reactors use UO_2 reactor fuel with zirconium cladding. However, changes to the fuel and cladding materials are being considered to make light water reactors more accident tolerant. In addition generation IV reactors as well as small modular reactors are all likely to employ different fuel and cladding than what we are familiar with now. To accelerate the generation of these modified fuel concepts, it is essential to combine state of the art experiments and materials characterization with advanced modeling and simulation techniques. However, to maximize the benefit of combining these two different approaches requires changes on both sides, as well as improved communication. In this presentation I discuss current efforts in the US to combine simulation and experiments for the investigation and development of reactor fuel. I will give examples of successes as well as some failures.

4:15 PM

(PACRIM-S25-031-2017) DFT calculations on the role of Cr-doping for enhanced UO_2 sintering

M. W. Cooper*[1]; D. A. Andersson[1]

1. Los Alamos National Lab, Materials Science and Technology Division, USA

The development of nuclear fuel with improved accident tolerance has focused in part on materials suitable for use in conventional LWRs. AREVA and Westinghouse have developed advanced fuel concepts by blending UO_2 and Cr_2O_3 powders for improved sintering. The 5 fold larger gain size achieved compared to

conventional UO_2 pellets is thought to reduce fission gas release by increasing the distance to the grain boundaries. Furthermore, higher creep rates and increased fuel plasticity are linked to improved pellet clad interaction (PCI) performance. Using density function theory we have investigated the effect of Cr-doping of UO_2 on the intrinsic defect concentrations as a function of oxygen partial pressure and temperature. We have considered Cr accommodation in the 3+, 4+, 5+, and 6+ charge states. The results are discussed in the context of pellet sintering, creep, and fission gas migration in the bulk.

4:30 PM

(PACRIM-S25-032-2017) Uranium Silicide and Nitride-Silicide Composite Fuels: Phase Behavior in Processing and Irradiation

T. M. Besmann*[1]; M. Noordhoek[1]; T. Wilson[1]; M. Bogala[1]; A. T. Nelson[2]; E. Sooby Wood[2]; J. W. McMurray[3]; S. Middleburgh[5]; P. Xu[4]; E. J. Lahoda[6]

1. University of South Carolina, Nuclear Engineering, USA
2. Los Alamos National Lab, USA
3. Oak Ridge National Lab, USA
4. Westinghouse - Columbia, USA
5. Westinghouse - Vasteras, Sweden
6. Westinghouse - Cranberry Township, USA

Uranium silicide and uranium nitride are of significant interest as next generation LWR fuels due to their significantly higher uranium atom density and high thermal conductivity. These properties will allow development of more economic cores as well as fuel that operates at significantly lower temperatures. Nitrides are particularly of interest, yet their susceptibility to both cracking and reaction with water in the event of a breach of the cladding have curbed development. A current concept where U_3Si_2 is present as a grain boundary phase in UN could increase fracture toughness and provide an improved barrier to attack by water or steam. This presentation will discuss the phase equilibria and thermochemistry for these systems developed from ab initio calculations and thermochemical assessments supported by the results of characterization of silicide and composite samples. This research was supported by the U.S. Department of Energy, Office of Nuclear Energy Fuel Cycle R&D Program under a Nuclear Energy University Programs award.

4:45 PM

(PACRIM-S25-033-2017) Thermophysical properties and oxygen transport in $(Th_x,Pu_{1-x})O_2$

C. Galvin*[1]

1. Imperial College, Materials, United Kingdom

The feasibility of using $(Th,Pu)O_2$ fuel has been discussed for various reactor systems. These studies concluded that Th based fuels can efficiently reduce Pu stockpiles while maintaining acceptable safety and control characteristics of the rector system. Computer simulations are a useful tool for examining the properties of these materials under extreme conditions in a cost effective, safe manner. Using Molecular Dynamics the thermophysical properties and oxygen transport of $(Th_x,Pu_{1-x})O_2$ $(0 \leq x \leq 1)$ in the temperature range 300-3500 K are examined. In particular, the superionic transition is investigated and viewed via the thermal dependence of lattice parameter, linear thermal expansion coefficient, enthalpy and specific heat at constant pressure. Oxygen diffusivity and activation enthalpy are also investigated. Below the superionic temperature an increase of oxygen diffusivity for certain compositions of $(Th_x,Pu_{1-x})O_2$ compared to the pure end members is predicted. Oxygen defect formation enthalpies are also examined, as they underpin the superionic transition temperature and can be used to explain an enhancement in oxygen diffusivity. The increase in oxygen diffusivity for $(Th_x,Pu_{1-x})O_2$ is explained in terms of lower oxygen defect formation enthalpies for $(Th_x,Pu_{1-x})O_2$ than PuO_2 and ThO_2, while links are drawn between the superionic transition temperature and oxygen Frenkel disorder.

PACRIM Symposium 28: Advanced Materials and Technologies for Electrochemical Energy Storage Systems

Characterization I

Room: Queen's 5
Session Chair: Stefan Adams, National University of Singapore

1:15 PM

(PACRIM-S28-020-2017) Near-Field Optical Spectroscopy and Imaging of Interfaces and Interphases of Li-ion Electrode Materials (Invited)

R. Kostecki*[1]; M. Ayache[1]; I. Lucas[1]; J. Syzdek[1]

1. LBNL, USA

Fundamental investigations of the electrode material properties of electrochemical systems are essential for improvements in electric energy storage technologies. Most Li-ion battery chemistries operate beyond the thermodynamic stability limits of electrode materials and/or electrolytes. Reactions between electrodes and electrolyte result in the formation of new phases and interphases, which assure safe battery operation over the lifespan of the application. The chemical composition and functional mechanism of the electrode materials, interfaces and interphases is not well understood, due to the technical barriers associated with characterization methodologies across length and temporal scales that correspond to the basic components and processes. This presentation provides an overview of infrared apertureless near-field scanning optical microscopy (IR aNSOM) as a valuable emerging tool in the chemical characterization of materials and interfacial layers at the nanometer scale in electrochemical systems. This work demonstrates an IR aNSOM study of model model Sn, HOPG and LiFePO4 electrodes. IR aNSOM images recorded at several wavelengths reveal significant chemical contrast variations tied to specific topographic features and variation of chemical composition.

1:45 PM

(PACRIM-S28-021-2017) Reaction mechanism of the Li-ion negative electrode TiSnSb using ^{119}Sn Mössbauer and ^{7}Li MAS NMR spectroscopies (Invited)

N. Dupre*[1]; K. Johnston[2]; M. Sougrati[3]; L. Steviano[3]; A. Darwiche[3]; C. P. Grey[4]; L. Monconduit[3]; D. Guyomard[1]

1. CNRS-IMN, ST2E, France
2. Durham University, United Kingdom
3. ICG, France
4. University of Cambridge, Chemistry, United Kingdom

Conversion type materials, such as TiSnSb, have recently been considered as plausible alternatives to conventional Lithium battery electrode materials due to their large energy densities. During the first discharge, TiSnSb undergoes a conversion process, leading to the simultaneous formation of Li-Sb and Li-Sn intermetallic compounds. However, some ambiguities remain concerning the phases formed upon the electrochemical process and the interfaces between them. Ex situ ^{7}Li MAS NMR, in-situ ^{119}Sn Mössbauer and model compounds have been used to obtain information on the local environments forming upon reduction. Two distinct groups of resonances are observed in the ^{7}Li solid-state NMR spectra obtained at the end of discharge, tentatively assigned to the solid electrolyte interphase (SEI), Li_3Sb, Li_7Sn_2, Li_7Sn_3 and a second non stoichiometric Li-Sb phase. The presence of metallic nanoparticles at the end of lithiation appears to affect both the chemical shift of Li_3Sb, appearing at a negative value, and the reactivity of low potential phases. The ternary alloy NbSnSb has also been investigated, as a direct comparison to TiSnSb. The study model compounds, confirms the influence of the so-called "inactive" elements in ternary alloys, e.g., Ti or Nb and suggest a preferential distribution of Ti and Nd nano particles around the LiSb phases.

2:15 PM

(PACRIM-S28-022-2017) Advancing Alkali-Ion Battery Technology Through Understanding Function: X-Ray and Neutron Studies of Electrode Structure and Operational Mechanism (Invited)

V. K. Peterson*[1]; W. Pang[1]

1. Australian Nuclear Science and Technology Organisation, Australian Centre for Neutron Scattering, Australia

Functional materials form the central part of many important energy technologies, with their atomic-scale structure and chemistry underpinning performance of the whole device. Electrodes are the functional materials at the heart of alkali-ion batteries, and are host compounds that allow reversible and usually topotactic ion-insertion. Central to advancing alkali-ion batteries is the characterization of the operational mechanism of these electrodes, and both X-ray and neutron methods have made important contributions to this. Key to the success of such characterization is understanding the response of the electrode during the ion insertion/extraction processes. In this presentation, examples of where both X-ray and neutron analysis methods, mostly applied in real-time, have been used to understand alkali-ion electrode function will be given. These include to understand the phase and structural evolution of the P2-type sodium-ion positive electrode $Na_{2/3}(Fe_{1/2}Mn_{1/2})O_2$, transition-metal ordering in the positive electrode $LiNi_{0.5}Mn_{1.5}O_4$, the lithium-ion migration pathway in the zero-strain negative electrode $Li_4Ti_5O_{12}$, and the origin of capacity fade of the positive electrode $Li_2MnO_3 \times Li_{0.96}Ni_{0.04}(Li_{0.25}Ni_{0.21}Mn_{0.42}Co_{0.12})O_2$.

2:45 PM

(PACRIM-S28-023-2017) Phase assemblage/transformations and dimensional aspects effecting stress developments and electrochemical behavior of battery electrode materials (Invited)

A. Mukhopadhyay*[1]

1. Indian Institute of Technology (IIT) Bombay, Metallurgical Engineering and Materials Science, India

The overall performances of metal-ion batteries depend critically on facile electrochemical insertion/removal of relatively large amounts of the concerned metal ions (viz. Li, Na etc.) into the electrode materials (preferably resulting in ‘flat’ potential profiles); but causing minimal damage to the same. Dimensional scales of the electrode materials, phases originally present (the composition) and phase transformations upon insertion/removal of the metal-ions impart considerable influences on the overall performances. These aspects also impact the stress developments during metal-ion insertion/removal; which in turn affect the capacities, integrity and cycle life of the electrode materials. In these contexts, based on some recent results obtained with real-time monitoring of stress developments in electrode materials during electrochemical cycling, the talk will throw important insights into the occurrence of plastic deformation and concomitant mechanical instability just during phase transformations in ceramic ($LiCoO_2$), metallic (Sn) and graphenic carbon based electrode materials. Additionally, some interesting observations associated with phase assemblage/transformation in ‘ultra-fine’ $LiFePO_4$ and Na-titanate nanoparticle based electrode materials, in the presence/absence of conducting/‘reinforcing’ additives, will be discussed.

3:15 PM

(PACRIM-S28-024-2017) Fabrication and characterization of structure-controlled cathodic thin films for lithium ion secondary batteries

Y. H. Ikuhara*[1]; X. Gao[1]; Y. Sugawara[1]; C. Fisher[1]; A. Kuwabara[1]; H. Moriwake[1]; K. Kohama[2]; Y. Ikuhara[3]

1. Japan Fine Ceramics Center, Nanostructures Research Laboratory, Japan
2. Toyota Motor Corporation, Japan
3. The University of Tokyo, Japan

Rechargeable Li-ion secondary batteries are being developed for use in high power applications, such as hybrid and fully electric vehicles, because of their high energy density and high power density. Future application of all-solid-state lithium ion batteries requires multilayer composite structure analysis of the cathode, electrolyte and anode to understand the influence of microstructure on battery performance. In particular, cathode-substrate and cathode-electrolyte interfaces are known to affect charge/discharge rates, cyclability, and battery lifetime. In this study, oriented spinel $LiMn_2O_4$ and olivine-type $LiCoPO_4$ thin films were successfully fabricated from precursor solutions on single-crystal substrates. It was found that the film/substrate lattice misfit affects the degree of epitaxy of both types of thin films. Direct observation of atom columns using high-angle annular dark-field (HAADF) - and annular bright-field (ABF) -STEM showed that epitaxial $LiMn_2O_4$ films form atomically flat and coherent heterointerfaces with the substrate, although the crystal lattice is distorted near the interface and there is a compositional gradient between the interface and film bulk. ABF-STEM also confirmed that highly oriented $LiCoPO_4$ cathodic films could be fabricated that allow Li extraction and insertion along [010] Li-ion channels.

Characterization II

Room: Queen’s 5
Session Chair: Kiyoshi Kanamura, Tokyo Metropolitan University

3:45 PM

(PACRIM-S28-025-2017) Real-Time Observation of Electrochemistry in Nanoscale Ceramics (Invited)

R. S. Yassar*[1]

1. University of Illinois, Department of Mechanical & Industrial Engineering, USA

Electrodes in rechargeable batteries undergo complex electrochemically-driven phase transformations upon driving Li ions into their structure. Such phase transitions in turn affect the reversibility and stability of the battery. This presentation gives an overview of the PI’s research program on in-situ transmission electron microscopy (TEM) of ceramic battery materials. In-situ TEM has been shown to be a very powerful technique in shedding light to some of the mysteries in electrochemical performance of new materials. Various anode materials including SnO_2 and MnO_2 were subjected to lithiation process and the transport of Li ions was visualized within their atomic structure. For SnO_2 nanowires, it was observed that the Li ion transport results in local strain development preferably along (200) or (020) plans and [001] crystallographic directions. The lithiation behavior in the presence of twin boundary defects was completely different compared to pristine state with no twin boundary defect. We showed that twin boundaries in general provide a more accessible pathway for Li ion transport. Anisotropic plastic deformation was also observed along [010] directions of MnO_2 nanowires. We investigated the microstructural changes and phase evolution of such intermetallic nanowires using in-situ TEM.

4:15 PM

(PACRIM-S28-026-2017) Non-intrusive operando battery diagnosis and prognosis (Invited)

M. Dubarry*[1]

1. Hawaii Natural Energy Institute, USA

In recent years, HNEI developed a balanced technique that, while being non-intrusive, requiring little resources, can deliver excellent accuracy for diagnosis and ultimately, enable prognosis. The methodology is based on the study of the evolution of the voltage response of the cells with aging (1). Based on the changes in voltage, it is possible to quantify the evolution of a battery's three main degradation modes: the loss of active material, the loss of lithium inventory and the changes in kinetics (2). This knowledge can then be extended form prognosis (3). This technique was proven useful for both R&D and onboard diagnosis. In terms of R&D it can give a head start on where additional characterizations are needed to comprehend the origin of the observed degradation modes and thus save time and money. In terms of on-board applications, it allows to gather electrochemical insight from simple maintenance cycles and lead to better state of charge, state of health and imbalance tracking as well as possibly delivering early warning signs of failure. This presentation will introduce the theoretical background behind the technique as well as examples of its implementation for single cell and battery packs.

4:45 PM

(PACRIM-S28-027-2017) Fundamental understanding of batter materials at atomic and electronic levels using in-situ/operando synchrotron x-ray and neutron techniques (Invited)

Y. Ren*[1]

1. Argonne National Lab, X-ray Science Division, USA

Synchrotron x-ray and neutron facilities are very popular and indispensable scientific resources and provide powerful instruments and experimental techniques for both fundamental and applied researches. X-rays and neutrons interact with matter in different ways, thus are often used as complementary tools for studying materials in order to understand their properties at the electronic, atomic and molecular levels. We have been utilizing synchrotron x-ray and neutron techniques to investigate a large variety of advanced materials for electrochemical energy storage applications, including lithium-ion, lithium-sulfur and lithium-air batteries. In this talk, we will present our recent results on in-situ/operando studies of battery materials using various neutrons and synchrotron x-ray techniques, including real-time monitoring material synthesis, in-situ probing electrochemical performance and investigating commercial battery safety. The knowledge of the atomic and electronic level structures and their evolution in realistic conditions provides important information for deeper and fundamental understanding battery materials-property relationship and for further improvement of their performance and functionality. We will also discuss the challenges in battery materials research, and our future experimental approaches.

5:15 PM

(PACRIM-S28-028-2017) Insight into Microstructural Evolution in Lithium-based Batteries by Electron Microscopy

D. Miller*[1]

1. Argonne National Laboratory, USA

The evolution of new phases and interfaces can have a profound effect on the performance of lithium-based batteries. As an example for Li-ion batteries, grain-to-grain separation and cracking can lead to loss of capacity in Ni- and Mn-rich cathode materials when grains become electrically isolated and no longer fully contribute to performance. For cathode materials, the crystal structure and chemistry can play an important role in capacity and long-term stability. For lithium-oxygen batteries, nanoparticle catalysts, reaction products, and coatings to passivate defects all influence charge overpotential and the charge/discharge profile. Electron microscopy provides insight into each of these performance issues. For example, correlated electrochemistry and electron microscopy has shown how particle fragmentation contributes to loss of capacity by decreasing grain-to-grain connectivity in Ni-Mn-based cathode oxides. Aberration-corrected HREM showed that a "composite" strategy for cathode oxides provides a thermodynamically favorable structure that yields better performance than the end member constituents and how surface and catalyst control can influence the reaction pathway and microstructure of the reaction product in lithium-oxygen batteries. This presentation will detail our approaches to these issues and the insights gained from them.

PACRIM Symposium 29: Advances in Polar, Magnetic and Semiconductor Materials: Extending Temperature Limits

High Temperature Dielectrics

Room: Queen's 4
Session Chairs: Do-Kyun Kwon, Korea Aerospace University;
Beihai Ma, Argonne National Laboratory

1:15 PM

(PACRIM-S29-017-2017) Ceramic and Nano-Polymer Capacitors for Energy Storage and Energy Transduction Applications (Invited)

C. Randall*[1]; M. Lanagan[1]; R. Rajagopalan[1]

1. Penn State University, Materials Science and Engineering, USA

Starting first with the dielectric materials necessary for power invertors, we need capacitor devices that perform with high volumetric efficiencies and have low high field losses under high drive conditions, the dielectric materials also need high reliability and high dielectric breakdown strengths over broad temperature ranges. In developing new inorganic dielectrics materials based upon nonlinear dielectrics, we investigated new compositions with antiferroelectric based phase transitions, linear and weakly coupled relaxor ferroelectric phenomena, permitting high electrostatic energy storage with minimum dielectric loss at elevated temperatures. We will also report on nanocomposite designs with dielectric thermoplastic polymers with exfoliated clay based nanofillers, where the inclusions are dispersed and structured by a bi-axial stretching perpendicular to the electrodes that maximize dielectric breakdown and minimize space charge losses. The textured nanocomposites show superior dielectric properties in terms of lower losses, high breakdown strengths, and better dielectric endurance. Finally, our recent work on ultracapacitors is showing extremely good leakage characteristics ideal for energy harvesting applications.

1:45 PM

(PACRIM-S29-018-2017) Fabrication of Multi-Layer Glass Capacitors (Invited)

R. H. Wilke*[1]; H. J. Brown-Shaklee[1]; A. Casias[1]; B. Cunningham[1]; M. Vecchio[2]; R. Vudatha[3]

1. Sandia National Laboratories, USA
2. Pennsylvania State University, USA
3. Cornell University, USA

Alkali-free glasses show immense promise as a potential high dielectric energy density storage material. Commercially available alumino-borosilicate compositions exhibit high breakdown strengths (exceeding 1000 MV/m), low loss (tan d < 0.01), modest relative permitivities (5-7), and high dielectric energy storage densities (35 J/cc). In order to take advantage of the intrinsic properties of these materials it is necessary to develop processing and packaging strategies for fabricating devices with appreciable capacitance values.

We have fabricated multi-layer devices using Epon 828/Jeffamine T403 to bond individually processed sheets of glass. The thickness of this layer is controlled by bonding under uniaxial pressure. The capacitors are then fabricated from bonded sheets by laser singulation followed by end termination. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

2:15 PM

(PACRIM-S29-019-2017) The influence of non-stoichiometry and chemical doping on the electrical properties of $Na_{1/2}Bi_{1/2}TiO_3$ ceramics (Invited)

D. C. Sinclair*[1]

1. University of Sheffield, Materials Science & Engineering, United Kingdom

We will review the structure-composition-property relationships of $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) materials based on a combination of A-site non-stoichiometry and chemical doping. Nominally Na-rich or Bi-deficient NBT ceramics (i.e. Na:Bi >1) are excellent oxide-ion conductors with oxide-ion transfer numbers (t_{ion}) exceeding ~ 0.9 at 600 °C whereas nominally Na-deficient or Bi-excess NBT ceramics (i.e. Na:Bi<1) are electrically insulating but retain t_{ion} ~ 0.1 at 600 °C. Undoped NBT ceramics should be viewed as mixed ion-electron conducting materials where the magnitude of the bulk conductivity and t_{ion} are heavily dependent on the nominal Na:Bi ratio in the starting composition. We attribute the source of oxygen vacancies in nominally stoichiometric NBT to be associated with low levels of Bi_2O_3-loss during ceramic processing. Acceptor dopants such as Sr for Bi or Mg for Ti significantly increase the oxide ion conductivity to promote solid electrolyte behaviour whereas donor dopants such as Nb for Ti can suppress the oxygen vacancy concentration and exhibit excellent dielectric behaviour with tan d < 0.02 at 600 °C. Such behaviour is desirable for NBT-based dielectric applications, eg as Pb-free piezoelectrics and/or as a solid solution member in temperature stable, high permittivity multilayer ceramic capacitors (MLCCs) operating at > 175 °C

2:45 PM

(PACRIM-S29-020-2017) Development of PLZT-based Ceramic Capacitors for High-Temperature Power Inverters in Electric Drive Vehicles (Invited)

B. Balachandran*[1]; B. Ma[1]; T. H. Lee[1]; S. E. Dorris[1]

1. Argonne National Laboratory, Energy Systems Division, USA

Advanced power inverters in electric vehicles require capacitors that operate at high voltages at under-hood conditions. Funded by the U.S. Department of Energy's Vehicle Technologies Program, Argonne is developing lead lanthanum zirconium titanate (PLZT)-based film capacitors for vehicular applications. We have deposited PLZT dielectric films on metal foils and characterized the dielectric properties over a wide temperature range between -50 and 200°C. With 300 V bias, we measured a dielectric constant of ≈110 and loss of ≈0.004 at room temperature, and a dielectric constant of ≈185 and loss of ≈0.008 at 200°C. Leakage current densities of 6.6×10^{-9} A/cm^2 at 25°C and 1.4×10^{-8} A/cm^2 at 150°C were also measured. The breakdown field strength of PLZT films deposited on nickel foils was 2.4 MV/cm. Polarization – electric field hysteresis loop measurement showed recoverable energy density of ≈15 J/cm^3 at 600 V. These results suggest that Argonne's dielectric film capacitors have the potential to operate at high voltage in an under-hood temperature environment. An update on the fabrication procedures and dielectric properties of the PLZT films will be presented in this talk. Work supported by the U.S. Department of Energy, Vehicle Technologies Program.

3:15 PM

(PACRIM-S29-021-2017) Effects of Residual Stress on Dielectric Properties of PLZT Film Capacitors

B. Ma*[1]; T. H. Lee[1]; S. E. Dorris[1]; B. Balachandran[1]

1. Argonne National Laboratory, USA

Research interest in the development of high-temperature ceramic film capacitors is increasing because their dielectric properties are desirable for applications in power electronics and energy conversion. Using X-ray diffraction, we characterized residual stresses in lanthanum-doped lead zirconate titanate (PLZT) films grown on metal and metalized silicon substrates. Residual stresses in PLZT films depend on the fabrication conditions, annealing temperature, film thickness, and substrate type. The dielectric properties of PLZT film capacitors were examined and correlated with residual stresses in the films. Detailed relationships among processing conditions, dielectric properties, and residual stresses of PLZT films will be presented. This work was supported by the U.S. Department of Energy, Vehicle Technologies Program, under Contract DE-AC02-06CH11357.

3:45 PM

(PACRIM-S29-022-2017) High temperature dielectric capacitors based on doped-HfO_2 thin films (Invited)

Z. Hu*[1]; J. G. Jones[1]; N. X. Sun[2]; G. J. Brown[1]

1. Air Force Research Laboratory, Materials and Manufacturing Directorate, USA
2. Northeastern University, Department of Electrical and Computer Engineering, USA

The development of advanced energy storage technology is critical in integrated circuits with exponentially increasing electronic devices. Polar materials could be feasible candidates for next-generation film capacitors considering their large energy density and high working temperature. The recently discovered ferroelectricity and antiferroelectricity in doped-HfO_2 thin films reveal their potential applications in high temperature integrated capacitors. In this work, doped-HfO_2 thin films were deposited on Si substrates by reactive co-sputtering of metal targets. It is found that the doped-HfO_2 films crystallize as monoclinic phase (m-phase) at room temperature, which are non-polar and will not transfer to polar orthorhombic phase (o-phase) after rapid thermal annealing (RTA). In order to obtain the polar o-phase that is not conventionally stable, the first step is to grow amorphous doped-HfO_2 films by reducing the sputtering power. After being treated by RTA, the amorphous films are transferred to o-phase. The doped-HfO_2 films exhibit high remanent polarization, low leakage current density, and high breakdown strength. The energy storage performance and thermal stability are also investigated. These results demonstrate great potential of using doped-HfO_2 thin films for high-temperature dielectric capacitor applications.

4:15 PM

(PACRIM-S29-023-2017) High Temperature Dielectric and Energy Storage Properties of $Bi_{0.5}Na_{0.5}TiO_3$-$NaNbO_3$ Ceramics and Multilayer Ceramic Capacitors (Invited)

H. Liu*[1]; Q. Xu[1]; C. Su[1]; H. Hao[1]; S. Zhang[1]; Z. Yao[1]; M. Cao[1]

1. Wuhan University of Technology, School of Material Science and Engineering, China

The dielectric and energy-storage properties of $(1-x)Bi_{0.5}Na_{0.5}TiO_3$-$xNaNbO_3$ (x = 0.20, 0.25, 0.30,0.35) (BNT-NN) ceramics were investigated. BNT-NN ceramics show excellent dielectric temperature stability. For compositions with x = 0.25–0.35, the temperature coefficient of capacitance (TCC) was found to be lower than 11% over the temperature range of 60°C–400°C, with moderate permittivity (>1000) and low dielectric loss (≤1.2%), promising for temperature stable capacitor applications. In addition, all the BNT-NN ceramic samples show relatively large critical electric field, being higher than 12kV/mm. The optimum energy-storage property was obtained for the composition of x = 0.30, with energy-storage density of 1.3 J/cm^3 and efficiency of 84.5%. BNT-NN multilayer ceramic capacitors (MLCC) were prepared using Ag0.7Pd0.3 as inner electrodes. BNT-NN MLCCs show excellent dielectric properties with capacitance variation $\Delta C/C_{25°C} < 11\%$ over the temperature range of -55 to 205°C with breakdown strength of 26 kV/mm. Together with the high resistance of $1.87\times10^{11}\Omega$ at room temperature, the BNT–NN ceramics are regarded as the potential dielectric materials for the MLCCs application at the high temperature.

4:45 PM

(PACRIM-S29-024-2017) Novel Dielectric Composite Films Incorporated with Two-Dimensional Oxide Nanosheet Fillers (Invited)

H. Bae[1]; B. Kim[1]; D. Kwon*[1]

1. Korea Aerospace University, Materials Engineering, Republic of Korea

2-D nanosheets obtained via exfoliation of layered aluminosilicate minerals were incorporated as nano-fillers of polymer based dielectric composite films. 2-D nanosheets are expected to be promising fillers of nanodielectrics due to their unique structure and electrical properties. However effective dispersion of the nanofillers and filler/matrix nanoscale interfacial adhesion are still challenging to realize the enhanced dielectric performances of the dielectric nanocomposites. In this study, a layered aluminosilicate mineral, muscovite ($KAl_3Si_3O10\ (OH)_2$), which has severe layer charge deficiency and low cation exchange capacity could be successfully exfoliated into nanosheets with atomically thin thickness and micrometer-scale lateral size using an amphiphilic polymer in aqueous solution. The polymer assisted exfoliation process by PVP molecule was very effective to achieve nanosheets in relatively large lateral size. The FTIR and Raman spectroscopy results indicated presence of PVP molecules on the the muscovite nanosheet surfaces, where the hydroxyl groups were tightly bonded with carbonyl groups of the pyrrolidone moiety. The resulting PVP coated muscovite nanosheets exhibited excellent dispersion in the polymer matrix and strong interfacial adhesion with the matrix, leading to significant enhancements in dielectric properties and their stability at elevated temperatures.

PACRIM Symposium 31: Advances in Bioceramics: Biomineralization and Bioinspired Materials

On Bone: Formation of a Complex Bioceramic

Room: Monarchy
Session Chairs: Stephan Wolf, Friedrich-Alexander-University Erlangen-Neurnberg; Hortense Le Ferrand, ETH Zürich

1:15 PM

(PACRIM-S31-019-2017) Formation of hard-soft tissue interfaces: Lessons from collagen biomineralization (Invited)

E. Sone*[1]

1. University of Toronto, Institute of Biomaterials & Biomedical Engineering and Department of Materials Science & Engineering, Canada

Collagen biomineralization is a complex process for which the controlling factors, at the molecular level, are still not well understood. A particularly high level of spatial control over collagen mineralization is evident in the anchorage of teeth to the jawbone by the periodontal ligament: unmineralized collagen fibrils of the ligament become a fully-mineralized part of the cementum layer of the tooth at an unusually abrupt interface. The close juxtaposition of mineralized and unmineralized tissues provides an excellent model in which to study the molecular factors that control collagen biomineralization. This knowledge will be critical in the design of collagen-based scaffolds for tissue engineering of hard-soft interfaces such as the periodontal ligament-cementum junction, or for the reattachment of tendons and ligaments to bone. We developed a novel in vitro model, in which we demonstrate that the demineralized extracellular matrix of periodontal tissues contains sufficient information to reproduce with high fidelity the pattern of mineralization in native tissues in metastable calcium and phosphate-containing solutions. This model provides a unique platform with which to probe which extracellular matrix and solution molecules are responsible for this control, through selective enzymatic removal of different components.

1:45 PM

(PACRIM-S31-020-2017) Apatite Glass-Ceramics as a Substrate for Studying Protein-guided Mineralization

S. Habelitz*[1]; C. Russel[2]; W. Li[1]

1. University of California, San Francisco, PRDS, USA
2. University of Jena, GlassChemie, Germany

The formation of aligned fibrous apatite crystals in enamel is predominantly attributed to the involvement of amelogenin proteins. We developed a model to study interactions of matrix proteins and proteases with apatite mineral in vitro and tested the hypothesis that amelogenin solubility affects the ability to induce protein- guided mineralization. Crystal growth experiments were performed on fluoroapatite (FAP) glass- ceramics in mineralizing solutions containing recombinant full- length amelogenin (rH174), c-terminal modifications of this protein or a self-assembling amelogenin peptide. Using atomic force microscopy, we observed that mineral precipitated randomly on the substrate, but also formed thin layers (height, 10 nm) on FAP within 24 hrs. This growth pattern was unaffected when 0.4 mg/ mL of rH174 was added. In contrast, crystals grew on FAP at a rate up to 20 times higher, at 1.6 mg/ mL protein. Furthermore, in the presence of high concentrations of protein mineral bound specifically to FAP and aligned in strings approximately parallel to the c- axis of FAP, leading us to the conclusion that amelogenin proteins controls the direction and rate of growth of apatite in enamel. Glass-ceramics containing oriented apatite crystals are useful substrates for atomic force microscopy of molecular events in biomineralization.

2:00 PM

(PACRIM-S31-021-2017) Self-assembly of type I collagen molecules into fibrils (Invited)

F. Nudelman*[1]; J. Sindt[1]; B. Marzec[1]; A. Young[3]; N. Sommerdijk[2]; P. Murray[3]; P. Camp[1]

1. University of Edinburgh, Chemistry, United Kingdom
2. Eindhoven University of Technology, Dept. of Chemical Engineering and Chemistry, Netherlands
3. University of Strathclyde, Electronic and Electrical Engineering, United Kingdom

Type I collagen is an important constituent of many biological tissues, such as skin and bone. The collagen fibril is characterised by the highly organised arrangement of the molecules in staggered parallel arrays that give rise to a periodicity of 67 nm and the characteristic banding pattern. Fibril formation is a multi-scale, self-assembly process that is driven by electrostatic interactions between the molecules, leading to fibrils that can be several microns long. Little is known, however, about the self-assembling mechanisms of the molecules into fibrils. This issue is fundamental to understanding the structural basis of imperfect fibril formation in congenital disorders such as osteogenesis imperfecta, as well as the mineralisation mechanisms during bone formation. Here, we use time-resolved high-resolution cryo-transmission electron microscopy (cryoTEM) in combination with computer simulations study collagen assembly from the nano to the micron scale. We demonstrate that the self-assembly of collagen molecules into fibrils starts with the formation of molecular aggregates, followed by their association into microfibrils. Subsequently, the microfibrils associate into parallel, loosely-packed and disorganised arrays. These arrays further self-organise into a highly ordered fibril with the periodic 67 nm banding pattern.

2:30 PM

(PACRIM-S31-022-2017) Pre-nucleation clusters versus polymer-induced liquid precursors in collagen intrafibrillar mineralization

X. Huang*[2]; L. Niu[3]; C. S. Tay[4]; T. Luo[5]; F. Tay[1]

1. Augusta University, USA
2. Guanghua School and Hospital of Stomatology, Sun Yat-sen University, China
3. The Fourth Military Hospital, Prosthodontics, China
4. University of Toronto, Canada
5. School of Stomatology, Guangzhou Medical University, China

Intrafibrillar collagen mineralization is consistently achieved using liquid-like amorphous calcium phosphate (CaP) phase produced by stabilizing CaP pre-nucleation clusters (PC) with polyelectrolytes (PILP). Mineralization without PILP is only possible using high CaP concentrations during collagen self-assembly. This study compared the use of PC vs PILP at physiologic CaP concentrations for collagen mineralization. Collagen sponges were loaded into dialysis tubings (MWCO 500 Da) containing 4.2 mM Na_2HPO_4. The assembly was placed in 9 mM $CaCl_2$ and 1 mg/mL poly(allylamine) hydrochloride (PAH; Mw 17500 Da). This experimental design enabled PAH to exert a Donnan effect for precursors infiltration into collagen but prevented it from entering the tubing. Absence of PAH in the tubing was confirmed using fluorescamine assay. The aforementioned scheme was repeated in the control group without PAH. Results were compared with collagen sponges mineralized directly in $CaCl_2$, Na_2HPO_4 and PAH. Sponges were processed for TEM after 7 days. Intrafibrillar mineralization is possible using pre-nucleation clusters alone, when a polyelectrolyte is used to establish Donnan equilibrium. However, this process is inefficient, constrained by competition from extrafibrillar mineral precipitation. Intrafibrillar mineralization with PILP produces more predictable outcomes.

2:45 PM

(PACRIM-S31-023-2017) A new model of collagen intrafibrillar mineralisation based on establishment of Gibbs-Donnan equilibrium (Invited)

F. Tay*[1]

1. Augusta University, USA

Mineralization of fibrillar collagen with biomimetic process-directing agents has enabled scientists to gain insight into the potential mechanisms involved in intrafibrillar mineralization. By using polycation- and polyanion-directed intrafibrillar mineralization, the popular paradigm that electrostatic attraction is solely responsible for polyelectrolyte-directed intrafibrillar mineralization is challenged in this presentation. Because there is no difference when a polycationic or a polyanionic electrolyte is used to direct collagen mineralization, we argue that additional types of long-range non-electrostatic interaction are responsible for intrafibrillar mineralization. Molecular dynamics simulations of collagen structures in the presence of extrafibrillar polyelectrolytes show that the outward movement of ions and intrafibrillar water through the collagen surface occurs irrespective of the charges of polyelectrolytes, resulting in the experimentally verifiable contraction of the collagen structures. The need to balance electroneutrality and osmotic equilibrium simultaneously to establish Gibbs–Donnan equilibrium in a polyelectrolyte-directed mineralization system establishes a new model for collagen intrafibrillar mineralization that supplements existing collagen mineralization mechanisms.

3:15 PM

(PACRIM-S31-024-2017) Bone as an interpenetrating composite - 3D-printed models and finite element simulation

F. A. Sabet*[1]; F. Y. Su[2]; S. Pang[1]; J. Mok[3]; M. Tolley[4]; I. M. Jasiuk[1]; J. McKittrick[4]

1. University of Illinois at Urbana-Champaign, Department of Mechanical Science and Engineering, USA
2. University of California, San Diego, Department of Materials Science and Engineering, USA
3. University of California, San Diego, Department of Structural Engineering, USA
4. University of California, San Diego, Department of Mechanical and Aerospace Engineering, USA

Bone is a natural composite material that is mainly composed of collagen and biogenic hydroxyapatite. However, there is no full consensus among researchers regarding the bone nanostructure. While most of the previous studies assume that isolated crystals of hydroxyapatite are arranged in the collagen matrix, it is hypothesized here that the collagen and minerals in bone form an interpenetrating composite. Simplified models of an interpenetrating, an inclusion-matrix, and a no-network composite with collagen-hydroxyapatite volume ratios consistent with bone were developed. Models were 3D printed with a stiff and a soft polymer to represent the mineral and collagen phases, respectively. Mechanical properties were compared among composites. Models were also simulated under compression using finite element software ABAQUS. In the simulations an elastoplastic behavior was assumed for the stiff polymer, while the soft polymer was assumed to have an elastic behavior. Boundary conditions mimicking the experiments were applied and the effective response from finite element simulations was compared with experiments. This research is supported by the National Science Foundation (DMR-1507978).

Engineering of Hard Tissues I

Room: Monarchy
Session Chairs: David Kisailus, UC Riverside; Po-Yu Chen, National Tsing Hua University

3:45 PM

(PACRIM-S31-025-2017) Fabrication of porous carbonate apatite bone replacement using calcium sulfate granules as precursor (Invited)

K. Ishikawa*[1]; T. I. Arifta[1]; K. Tsuru[1]

1. Kyushu University, Department of Biomaterials, Japan

Although interconnected porous CO_3Ap may be a promising artificial bone replacement, introduction of porogen cannot be used for its fabrication since both CO_3Ap and calcite which is a precursor of CO_3Ap decompose at temperature required to burn out the porogen. On the other hand, calcium sulfate that has self-setting ability and stable at high temperature can be a precursor for porous calcium carbonate. First, calcium sulfate dihydrate (CSD) granules containing NaCl were prepared by mixing calcium sulfate hemihydrate CSD, 20wt% NaCl and distilled water. The granules was sintered at 750°C for 6 hours. Then, the obtained porous calcium sulfate was immersed in Na_2CO_3 solution followed by Na_2HPO_4 solution for compositional transformation through dissolution–precipitation reaction. XRD analysis and SEM observation revealed that porous calcium sulfate transformed to porous calcite and then CO_3Ap maintaining their fully interconnected macroscopic structure. Bone defect at the tibia of rat was reconstructed by porous and dense CO_3Ap granules. Both CO_3Ap exhibit excellent tissue response and osteoconductivity. New bone penetration was observed interior to the granules only in the case of porous CO_3Ap granules. It is concluded, therefore, that porous CO_3Ap has good potential value to be ideal artificial bone replacement.

4:15 PM

(PACRIM-S31-026-2017) Hydorxyapatite/collagen bone-like nanocomposite for medical applications (Invited)

M. Kikuchi*[1]; T. Sato[2]; Y. Shirosaki[3]; M. Aizawa[2]; K. Kadowaki[4]; M. Uezono[4]; K. Moriyama[4]; K. Takakuda[4]

1. National Institute for Materials Science (NIMS), Bioceramics Group, Japan
2. Meiji University, Japan
3. Kyushu Institute of Technology, Japan
4. Tokyo Medical and Dental University, Japan

Bone is a typical nanocomposite composed of nonstoichiometric hydroxyapatite (HAp) nanocrystals and type-I collagens. They form an oriented nanostructure that c-axis of HAp nanocrystals and lengthwise direction of collagen molecule align along each other. This nanostructure allows both mechanical toughness and biochemical activeness of bone. The authors succeeded in fabrication of HAp/collagen bone-like nanocomposite (HAp/Col). The HAp/Col dense and porous bodies are completely incorporated into bone remodeling process when they are implanted into bone defects. In the present lecture, the authors will deliver recent topics in the HAp/Col researches. One is a self-setting injectable HAp/Col paste. The HAp/Col powder and 3-glycidoxypropyl)trimethoxysilane aqueous solution mixed at powder/liquid ratio of 0.33 to 1.50 showed appropriate properties for an injectable bone filler. A twelve-week implantation of the paste in pocine tibia was completely substituted with newly formed bone without any adverse events. Another is coating of the HAp/Col onto titanium. The HAp/Col coating on titanium showed greater surrounding new bone formation and 3 times faster osseointegration in comparison to biomimetic HAp coating on titanium when they implanted into sub-periosteum of rats' cranium. Detailed data will be shown at the podium.

4:45 PM

(PACRIM-S31-027-2017) Development of Functional Heterostuctured Bone Substitute for Cell loading and Drug Delivery

N. Raja*[1]; H. Yun[2]

1. Korea University of Science and Technology, Advanced Materials Engineering, Republic of Korea
2. Korea Institute of Materials Science, Engineering Ceramics Department, Republic of Korea

Recent advances in bone tissue engineering have shown inclination towards cell printing within the bone substitutes which substantially increase their function and application. Conventional cell printing employs soft hydrogels which, due to fast degradation lack the long term stability required for balanced regeneration of hard tissue. Using our novel core-shell nozzle system, progressive formation of beads was enabled by simultaneous extrusion alginate hydrogel and ceramic paste. Homogeneous ceramic paste was extruded into cell loaded alginate droplet forming a ceramic coil providing the prolonged structural stability. Rigid hydrogel shell was produced by ionic crosslinking of bead with calcium chloride solution. The setting of ceramic core was achieved by cementation reaction which involves hydrolysis reaction. The cementation resulted in the formation of calcium deficient hydroxyl apatite, a well-known biocompatible and osteoconductive material. This promoted the growth and spreading of MC3T3-E1 cells, specifically on the surface of the ceramic core. Encapsulated cells were observed to be alive for up to 50 days in the hydrogel shell. Subsequently drug loaded ceramic pastes were also tested for positive cell growth. The hydrogel shell – ceramic core model gives an opportunity to print cells as well as transport various biomolecules to enhance and support bone tissue regeneration.

5:00 PM

(PACRIM-S31-028-2017) Novel Nanofibrous Bilayer Scaffolds Incorporated with Different Cells for Regenerating Complex Body Tissues

Y. Zhou*[1]; M. Wang[1]

1. The University of Hong Kong, Hong Kong

Tissue engineering has advanced significantly but regenerating complex body tissues is still a formidable task. Complex tissues generally display multilayer structures involving different cells. It is therefore important to develop multilayered scaffolds incorporated with different cells. In this study, a continuous process of concurrent electrospinning and electrospray was investigated to produce nanofibrous scaffolds with a bilayer structure incorporated with different cells. PLGA (LA:GA at 50:50 and 75:25) was electrospun into bilayer scaffolds: one layer of PLGA(50/50) fibers and another layer of PLGA(75/25) fibers. Coaxial electrospray was used to fabricate cell-encapsulated sodium alginate (SA) microspheres. SA microspheres containing human umbilical vein endothelial cell (HUVEC) or human aortic smooth muscle cell (HASMC) were respectively incorporated in the PLGA(50/50) layer and PLGA(75/25) layer. After dissolving SA shell, cells were released in scaffolds. The structure of cell-laden scaffolds was studied. The viability, distribution and proliferation of HUVECs and HASMCs in scaffolds were investigated. Results showed cell viability was well maintained in the scaffold fabrication process and cells were distributed in respective layers of the scaffolds. This study demonstrates the potential of the new technology for making novel cell-laden scaffolds.

5:15 PM

(PACRIM-S31-029-2017) Comparison of Demineralization Methods for Porcine Femur Cortical Bone

F. Y. Su*[1]; S. Pang[2]; R. Hsiong[1]; I. M. Jasiuk[2]; J. McKittrick[1]

1. University of California, San Diego, USA
2. University of Illinois at Urbana-Champaign, USA

It is well known that bone's impressive mechanical properties are a result of its intricate hierarchical structure from the nano- to macroscale. To gain a better understanding of the effect of collagen on the mechanical properties of bone, it is important to determine an efficient and effective method of demineralization that also preserves the collagen macromolecular organization. Previous studies have shown that 10% citric acid, 0.376 M ethylenediaminetetraacetic acid, 10% formic acid, 0.6 M hydrochloric acid are effective at removing mineral from bone and other mineralized collagen. However, most studies use bone powder instead of whole bone tissue and many do not directly observe whether the macromolecular organization is intact. This study tested previously mentioned demineralization methods on porcine femur cortical bone. Demineralization was evaluated using micro-computed tomography, thermogravimetric analysis, and Raman spectroscopy. Preservation of collagen macromolecular structure was observed using scanning electron microscopy, small angle x-ray scattering, and atomic force microscopy. This work is supported by the National Science Foundation (DMR – 1507978).

GOMD Graduate Student Posters

Room: Grand Promenade

5:30 PM

(GOMD-GSP-001-2017) Measurement of the Forward Dissolution Rate of the International Simple Glass using the Single-Pass-Flow-Through Method

A. J. Fisher*[1]; C. L. Corkhill[1]; R. J. Hand[1]; N. C. Hyatt[1]

1. The University of Sheffield, Material Science and Engineering, United Kingdom

Vitrified high level waste (HLW) is destined for final disposal in a geological disposal facility, where the release of radionuclides to the geo-sphere will be controlled by the dissolution of the glass matrix. Developing an understanding of glass dissolution is critical to building a robust safety case for geological disposal. In particular, an assessment of the kinetics of glass dissolution is required, as a function of the long-term conditions within the repository (e.g. pH and temperature). The forward rate of dissolution of the International Simple Glass (ISG), a reference HLW simulant base glass, was determined in this investigation. Using the Single-Pass-Flow-Through (SPFT) method we determined the inherent forward rate of ISG dissolution over the temperature range 40°C to 70°C and alkaline pH range of 7 to 11. Through application of the transition state theory, we obtained the fundamental parameters necessary to model the dissolution kinetics; activation energy (E_a), pH power law coefficient (η) and the intrinsic rate constant (k_0). These results are discussed in comparison with those obtained on the same glass using the micro-channel flow through method, and also with those for a UK simulant nuclear waste glass.

(GOMD-GSP-002-2017) Interactions between Simulant Vitrified Nuclear Wastes and Idealised Cement Leachates

C. Mann*[1]; E. M. Pierce[2]; J. R. Eskelsen[2]; C. L. Thorpe[1]; N. C. Hyatt[1]; J. Provis[1]; C. L. Corkhill[1]

1. University of Sheffiled, Material Science and Engineering, United Kingdom
2. Oak Ridge National Lab, USA

Within the United Kingdom (UK), it is proposed that nuclear waste will be disposed of in a geological repository, utilising an engineered barrier system that will be optimised to physically and chemically impede the transport of radionuclides to the biosphere. Interaction of groundwater with the cementitious components of the facility will lead to the presence of high pH conditions within a repository. The effect of such cement leachates on the durability of vitrified wasteforms is not well understood. Here we present results from a glass durability study using simulated cement leachates to elucidate the mechanisms that govern glass corrosion under these complex geochemical conditions. The normalised mass loss and normalised leaching rate as a function of cement leachate composition was determined by effluent solution analysis. Additionally, we present characterisation results collected on alteration layers by conducting glancing-angle x-ray diffraction and electron microscopy measurements on monolith samples. Collectively, these data provide new insight into the mechanisms that govern glass dissolution in the complex geochemical conditions expected for vitrified UK waste if water breaches the engineered barrier system in a geological repository.

(GOMD-GSP-003-2017) Influence of bubble-induced motion on the mixing of glass melts

D. Boloré*[1]; F. Pigeonneau[1]; P. Chamelot[2]; M. Gibilaro[2]; L. Massot[2]; O. Masbernat[3]; E. Cid[3]

1. Saint-Gobain Recherche, France
2. Laboratoire de Génie Chimique, Procédés Electrochimiques, France
3. Laboratoire de Génie Chimique, Génie des Interfaces & Milieux Divisés, France

Bubbles are produced at all steps of the melting process: closing of the pore network, carbonates reactions, sulfates decomposition or reboil at the end of the furnace. Consequently, it is one of the main defect in glass. But bubbles also play a useful role during the melting process: they participate in glass homogenization. Indeed, homogenization needs momentum which is mainly brought by thermal convection and bubbles motions. It is interesting to note that the motion induced by bubbles can put into contact reactive species which can potentially create a self-sustaining system. As recycling is already a major trend in our societies, we have to consider the impact of glass cullet additions on the melting process. First, we examine the nucleation rate of bubbles at the interface between two glasses, chemically different or not. We measure the velocity field around a bubble in order to look at the effect of the bubbles on the mixing rate of the two glasses. For this purpose, an X-Ray imaging device was used in transmission mode. Studied glasses are seeded with oxides particles. Bubbles rise in the glass and induce seeding particles motion. Applied on these time resolved particle images, an optical flow alorithm allows to calculate vector velocity fields around bubbles. Data obtained could be injected in finite elements codes.

(GOMD-GSP-004-2017) Foaming Glass Using High Pressure Sintering

M. B. Østergaard*[1]; R. R. Petersen[1]; J. Konig[2]; M. Bockowski[3]; Y. Yue[1]

1. Aalborg University, Chemistry and Bioscience, Denmark
2. Jozef Stefan Institute, Advanced Materials Department, Slovenia
3. Polish Academy of Sciences, Institute of High Pressure Physics, Poland

Foam glass is a high added value product which contributes to waste recycling and energy efficiency through heat insulation. The foaming can be initiated by a chemical or physical process. Chemical foaming with aid of a foaming agent is the dominant industrial process. Physical foaming has two variations. One way is by saturation of glass melts with gas. The other involves sintering of powdered glass under a high gas pressure resulting in glass pellets with high pressure bubbles entrapped. Reheating the glass pellets above the glass transition temperature under ambient pressure allows the bubbles to expand. After heat-treatment foam glass can be obtained with porosities of 80–90 %. In this study we conduct physical foaming of cathode ray tube (CRT) panel glass by sintering under high pressure (5-25 MPa) using helium, nitrogen, or argon at 640 °C (~10^8 Pa s). Reheating a sample in a heating microscope above maximum foaming temperature gives a suitable foaming temperature for the remaining samples. We show that the foaming kinetics depend on the type of gas and the pressure. A critical pressure of around 20 MPa is found to give the largest expansion for all gasses. Samples are obtained with 100 % closed porosity for argon and nitrogen samples (5-20 MPa) and for helium samples (5-15 MPa). The pore structure of the samples is analysed to understand the critical pressure.

(GOMD-GSP-005-2017) Synthesis, Sintering, and Thermal Properties of ThN

S. S. Parker*[1]; A. Parkison[1]; J. T. White[1]; A. T. Nelson[1]

1. Los Alamos National Laboratory, Material Science and Technology Division, USA

Thorium-based nuclear fuel cycles represent an intriguing alternative to conventional nuclear fuels. The majority of thorium fuels tested and analyzed to date are oxide or metal fuel forms, but a thorium cycle constituted using a nitride architecture would offer a number of performance benefits. Thorium mononitride (ThN) has considerably higher actinide density than thorium oxide, and has a significantly higher melting point than thorium metal. The thermal conductivity of ThN far exceeds that of UO_2 in temperature ranges relevant to nuclear reactor operation. However, to date the only demonstrated means of producing ThN has been direct nitration of the metal. In this work, a novel carbothermic reduction to nitridation (CTRN) synthesis pathway to produce high purity ThN from ThO_2 is presented. The ThN feedstock produced by the CTRN process was then milled, pressed, and sintered to produce high density (< 90% theoretical) properties for initial thermophysical property measurements. The thermal conductivity, heat capacity, and thermal expansion data for ThN from room temperature to 1800 K are presented and discussed with respect to the benefits of a thorium nitride fuel cycle.

(GOMD-GSP-006-2017) Impact of Hot Compression on the Stress Optic Coefficient of Oxide Glasses

T. K. Bechgaard*[1]; L. M. Thirion[2]; S. Rzoska[3]; M. Bockowski[3]; J. C. Mauro[2]; M. M. Smedskjaer[1]

1. Aalborg University, Denmark
2. Corning Incorporated, USA
3. Institute of High-Pressure Physics, Polish Academy of Sciences, Poland

The stress-induced birefringence (termed photoelastic response) in oxide glasses has important consequences for several applications. The effect of composition on the photoelastic response is relatively well understood, but here we evaluate the effect of hot isostatic compression on the photoelastic response of ten oxide glasses within the aluminosilicate and boroaluminosilicate glass families. Hot isostatic compression normally results in decreasing modifier-oxygen bond lengths and increasing network-former coordination numbers. These structural changes should lead to an increase in the stress optic coefficient (C) according to the model of Zwanziger et al., which can successfully predict the composition and structure dependence of C. However, the model fails to predict C for compressed glasses as we observe a pressure-induced decrease in the stress-optic coefficient. We discuss this finding based on measured refractive indices and elastic moduli and the atomic and lattice effects from the pioneering work of Mueller in 1935. We propose that changes in the lattice effect and changes in shear modulus due to topological changes are the origin of the pressure-induced decrease in C.

(GOMD-GSP-007-2017) Origin of the Mixed Alkaline Earth Effect on the Hardness of Silicate Glasses

Y. Yu*[1]; A. N. Krishnan[1]; M. M. Smedskjaer[2]; J. C. Mauro[3]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA
2. Aalborg University, Denmark
3. Corning Incorporated, USA

Most oxide glasses containing a combination of two (or more) types of alkali or alkaline earth cations tend to exhibit non-additive variations of their properties, when one cation is gradually substituted by the other one. This behavior, known as the mixed alkali effect (MAE), has remained an enigma in glass science. In particular, hardness – a property of primary interest for applications such as protective screens, can exhibit a positive or negative deviation from linearity with respect to the fraction of mixed ions. Here, based on molecular dynamics simulations, we investigate the hardness of mixed calcium/magnesium aluminosilicate glasses. We observe a minimum of hardness for mixed glasses, in agreement with micro-indentation experiments. Such anomalous behavior is found to arise from an increase propensity for shear flow relaxation under load, which is stimulated by the presence of internal stress in the atomic network. Finally, we demonstrate that the internal stress originates from a mismatch between the alkaline earth cations and the rest of the silicate network for mixed compositions. The present results offer a clear atomic picture of the origin of the MAE on hardness and highlight the potential for the nano-engineering of high-performance glasses.

(GOMD-GSP-008-2017) Structural investigation on hydrous phosphate glasses

R. Balzer*[1]; H. Behrens[1]; U. Bauer[1]; M. Fechtelkord[2]; A. Welsch[3]

1. Leibniz University of Hannover, Institute of Mineralogy, Germany
2. Ruhr-Universität Bochum, Institute of Geology, Mineralogy and Geophysics, Germany
3. The University of Sydney, Vibrational Spectroscopy Core Facility and School, Australia

This study focuses on the effect of water on structural and mechanical properties of lithium-magnesium-metaphosphate (LiMgP) and lithium-magnesium-aluminum-metaphosphate (LiMgAlP) glasses. Dry glasses were produced by melting at ambient pressure in a corundum crucible at 1100 °C (LiMgP) and 1200 °C (LiMgAlP). Hydrous glasses containing 0 - 8 wt% H_2O were synthesized within 15 h at same temperatures and a pressure of 500 MPa in an internally heated pressure vessel. Water contents were determined by Karl-Fischer titration. Pressurization increased the density of dry glasses by 2-3 %. Addition of 2-3 wt% H_2O has only weak effect on density, while higher water contents result in a pronounced density decrease. These trends point to large structural changes, i.e. denser packing, when water is added to the dry glasses. Infrared spectroscopy gives evidence of homogeneous water distribution in the glasses. Combination bands of OH groups and H_2O molecules in the near infrared are weak and poorly resolved. First evidence for molecular H_2O is give at 4 wt% The structure of the glasses has been investigated using Raman spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. Dry metaphosphate glasses contained predominately phosphate tetrahedra that are linked with two bridging oxygen (Q^2 species). Addition of water results in strong depolymerization of the network with formation of large fractions of Q^1 species.

(GOMD-GSP-009-2017) The structural role of Ta_2O_5 in SiO_2-CaO-ZnO-SrO-P_2O_5 glasses

A. Alhalawani[1]; M. Towler*[1]

1. Ryerson University, Mechanical and Industrial Engineering, Canada

Bioactive glasses are candidate materials for a wide variety of biomedical applications as they can bond to bone and be formulated to release bioactive ions into the local environment. Tantalum is a bioactive transition metal that has been used as an orthopedic medical device. It has a range of biological and physical properties that make its incorporation into bioactive glass systems promising for various clinical applications. A series of glasses based on the system $48SiO_2$-(36-X)ZnO-6CaO-8SrO-$2P_2O_5$-XTa_2O_5 with X varying from 0 mol% (TA0) to 0.5 mol% (TA2) were synthesized. The addition of small amounts of Ta_2O_5 did not cause crystallization of the glasses but increasing Ta_2O_5, replacing ZnO, was found to result in an increased number of bridging oxygens. This, along with the data recorded by differential thermal analysis and magic angle spinning-nuclear magnetic resonance, confirms that Ta acts as a glass former in this series. Solubility experiments showed that minor changes in the glass structure caused by Ta incorporation exhibited greater cumulative %weight loss, pH values and cumulative Zn^{2+} and Sr^{2+} ion concentration over a period of 30 days of maturation, when compared to Ta_2O_5-free glasses. The results confirm that replacing ZnO with Ta_2O_5 in silicate glasses results in the formation of stronger bonds within the glass network without any adverse effects on the solubility of the glasses prepared from them.

(GOMD-GSP-010-2017) Iron specification in lithium iron phosphate glasses

M. Stranghoener*[1]; H. Behrens[1]; A. Welsch[2]

1. Leibniz University Hannover, Institute of Mineralogy, Germany
2. The University of Sydney, Vibrational Spectroscopy Core Facility and School of Chemistry, Australia

Structure and properties of glasses are strongly influenced by the Fe^{3+}/Fe^{2+} ratio of which is little known for lithium iron phosphate glasses, a possible electrode material in rechargeable Li-ion batteries. A starting glass ($30Li_2O$ $10Fe_2O_3$ $60P_2O_5$) was prepared by melting raw materials in a corundum crucible at 1200°C in air. Contamination by 1.43 mol% Al_2O_3 was detected by electron microprobe. Further experiments were conducted in gas mixing furnaces using different gases (from air to Ar/H_2) to control oxygen fugacity. Colorimetric wet chemistry analysis revealed a continuous increase of Fe^{2+}/Fe_{tot} from 0.16 (air) to 0.81 (Ar/H_2). Optical absorption spectra show two pronounced peaks of Fe^{2+} at 4500 and 9500 cm^{-1} and a weak peak of Fe^{3+} at 23500 cm^{-1}. Upon reduction both Fe^{2+} peaks shifts towards higher wavenumber indicating a stabilization of octahedral coordination of Fe^{2+}. A broad absorption band centered at 20000 cm^{-1} has maximum intensity at intermediate redox state of iron and is assigned to Fe^{2+}-Fe^{3+} charge transfer. Raman spectroscopy indicate that Fe^{3+} acts as a network former linking phosphate chains whereas Fe^{2+} act as a network modifier occupying interstitial sites. The results of this work demonstrate the dramatic changes in the glass structure with changing Fe^{2+}/Fe^{3+} ratios. The presence of significant ferric iron even at lowest fO_2 may cause severe problems during crystallization, i.e. formation of magnetite.

(GOMD-GSP-011-2017) Nd^{3+}-doped silicate glasses as a color filter for white LED with wide color gamut coverage

K. Han*[1]; S. Kim[1]; Y. Kim[1]; C. Shin[2]; K. Chung[2]; H. Hwang[2]; W. Chung[1]

1. Kongju National University, Advanced Materials Engineering, Republic of Korea
2. NEPES, Republic of Korea

In order to improve color rendering index (CRI) of conventional white LEDs (wLEDs) which employ only yellow phosphor, combination of red phosphors either with green or yellow phosphors are normally used. Liquid crystal display (LCD) requires back light units with high color rendering index as well as wide color gamut coverage for the improved picture quality. Narrow emission bandwidth of green and red phosphor is required for wide color gamut coverage and thus wLEDs with quantum dots (QDs) as a color converting material are recently used for high quality LCD displays. However, QDs require high production cost and have weak thermal and chemical stability. In this study, thus, we achieved wLED with narrow green and red emission bandwidth by introducing Nd-doped silicate glasses as a color filter for commercial wLED with green and red phosphors. Nd^{3+}-ion has a strong absorption band around 580 nm which is hypersensitive and thus good for bandwidth control of the LED. Various silicate glasses were fabricated varying Nd_2O_3 content and their absorption peak and bandwidth were measured. Glasses were mounted on commercial wLED varying thickness. The wLED with Nd-glass showed green and red emission with effectively reduced bandwidth improving NTSC color gamut of the wLED.

(GOMD-GSP-012-2017) Phosphor-in-Glass composed of red-green phosphors for white LED with wide color gamut coverage

S. Kim*[1]; K. Han[1]; W. Im[2]; C. Shin[3]; K. Chung[3]; H. Hwang[3]; W. Chung[1]

1. Kongju National University, Division of Advanced Matrials Engineering, Republic of Korea
2. Chonnam National University, School Materials Science and Engineering, Republic of Korea
3. Nepes Institute of Science and Technology, Republic of Korea

Various inorganic color converters such as phosphor ceramics and phosphor-in-glass (PiG) were suggested for high power wLED applications. Among them, PiG can be easily fabricated with a transparent glass frit and phosphors and provide color tunable wLEDs simply varying phosphor content or thickness of PiG plate. It showed also improved thermal stability and recently applied to an automobile headlamp. However, commercial PiGs use yellow phosphor and have high sintering temperature of 750 ºC at which red phosphor such as CaAlSiN3:Eu^{2+} (CASN) cannot be incorporated due to thermal degradation. Moreover, in order to achieve wide color gamut of LCD display, wLEDs for back light unit should provide green and red emission at the same time with high thermal stability. In this study, thus in order to provide a PiG plate for BLU application, we employed a SiO_2-ZnO-B_2O_3-R_2O (R=Li, Na) glass which has low sintering temperature of 550 ºC to embed green and red phosphors. $Lu_3Al_5O_{12}:Ce^{3+}$ (LuAG) and CASN were used for green and red phosphors, respectively. Mixing ratio of glass to LuAG was varied and CASN was added to obtain wLED. After mounting on 450nm blue LED, color coordination, color rendering index (CRI) and luminous efficacy were measured using integrating sphere. Thermal quenching property as well as their color gamut coverage were examined comparing with those of PiG with yellow phosphor.

(GOMD-GSP-013-2017) Effects of Rare-Earth Co-doping and Heat Treatment on Zinc Borosilicate Glass Phosphors

S. Bosna*[1]; H. Sade[1]; S. Dayioglugil[1]; G. Soydan[1]; N. Solak[1]

1. Istanbul Technical University, Metallurgical and Materials Engineering, Turkey

Persistent luminescence materials can emit light even for several hours after the removal of the light source. These types of material have received special attention due to their applications in optoelectronics, LEDs and sensors. Optoelectronic devices are made from glasses thanks to their optical properties; therefore, glass phosphors have potential application for optoelectronic devices. However, persistent phosphorescence in glasses has been recently developed and there are limited studies on this topic. In this study, Zinc borosilicate glass phosphors (Tb^{3+} doped) with persistent phosphorescence properties are synthesized and characterized by using, SEM, XRD, DTA, Dilatometer and Spectrophotometer. The effects of cooling rate, heat treatment temperature/time and rare-earth co-doping have been investigated. La, Ce, Sm, Gd and Dy oxides were used as co-dopant and it is directly observed that the ionic radius of the rare-earth oxides has significant effect on the phosphorescence properties.

GOMD Undergraduate Student Posters

Room: Grand Promenade

5:30 PM

(GOMD-UGSP-001-2017) Thermal Study of Bio Active Borosilicate Glass that Contains Cerium Oxide Nano Particles

J. Ard*[1]; K. S. Ranasinghe[1]; R. Singh[1]; D. E. Day[2]; G. Humble[3]

1. Kennesaw State University, Physics, USA
2. Missouri University of Science & Technology, USA
3. Paulding High School, Physics and Physical Science Science Department, USA

Borosilicate glass doped with varying wt% of cerium oxide is used to create cerium oxide nano particles. Thermal studies of each concentration of both glass and nano particles were carried out using an SDT Q600 differential scanning calorimeter. A strong crystalline phase of CeO_2 is clearly visible above the melting of the glass phase indicating the presence of ceria in the as-melted glass. Several studies indicated a possible crystalline phase at a higher temperature with a peak more prominent at heating rates above 20C per min.

(GOMD-UGSP-002-2017) Technological aspects and characterization of solution-based arsenic selenide thin films

M. White*[1]; J. Allen[1]; J. Bunton[1]; B. Gaither[1]; A. Kovalskiy[1]

1. Austin Peay State University, Department of Physics and Astronomy, USA

Spin coated thin films of chalcogenide glasses have quite different structure and properties than the films obtained by other methods such as thermal evaporation or sputtering. Solution-based method provide lower sensitivity of glass matrix to the influence of bandgap and superbandgap light. Such a feature can be very useful for non-linear optical applications based on high transparency in IR region. Arsenic selenide films were obtained by chemical dissolution of bulk arsenic selenide glasses in ethylenediamine with subsequent spin-coating and thermal treatment. Technological features of the spin-coating method for the arsenic selenide and role of chemical environment were studied with the aim to obtain optical quality film and avoid surface oxidation. Raman spectroscopy was used for structural characterization of the prepared samples. Photo-induced optical effects were studied by irradiating the thin chalcogenide film with light of different energy and intensity. Kinetics of photodarkening was analyzed.

(GOMD-UGSP-003-2017) Specific Heat Capacity of Amorphous Materials near the Absolute Zero

R. Karsdorf*[1]; F. Werr[1]; A. Lenhart[1]; D. de Ligny[2]

1. TH Nürnberg, Materials Engineering, Germany
2. FAU Erlangen, Materials Science, Germany

The temperature dependency of specific heat capacity for crystalline bodies is usually well described by Debye's model which predicts that the ratio c_p/T^3 should remain constant over all temperatures[1]. For glasses a significant deviation is observed in the range between 5 and 25 Kelvin. This feature evidences their Excess Heat Capacity (EHC) which varies with the composition as evidenced in the alkaline silicates[2]. This gives an insight in the relationship between composition and entropy of glass. This additional entropy in the EHC is the consequence of additional vibrational modes in the amorphous system. Raman spectroscopy is a well know technique to study vibrational modes and allows to measure the so-called Boson peak[3]. Hence, we compare the evolution of the EHC with the Boson Peak over different binary glass compositions. The two phenomena follow a similar trend with the compositional changes. A better understanding of the relationship between them could be an interesting contribution to the comprehension and description of the structure and mid-range order of glasses.

(GOMD-UGSP-004-2017) Glass technology and use in ancient Byzantine Turkey: Color, composition, deterioration, and field identification of glass at Çadir Höyük

E. Fergerstrom*[1]; H. Meredith[2]; J. McCloy[1]

1. Washington State University, School of Mechanical and Materials Engineering, USA
2. Washington State University, Department of Fine Arts, USA

Çadir Höyük, Turkey, is home to a unique trade settlement that spanned from the 4th – 11th centuries beginning in the Middle Chalcolithic Era and ending in the Late Byzantine. Stratification of the layers have allowed for precise excavation with regard to dating and compositional information of the materials and technology used during this era. The glass compositions of this time mark a change from a medium characterized by Roman glassmaking to that of Byzantine glassmaking due to a variation in regional patterns such as trade and production. There is potential to provide a basis for understanding these regional patterns using typological and compositional analyses. Using a hand-held x-ray fluorescence, distinguishing these compositions in the field will allow for better understanding of glass among Byzantine inhabitants of Çadir Höyük. Additionally, the possibility of multiple glass compositions buried under similar conditions for long times promises to provide valuable data regarding long term glass corrosion, which is of great current interest to the nuclear waste glass community.

(GOMD-UGSP-005-2017) Producing Amorphous Tellurium Dioxide

A. DeCeanne*[1]; S. Feller[1]; B. Hauke[1]; B. Smith[1]; K. Bozer[1]; Z. Thune[1]; I. Tillman[1]; M. Affatigato[1]; D. Holland[2]; E. Barney[3]; R. Orman[2]; A. Hannon[4]

1. Coe College, Physics, USA
2. University of Warwick, Physics, United Kingdom
3. University of Nottingham, United Kingdom
4. Rutherford Appleton Laboratory, United Kingdom

Over the past few years we have produced amorphous TeO_2 using three methods: roller quenching, laser levitation, and most recently[1] rapidly cooling a platinum crucible with small amounts (less than one gram) of molten TeO_2. The resulting samples were checked for glassiness using various methods including X-ray diffraction, neutron scattering, Raman spectroscopy, and differential scanning calorimetry. The yellow and green tinted glasses were subjected to physical property and spectroscopic analysis. A model was developed for the structure of these glasses. We will also review other recent reports of vitreous TeO_2. [1] Synthesis, thermal and structural properties of pure TeO2 glass and zinc-tellurite glasses N.S. Tagiaraa, D. Pallesa, E.D. Simandirasa, V. Psycharisc, A. Kyritsisb, E.I. Kamitsos, accepted by Journal of Non-Crystalline Solids (2016) Work supported by the National Science Foundation through grant NSF-DMR-1407404

(GOMD-UGSP-006-2017) Temperature-resolved ToF-SIMS of Display Glass Surfaces

C. T. Dahlquist*[1]; C. V. Cushman[1]; B. M. Lunt[1]; M. R. Linford[1]; N. J. Smith[2]

1. Brigham Young University, Chemistry, USA
2. Corning Incorporated, Science and Technology Division, USA

Multicomponent glasses are preferred substrates for manufacturing flat panel displays, and their surface properties can influence the display manufacturing process. Among the relevant surface attributes, the hydroxylation state of the surface is thought to be important in mediating properties such as adhesion and charging. Few studies address the surface hydroxyl concentration of planar substrates, and fewer still attempt to quantify them on multicomponent glass surfaces. This is a challenging analytical task because (i) planar substrates have low surface area and relatively low hydroxyl density, (ii) glass surface composition typically varies from its bulk composition, and (iii) multicomponent glasses can have hydroxyl groups of different identity, and analyses are complicated by the presence of mobile modifier ions. Here, we use temperature-resolved time-of-flight secondary ion mass spectrometry (ToF-SIMS) to evaluate the surface-hydroxyl concentration on glass substrates representative of display glass materials. These samples were exposed to various surface treatments, including aqueous solutions, believed to significantly alter surface chemistry. We have previously characterized how similar treatments alter the inorganic surface composition of such glasses. Accordingly, in this study, we aim to link complex interactions between surface composition and hydroxylation.

GOMD Poster Session (non-student)

Room: Grand Promenade

5:30 PM

(GOMD-P-001-2017) Phase separation in ancien Chinese glazes

W. Li*[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Ancient Chinese high-fired glaze falls into the category of lime glass or lime-alkali glass, which was derived from the plant ash glaze of the

Shang Dynasty (1600-1046BC). In this study, the chemical compositions and microstructures of ancient high-fired glazes have been investigated by means of EDXRF, XRD, OM and FESEM/EDS. The physico-chemical foundation for the glazes can be supposed within the confines of the phase equilibrium relationships and the metastable liquid–liquid immiscibility region in $CaO–Al_2O_3–SiO_2$ system. With nucleation and growth of anorthite, liquid–liquid immiscibility develops simultaneously with coarsening of the phase separation structure. Liquid–liquid phase separation turns out diversiform variations in shape, scale and distribution, closely associated with the size and crowding level of crystal crystallization, which on one hand shows local chemical heterogeneity of glaze, on the other hand demonstrates the essential impact of the un-equilibrium thermodynamic firing process on the formation of the glaze microstructure. For the first time, the crystallization-accompanied phase separation structure has been revealed as the most important feature for many ancient Chinese high-fired glazes.

(GOMD-P-003-2017) Charge Transfer (C T) Spectra of Vanadyl (VO^{2+}(VS) and Vanadyl (VO^{2+}(VP)) doped lead phosphate glasses

C. Churya*[1]

1. Tirumala Engineering College, Jawaharlal Nehru Technology University, Hyderabad, India

The lead Phosphate glasses doped with vanadyl with different compositions have been prepared by melt quenching technique. These glasses are doped with the transition metal ion as Vanadyl, VO^{2+} ion derived from $VOSO_4$ $5H_2$ O referred as VO^{2+}(VS) and another Vanadyl VO^{2+} derived from vanadium pentoxide V_2O_5 referred as VO^{2+}(VP) system were prepared by a single step process from PbO and NH_4 $H_2.PO_{4.}$ The Optical absorption spectra of all these glasses were recorded on Shimadzu3000 UV-VIS-NIR model Spectrophotometer. The Charge Transfer (CT) spectra of these glasses were studied in the region of 225nm to 300nm. It is significant to note that in both LP(VS) and LP(VP) glasses, the peak-position of CT band shows a gradual shift to higher wavelengths (lower energies) with increase in the PbO content. This is probably due to the orientation of V=O in the VO_5 towards Pb^{2+} ion. The CT(C) band of VO^{2+}(VS) in crystalline phase appears at lower energies for $x > 0.5$ correlating well with the appearance of (C)band. The results offer sufficient support to the conclusion that VO^{2+}(VS) and VO^{2+}(VP) behave as distinct, independent chemical species.

(GOMD-P-004-2017) IR Study of vanadyl ion doped lead phosphate Glasses

C. Churya*[1]

1. Tirumala Engineering College, Jwaharlal Nehru Technology University, Hyderabad, India

Investigation of Lead phosphate glasses doped with vanadyl ion employing IR technic have been studied. The IR band position of V=O by recording the IR spectra of vanadyl doped glasses. The IR spectra of these glasses are recorded in the region of 1600cm^{-1} -700cm^{-1}. The IR spectra of these glasses consists of mainly three bands for the purpose of discussion only as I,II,III regions, in the region of 1220cm^{-1}-1252 cm^{-1} designated as region I attributed as [P=O], and region II as 1038cm^{-1}-1057 cm^{-1} designated as[$PO_{4,}$ $\upsilon_3(T_2)$ mode] and region III 883cm^{-1}-904cm^{-1} designated as P-O-P bending.

(GOMD-P-005-2017) From Nano-Ductility to Macroscale Brittleness: Modeling the Fracture of Glass at Different Scales via Molecular Dynamics and Peridynamics Simulations

N. Krishnan*[1]; B. Wang[1]; J. C. Mauro[2]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA
2. Corning Incorporated, USA

Although they are archetypical brittle materials at the macroscale, the existence of metal-like ductility at the nanoscale in glasses remains controversial. Here, based on molecular dynamics simulations, we show that multi-component silicate glasses feature some intrinsic nano-ductility. This deviation from brittleness is shown to arise from the existence of heterogeneities in the local rigidity of the atomic network, which, in turn, induce crack deflections. Finally, the influence of such nano-ductility at larger scales is assessed through peridynamics simulations, which are directly parameterized from the outcomes of the molecular dynamics simulations. We show that, although glasses eventually break in the brittle fashion at the macroscale, the existence of nano-ductility should be accounted for, to properly predict the fracture toughness of glass in conventional tests or the characteristics of the crack pattern induced by a ballistic impact.

(GOMD-P-006-2017) In-situ observation of the structural change in $MgO-B_2O_3-SiO_2$ glass at high pressure

A. Yamada*[1]; M. Harada[1]; A. Masuno[2]; K. Yamanaka[3]; K. Mitsuhara[3]; S. Yoshida[1]; J. Matsuoka[1]

1. The University of Shiga Prefecture, Japan
2. The University of Tokyo, Japan
3. SR Center, Ritsumeikan University, Japan

The structural change in magnesium borosilicate glass under hydrostatic pressure was investigated by high-pressure Raman spectroscopy. 4MgO-3B2O3-3SiO2 glass has been synthesized by levitation method. The elastic moduli of the glass showed relatively higher value compared with $Na_2O-B_2O_3-SiO_2$ glass. In particular, bulk modulus was more pronounced. The structure of as-made glass was investigated by B and Mg k-edge x-ray absorption near edge structure (XANES), which indicate that the coordination number of B could be almost 3 and that Mg may have higher coordination number (i.e., 5 and 6). The structural response in compression was examined within diamond anvil cell, up to 8 GPa. As for silicate group, Q^2 and Q^3 structure were responsible to compression. Specifically, Q^2 structure could be replaced by Q^3 structure with elevating pressure, which means that the silicate network becomes polymerized with pressure. However, the structural change was almost reversible. On the borate group, metaborate group, which consists of three triangular boron with one non-bridging oxygen, decreased with pressure. In contrast, triborate group, which includes four-fold coordinated boron and has fully polymerized borate network, increased. Present structural change in borate group could be interpreted as the pressure-induced coordination number change of B and the polymerization.

(GOMD-P-007-2017) A new model for medium-range structure in vitreous silica

S. Cheng*[1]

1. Lawrence Berkeley National Laboratory, Molecular Foundry, USA

Vitreous silica is the simplest silicate glass. Understanding its structure is fundamental to deciphering the structure of all other silicate glasses. The most common model for vitreous silica is the continuous random network theory (CRN) It is based on the original idea of Zachariasen and X-ray diffraction studies by Warren. Although the original CRN model is presented in many textbooks, it has to be regarded as a first-order approximation of the glass structure. Many experimental data show that in the medium range (about 0.5 nm to 2 nm), the SiO_4 tetrahedra are not randomly connected, but has some unidentified ordering. In order to describe the medium-range ordering (MRO) in vitreous silica, various models have been proposed and explain some of the contradicting data, but not all of them. This poster will present a new nano-flake model and the TEM supporting evidence. The newly proposed model is found to be consistent with various analytical data and may explain well the mechanical and optical properties of vitreous silica.

(GOMD-P-008-2017) First-principles K-edge XANES simulation for doped Ti in CaO-P_2O_5 invert glass

T. Tamura*[1]; H. Maeda[1]; M. Kohyama[2]

1. Nagoya Institute of Technology, Japan
2. National Institute of Advanced Industrial Science and Technology (AIST), Japan

We simulated pre-edge fine structures in Ti K-edge x-ray absorption near-edge structure (XANES) spectra for doped Ti ion in calcium phosphate glass within first-principles full projector-augmented wave (PAW) method. Based on detailed analysis of dipolar and quadrupolar contributions, we proposed the systematic interpretation for the origin of the pre-edge peaks for crystalline and glass materials. The pre-edge region in Ti K-edge XANES spectra consists of three contributions; (i) quadrupolar contribution of core-holed Ti d orbital, (ii) dipolar contribution of Ti p orbital hybridized with on-site core-holed Ti d orbital, and (iii) dipolar contribution of Ti p orbital hybridized with neighboring ground-state Ti d orbital. The energy splitting and the intensity of each contribution depend on the symmetry of Ti-centered polyhedra. We found that the third contribution is absent for an isolated Ti ion in glass materials.

(GOMD-P-009-2017) Study of radiation resistance of erbium-doped-nanoparticles optical fiber for space applications

M. Lancry*[1]; B. Hari Babu[2]; N. Ollier[2]; H. El Hamzaoui[3]; A. Pastouret[4]; M. Bouazaoui[3]; L. Bigot[3]; B. Poumellec[1]

1. University Paris Sud, France
2. Laboratoire des Solides Irradiés, CEA-CNRS-Ecole Polytechnique, France
3. University Lille 1, PhLAM, France
4. Draka - Prysmian, France

Here we report on the γ radiation resistance of optical fibers doped by Al_2O_3 or SiO_2 nanoparticles containing Er^{3+} ions. The nanoparticles (NP) have been synthesized and then incorporated by solution doping inside the soot core fabricated, using MCVD technique. The generation of point defects in γ-irradiated optical fibers are explored systematically as a function of Al/Ge ratio ranging over 0.1-150, NP presence and their composition. Even with a high amount of Ge, Er-SiO_2-nanoparticles derived-optical fibers exhibit lower RIA than those with a low Ge content un-doped or doped with Er-Al_2O_3 nanoparticles. From RIA results, the optimum Al/Ge ratio should be at around 1 implying a better performance of NP doped optical fibers. Silica NP and high Al/Ge ratio (Al/Ge>10) standard fibers revealed a large concentration of GeE' centers. The H(I) defect centers are also observed, but we do not observe the related Ge defects i.e. no H(II) defects. Based on RIA and EPR measurements, SiNP fiber is the better one despite it has a slight amount of Al_2O_3, Our experimental results bring a new insight on the radiation resistance of SiO_2 and Al_2O_3 nanoparticles doped germano-silica fibers. This NP based doping technology is a significant way for improving the radiation resistance of erbium doped fiber amplifiers enabling their use of in photonic sub-systems for satellite communications.

(GOMD-P-010-2017) Photoluminescence from lead selenide quantum dots embedded in glasses

J. Wang*[1]; J. Han[1]; J. Xie[1]; X. Zhao[1]

1. Wuhan University of Technology, State Key Lab of Silicate Materials for Architectures, China

Glasses containing quantum dots (QDs) have been extensively investigated in the past few years due to the tunable band gap that enables widespread technological applications in optoelectronics [1]. Even though QDs with high photoluminescence efficiency and various structures have been successfully synthesized through chemical methods, incorporation of these QDs into solid matrices with good thermal, mechanical and chemical properties such as glasses can expand their potential applications [2-3]. Formation of QDs in glasses to achieve tunable absorption and photoluminescence of QDs through the thermal treatment is well established [4]. In this work, impurity co-doping and modification of glass compositions were investigated to realize the flexible tuning of the optical properties of PbSe QDs embedded in glasses. PbSe QDs were precipitated in the glass system with nominal composition of $50SiO_2$-$25Na_2O$-8.2ZnO-10BaO (or SrO)-$5Al_2O_3$-0.6PbO-1.2ZnSe (in mol%). When BaO was replaced by SrO, the blue-shift with significant enhancement in the photoluminescence intensity were observed because of the formation of PbSrSe tenary QDs. In addition, a new family of germanosilicate glass was developed and mid-infrared photoluminescence at ~2.6 μm was obtained from pure PbSe QDs.

(GOMD-P-011-2017) Tuning luminescence and electrical properties in $CuAlO_2$ by chemical unit substitution

Y. Liu*[1]; Y. Wu[1]

1. Alfred University, Materials Science, USA

Tuning the physical properties of $CuAlO_2$ transparent conducting oxide has become a major task in the development of multifunctional building blocks for optoelectronic devices. Due to its AlO_6 octahedron layer and O-Cu-O dumbbell chains, the delafossite structure of $CuAlO_2$ exhibits anisotropic physical properties and excellent suitability for cation accommodation. In the current research, a chemical unit substitution strategy was utilized to modify the subunit of $[Al^{3+}]O_6$ and $[Cu^+]O_2$ through charge compensation. Rare earth and Eu^{3+} ions were co-doped to probe the modification of the host structure that occurs with charge compensation, and a large shift in emission spectra was observed. The relevant electrical properties were characterized and compared at different substitution conditions. It is theorized that to a small degree, the chemical unit substitution may alter the confinement of the O-Cu-O link through Cu 3d/4p hybridization, and consequently generate new and tunable photoluminescence behavior in the delafossite structure.

(GOMD-P-012-2017) Effects of Particle Size on Microstructure using Laser Sealable Frit

J. A. Duprey*[1]; A. Hall[2]; L. Lamberson[1]; R. Morena[1]

1. Corning Incorporated - CRDC, Glass Research, USA
2. Corning Incorporated, Chemical Analysis, USA

Laser sealing is the preferred method to achieve high quality hermetic frit seals for OLED and other sealed assemblies. Laser sealing frit technology depends on many variables to obtain quality and specifications for product development. Variables range from screen printing frit pastes to profile uniformity and measured frit heights. One critical component is a well consolidated and low-pore microstructure after pre-sintering. Microstructure depends heavily on firing schedule and particle size of the powdered glass. Good consolidation of the glass ensures organic burn out and improves sealability. Porous microstructures lead to lower adhesion and compromise hermeticity of sealed products. The effect of particle size for a designed low Tg frit glass and filler were studied to determine the effects on microstructure following pre-sintering and laser sealing. Using a designed firing schedule for glass with a coarser particle size resulted in less consolidation than that of finer particle size glass. Results using the coarse particle size glass also show defects after sealing. Results with fine glass are smoother seals and lower surface roughness. Smoother seals can encourage better adhesion after sealing due to increased glass to frit contact. Microstructure can be used as a precursor for seal quality, adhesion strength, and hermetic durability which are critical in meeting specifications for a quality product.

(GOMD-P-013-2017) Glass forming ability in the TeO_2-ZnO-NiO system

O. Zamyatin*[1]; Y. Medvedeva[1]; E. Zamyatina[1]

1. Lobachevsky State University of Nizhni Novgorod, Chemistry, Russian Federation

Tellurite glasses have been studied extensively in the recent years due to their applications in the field of glass ceramics and electronic devices. The addition of ZnO to tellurite glass increases the forming ability and thermal stability of glasses. The introduction of transition metal oxides (like NiO, Co_3O_4, CuO) to the glasses changes both the physical and optical properties. These glasses are used to produce materials with semiconducting properties and the development of optical filters. The purpose of this study was to establish a glass-forming region in the TeO_2– ZnO – NiO ternary system and study the thermal and optical properties of glasses. Samples were synthesized by the conventional melt quenching method and the maximum concentration of nickel oxide for the vitrification was found. The glass transition temperature and crystallization temperature were determined as a function of composition. The optical properties in the entire range transparency of the glasses were studied and characteristic absorption bands in the visible and near-IR region due to the ion Ni^{2+} were registered. Amorphous nature of the glasses and crystalline phases, formed by heating a mixture of oxides were confirmed by X-ray diffraction analysis.

(GOMD-P-014-2017) Optical properties of the TeO_2– ZnO glasses doped with Cu^{2+}

O. Zamyatin*[1]; E. Zamyatina[1]; V. Plotnichenko[2]

1. Lobachevsky State University of Nizhni Novgorod, Chemistry, Russian Federation
2. Fiber Optics Research Center of the Russian Academy of Sciences, Russian Federation

TeO_2-based glasses have a wide range of properties that make them an attractive material for optoelectronics and photonics. The tellurite-zincate system has been extensively researched as suitable materials for optical fiber amplifiers and lasers. Despite all these possibilities and prospects, their wide application inhibits a high level of optical losses. Transition elements such as nickel, cobalt and copper have the intense absorption bands in the visible and near-IR region. There is only partial information about the behavior of these elements in this system included in the literature. The purpose of this study was to investigate the optical properties of tellurite-zincate glasses doped with Cu^{2+}. The transmission spectrums of the glass samples in the range of 0.3 to 2.8 microns contain an intense absorption band at 820 nm. The specific absorption coefficient and the integral absorption coefficient were calculated. The absorption bands in the mid-IR region due to impurity absorption of OH groups was registered.

(GOMD-P-015-2017) Complex oxides as a starting material for synthesis of the ternary tellurite glasses

O. Zamyatin*[1]; E. Zamyatina[1]; A. Sibirkin[1]

1. Lobachevsky State University of Nizhni Novgorod, Chemistry, Russian Federation

Glass materials based on the tellurium dioxide have attractive physical, optical and thermal properties and they promising candidates for the various branches of science and technology. One of the most interesting systems is tellurite-molybdate. It has one of the most extended glass-forming regions and can be significantly expanded and modified the beneficial glass properties by introducing bismuth oxide. However, the glasses prepared from TeO_2, MoO_3 and Bi_2O_3 possess reduced optical transparency in the visible and near infrared region. In this research, a new approach to significantly improve the optical properties of the glass was proposed and implemented. Molybdenum and bismuth tellurates (Te_2MoO_7, Bi_2TeO_6, $Bi_2Te_2O_8$ et al.) and the bismuth molybdate (Bi_2MoO_6 and $Bi_2 (MoO_4)_3$) were used for preparing glasses. Glass-forming range in the TeO_2 – MoO_3 – Bi_2O_3 system was studied and phases formation by heating the batch to the melting and on the crystallization of glass samples were investigated. Optical and thermal properties were studied for the synthesis of glasses and the dependence of the glass composition on the energy band gap and cut-off wavelength were established.

(GOMD-P-016-2017) Introduction to the new 20-inch MCP-PMT glass bulb production

X. Zhang*[1]

1. Insitute of High Energy Physics, Chinese Academy of Sciences, China

Photomultiplier is an essentially important device for particle physics experiments especially for low background experiments such as neutrino experiments. A new 20-inch MCP-PMT has been developed for the Jiangmen Underground Neutrino Observatory (JUNO). To meet the low radioactive background requirement of JUNO, the production technique of the glass bulb of MCP-PMT was studied and improved. This poster introduces the improvement of the glass bulb production technique, including the low radioactive glass bulb and the transition section production, bonding between bulb and transition section and annealing.

(GOMD-P-017-2017) Eu^{3+} and Er^{3+} environment modification by Electron and femtosecond Laser irradiation in phosphate glasses

M. Mahfoudhi[1]; R. Desmarchelier[2]; M. Lancry[2]; N. Ollier*[1]

1. CEA, France
2. ICMMO, France

Phosphate glasses are interesting in different fields (nuclear industry, batteries, medical) and also in optics because of their high ability to dissolve the rare earth ions (i.e amplifier elements of powerful laser systems). Fs laser writing is commonly used to modify refractive index in various glassy matrix and can also impact the rare earth ion dopant environment. At integrated doses of GGy, under high energy electrons irradiation, the migration of alkali ions in glasses can also lead to a strong modification of the glassy network. We want to provide a better understanding of those structural modifications in order to control the rare earth environment evolution in phosphate glasses. We are particularly interested in evaluating the role of electronic and thermal processes or migration induced by the electrical field by playing on the glass composition (mixed alkali effect), energy of electrons and dose of irradiation and repetition rate of the fs laser. We will present some results obtained on metaphosphate and ultraphosphate glasses irradiated by fs laser and 700 keV /2.5 MeV electrons. The local environment modification of Eu^{3+} (asymmetry ratio, Eu^{2+} formation) will be compared to the luminescence properties evolution of Er^{3+} ions. Those sytems do not present same features, as the Second Harmonic Generation signal obtained in Er doped ultraphosphate only

(GOMD-P-018-2017) Photoluminescence properties of Ce^{3+}-doped $Y_3Al_5O_{12}$ phosphors obtained by controlled crystallization of eutectic Y_2O_3-Al_2O_3 glass microspheres

K. Haladejová[1]; R. Klement*[1]; A. Prnová[1]; D. Galusek[1]

1. University of Alexander Dubcek in Trencin, Vitrum Laugaricio – Joint Glass Centre of the IIC SAS, TnU AD and FChPT STU, Slovakia

The glass in the systems Y_2O_3-Al_2O_3 with eutectic composition (76.86 mol.% (60 wt.%) Al_2O_3 and 23.13 mol.% (40 wt.%) Y_2O_3) was prepared by flame-spraying synthesis in the form of glass microspheres. The Ce^{3+} doping level was 0.25 at.%. The crystallization of glass was examined by DSC analysis and high temperature XRD (HTXRD). HTXRD revealed the crystallization of YAG phase up to 1200 °C and a-Al_2O_3 phase above 1300 °C. The observed two exothermic effects in DSC trace unusually correspond to YAG phase crystallization. The crystallization kinetics of glass was interpreted in terms of Johnson–Mehl–Avrami–Kolmogorov (JMAK) model. The polycrystalline phosphors were prepared from the glass by controlled crystallization at selected temperature-time regimes. The photoluminescence properties of glass and polycrystalline phosphors were studied in detail. While Ce^{3+} doped glass under UV excitation at 345 nm exhibits intensive blue emission, Ce^{3+} in YAG host green emission. As temperature of the heat-treatment increases, the intensity of blue emission decreases and green emission increases. The heat-treated sample at 935°C/3h shows however the balance of the blue and green emissions thus producing the white light under UV excitation at 345 nm. The lifetime and temperature dependent luminescence of selected samples were also investigated.

(GOMD-P-019-2017) Elaboration and structural study of Yb-doped optical fibers preforms'cores prepared by a plasma process

A. Barnini[1]; T. Robin[2]; D. Caurant*[1]; B. Cadier[2]; T. Gotter[2]; C. Guyon[1]; G. Aka[1]; T. Charpentier[3]

1. Chimie Paristech CNRS, IRCP, France
2. iXblue, France
3. CEA Saclay, France

In the race for high power fiber lasers, the rare earth-doped optical core quality is essential. Modern large-mode-area fibers require a fine radial control of the core refractive index (RI) that remains close to the silica level. These low RI can be achieved with multi-component materials, not using the conventional solution doping-based CVD technology, but rather through a full-vapor phase Surface Plasma Chemical Vapor Deposition (SPCVD), developed in our laboratory. These process generates straight glassy films on the inner surface of a thermally regulated synthetic silica tube under vacuum. In this paper, by varying process conditions and gases nature ($SiCl_4$, $AlCl_3$, $YbCl_3$, BCl_3, C_2F_6), several core compositions with various Al/Si and Yb/Al ratios (with B or F) were obtained. Their optical properties (RI) and homogeneity (electron microprobe) have been studied. After preform drawing, optical fibers were obtained with numerical apertures ranging from 0.06 to 0.09, power conversion efficiency between 65 and 75% and low background losses (<20 dB/km at 1100nm). In order to follow the evolution of Yb environment and dispersion in these samples, both optical fluorescence (spectra and luminescence lifetimes) and electron paramagnetic resonance were used. Moreover, the structure of the different matrices was probed using MAS NMR (Si, Al, B, F) and Raman spectroscopy.

(GOMD-P-020-2017) The Generation of The Residual Stress in ABS type Glaze of Bone China

J. Choi*[1]; H. Park[1]; Y. Han[1]; H. Kim[1]

1. Korea Institute of Ceramic Engineering and Technology (KICET), Engineering Ceramic Center, Republic of Korea

We investigated why the residual stress in ABS type glaze was generated in bone china product. The residual stress calculated in ABS type glaze was expected to be 15MPa or lower due to the difference between the coefficient of thermal expansion (CTE) of glaze and body according to Goodier's theory cited by Kingery. However, the residual stress measured by a stress meter was more than 50MPa. During glost firing, the interface layer appeared, which was thought to be hydroxyapatite(HAp) or β-tricalcium phosphate (TCP). A finite element simulation confirmed that CTE of interface layer have to be higher than $14x10^{-6}$/degrees Celciusand its thickness had to have 30 mm or thicker to be similar to measured value, 50MPa. Thus, it was thought that the difference of CTE between glaze and interface had a stronger influence than that between glaze and body to develop the residual compressive stress in glaze of bone china.

(GOMD-P-021-2017) Elasticity/Plasticity of Network Bonds in Chemically Strengthened Glasses

S. Tietje*[1]; R. Schaut[1]

1. Corning Incorporated, S&T, Glass Research, USA

Chemical (or ion-exchange) strengthening in glass induces positive strain as larger ions occupy the structural sites originally occupied by much smaller ions during melting and forming. It is believed that this strain is perfectly elastic, and any changes in the atomic structure are reversible upon removal of the strain. However, disagreements between measured and theoretical network dilation coefficients and reports of anomalous stress generation (tensile rather than compressive) suggest the possibility of plasticity of the local atomic network during the ion-exchange process. Here we prepare samples before and after various ion-exchange processes, including reverse ion-exchange back to the original as-melted chemistry. The samples are then characterized for chemistry by electron microprobe analysis, strain by dimensions and density, and elasticity (or plasticity) of the glass network by Brillouin scattering. Hysteresis of the sample dimensions and attributes during the forward and reverse ion-exchange processes will be discussed in relation to local atomic elasticity or plasticity during the ion-exchange process.

(GOMD-P-022-2017) Chemical strengthening of soda-lime-silicate glass: Effect of impurities and Na enrichment of the KNO_3 bath

V. M. Sglavo*[1]; H. Hassani[1]

1. University of Trento, Italy

Chemical strengthening of glass has gained notable interest during the last years because of its flexibility in the reinforcement of components with different geometry and thickness. Several variables like glass and molten bath composition, temperature and time can affect the efficiency of the process. During a typical industrial process, sodium atoms contained in the glass are substituted by potassium ions diffusing from the molten salt. An interesting aspect regards the poisoning of the bath after each process and its enrichment in sodium. In addition, the presence of several impurities in the bath can influence the ion-exchange efficiency. In the present work, the effect of variable sodium concentration in the molten bath and of typical impurities present in KNO3 commercial salts on the performances of the strengthened glass was analyzed. Soda-lime-silicate float glass was considered and, after the chemical strengthening process, it was characterized from a mechanical and chemical point of view to point out the efficiency of the ion-exchange process. The results point out that potassium surface concentration, residual compression and strength decrease in a non linear fashion as a function of the sodium content within the bath. The presence of some specific impurities like Ca also appear to be detrimental although the inefficiency is reversible to some extent.

(GOMD-P-024-2017) Development of chalcogenide glasses for mid-IR fiber sensors

V. Shiryaev*[1]; A. Velmuzhov[1]; M. Sukhanov[1]

1. Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, Russian Federation

The glasses in the Ge-Se, Ge–Se–I, Ge-As-Se-Te, Ge–Se-Te and Ge-Te-I systems are considered to be the promising materials for fabrication of mid-IR fiber sensors. They are characterized by high transparency in the near and middle IR-range and good stability against crystallization. The goal of the work is to develop the techniques for preparation of these glasses with low content of optically active impurities, investigation of properties of glasses, determination of the compositions with low tendency to crystallization, fabrication of low loss optical fibers, and their testing as chemical sensors. The present work represents the different approaches to preparation technique of special purity chalcogenide glasses providing the decrease in the contaminating effect of apparatus material. In the best examples of these glasses, the content of residual impurities was: hydrogen in the form of Se–H bonds - 0.005-0.02 ppm(wt), oxygen -<0.1 ppm(wt), silicon - £0.1 ppm(wt), of metals - <0.5 ppm(wt). Thermal, optical properties and stability to crystallization of different chalcogenide glass compositions were investigated. The possibility of use of different glass compositions and geometrical forms of fiber sensor zone for infrared chemical analysis of liquids has been demonstrated. This work was supported by the Russian Science Foundation (Russia, Grant No. 16-13-10251).

(GOMD-P-025-2017) Mid-infrared Luminescence of Dysprosium ions in modified Ga-Sb-S Chalcogenide Glasses and Fibers

A. Yang[1]; Z. Yang*[1]; J. Qiu[1]; M. Zhang[1]; H. Ren[1]; C. Zhai[1]; S. Qi[1]; D. Tang[1]

1. Jiangsu Normal University, China

$Ga_8Sb_{32}S_{60}$ chalcogenide glass is modified by arsenic (As) to further improve its thermal stability against crystallization, and the 3-5 μm mid-infrared (MIR) luminescent properties of Dy^{3+} ions in the modified glasses are studied. Furthermore, fibers consisting of Dy^{3+}-doped glass core and undoped glass cladding are drawn, and the transmission losses and MIR luminescence of the fibers are investigated. The substitution of a small amount of Sb by As could remarkably improve the thermal stability of the glass without leading to significant changes on the optical transparency and the effective phonon energy. Although Dy^{3+} addition has a negative effect on the thermal stability of the modified glasses, the doped glasses are still sufficiently stable for fiber drawing. Dy^{3+} ions in the modified glasses show strong MIR emissions around 2.95 μm and 4.40 μm with high quantum efficiencies and large stimulated emission cross sections. The fabricated fibers exhibit a background loss of less than 2 dB/m in the 2-6 μm spectral range and intense MIR emissions. These favorable properties indicate good potential of the fibers as MIR gain media.

(GOMD-P-026-2017) Nontoxic Chalcogenide Fibers for 2-12 μm Mid-infrared Supercontinuum Generation

Z. Yang*[1]; B. Zhang[1]; Y. Yu[2]; C. Zhai[1]; S. Qi[1]; B. Luther-Davies[2]

1. Jiangsu Normal University, China
2. Australian National University, Australia

Environment friendly nonlinear chalcogenide glass fibers with a Ge-Sb-Se core and a Ge-Se cladding are designed and fabricated for bright broadband mid-infrared (MIR) supercontinuum (SC) generation. The fabricated Ge-Sb-Se/Ge-Se fiber with a core diameter of 6 μm shows zero group velocity dispersion at ~4.2 μm and ~7.3 μm. By pumping the fiber with a length of 11 cm at ~4.5 μm with 330 fs pulses, we achieve a SC covering the ~2-12 μm spectral range and with an output average power of ~20 mW. This bright broadband SC source is promising for high-resolution MIR spectroscopy.

PACRIM Graduate Student Posters

Room: Grand Promenade

5:30 PM

(PACRIM-GSP-001-2017) Condition of deposit and prediction of internal structure of CeO_2 thin films fabricated by RF sputtering method

S. Miwa*[1]; T. Hashizume[2]; A. Saiki[2]

1. University of Toyama, Graduate School of Science and Engneering for Education, Japan
2. University of Toyama, Graduate School of Science and Engneering for Research, Japan

Solid oxide fuel cells (SOFC) are receiving attention with the co-generation system (improvement of energy efficiency by heat recovery during operation) as one of next-generation energy. It is becoming popular as the household generator. A major problem of YSZ-based SOFC is it has to be operated at a high temperature (900 ºC). For that reason, a long heating time for the start-up is required, and also the material to be used is limited. In addition, degradation of SOFC internal components will be faster. Thus, we use ceria (CeO_2) as electrolyte instead of YSZ. It can be reduced the operating temperature to 500-600 ºC. Also for the efficiency of power generation, the thickness of the electrolyte should be thin. So We deposited ceria on the Si(100) substrate by RF sputtering method, searched the deposition conditions. And we predict the internal structure and orientation of the membrane surface by using First-principles calculation.

(PACRIM-GSP-002-2017) Electrical, Thermal, and Mechanical Properties of SiC-BN Composites

H. Yeom*[1]; Y. Seo[1]; Y. Kim[1]

1. Functional Ceramics Laboratory, Department of Materials Science and Engineering, Republic of Korea

SiC-BN composites were fabricated by conventional hot-pressing from β-SiC and h-BN powders with 2 vol% Y_2O_3 as a sintering additive. Electrical, mechanical, and thermal properties of SiC-BN composites were investigated as a function of the BN content in the starting materials. The addition of BN suppressed the grain growth of the SiC and triggered the $\beta \rightarrow \alpha$ phase transformation of the SiC in SiC-BN composites. A minimum electrical resistivity of $3.7 \times 10^{-2}\Omega$cm was obtained for the SiC-4 vol% BN composite (SBN4). This low electrical resistivity was ascribed to N-doping in the SiC lattice, which acts as a donor for supplying electrons to the conduction band. Typical values for the electrical conductivity, fracture toughness, flexural strength, and thermal conductivity of The SiC-10 vol% BN composite at room temperature were 14 Ω^{-1}cm^{-1}, 4.3 MPam$^{1/2}$, 550 MPa, and 86 W/mK, respectively. The SiC-4 vol% BN composite can be electrical discharge machined to form complex shapes.

(PACRIM-GSP-003-2017) Bioactive Layers On Titanium Substrates Based On The Black Glasses

M. Lesniak[1]; M. Gaweda[1]; P. Jelen[1]; E. Dlugon[1]; M. T. Sitarz*[1]

1. AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Poland

Oxycarbide glasses, so called “black glasses”, are very interesting and promising materials from the point of their chemical and mechanical resistance. They can be used as modifying layers on different kind of substrates for example on steel. Controlling amount of carbon introduced to its structure is crucial for the properties of the material. We have proposed using as precursors of black glasses, well-defined ladder-like silsesquioxanes. As a result after pyrolysis under argon atmosphere, of such silsesquioxanes, visually homogeneous glasses in the bulk form and as layers on titanium substrates were received. Microscopic and spectroscopic examination showed that we obtained practically homogenous glasses containing in its structure carbon – black glasses. On the basis of microscopic examinations we also found that the resulting layers are tight without any cracks. The bioactivity of the resulting coatings, we have identified on the basis of in vitro tests in artificial plasma according to the Kokubo test. For bioactive materials are considered those on which surface occurs the accumulation of phosphate phase (preferably hydroxyapatite). The microscopic and spectroscopic studies clearly showed the presence of nanoscale hydroxyapatite on the surface of the samples after the incubation process. This work was supported by National Science Centre Poland under project no 2014/15/B/ST8/02827.

(PACRIM-GSP-005-2017) Influence of sulfate ion on phase and dispersion of $Y_3Al_5O_{12}$ nanopowders with the co-crystallization method

G. Fan*[1]; Z. Zeng[1]; X. Wang[1]; X. Wang[1]; W. Lu[1]; F. Liang[1]

1. Huazhong University of Science and Technology, Huazhong University of Science and Technology, China

Yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG) was synthesized from co-crystallized precursor of $Y_2(SO_4)_3$, $Al(NO_3)_3$-$Al_2(SO_4)_3$ and $Y(NO_3)_3$ formed three-layer core-hell structure. X-ray powder diffraction (XRD) pattern indicated that the increasing SO_4^{2-}content in the crystallized precursor was not conductive to the synthesis of the pure phase YAG, resulting from the huge segregation between $Y_2(SO_4)_3$ and $Al(NO_3)_3$-$Al_2(SO_4)_3$. Transmission electron microscopy (TEM) revealed that the increasing SO_4^{2-} content was beneficial for the dispersion of the powders, owing to the high decomposition temperature of SO_4^{2-} . The powders with the $n(SO_4^{2-}$)/$n(Y^{3+})$ mole ratio of 1.5 calcined at 1050ºC from the precursor showed good sintering activity and the the relative density of YAG ceramics sintered at 1550 °C is more than 80%, which is significantly higher than that of YAG ceramics synthesized by pure nitrate precursor.

(PACRIM-GSP-006-2017) Crystal-oriented tetragonal (Li,Na,K)NbO_3 ceramics

Y. Ono*[1]; S. Tanaka[1]; T. Harada[2]; H. Shimizu[2]; Y. Doshida[2]

1. Nagaoka University of Technology, Japan
2. Taiyo Yuden Co., Ltd., Japan

(Li,Na,K)NbO_3 (LNKN) ceramic has well-balanced piezoelectric properties and better environmental compatibility. The property of LNKN can be improved by controlling the microstructure as crystal orientation. The objective of this study is to fabricate crystal-oriented LNKN ceramics by colloidal processing in a magnetic field, and to demonstrate improvement of their piezoelectric properties. (x$LiNbO_3$-(1-x)$Na_{0.5}K_{0.5}NbO_3$, LNKN) particles with tetragonal crystal system was synthesized by solid phase reaction. A dispersed slurry was prepared by ball-milling of powder, isopropyl alcohol, and a dispersant. The slurry was poured into a mold and set in the superconducting magnet 10T until drying. A random LNKN was also fabricated as a reference. The powder compact was sintered at 1000°C under the oxygen atmosphere. The orientation of the powder compact and ceramics were evaluated by XRD. The P-E hysteresis loops were analyzed by a Sawyer-tower circuit, and the piezoelectric constant was measured by the d_{33} meter. The XRD pattern of the powder compact showed the c-axis orientation to the magnetic field. The c-axis-oriented structure changed to the c- and a-axis orientation after sintering. The relative density of sintered LNKN ceramics were ~96%. While the hysteresis loop of the oriented LNKN was almost same with that with random structure, the d_{33} of oriented sample was 143 pC/N and higher than non-oriented sample 103 pC/N.

(PACRIM-GSP-007-2017) Flash sintering of porcelain stoneware

M. Biesuz*[1]

1. University of Trento, Department of Industrial Engineering, Italy

Flash Sintering (FS) represents a very promising processing route for ceramic materials that allows to reduce drastically sintering time and temperature with undoubtable advantages in terms of limited CO_2 emissions, energy consumption and plants degradation. Flash sintering has been applied to crystalline materials with very different electrical and physical properties. Recently, it has been shown that also bulk glass specimens can undergo to a flash event, followed by a drop in glass resistivity, which was defined as Electric Field-Induced Softening (EFIS). In this work we extended the application of FS to porcelain stoneware, which is typically consolidated by viscous flow sintering or vitrification. In this way a sort of viscous flow flash sintering was produced. The specimens were produced by uniaxial pressing and sintered under the effect of an external electrical field. The results show that the material can be efficiently densified and nearly full density can be achieved in about 30 s.

(PACRIM-GSP-008-2017) Synthesis of Ti-Rich *BEA-Type Zeolite and Characterization of Ti Species during Crystallization

H. Horikawa*[1]; T. Iida[1]; R. Osuga[2]; K. Ohara[3]; J. N. Kondo[2]; T. Okubo[1]; T. Wakihara[1]

1. The University of Tokyo, Engineering, Japan
2. Tokyo Institute of Technology, Japan
3. Japan Synchrotron Radiation Research Institute, Japan

Zeolites containing titanium inside the framework have played a critical role as oxidizing catalysts, and reducing the molar ratio below Si/Ti = 50 is a critical challenge for increasing the number of active sites. In this study, *BEA-type zeolites rich in titanium were synthesized using Ti-Si oxide composites as ingredients. The composites were prepared through two routes: 1) mechanochemical treatment using a planetary ballmilling apparatus, and 2) sol-gel method. The molar composition as low as Si/Ti = 24 was achieved in the product prepared via the mechanochemical route. Especially, to accelerate the crystallization rate of *BEA-type zeolite, aluminum was added to the synthesis mixture in addition to incorporation from milling balls, and after the hydrothermal synthesis, an acid treatment was conducted to remove the aluminum to obtain products with only Ti, Si and O in the framework. It was clarified the Si/Ti ratio was preserved before and after the acid treatment. The state of Ti species during crystallization was examined using the X-ray total scattering (performed at SPring-8 BL04B2), physisorption, and elemental analysis. The difference in the crystallization behavior between the mechanochemical and the sol-gel routes was investigated.

(PACRIM-GSP-009-2017) Tensile Mechanical Behavior of Three-Dimensionally Networked Porous Carbon Materials

M. Nakajima*[1]; R. Inoue[1]; E. Kojo[1]; Y. Kubota[2]; Y. Kogo[1]

1. Tokyo University of Science, Japan
2. Japan Aerospace Exploration Agency, Japan

Porous carbon materials are expected as heat-resistant lightweight structural materials in aerospace field, because they have high strength relative to their low density with extremely high heat resistance. Among them, newly developed three-dimensionally networked porous carbon materials (TNPCs) are one of the most attractive materials. Since mechanical properties are fundamental and indispensable for actual uses, understanding of mechanical behavior is quite important. Experimental investigation into mechanical behavior of TNPCs, however, are limited, and it remains unclear whether or not mechanical behavior is identical to that of bulk materials. In this study, therefore, tensile mechanical behavior of the TNPC with three different pore sizes ranging from 4.5 μm to 10 μm were investigated. On the tensile tests, in addition to smooth specimens, open-hole and notched tensile specimens were prepared to investigate effect of stress concentration. The results showed that tensile strength of smooth specimens were proportionally increased with pore size. In tensile tests of open-hole specimens, strength was decreased by stress concentration, which was qualitatively similar to the behavior of bulk materials. In this presentation, effects of pore size and of stress concentration on the tensile strength of the TNPC will be discussed with reference to those of the bulk materials.

(PACRIM-GSP-010-2017) Porous Al_2O_3 Catalyst Carrier by 3D Additive Manufactureing for Syngas Reforming

N. Fan[1]; Y. Huang*[1]; Y. Chen[1]; W. Wei[1]; B. Liu[2]; A. Wang[1]; R. Luo[1]

1. National Taiwan University, Taiwan
2. National Cheng Kung University, Taiwan

This research selects two Al_2O_3 powders (α- and high-surface-area θ-Al_2O_3) and two polymeric binder systems [1], kneading of the polymers with the ceramic powders, and extruding to produce feedstocks and filaments, which are melted and used for 3D additive manufacturing (AM). The processing parameters (sequence of addition, viscosity of the feedstocks, etc.), the phase transformation of the θ-powder, and catalytic properties of the carrier with nano-catalyst are investigated. The made alumina parts are densified to a relative density (RD) of 40-45%. Porous disks (θE60-40 and θE60-30) are coated with catalyst NiO and CeO_2, and used to reform syngas made from waste paper. The best case reforms the CH_4 content from 25.7% down to 0.14% or lower, which is suitable as a gaseous fuel of solid oxide fuel cells (SOFCs).

(PACRIM-GSP-011-2017) Evaluation of Ceramic/Ceramic (SIC/SIC) Joint interface prepare via brazing

A. Ghazi Daryani*[1]

1. Sharif University Technology, Material Science & Engineering, Islamic Republic of Iran

This joint is performed by brazing method and under certain conditions in a furnace with controlled atmosphere, using the appropriate filler metal. The properties and characteristics of connection has finally been studied by using mechanical test (shear strength test) and microscopic examination (SEM) and phase analysis (XRD) and elemental distribution was conducted by EDAX. Heat treatment was performed (at different time and temperature) according to phase diagram to gain the desirable joint. The results showed that the proper joining of SiC/SiC was obtained applying a metal layer of Ag-Cu as well as an active metal of Ti-6Al-4V. The second one was used to increase the wet ability and proper strength. Microscopic investigations revealed penetration and activation of elements from interface to the bulk of ceramic body and this “in turn” was the major reaction in the joints. Both joints showed the deepest penetration of Ti atoms from interface to ceramics. According to the XRD results, TiC and Ti5Si3 were the most important phases in the SiC/SiC interface. The strength of this joint was increased till optimum time and temperature condition and diminished after that by forming of some phases as TiC in (SiC /SiC) which inhibit the formation of more strong interface. The optimum time and temperature were suggested to be 900 °C and 90 min for SiC/SiC.

(PACRIM-GSP-012-2017) Removal of methyl orange over the Cu^{2+} substituted $MgAl_2O_4$ spinel prepared via the coprecipitation method

J. Tang*[1]; Y. Liu[1]; D. Chen[1]; J. Chen[1]; B. Wang[1]

1. China University of Geosciences, Beijing, China

5% Cu^{2+} substituted $MgAl_2O_4$ spinel nanoparticles were prepared via the chemical coprecipitation method. The obtained samples were characterized by thermal gravimetric analysis (TGA), specific surface area (BET), X-ray diffraction (XRD), UV-vis diffuse reflection spectrum (UV-vis DRS) and Fourier transform infrared spectroscopy (FT-IR). Only the diffraction peaks of cubic magnesium aluminium spinel $MgAl_2O_4$ were detected in the Cu^{2+} substituted $MgAl_2O_4$ spinel. The crystallinity of the spinel calcined at 800 °C is higher than that calcined at 700 °C. Removal of methyl orange using the obtained $MgAl_2O_4$ spinel were carried out under the dark and the irradiation of UV and visible light. It was found around 95% methyl orange was removed within 80 mins. The induction of UV and visible light irradiation didn’t play obviously. The mechanism of the removal methyl orange is still unclear.

(PACRIM-GSP-013-2017) Enhancement of Red Phosphorescence Properties of Pr^{3+} activated Calcium Titanate

H. Sade*[1]; S. Dayioglugil[1]; S. Bosna[1]; G. Soydan[1]; N. Solak[1]

1. Istanbul Technical University, Metallurgical and Materials Engineering, Turkey

Recently, rare-earth doped titanate phosphors which are novel luminescent materials with advanced physical-chemical properties, have attracted significant attention owing to their promising photoluminescent properties and potential applications in white light-emitting diodes (LEDs) due to very close to the chromaticity coordinates of the ideal red. Calcium titanate ($CaTiO_3$) is preferred as a host material thanks to exhibited good chemical and thermal stability as well as its better mechanical resistance. However, $CaTiO_3 : Pr^{3+}$ only radiate under UV lamp; therefore, rare earth elements are used as co-dopant material in order to enrich red fluorescence and the afterglow intensity. This study includes a promising approach for the improvement of a red-light emitting $CaTiO_3 : Pr^{3+}$ phosphor with addition of Lu^{3+}, Dy^{3+}, Gd^{3+}, La^{3+}, and Tb^{3+}. $CaTiO_3 : Pr^{3+}$ was synthesized by wet chemistry in nano size and solid state method in micron size. The samples were characterized by using, SEM, XRD, FTIR-RAMAN and Spectrophotometer. The effects of sintering paremeters and particle size on the phosphorescence properties were also investigated. A significant enhancement on the luminescent intensity was observed with the addition of the rare-earth co-doping in both micron and sub-micron scale.

(PACRIM-GSP-014-2017) Influence of Si Particle Size Distribution and Milling Fluid on SRBSN Ceramic Substrate with High Thermal Conductivity for Powder Modules

H. Oh*[1]; H. Lee[1]

1. Kumoh National Institute of Technology, Advanced Material Science and Engineering, Republic of Korea

Si_3N_4 ceramic substrate with high thermal conductivity has been developed for next-generation high power devices due to its high electric insulation, high heat dissipation and excellent mechanical reliability. In general, highly thermal conductive Si_3N_4 ceramics are fabricated via reaction-bonding of Si, and post-sintering (SRBSN) process. It is well known that, for highly thermal conductive Si_3N_4 ceramics, characteristics of starting Si powder, i.e., a purity as well as an average particle size and its distribution play an important role. However, the effect of Si particle size distribution after milling as well as milling fluid have not been studied. In order to fabricate highly-thermal conductive silicon nitride ceramic substrate, Si scrap (~700 um) was pulverized to ~l um of average particle size with different particle size distributions, W_{PSD}, by controlling the milling parameters including the kind of milling fluids. After mixing the sintering additives with milled Si, the CIPed compact was nitrided (RBSN) and post-sintered (SRBSN) at 1450 and at 1900 degrees celcius under a nitrogen atmosphere, respectively. Thermal conductivity of SRBSN ceramics were affected by different milling condition, amount of sintering additives, the existence of O impurities and particle size distribution of milled Si scrap.

(PACRIM-GSP-015-2017) Electrochomic properties of WO_3 films synthesized by direct agent assisted hydrothermal metheods

S. Park*[1]; C. Nam[1]

1. Hannam University, Photonics and Sensors, Republic of Korea

WO_3 nanorods with a hexagonal structure were synthesized by hydrothermal methods, where directional capping agents of citric acid and oxalic acid were added to modify the morphology of WO_3 nanostructures. Synthesized WO_3 powders were characterized by using scanning electron microscopy (SEM) and X-ray diffraction (XRD), revealing that well-crystallized nanorods have a hexagonal structure with [0001] direction. Powder WO_3 samples were coated on ITO or FTO substrates by using doctor-blade methods to investigate electrochromic properties of WO_3 nanostructures. The electrochromic properties were varied depending on post-annealing temperatures, i.e., coloration, bleaching, and switching speed. Cyclic voltammograms of the WO_3 films and UV-vis transmittance spectrum will be presented in detail to understand their morphology and structure effects on the electro-optical properties.

(PACRIM-GSP-016-2017) Effect of the ZnO addition on the structure and technological properties of the ceramic glazes by variable molar ratio of the SiO_2/Al_2O_3

M. Lesniak*[1]

1. AGH University of Science and Technology in Krakow, Faculty of Materials Science and Ceramics, Poland

Currently glass-ceramic materials have a variety of applications. They are used to produce surface coatings on a range of everyday wares including ceramic tiles, tableware and sanitary ware, materials for thermal shock resistant applications, biomaterials, glass-ceramic construction materials, abrasives and cutting materials, materials used in electronics, optics. One field for which glass-ceramics have been developed is that of glazes. Glass-ceramic glazes are characterised by a range of properties that include a mechanical strength, chemical durability and resistance to thermal shock. The presence of crystals in the glass matrix is influenced by many factors. A crucial role is played by the molar ratio of SiO_2/Al_2O_3 oxides. In this work we examined a number of glazes from SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O system in which the variable is the molar ratio of the SiO_2/Al_2O_3 and ZnO amount at a constant content of other components (CaO, MgO, K_2O, Na_2O) were examined. For all selected glazes, structural studies - X-ray diffraction (XRD) and spectroscopic in the middle (MIR) and far (FIR) infrared were performed. In order to determine the state of the surface (microstructure) research on the scanning electron microscope (SEM) with EDX and confocal microscopy were done.

(PACRIM-GSP-017-2017) Advanced photocatalytic properties of UCNP supported TiO_2 nanotube photocatalyst for air purification

B. Ye*[1]; J. Baik[2]; B. Jeong[1]; E. Kim[1]; H. Kim[1]

1. Korea Institute of Industrial Technology, Republic of Korea
2. Ulsan National Institute of Science and Technology, Republic of Korea

As the air environment regulations become more and more strict, many studies are being actively carried out in various countries around the world to reduce the generation of air pollutants. Air pollutants are generated by almost all industry and these are harmful to the human body and form a secondary air pollutant causing atmosphere problems. Especially, VOCs also occur in indoor or interior materials and cause sick house syndrome. In this study, we first attempt to disassemble air pollutants by applying a photocatalyst that can decompose air pollutants using finite resource of sunlight. TiO_2 is used as a typical photocatalyst, but the problem is that the active wavelength range is restricted to the UV region. In order to activate these catalytic reactions, it is necessary to improve the surface area characteristics through the modification of the nanostructures, and to improve the photoactive wavelength range upconversion nanoparticle (UCNP) was applied to TiO_2 nanotube photocatalyst. After the synthesis process, as a result of comparing the improvement of the photocatalyst by application of nanostructure and UCNP, it was confirmed that the decomposition rate was improved in the UV region when the structure was changed to TiO_2 nanotube compared to the existing TiO_2. It was also confirmed that UCNP was active in visible region compared to existing TiO_2 nanotubes.

(PACRIM-GSP-018-2017) Y_2O_3-Al_2O_3-SiO_2 (YAS) Coatings for High-Plasma resistant Al_2O_3 ceramics in Semiconductor Etching Process

E. Park*[1]; H. Lee[1]

1. Kumoh National Institute of Technology, Advanced Materials Science and Engineering, Republic of Korea

Recently, owing to high density and severe plasma dry etching process in semiconductor industry, highly plasma resistant ceramic components have been increasingly required. The typical plasma resistant ceramics are known to be Y_2O_3 and CVD-SiC. Especially, the Y_2O_3 bulk ceramics and the Y_2O_3-coated ceramic components by plasma thermal spray process have been paid great attentions due to their excellent plasma resistances. However, the Y_2O_3 bulk ceramic as well as The CVD-SiC components are highly expensive, furthermore, surface failure of the Y_2O_3-coated ceramic components causes serious problems. In order to solve these problems, this study aims to develop the economical and high-plasma resistant Al_2O_3 ceramics by a simple Y_2O_3-Al_2O_3-SiO_2 (YAS) coating process. In this study, a number of batch compositions in YAS materials system were examined, and uniform and dense YAS coating layers were formed on the sintered Al_2O_3 ceramics. And then, effects of the YAS compositions and the coating processing on the plasma resistance of YAS coated Al_2O_3 ceramics were thoroughly studied. The plasma resistance of the YAS-coated Al_2O_3 ceramics thereby showed significantly high plasma resistance, that is, 8 times higher than quartz, 2.7 times than Al_2O_3 and ~ 70% of bulk Y_2O_3 ceramics.

(PACRIM-GSP-019-2017) Synthesis and characterisation of alkali aluminosilicate ceramics

G. Christopoulou*[1]; P. A. Bingham[1]; H. A. Jones[1]; G. A. Jubb[2]; F. Modarresifar[2]

1. Sheffield Hallam University, Materials and Engineering Research Institute, United Kingdom
2. Morgan Advanced Materials, United Kingdom

According to ternary phase diagrams, certain alkali aluminosilicate phases such as leucite or nepheline can exhibit very high melting points. Here we present the initial results of systematic synthesis experiments with the aim of producing single-phase alkali aluminosilicate ceramics in the ternary systems SiO_2-Al_2O_3-Na_2O and SiO_2-Al_2O_3-K_2O through a solid state reaction route. Thermal transformations have been studied by means of differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA). The microstructures of the resulting ceramics have been analyzed using Scanning Electron Microscopy (SEM) with Energy-Dispersive X-Ray Spectroscopy (EDX). Literature data for the phase diagrams is compared with the experimental data. The major initial outcomes of this work will be presented here.

(PACRIM-GSP-020-2017) Preparation of $ZrW_{2-x}Mo_xO_8$ ceramic by a hydrothermal process combined with spark plasma sintering method and evaluation of its thermal properties

H. Wei*[1]; M. Hasegawa[1]; Y. Yamaguchi[2]; K. Fujimoto[2]; K. Nishio[1]

1. Tokyo University of Science, Department of Materials Science and Technology, Japan
2. Tokyo University of Science, Department of Pure and Applied Chemistry, Japan

Zirconium tungstate (ZrW_2O_8) is one of the most promising negative thermal expansion (NTE) materials because it has a three-dimensional isotropic large coefficient of NTE in a wide temperature range. However, an order–disorder phase transition occurs around 450 K as the coefficient of thermal expansion (CET) changes from -9 ppm up to 450 K to -5 ppm above 450 K, and this CET changes prevents the use of this material in several devices. Tungsten and Mo have the same coordination number and very similar ionic radii and electronegativity values. In this study, we prepared Mo doped ZrW_2O_8 ceramics and evaluated their thermal properties (i.e., phase transition temperature and CET). $ZrW_{2-x}Mo_xO_8$ (0.0%x%1.0) ceramics were prepared by using a hydrothermal process with the Spark Plasma Sintering (SPS) method. We succeed in obtaining a $ZrW_{2-x}Mo_xO_8$ sintered body without impurities. The phase transition temperature of $ZrW_{2-x}Mo_xO_8$ was found to shift to the lower temperature side as the amount of doped Mo increased. However, this was not observed above room temperature when $x \geq 0.7$. Furthermore, the CET of b-phase $ZrW_{2-x}Mo_xO_8$ was increased by increasing the amount of doped Mo from -7.85 ppm (x=0) to -2.50 ppm (x=1.0).

(PACRIM-GSP-021-2017) Thermal conductive h-BN/CNT flexible paper using recycling waste paper

M. Lee*[1]; H. Lee[2]; B. Ye[1]; D. Kim[3]; H. Kim[1]

1. Korea Institute of Industrial Technology, Republic of Korea
2. Pusan National University, Republic of Korea
3. Korea University, Republic of Korea

Hexagonal Boron nitride(h-BN) is known as functional 2D material which has the layered structure. It has been widely noticeable in lots of fields in electric devices so on, due to the properties of a superior thermal endurance and heat conductivity. And we chose carbon nanotube(CNT) to connect h-BN flakes each other for improving the conductivity, because the flakes should be connected themselves to have the higher property. Hence, h-BN and CNT were adapted in to make the paper thermal conductive. In this study, we mixed shredded A4 paper with h-BN and multi-walled CNTs(MWCNTs) in different ratio and ground them in water without dispersion agent. Thermal conductive paper was obtained after filtering and drying the mixture of h-BN, MWCNTs and the waste paper. The thickness of the paper could be controlled by the volume of the mixture. Thermal conductivity and resistance of the paper were varied according to the thickness of the paper and the amount of the h-BN and MWCNT. The uniform dispersion of MWCNTs and h-BN in the paper on the surface of the cellulose was observed by Scanning Electron Microscope. In addition, the optimum ratio of h-BN and MWCNTs contents will be set through the more experiments to enhance the thermal conductivity. As the result of that, we could fabricate the thermal conductive and also flexible paper with a low cost and simple process.

(PACRIM-GSP-022-2017) A Study on the Wear Characteristics of AISI 4140 steel by Nitriding Treatment Methods

M. Kim*[1]; H. Park[1]; H. Kim[2]; K. Moon[1]

1. Korea Institute of Industrial Technology, Heat Treatment R&D Group, Republic of Korea
2. INHA University, Materials Science and Engineering, Republic of Korea

In this study, the effects of the various nitriding layers such as compound and compound free layer with different case depth and the various post nitriding layer such as sulfric and oxy-nitride layer producted by various nitring processes on the mechanical and wear resistance properties of AISI4140 steels were investigated. Nitriding processes were carried out; plasma sulfer, oxidation, gas and ion nitriding. In the gas and ion nitriding processes, compound and compound free layers with different case depth of AISI4140 steels were prepared. For this, AISI4140 steels were nitrided at different temperatures and gas ratio between 400~600°C. The effects of the temperature on the formation of compound layer and the thickness of hardened layer were examined. The nitrided specimens from the four kinds of nitriding process were characterized by means of optical and scanning electron microscopy, X-ray diffraction, hardness, wear test. The hardness tests were conducted to measure the surface hardness and the effective case depth of nitride layer. The O.M. were examined to find out the cross-sectional views of compound layer and case depth of the nitride layer. The wear resistance tests were performed using three types of oil for engine and construction machinery. Also, the effects of the compound layer on the mechanical properties such as friction coefficient, toughness and fatigue life were reviewed.

(PACRIM-GSP-023-2017) Piezoelectric Enhancement of Thermally Annealed Fine and Coarse-Grained Barium Titanate Ceramics

G. P. Khanal*[1]; S. Kim[1]; S. Ueno[1]; S. Wada[1]

1. University of Yamanashi, Japan

High performance lead-free piezoelectric ceramics system is needed to replace the lead-based one. Barium titanate (BT), the typical lead-free piezoelectric ceramics, is used in multilayer ceramic capacitors (MLCCs) and is one of the extensively investigated ceramics in the electroceramics field. In this study, we investigated an influence of thermal annealing on the electrical properties of the fine and coarse-grained BT ceramics with a range of grain sizes from 4 μm to 30 μm, which were prepared from hydrothermally synthesized BT nanoparticles with a particle size of 100 nm and 300 nm (Sakai Chemical Industry) by a two-step and conventional one-step sintering methods. The sintered BT ceramics were polished and cut into a plate and bar-type samples, and then thermal annealing was carried out in air at different temperatures for different durations. The crystal structures and microstructures of these BT ceramics before and after thermal treatment were investigated by X-ray diffractometer and scanning electron microscopy, respectively. The d_{33} value of 529 pC/N was measured after thermal annealing by a d_{33} meter for the BT ceramics with a grain size of 4.9 μm, while the d_{33} value was 330 pC/N before thermal annealing for the ceramics with a grain size of 4.7 μm. The crystal structure analysis suggests the relaxation of the sample surface contributed to the piezoelectric enhancement.

(PACRIM-GSP-024-2017) Appropriate suspension for the preparation of $(Bi_{0.5}Na_{0.5})TiO_3$-hexagonal $BaTiO_3$ ceramics by electrophoretic deposition (EPD) method

M. Kim*[1]; R. Itou[1]; T. S. Suzuki[2]; T. Uchikoshi[2]; S. Wada[1]

1. University of Yamanashi, Interdisciplinary Graduate School of Medicine and Engineering, Japan
2. National Institute for Materials Science (NIMS), Ceramics Processing Group, Japan

Lead-based Pb(Zn, Nb)O_3-$PbTiO_3$ (PZN-PT) single crystals have an extremely high piezoelectric constant of about 2,000 pC/N. On the other hands, lead-free piezoelectric materials have been attracting attention as eco-friendly materials but their properties are still quite poor. To enhance piezoelectric properties, we have studied lead-free ceramics prepared by EPD (electrophoretic deposition) method because textured ceramics can be obtained using high magnetic field and could achieve high domain wall density by controlling the grain size. However, a limited number of articles have been reported for lead-free piezoelectric ceramics prepared by EPD method. In this work, we tried to find optimum preparation condition of $(Bi_{0.5}Na_{0.5})TiO_3$ – $BaTiO_3$ (BNT-BT) ceramics using EPD method. BNT-BT ceramics were prepared with various experimental conditions, which includes the driving voltage, surfactants, and acid-base usage. The preparation condition using EPD method was optimized and the electrical properties of the ceramics prepared accordingly was investigated and compared with the ceramics prepared by conventional solid state reaction method. The obtained results are almost similar for both of the cases. However, we could expect superior electrical properties under certain modification in this process, which we will focus now onwards.

(PACRIM-GSP-025-2017) Direct Fabrication of $CuFeO_2$/Fe photocathode by Hydrothermal method for solar hydrogen evolution

M. Ito*[1]; C. Izawa[1]; T. Watanabe[1]

1. Meiji University, Japan

Water splitting using semiconductor photoelectrodes is expected as a method of storing and converting solar energy into chemical energy (hydrogen). Currently, for efficient water decomposition, it is necessary to apply an external voltage between a photoanode and a counter electrode to compensate for the potential deficiency. Combining the suitable photoanode and the photocathode is included as one solution to avoid applying the external voltage. In this situation, the maximum photocurrent and the working potential are estimated from the intersection of the steady current–potential curves of the respective photoelectrodes. Therefore, the performance of the photocathodes comparable to that of the photoanodes is demanded. Among photocathode materials, we focused on $CuFeO_2$, cuprous ferrite. $CuFeO_2$ has a delafossite-type structure, with which metal oxides containing Cu^{1+} are desirable as p-type semiconductors. However, $CuFeO_2$ is limited its photocuurent by its non-optimal film thickness or morphologies. Thus, we focused on direct fabrication on metal substrates by hydrothermal method. Hydrothermal method is prospective process for fabricating, sizing, and shaping metal oxide films by operating reaction conditions. So far, we have succeeded fabricating $CuFeO_2$ films on Fe substrates by hydrothermal method. In this study, effects of reaction conditoions on products has been studied.

(PACRIM-GSP-026-2017) Microwave-Assisted Solvothermal Synthesis of Potassium Niobate Nanocubes

R. Kunisada*[1]; S. Ueno[1]; T. Chikata[1]; S. Wada[1]

1. University of Yamanashi, Japan

Strained dielectric nanocrystal and nanocomposite materials have attracted much attention because of their unique properties different from bulk ceramics. It is reported that the closely-packed dielectric perovskite cube-shaped nanoparticles, which are enclosed by the {100} facets, exhibit the excellent dielectric properties arising from distortion at the epitaxial interfaces between nanocubes. To prepare such ordered assemblies, monodisperse nanocubes are required. In this study, to synthesize $KNbO_3$ nanocubes by controlling nucleation and crystal growth in solution, a microwave-assisted solvothermal synthesis method was employed. In this method, reaction solutions can be heated homogeneously up to around 200°C within a couple of minutes, and thereby we can expect to synthesize the nanoparticles with a narrow size-distribution due to the rapid nucleation rate. KOH and Nb_2O_5 were added to mixed solvent of ethanol and methanol, and the microwave-assisted solvothermal treatment was performed at 200°C. The product was collected by centrifuging, and crystal structures and morphologies of dried powders were investigated by X-ray diffraction, scanning electron microscopy, and so on. $KNbO_3$ nanocubes with round corners (particle size < 80 nm) could be obtained by the microwave-assisted solvothermal treatment at 200°C for 5 min. The corners of nanocubes turn into sharp with prolonging reaction time.

(PACRIM-GSP-027-2017) In-situ electric filed induced lattice strain observation and crystallographic structures of $BiFeO_3$-$BaTiO_3$ lead-free ceramics

S. Kim*[1]; G. P. Khanal[1]; C. Moriyoshi[2]; Y. Kuroiwa[2]; S. Wada[1]

1. University of Yamanashi, Japan
2. Hiroshima University, Japan

Recently, $BiFeO_3$-$BaTiO_3$ lead-free ceramics are one of replacement for lead-base piezoelectric materials, because of their high Curie temperature. The phase diagram of BF-BT system was suggested with two different type which structure were changed from rhombohedral to pseudo-cubic structure at 0.33 and 0.25 $BaTiO_3$ concentration composition. The phase diagram of BF-BT lead-free system is not clearly yet. In this study, (1-x)$BiFeO_3$-x$BaTiO_3$ (x= 0.20, 0.25, 0.30, 0.33, 0.35, 0.40) lead-free ceramics were fabricated using solid state reaction method. The structures were investigated by x-ray diffraction (XRD). The crystal structures are rhombohedral for BF20BT, pseudo-cubic for BF30BT, BF33BT, BF35BT, and BF40BT. The electrical properties were investigated with polarization–electric filed and strain–electric filed hysteresis loops. The electrical properties were observed in the pseudo-cubic structure. In order to study crystal structure, the temperature and electric field dependent synchrotron radiation powder x-ray diffraction (SR-PXRD) were measured in the Spring-8. The cubic-like XRD patterns were observed at the below Curie temperature in the BF30BT, BT33BT, BT35BT, BF40BT. The rhombohedral structure was observed by SR-PXRD in the BF25BT. More detail crystal structures and electrical properties will be discussed in the presentation.

(PACRIM-GSP-028-2017) Microwave dielectric and ferroelectric properties of strontium and tantalum based ferroelectric ceramics

F. Marlec[1]; C. Le Paven*[1]; R. Benzerga[1]; L. Le Gendre[1]; F. Cheviré[2]; V. Laur[3]; B. Guiffard[4]; T. Dufay[4]; F. Tessier[2]; A. Sharaiha[1]

1. University of Rennes 1, Institute of Electronics and Telecommunications of Rennes (IETR), France
2. University of Rennes 1, Institut des Sciences Chimiques de Rennes, France
3. University of Bretagne Occidentale, LAB-STICC, France
4. University of Nantes, Institute of Electronic and Telecommunications of Rennes, France

The present study concerns the microwave dielectric and ferroelectric characterization of new layered-type perovskite ferroelectric materials. They correspond to $(Sr_2Ta_2O_7)_{1-x}(La_2Ti_2O_7)_x$ solid solutions with compositions in the 0.00-0.05 range, tailored to attain Curie temperatures (T_C) close to ambient temperature. The end members are two ferroelectrics: $Sr_2Ta_2O_7$ (STO) with T_C = -107°C and $La_2Ti_2O_7$ (LTO) with T_C = 1461°C. Compounds were first synthesized as powders using a high-temperature solid-state reaction route starting from stoichiometric amounts of $SrCO_3$, Ta_2O_5, La_2O_3 and TiO_2. Dense ceramics were then obtained by sintering pellets at 1400°C for 3h. X-ray diffraction analysis confirmed the elaboration of phase pure compounds and Rietveld crystal structure refinement pointed out a linear variation of the lattice parameters within the studied solid solution domain. At 1 kHz and ambient temperature, dielectric measurements show permittivities in the 50-350 range. Polarization measurements (@10Hz, 40kV/cm) pointed out ferroelectric hysteresis for x concentrations in the 0.0165 – 0.03 range. Final contribution of this work will include microwave dielectric characterization of the ceramics by means of a coaxial probe. It will also present ferroelectric measurements of the compounds as thin films, deposited by magnetron reactive rf sputtering.

(PACRIM-GSP-029-2017) Evaluation of residual stress in glass using optical measurement methods

F. Werr*[1]; R. Karsdorf[1]; A. Lenhart[1]; D. de Ligny[4]; H. Katte[2]; A. Cornet[3]; V. Martinez[3]

1. TH Nuernberg, Materials Technology, Germany
2. ilis gmbh, Germany
3. Université Claude Bernard Lyon 1, Institut Lumière Matière, France
4. Friedrich-Alexander-University Erlangen-Nuernberg, Institute of Glass and Ceramics, Germany

The quantitative knowledge of the residual stress in glasses is a challenging problem. As long as the sample geometry is simple and the stress tensor is known, experiments taking advantage of the effect of birefringence are showing good results. The laser scattering method, due to its high resolution of local stress in the inside of the glass, also can be used. If the geometry is getting more complex, these methods reach their limits and experiments using the effect of luminescence can be a good alternative. Nd^{3+} presents sharp emissions in glass that can be easily followed by using luminescence-spectroscopy. The dependence of the emission band with pressure was measured under hydrostatic conditions using diamond anvil cell. A constant shift of $5cm^{-1}$/GPa was found between 0 and 4GPa. This newly determined relation was then used to characterize well known residual stress as the one founded in thermally toughened glasses. The emission spectra of Nd^{3+} is used to compare the results with the onion peeling method to evaluate the residual stress distribution in glass rods and to determine the local stress in thermally toughened glass panes. Regarding the obtained data of the glass pane, laser scattering and the evaluation via Nd^{3+} show congruent results. This novel method is an encouragement to evaluate more complex geometries as Prince Rupert's drops.

(PACRIM-GSP-030-2017) M-doped SnO_2/metal/M-doped SnO_2 multilayer deposited on PET for transparent conducting thin films

J. Jang[1]; Y. Cho[1]; J. Choi*[1]

1. Korea Institute of Science and Technology, Center for Electronics Materials, Republic of Korea

The transparent conducting oxides (TCOs) thin films are significant component for a large variety of photosensitive electronic devices, acting as transparent electrical contacts in flat panel displays, and touch panels. Transparent and conducting oxide such as In_2O_3, ZnO, or SnO_2 have been studied but advanced devices require better electrodes with much lower resistivity, superior optical properties and flexibility. Oxide-metal-oxide (OMO) multi-layer structure was designed to achieve high conductivity, transparency and flexibility. In order to apply oxide layer to OMO structure, low surface roughness of oxide layer is preferred as metal layer is very thin and it needs to be deposited uniformly on oxide layer. SnO_2 based thin films which has high crystallization temperature have been researched as oxide layer. Optical and electrical properties of SnO_2 thin film can be improved by doping. In this work, we found that optimized composition of M-doped SnO_2 by continuous composition spread (CCS) method and fabricated M-doped SnO_2/Ag/M-doped SnO_2 multilayer structure on PET substrate with on-axis radio frequency (RF) sputter. The optimized composition of M-doped SnO_2 was analyzed using secondary ion mass spectrometry (SIMS). Electrical and optical properties of M-doped SnO_2/Ag/M-doped SnO_2 thin film were investigated by Hall measurement and UV-Visible-spectrometer, respectively.

(PACRIM-GSP-031-2017) Fabrication of $(K_{0.5}Na_{0.5})NbO_3$ based transparent ceramics by a pressureless, conventional sintering technique

K. Hirai*[1]; I. Fujii[1]; T. Wada[1]

1. Ryukoku University, Materials Chemistry, Japan

Li-doped $(K_{0.5}Na_{0.5})NbO_3$ ceramics were fabricated by a pressureless, conventional sintering technique, with varied contents of Bi_2O_3 powder as sintering aid, and the transparency and crystal structure aswell as electric properties were characterized. $(Li_x(K_{0.5}Na_{0.5})_{1-x})NbO_3$ + y wt%Bi_2O_3 (x=0, 0.02, 0.04, 0.05, 0.06, 0.08, and 0.10; y=0, 3, 5, and 7) ceramics were fabricated by a modified solid-state reaction method. The relative density of the ceramics with x=0.05 was 70.5, 99.5, 99.9, and 98.9% at y=0, 3, 5, and 7, respectively. X-ray diffraction patterns indicated the crystal system of the ceramics with x=0.05 were a mixture of orthorhombic and tetragonal phases, and crystallographic anisotropy decreased at y=5 and 7. For the ceramics with x=0.05, the transmittance was nigligible at y=0, and it increased to about 8% at the wavelengh l of 2000 nm at y=3. At y=5 and 7, the transmittance gradually increased near $\lambda\approx400$ nm, which was associated with a band edge of the ceramics, and reached 70 and 64% at $\lambda=2000$ nm, respectively. These results indicated that the transparency of the ceramics depended not only the relative density but also the crystallographic anisotropy. Optical and electric properties of the ceramics with x=0–0.10 and y=7 will be also presented.

(PACRIM-GSP-032-2017) Luminescence properties of Eu^{3+} doped glass ceramics containing $ZnAl_2O_4$

Q. Wei*[1]; C. Liu[1]; J. Han[1]

1. Wuhan University of Technology, China

Glass ceramics containing RE^{3+} (RE =rare earth ions) have attracted a great interest in past decades due to their possible applications in solid-state lasers, fiber amplifiers, white light emitting diodes etc. Eu^{3+} have attracted a lot of attention due to their intense emission related to $^5D_0$-^7F_J (J=0-4)transitions. The emission of Eu^{3+}-doped materials located in orange and red light region depending on the crystal field and structural environment surrounding Eu^{3+}. Eu doped oxyfluoride glass ceramics containing CaF_2, SrF_2, PbF_2 have been reported. However, little attention in literature has been drawn on Eu doped silicate glass ceramics containing $ZnAl_2O_4$. In our present study, Eu^{3+} doped glass ceramics containing $ZnAl_2O_4$ were prepared by heat treating the glass samples at different temperatures; the changes of the structure and luminescent properties of the samples were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and luminescence spectrometer.

(PACRIM-GSP-033-2017) Two-Step Sintering of Partially-Stabilized Zirconia for Applications in Ceramic Crowns

B. A. Darmawan*[1]; J. G. Fisher[1]; G. Oh[2]; S. Park[2]

1. Chonnam National University, Materials Science and Engineering, Republic of Korea
2. Chonnam National University, Department of Prosthodontics, School of Dentistry, Republic of Korea

Partially-stabilized ZrO_2 is used in ceramic crowns due to its excellent mechanical properties and bio-inertness. Being white and opaque, ZrO_2 does not match the natural color and translucency of tooth enamel. A translucent ZrO_2 material would improve the aesthetics of ceramic cores. In polycrystalline ceramics, the main sources of scattering are grain boundaries and pores. To reduce scattering of light, the grain size of ZrO_2 ceramics should be less than the wavelength of visible light and porosity should be eliminated. Hot pressing and spark plasma sintering can be used but the equipment costs are prohibitive. Two-step sintering (TSS) is a sintering schedule that has been developed to sinter samples to high density while controlling the grain growth. The sample is sintered at a high temperature (T_1) for a short time to achieve >75% TD and then at a temperature about 100–150ºC lower (T_2) for a long period to induce densification with minimal grain growth. In this work, samples of a commercial powder (ZPex, Tosoh Corp., Japan) were sintered under two-step sintering conditions. The first step temperature (T_1) is 1300ºC holding for 5 minutes, followed by second step temperature (T_2) at 1200ºC, 1250ºC and 1275ºC and holding for 5 – 20 hours. The density and grain size of specimens are measured. Crystallographic phase, translucency and mechanical properties of selected samples are studied.

(PACRIM-GSP-034-2017) Fabrication of Photo-functional Xanthene Dye/ZnO Hybrid Films by a Chemical Bath Deposition Method

D. Hyakutake*[1]; E. Hosono[2]; M. Hagiwara[1]; H. Matsuda[2]; S. Fujihara[1]

1. Keio University, Japan
2. AIST, Japan

In this study, we aimed to fabricate photo-functional hybrid films consisting of transparent semiconductor ZnO and pH- or redox-responsible xanthene dyes, namely eosin Y (EY) and fluorescein (FL), by a chemical bath deposition (CBD) method. EY/ZnO and FL/ZnO hybrid films were grown on glass substrates coated with a sol-gel-derived ZnO seed layer in CBD solutions including zinc acetate and EY or FL. The resultant films were transparent in the visible range and showed an absorption due to the xanthene dyes. These films were composed of single-crystalline c-axis-oriented ZnO rods grown perpendicular to the substrate. Furthermore, these rods were mesocrystals with a chain-like structure of interconnected nanoparticles with a size around 50 nm. The ZnO films prepared from a CBD solution without the xanthene dyes did not have such the chain-like structure. These results indicate that dye molecules are adsorbed on (100) or (110) planes of ZnO during the crystal growth, acting as structure directing agents in the CBD process. In conclusion, we could fabricate the transparent xanthene dye/ZnO hybrid films with the c-axis oriented single crystalline chain-like structure by the CBD method.

(PACRIM-GSP-035-2017) Scintillation and Optical Properties of Sm-doped C12A7 Single Crystals

N. Kumamoto*[1]; D. Nakauchi[1]; G. Okada[1]; N. Kawaguchi[1]; T. Yanagida[1]

1. Nara Institute of Science and Technology, Japan

Scintillators are one of the inorganic phosphors applied for radiation detectors used in various applications such as security, high energy physics and medical. They convert the incident ionizing radiation to visible photons immediately. The most common scintillators are rare-earth doped oxide or fluorides bulk crystalline materials. $12CaO{\cdot}7Al_2O_3$ (C12A7) are transparent in the near-UV and visible range, hence the application for optical devices will be interesting. In this study, we synthesized Sm-doped C12A7 (Sm:C12A7) single crystals with various Sm concentrations (0.1-2.0 mol%) by Floating Zone (FZ) method, and investigated scintillation and optical properties by using Quantaurus-QY (C11347, Hamamatsu Photonics), Quantaurus-τ (C11367, Hamamatsu Photonics) and equipments of our laboratory-constructed set-up. From the photoluminescence (PL) emission spectra of Sm:C12A7 crystals, some emission lines appeared at 570-580, 600-620 and 650–660 nm under excitation at 420 nm due to the 4f-4f transitions of Sm^{3+}. The scintillation spectra of Sm:C12A7 crystals show some emission lines appeared at 570-590, 600-620 and 650-660 nm. In the both of scintillation and PL, the decay time constants of Sm-doped samples were around

1.4 ms due to the 4f-4f transitions of Sm^{3+}. We are also planning to research thermoluminescence properties of these single crystals.

(PACRIM-GSP-036-2017) Improvement of critical current density in MgB_2 superconductors by NaF-doping

N. Takahashi*[1]; M. Nagao[1]; S. Watauchi[1]; Y. Takano[2]; I. Tanaka[1]

1. University of Yamanashi, Japan
2. National Institute for Materials Science (NIMS), Japan

Superconducting transition temperature of MgB_2 is 39 K. It is synthesized by low cost materials (Mg and B). Then, MgB_2 is useful for superconducting applications. We focus on superconducting wire. But the critical current density (J_c) under magnetic field of MgB_2 superconducting wire should be improved for commercial applications. Therefore, we attempt to improve the J_c by introducing of pinning-site. Previously reports described that C, SiC, B_4C and organic compounds are effective for pinning-site in MgB_2. Though, we focus on fluoride which is chemically stable. As a result, NaF-doped MgB_2 powder shows the enhancement of J_c in magnetic fields. The 10 mol% NaF-doped MgB_2 powder exhibits highest J_c under magnetic field. We will fabricate the MgB_2 superconducting wire with 10 mol% NaF doping by Powder-In-Tube method (PIT method).

(PACRIM-GSP-037-2017) Scintillation and Photoluminescence Properties of Sc:Al_2O_3 Ceramics

N. Noor Azman*[1]; T. Kato[1]; G. Okada[1]; N. Kawaguchi[1]; T. Yanagida[1]

1. Nara Institute of Science and Technology, Japan

Radiation dose monitoring has been a field of great interest for over years. Aluminium oxide (Al_2O_3) has been one of the materials that intensely studied for radiation monitoring applications. The irradiation dose by ionizing radiations such as X-ray can be measured immediately by a scintillator or can be stored by a dosimeter material. Many works have been done by using α-Al_2O_3, commonly known as sapphire or corundum, as a host and doping with various impurities such as carbon (C), chromium (Cr) and silicon (Si). In this study, we synthesized 1 mol% scandium (Sc) doped Al_2O_3 (Sc:Al_2O_3) ceramics by using Spark Plasma Sintering method (SPS) to investigate radiation-induced properties for radiation measurements. The sintering process was done in a vacuum atmosphere with a pressure of 7.8 kN at a temperature of 1300 °C. A disk-shaped ceramic with a diameter of 10 mm was obtained and undergone further scintillation and photoluminescence characterizations. X-ray induced scintillation spectrum was observed in between 350- 450 nm. Photoluminescence (PL) spectrum was obtained under the excitation wavelength of 250 – 350 nm. A broad emission band appeared around 550 nm. Additional scintillation and PL properties, as well as, dosimeter properties will be discussed in the presentation.

(PACRIM-GSP-038-2017) Carrier generation in p-type wide gap semiconductor, Sn-Nb-O system

S. Akane*[1]; N. Kikuchi[2]; S. Ikeda[1]; Y. Aiura[2]; K. Nishio[1]

1. Tokyo University of Science, Graduate School of Industrial Science and Technology, Japan
2. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Development of p-type transparent conducting oxide (TCO) showing high-mobility is required for fabricating transparent electric devices based on p-n junction. A strategy for realizing p-type TCOs is to delocalize the valence band maximum (VBN) composed of oxygen 2p orbital. Hybridization of oxygen 2p orbital with metal d orbital or the use of chalcogen p orbital instead of O 2p was carried out to delocalize the VBM. However, existing p-type TCOs are insufficient for practical use because of low mobility, durability and productivity. Hosono et al. proposed that the VBM composed of metal s orbital having large spatial spreading and isotropic nature was desirable to realize p-type TCOs with a high mobility. Recently, we succeeded in preparation of wide-gap Sn-Nb-O showing p-type conduction, where the VBM of Sn-Nb-O was composed of Sn 5s. In this presentation, we discuss the mechanisms of generating holes in Sn-Nb-O. Two defects, vacancy of Sn^{2+} (V''_{Sn}) and Sn^{4+} in Nb^{5+} sites (Sn'_{Nb}), could be considered for generation centers for holes. Since increasing carrier density with decreasing Sn/Nb (increasing Sn-deficiency) was found in this study, it seems that V''_{Sn} was of importance for hole generation. However stoichiometric Sn-Nb-O having large fraction of Sn4+ showed higher carrier density than that of Sn-deficient Sn-Nb-O, indicating that Sn'_{Nb} is thought to be a dominant defect for generation center for holes.

(PACRIM-GSP-039-2017) The Effect of Rare Earth Dopants on Sintering Behavior of Lead Zirconate Titanate (PZT)

S. Dayioglugil*[1]; S. Bosna[1]; H. Sade[1]; E. Kondakci[1]; N. Solak[1]

1. Istanbul Technical University, Metallurgical and Materials Engineering, Turkey

Lead zirconate titanate (PZT) is the most widely used piezoelectric materials due to outstanding properties and enable to enhance their properties by addition of different rare earth oxides and changing the composition. Piezoelectric materials have received special attention due to their applications in automotive industry as an acoustic sensor for online monitoring of crack detection in engine parts. In this study, stoichiometric and 3-mol %- PbO-excess PZT samples were prepared as reference undoped material. In order to improve piezoelectric performance, rare earth oxides were systematically doped such as oxides of La, Nd, Gd, Eu, Er. The samples were prepared by conventional solid state reaction method. Samples were cold isostatically pressed and sintered at various temperatures. As a result of the structural and electrical characterization, it is observed that the addition of rare earth oxides improves not only density but also the piezoelectric properties. The ionic radius of the rare earth has significant effect on the Curie temperature and approximately 100°C increment was observed by the addition of La_2O_3.

(PACRIM-GSP-040-2017) Optical Properties of Rare Earth Element Doped CeO_2 Thin Films Deposited by Mist Deposition Method

Y. Hara*[1]; T. Hashizume[3]; A. Saiki[2]

1. University of Toyama, Graduate School of Science and Engineering for Education, Japan
2. University of Toyama, Graduate School of Science and Engineering for Research, Japan
3. University of Toyama, Organization for Promotion of Research, Japan

In this study, thin films of CeO_2 and a rare earth element (yttrium, samarium and gadolinium) doped CeO_2 were fabricated by mist deposition method in atmospheric pressure. The effect of the doped element on optical properties of CeO_2 thin films were studied. The precursor solution was mixture of $Ce(NO_3)_3$-$6H_2O$ and $RE(NO_3)_3$-$6H_2O$ (RE: Y, Gd, Sm) with deionized water. The mist of the precursor solution was generated by ultrasonic atomizer. The films were deposited on heated glass substrates. Droplets made of the mist deposited and dried on the substrates. They overlapped each other and the films were fabricated. After deposition, the films were heat-treated to remove water and nitric acid at 673K for an hour. They were characterized by UV-Vis spectroscopy, scanning electron microscopy (SEM) and Raman spectroscopy. Optical absorbance became higher in the following order: CeO_2 > Y-CeO_2 > Gd-CeO_2 > Sm-CeO_2.

(PACRIM-GSP-041-2017) Fabrication of a Ni/MgO Nanocomposite Catalyst by Exolution

Y. Park*[1]; H. Hwang[1]

1. Inha University, Republic of Korea

Methane steam reforming reaction is the most important chemical process to produce hydrogen or synthesis gas. For effective production of hydrogen or synthesis gas, the role of the reforming catalyst becomes more significant. Especially, highly active and stable catalyst is necessary for an on-site reformer for fuel cell systems. In conventional technology, the methane steam reforming reaction is conducted on supported noble metals- or nickel-based catalysts. However, these catalysts suffer from the deactivation by agglomeration and carbon deposition. Noble metal-based catalysts are less sensitive to carbon deposition than nickel-based catalyst. However, high cost and limited availability are major concern. In this study, nickel-based nanocomposite catalysts were fabricated by exolution process. First, $Mg_{1-x}Ni_xO$ solid solution powders were synthesized from aqueous magnesium and nickel nitrate solution by precipitation technique and then the powder was heat-treated in reducing atmosphere at 600 to 900°C. SEM and TEM images revealed that the nano-sized nickel particles were homogeneously dispersed in the $Mg_{1-x}Ni_xO$ solid solution matrix and the size and morphology of nano nickel particles can be controlled by the heat-treatment condition. Catalytic activity for the methane steam reforming or methane particle oxidation reaction and durability of the $Ni/Mg_{1-x}Ni_xO$ was investigated in terms of nickel contents and sizes.

(PACRIM-GSP-042-2017) Synthesis of Pt/WO_3 nano-particle dispersed PDMS membrane for hydrogen gas leakage sensor

Y. Makino*[1]; Y. Yamaguchi[2]; R. Ishihara[1]; K. Nishio[1]

1. Tokyo University of Science, Department of Materials Science and Technology, Japan
2. Tokyo University of Science, Department of Pure and Applied Chemistry, Japan

Hydrogen energy generation systems are becoming widely known as clean and highly efficient. However, not only fuel cells but also transportation and storage techniques must be developed to increase the prevalence of hydrogen energy. To use hydrogen energy safely, a high-performance gas sensor is needed to detect hydrogen gas leaks. Platinum catalyst-loaded tungsten trioxide (Pt/WO_3) is a gasochromic material, and we have reported that Pt/WO_3 thin films can detect hydrogen gas from 4% to 100 ppm by using its optical and electrical properties. However, Pt/WO_3 thin solid films are difficult to use in complicated structures, i.e. gas transport pipes and valves. In this study, we tried to develop a flexible hydrogen gas leakage sensor using the WO_3. We found that synthesized Pt/WO_3 nanoparticles (Pt/WO_3 NPs) dispersed in polydimethylsiloxane (PDMS) and evaluated their ability to sense hydrogen gas. Pt/WO_3 powder was prepared by using a sol-gel process. The Pt/WO_3 NPs were dispersed into PDMS precursor solution. A Pt/WO_3 NPs dispersed PDMS membrane was obtained by heat treatment of the solution. The prepared membrane showed high transparency and flexibility. When it was exposed to 100% hydrogen gas, the membrane changed from translucent to blue. The response time of the membrane to hydrogen gas depended on amount of loaded Pt because Pt particles on the WO_3 particles work as a catalyst.

(PACRIM-GSP-043-2017) Improvement of Thermoelectric Properties and Phase Studies in p-type $Ca_3Co_4O_9$ Ceramics

A. Demirkesen*[1]; F. Kurt[1]; E. Yaris[1]; A. Ozdemir[1]; N. Solak[1]

1. Istanbul Technical University, Metallurgical and Materials Engineering, Turkey

The sol-gel method was used to synthesize the $Ca_3Co_4O_9$ type thermoelectrical materials. The thermoelectrical properties of the materials have been investigated by the substitution of Ca^{+2} ions by Ba^{+2}, La^{+3}, Sr^{+2}, Na^{+}. For the first time in the literature, solubility limits and phase diagram studies in $Ca_3Co_4O_9$ ceramics were experimentally and computationally conducted. Samples were cold isostatically pressed and sintered at elevated temperatures. Effects of sintering atmosphere, temperature and time on density, grain size and thermoelectrical properties as well as the solubility limits were systematically investigated. Structural and microstructural characterizations were conducted by using XRD, SEM, FTIR. Electrical – thermal conductivity and Seebeck coefficient of the samples were measured from 200 to 800°C. It has been directly observed that the dopand concentration and ionic radius has a significant effect on the Seebeck coefficient by changing the misfit ratio (Rock Salt-type block layers and CdI_2-type CoO_2 layers). Additionally, electronic conductivity and density improvements are obtained by the addition of La^{3+} and Na^{+} ions. An extended solubility of La^{3+} ions were determined in the form of $(Ca,La)_3Co_4O_9$.

(PACRIM-GSP-044-2017) Thermoelectric properties of V, Fe co-substituted $MnSi_\gamma$ synthesized by melt-grown method

M. Sato*[1]; H. Hamada[1]; K. Hayashi[1]; Y. Miyazaki[1]

1. Tohoku University, Applied Physics, Japan

Higher manganese silicides (HMSs) are known as good thermoelectric (TE) materials because of their low cost, less-toxicity and high chemical stability. Recently, we synthesized V-substituted HMSs by melt-grown method, and succeeded in enhancing TE properties owing to the increase of hole carrier density and dissipation of MnSi layered precipitates in HMSs. The aim of this study is to further increase TE properties by V, Fe co-substitution. Mixed powders of Mn, V, Fe and Si with the nominal composition of $(Mn_{1-x-y}V_xFe_y)Si_\gamma$ ($0 \le x \le 0.03$, $0 \le y \le 0.06$) were sealed in vacuumed quartz tubes, melted at 1200°C for 8 hours and cooled slowly to the room temperature. In X-ray diffraction patterns, no peak corresponding to the MnSi phase was found except for the x=0.03, y=0.05 sample. The V, Fe co-substituted samples exhibited higher Seebeck coefficient and lower electrical conductivity relative to the V-substituted sample. It is because the hole carrier density decreased by substituting Fe for Mn. Due to a difficulty to set the measurement direction parallel to the c-axis direction of the samples, there was no clear correlation between these TE properties and the amount of Fe substitution. The maximum power factor of 2.4 mW/mK^2 at 810 K was achieved for the x=0.03, y=0.04 sample. This study is supported by New Energy and Industrial Technology Development Organization (NEDO).

(PACRIM-GSP-045-2017) Preparation and thermoelectric properties of Sn_2S_3 with electron lone pairs

W. Saito*[1]; H. Nagai[1]; K. Hayashi[1]; Y. Miyazaki[1]

1. Tohoku University, Applied Physics, Japan

Thermoelectric materials that can directly convert waste heat to electricity have been attracted much attention recently. Thermoelectric performance is characterized in terms of the dimensionless figure of merit, $ZT = \alpha^2\sigma T/\kappa$, where α, σ, T, and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. In this study, we focused on Sn_2S_3, which is a mixed Sn valence compound leading to generate electron lone pairs in the crystal. Since SnS_6 octahedra and SnS_4 tetrahedra in the crystal are weakly bonded via the electron lone pairs, a satisfactorily low thermal conductivity can be expected. Mixed powders of Sn and S were heated in an evacuated quartz tube at 873 K for 12 hours, and gradually cooled down to room temperature for 10 hours. The obtained samples were pulverized and then densified by spark plasma sintering. Relative density of the sintered samples was 95% of theoretical density. As expected, a thermal conductivity as low as ~ 1.5 W/mK was realized from 300 K to 650 K. Although the Seebeck coefficient was high (> 300 μV/K), the electrical conductivity was low (~ 0.1 S/cm at 650 K). As a result, the highest ZT was 1.7×10^{-3} at 650 K. To increase the electrical conductivity, we have also attempted partial substitution of Ti for Sn. The improved thermoelectric properties of $(Sn,Ti)_2S_3$ will be also presented in the Conference.

(PACRIM-GSP-046-2017) Solvothermal Fabrication of Cesium Tungsten Bronze

Y. Yao*[1]; Y. Gao[1]

1. Shanghai University, School of Materials Science and Engineering, China

For the application as heat shielding materials, an excellent shielding ability of NIR rays as well as high visible light transparency is required. Tungstic acid and cesium chloride were used as raw materials, cesium tungsten bronze (Cs_xWO_3) powders were synthesized by hydrothermal method, and the Cs_xWO_3 films were prepared on the surface of PET by dispersing the Cs_xWO_3 powders into ethyl alcohol. The solvent is consisted of glycerol and water, with the increase of water, product yield increase. There is an optimal ratio of water and glycerol, above the ratio, with the increase of water Cs doping amount reduced, near infrared shielding performance degradation. The structure and morphology of the obtained Cs_xWO_3 powders were characterized by X-ray diffractometer and energy dispersive spectrometer. The light absorption of the as-prepared powder and film was investigated by an ultraviolet–visible spectrophotometer. The results indicated that the synthesized Cs_xWO_3 powders were hexagonal $Cs_{0.32}WO_3$ crystals. The obtained Cs_xWO_3 powders showed strong near-infrared absorption, and the film showed good near-infrared shielding properties with more than 60% of the visible light transmittance.

(PACRIM-GSP-047-2017) Fabrication of Depleted U_3O_8 Samples for use as a Fast Neutron Detector

B. Musicó*[1]; S. Lawson[1]; C. B. Shaver[1]; B. Rowell[1]; S. Dhungana[2]; G. Bhattarai[2]; M. Paquette[2]; A. Caruso[2]; T. T. Meek[1]

1. University of Tennessee, Materials Science and Engineering, USA
2. University of Missouri, Kansas City, Department of Physics and Astronomy, USA

Depleted U_3O_8 is being considered for use as a fast neutron detector. Polycrystalline samples of U_3O_8 were fabricated through powder processing followed by sintering at 1350°C for various lengths of time. Green pre-sintered samples were made by uniaxial pressing depleted U_3O_8 powder under pressures of 5 to 8 ksi for 1 minute. Green sample size was a diameter of 0.5 inches with thickness between 0.04 and 0.05 inches. These green samples were placed on an alumina setter plate in a Carbolite HTF 18/4 furnace and sintered in air at 1350°C from 1 to 10 hours with a heating rate of 1.5°C per minute and a cooling rate of 3°C per minute. Sintered samples had a diameter varying from 0.43 inches with a thickness of 0.03 to 0.04 inches. This paper will address in more detail the procedure described above and the resulting samples that were obtained.

(PACRIM-GSP-048-2017) Electrical Properties of Sintered U_3O_8

C. B. Shaver*[1]; S. Lawson[1]; B. Musicó[1]; B. Rowell[1]; S. Dhungana[2]; G. Bhattarai[2]; M. Paquette[2]; A. Caruso[2]; T. T. Meek[1]

1. University of Tennessee, Materials Science and Engineering, USA
2. University of Missouri, Kansas City, Department of Physics and Astronomy, USA

Depleted U_3O_8 is currently being considered for use as a fast neutron detector. Samples of depleted U_3O_8 were prepared by sintering in air as well as varying reducing and oxidizing atmospheres at temperatures from 900 to 1350°C for various times. Sample microstructures were investigated resulting in characterization of grain sizes allowing the measured electrical resistivity to be determined as a function of grain size. Samples were also fabricated with hypostoichiometric and hyperstoichiometric compositions by sintering reducing or oxidizing atmosphere. Electrical resistivity was also determined for samples under these conditions. This paper will discuss in more detail the impact of varying grain size and stoichiometry has on the electrical resistivity of U_3O_8.

(PACRIM-GSP-049-2017) Low temperature sintering of hydroxyapatite-based waste form

M. u. Hassan*[1]; H. Ryu[1]

1. Korea Advanced Institute of Science and Technology, Republic of Korea

Calcium hydroxyapatite (HAP) has been recognized as a matrix for the immobilization of I-129, one of the long-lived radioisotopes found in direct disposal facilities and fuel reprocessing industry. HAP has the potential to accommodate iodine with its ionic radius of 196 pm and also have stability in a radiation environment. However, Iodine under high temperatures is volatile and changes to I_2 which also reduces the incorporation of iodine into the matrix. In this regard, different methods have been adopted to synthesize iodide bearing and iodate substituted apatite with improved sintering properties. To further lower the sintering temperature of iodate-substituted hydroxyapatite, microwave sintering by adding some suitable microwave absorbents in the matrix will be investigated. Moreover the possibilities to enhance the matrix density as well as capture of the iodine will be investigated. Development of hydrated layer at the surface of nanocrystalline grains of the apatite will further be probed and its role in decreasing the sintering temperature may be investigated deeply. The achievement of low temperature sintering of waste matrices having good leaching resistance can be a breakthrough for long term safe disposal of radioactive waste and can contribute further to the development of clean energy options.

(PACRIM-GSP-050-2017) Characterization of the Stoichiometry of Sintered Depleted U_3O_8 using Automated Cerimetry

S. Lawson*[1]; C. B. Shaver[1]; B. Musicó[1]; B. Rowell[1]; S. Dhungana[2]; G. Bhattarai[2]; M. Paquette[2]; A. Caruso[2]; T. T. Meek[1]

1. University of Tennessee, Materials Science and Engineering, USA
2. University of Missouri, Kansas City, Department of Physics and Astronomy, USA

Depleted U_3O_8 is currently being considered for use as a fast neutron detector. Pellets of depleted U_3O_8 were prepared by sintering at temperatures from 900 to 1350°C in air as well varying argon oxygen mixes. Sample portions weighing 20-30mg were then dissolved in a heated sulphuric acid and phosphoric acid solution bubbled with inert gas to prevent interaction with dissolved oxygen. Dissolved uranium will be present in a mixture of states between U(IV), U(V), and U(VI). A fixed volume of 0.05M ceric sulfate is added, oxidizing all uranium to a U(VI) state. The reduced Ce(III) is determined by measure of excess Ce(IV) by titration of Fe(II) using autotitration and a photometric sensor, providing the average oxidation state of the starting uranium. This paper will address in more detail the procedure described above and the resulting stoichiometries that were obtained.

(PACRIM-GSP-051-2017) Physical properties of Inorganic Binder Based on Sodium Silicate Solution in Accordance with SiO_2/Na_2O ratio

W. Kim[2]; S. Ha[1]; W. Kim[1]; Y. Kim[2]; J. Park*[1]

1. DR AXION Enterprise Co. Ltd., Chemical Research Institute, Republic of Korea
2. Pusan National University, School of Materials Science and Engneering, Republic of Korea

The organic binder widely used in the casting industry generates odor and a large amount of volatile organic compound. These substances cause safety problems by accelerating the air pollution of industrial sites, and climate change. Thus, environmental regulations are being strengthened globally, It is urgent to come up with a fundamental solution to prevent the emission of pollutants from being exposed to the atmosphere. An inorganic binder based on sodium silicate solution is functioning mainly as a bonding agent through interaction with water, and is hardened by being dehydrated through heating. Thus, it is possible to suppress the emission of pollutants generated in the core manufacturing and casting process, and to reduce the defect rate of the product. Therefore, this study is to evaluate the strength of the core in accordance with the amount of SiO_2 and SiO_2/Na_2O ratio in the binder. The inorganic binder was produced by varying the mixing ratio of water and sodium silicate solution, SiO_2/Na_2O ratio, and the amount of SiO_2. The core was produced by mixing sand and inorganic binder at a weight ratio of 3 wt%. The strength of the core was evaluated using a universal testing system. Additionally, XRD, ICP, FT-IR, and Si-NMR analysis were performed to confirm the properties of the produced binders, also to clarify the probability between the strength and ingredients.

(PACRIM-GSP-052-2017) In-situ sol-gel synthesis of titanium dioxide-graphene oxide heterostructures for water purification technologies

U. Naknikham*[1]; V. Boffa[1]; Y. Yue[1]

1. Inorganic Chemistry, Chemistry, Bioscience and Engineering, Denmark

Titanium dioxide-graphene oxide (TiO2-GO) heterostructures presents superior photocatalytic properties, due to their efficient use of the solar light and to their ability to adsorb water pollutants. However, the synthesis of such heterostructures often involves tedious experimental steps, the reaction mechanisms of which are not well understood yet. In this context, we developed and optimized a synthetic path for the preparation of TiO2-GO heterostructures with large interphase and strong interaction between GO (or reduced GO) and TiO2. TiO2 nanoparticles were synthesized by in-situ sol-gel reaction. Synthetic conditions (pH and temperature) were optimized to enhance the interface interaction between TiO2 and GO.The new materials were characterized by XRD, SEM and TEM analysis, besides the study of Ti-O-C interface bonding was carried out by XPS. In addition, the impact of the GO loading (0.01, 0.5, 1, 2, 5, and 10 wt.%) on the photocatalytic performances of TiO2 was studied with model pollutants. Lastly, band gab energy and UV-VIS diffuse reflection were conducted to observe the degree of TiO2-GO composites which works under the visible light.

(PACRIM-GSP-053-2017) Structure and synthesis of a garnet-type lithium ion conductor $Li_7La_3Zr_2O_{12}$

E. Yi*[1]; K. Yoon[1]; H. Hwang[1]

1. Inha University, Republic of Korea

Li ion conductors with garnet structure and general formula $Li_5La_3Zr_2O_{12}$ was found to exhibit high lithium ionic conductivity ($\approx 5x10^{-4}$ S/cm at room temperature) and high decomposition voltage (6 V versus Li), promising for application as electrolyte in all-solid-state lithium secondary batteries. In this study, the ab initio calculations were performed to investigate the mechanism of the Li+ ion conduction in garnet-type solid electrolyte by using the Vienna ab initio simulation package (VASP) code based on the density functional theory (DFT). The crystal structure stability and the doping effect on the lithium ion conductivity were studied in terms of various doping elements. The garnet-type solid electrolyte powder samples were synthesized by solid state reaction method from lanthanum oxide, lithium carbonate, and zirconium oxide. A single phase cubic phase could be successfully obtained by calcining the powder mixture at 800 to 900°C and subsequently sintering at 1200°C. Lithium ion conductivity was measured by using a dense electrolyte disk covered by Pt blocking electrodes at room temperature. The measured lithium ion conductivity were compared with the simulation results.

(PACRIM-GSP-054-2017) Fabrication of all solid-state transparent thin film batteries using olivine structure

H. Lee*[1]; N. S. Parmar[1]; K. Kim[2]; J. Choi[1]

1. Korea Institute of Science and Technology, Center for Electronic Materials, Republic of Korea
2. Yonsei University, Department of Material science and Engineering, Republic of Korea

In recent years, transparent devices have attracted substantial attention. However, all components of transparent batteries, a key component in fully integrated transparent devices, have not yet been reported. The key factor in obtaining transparent Li-ion batteries (LIBs) resides mainly in the preparation of the cathode materials. A general method of making transparent devices is to reduce their thicknesses much less than the optical absorption length. Thus, we expect that the fabrication of a battery with fully covered thin film materials allows the battery to possess high transparency. Another important factor for thin film materials to possess large transparency is their band gap energies. Thin film materials with wide band gap energies, such as olivine compounds, are highly transparent. Our group previously studied exploration of composition by thin film cathode materials of olivine compound proved as $LiFePO_4$ without carbon. In this study, transparent all solid-state thin film batteries were fabricated on TCO substrate. Transparent all solid-state thin film batteries using olivine compound as cathode materials and SiNx were fabricated and the electrochemical properties were characterized on TCO substrate. The olivine cathode materials were deposited by RF magnetron sputtering.

(PACRIM-GSP-055-2017) Dynamic behavior of wood: Investigating microstructural effects on the impact resistance of wood

A. K. Matsushita*[1]; D. Gonzalez[1]; M. B. Frank[1]; J. Jae[1]; J. McKittrick[1]

1. University of California, San Diego, USA

Sporting goods and historic weapons make ubiquitous use of impact resistant timbers, yet the microstructural origins of wood dynamic behavior are poorly understood. Therefore drop-weight testing was conducted on wood samples in custom-built impact tower using modified ASTM standard D7136/D7136 M-07. Specimens were prepared from 8-10% moisture content plain-sawn planks cut into 20x20x7mm squares. Selected woods exhibited normalized failure impact energy superior to other biological materials including armadillo scute and abalone nacre and comparable to hydrated ram horn (~28 kJ/m2). Ashby diagrams of the relative density plotted against normalized impact energy of failure suggest that unlike in static loading conditions, density may not reliably indicate toughness in dynamic loading, however. Finite element models and wood-mimicking freeze-casted ceramics were constructed to identify whether specific microstructures contribute to this discrepancy. The results offer insight into identifying commonalities in the design of impact resistant biological materials. This work is supported by a Multi-University Research Initiative through the Air Force Office of Scientific Research (AFOSR-FA9550-15-1-0009).

(PACRIM-GSP-056-2017) Optimization of Artificial Bone Construct Fabrication via Paste Extrusion 3D Printing

C. M. Gigliotti*[1]; R. W. Marks[3]; Z. R. Wilczynski[1]; J. Moore[2]; J. H. Adair[4]

1. Pennsylvania State University, Bioengineering, USA
2. Pennsylvania State University, Mechanical Engineering, USA
3. Pennsylvania State University, Biomedical Engineering, USA
4. Pennsylvania State University, Materials Science and Engineering, USA

For bone tissue engineering, a delicate balance between bioactive material selection and scaffold porosity must be reached to permit sufficient implant mechanical properties and natural bone ingrowth. To accomplish this combination, a resolution test was developed to optimize spatial and shape accuracy for a 3D printing paste extrusion system used to create the intricate features associated with natural bone morphology. The results of this study outline various printing parameters including rheological requirements, print speed, and nozzle head shape and scale that are necessary to maximize print quality. In addition, artificial bone constructs were fabricated using a calcium phosphosilicate nanoparticle doped hydroxyapatite paste. This printing system will continue to be the foundation for fabricating future scaffolds and experimentation with design and material optimization for osteogenesis, angiogenesis, and suitable mechanical loading.

(PACRIM-GSP-057-2017) Current progress in the designing of novel polymer matrix composites by Streolithography (SL)

E. Kramer*[1]; L. Yutrzenka[1]; D. Blue[1]; R. Larson[1]; S. Gupta[1]

1. University of North Dakota, Mechanical Engineering, USA

This poster reports the synthesis and characterization of novel particulate reinforced polymer matrix composites by 3D printing (3DP). Novel Particulate-Photopolymer Resin composites were designed by adding different particulates in the Resin matrix. Microstructure studies by SEM studies were performed to understand the dispersion of these particulates in the resin matrix. Tensile testings and tribological behavior study by pin-on-disk method were performed to understand the mechanical and tribological behavior of these solids. In addition, we will also report some of the recent progress in designing of novel 3D printers.

(PACRIM-GSP-058-2017) On the Design of Novel Ceramics based Scaffolds and Composites

K. Hall*[1]; S. Gupta[1]

1. University of North Dakota, Mechanical Engineering, USA

In this poster, as a part of undergraduate research, we will present recent developments on the research and development of novel materials which can perform multifunctional functions like energy harvesting, energy storage, and solid lubrication, among others. Green design is an integral component of research for the 21st century. Scientists and researchers are being continuously challenged on a variety of global issues, including population growth, rapid urbanization, infrastructure decline, climate change, and water scarcity. Thus, there is a huge potential to deliver game-changing solutions by designing sustainable materials.

PACRIM Undergraduate Student Posters

Room: Grand Promenade

5:30 PM

(PACRIM-UGSP-001-2017) Effects of surface condition of HAp powders on microwave absorption behavior and Its catalysis Properties

R. Iwasaki*[1]; H. Nishikawa[1]; M. Fuji[1]; T. Shirai[1]

1. Nagoya Institute of Technology, Advanced Ceramics Research Center, Japan

We fabricate a novel altemate noble metal catalyst using hydroxyapatite (HAp) for reduction of VOC gas. In the fabricated novel catalyst of HAp, the trapped electron generates oxygen radical and promotes oxidative decomposition of VOC gas through the heat treatment. For the reducing heating energy, we apply to microwave heating on HAp powder. Microwave absorption property depends on its material, but also crystallization. In this study, the surface condition of HAp powder are modified by planetary ball mill, and effects of the difference of surface condition and microwave absorption are investigated.

(PACRIM-UGSP-002-2017) Fabrication of Electrical Conductive Alumina by Combination of Gel-casting and Inert Gas Sintering

M. Hattori*[1]; M. Nanko[2]; M. Fuji[1]; T. Shirai[1]

1. Nagoya Institute of Technology, Advanced Ceramics Research Center, Japan
2. Nagaoka University of Technology, Japan

Gelcasting is one of method which could fabricate homogeneity carbon-ceramics composite material with high electrical conductivity by sintering under argon atmosphere. But it is known that carbonization rate against to quantify of the polymer is low due to decomposition and vaporization of polymer. In order to increase the amount of carbon in sintered bodies and electrical conductivities, green bodies are impregnated with iodine solution as a doping substance. Carbon structure and electrical conductivity were evaluated by Raman spectrum and van der Pauw method. In these results, sintered body with iodine can fabricate graphite structure with less defect and higher electrical conductivity than it without iodine.

(PACRIM-UGSP-003-2017) Effects of Milling Process on the Powder Surfaces and Its Dispersion Properties

W. Shimizu*[1]; M. Ishihara[1]; M. Fuji[1]; T. Shirai[1]

1. Nagoya Institute of Technology, Advanced Ceramics Research Center, Japan

In generally, ball-milling are used as disperse process for slurry preparation. Through this process, excess energy is given to the surface of particles. This would form alumina hydrate on the surface and cause different desorption behavior of dispersant to alumina. It is important to investigate the effects of surface to slurry property. In this study, alumina slurries are prepared by ball-milling at different conditions. Binding energy, crystal structure and adsorbed amount of dispersant are evaluated by FT-IR, XRD and TOC. In these results, relation between slurry property and milling process are investigated.

(PACRIM-UGSP-004-2017) Preparation of highly dispersed Pd/SiO_2 catalysts: Effect of calcination temperature of SiO_2 on Pd dispersion

J. Kwon*[1]; J. Kim[1]; J. Park[3]; H. Lee[2]; M. Lee[1]

1. Korea Institute of Industrial Technology, Republic of Korea
2. Ulsan University, Chemical Engineering, Republic of Korea
3. DR AXION Co.Ltd, R&D center, Republic of Korea

The SiO_2 has suitable properties as support, such as high specific surface area and thermal stability. But there are many functional groups on the silica surface. Especially silanol groups lead to strong Pd Si-O interaction. And this strong interaction interrupt metal reduction for synthesis of noble metal catalysts, furthermore it leads to decrease of metal dispersion. In this study, SiO_2 was calcined from 573K to 1373K to remove the silanol groups on SiO_2. The thermal treated SiO_2 were characterized by N_2 adsorption-desorption, FT-IR, XRD and TPD. And the Pd supported on calcined SiO_2 catalysts prepared by ion-exchange method were characterized by H_2_TPR, CO-chemisorption, and FE-TEM. From the CO-chemisorption results, Pd catalysts supported on SiO_2 calcined at 973K has the highest Pd dispersion as 10.06%. According the FT-IR results, the concentration of silanol groups decreased with increasing the calcination temperature of SiO_2. Above the 973K, the silanol groups disappeared completely. Combination of FT-IR and CO-chemisorption showed that the increase of the Pd dispersion is associated with decrease in silanol group on the SiO_2. From these results, calcination of SiO_2 lead to remove the silanol groups, and this removal was favorable for the Pd dispersion.

(PACRIM-UGSP-005-2017) Influence of calcination temperature on Al_2O_3 structure properties and catalytic characteristics of Pd/Al_2O_3

M. Byun*[1]; J. Kim[1]; D. Park[2]; M. Lee[1]

1. Korea Institute of Industrial Technology, Republic of Korea
2. Department of Polymer Science and Chemical Engineering, Pusan National University, Republic of Korea

In this study, we investigate the influence of the Al_2O_3 structure properties by calcination temperature on characteristics of Pd/γ-Al_2O_3 catalysts. The 2 type Al_2O_3 of commercial γ-Al_2O_3(CM) and γ-Al_2O_3 (PM) synthesized by precipitation method were used as supports. The CM was calcined from 733 to 1423K. The PM was calcined at the 1173K. The Pd/γ-Al_2O_3 catalysts prepared by deposition-precipitation method. The prepared Pd/γ-Al_2O_3 catalysts were studied by XRD, N_2 Physisorption, FT-IR, CO-Chemisorption, and FE-TEM. The CO-Chemisorption results show that Pd/CM(1173) catalyst has the highest Pd dispersion of 29.82%. We suggest that metal dispersion is related to characteristics of supports. The CM support calcined up to 1173K, the ratio of tetrahedral is increased. However, CM supports calcined above 1173K, the ratio of tetrahedral is decreased and structure properties is dramatically changed due to γ to α phase transition. Also the tetrahedral surface appears negative charged, so positive charged Pd particle absorb on Al_2O_3 by electrostatic attraction. It is revealed that CM(1173) has high tetrahedral ratio compared to CM(773) and PM(900). From these results, CM(1173) has more elastostatic attraction with Pd ions than CM(733) and PMA(1173).

PACRIM Poster Session (non-student)

Room: Grand Promenade

5:30 PM

(PACRIM-P-001-2017) Modeling of structure and calculation of mechanical properties of ceramic nanoparticles with diamond-like structure

D. Zakarian*[1]; A. Khachatrian[1]; V. Kartuzov[1]; E. Kartuzov[1]

1. Frantzevich Institute for Problems of Materials Science NAS Ukraine, Ukraine

This effort was using ab-initio calculations based on pseudo potential method, to evaluate the energy of interaction of atomic layers accounting for free surface of ceramic nanoparticles with diamond-like structure. These crystals are easily deformed along the space diagonal [111] thus it is better to perform those in hexagonal axes. Thus in one elementary cell we obtain 6 parallel highly densely packed atomic planes, which are distanced from each other on c/4 and c/12. Here c – the parameter of hexagonal lattice, perpendicular to the basic planes. As a result of calculations it was found out that in brittle materials with a cubic structure, microcracks at first appear between the atomic planes {111}, distanced at c/4. Material fractures on layers made of two atomic planes distanced on c/12. As nanoparticles, a-priory, have crystal properties, their structure is described in hexagonal axes; space cube diagonal is taken as Z axis. We believe that a free surface coincides with basic highly dense atomic planes and posses the energy equal a half of energy of interplane interaction. The average value of strength is calculated for various models of nanoparticles. The dependence of strength vs. nanoparticles size and form has been investigated.

(PACRIM-P-002-2017) Deposition Kinetics and Characterizations of BN Coatings Deposited by Chemical Vapor Deposition

Y. Peng*[1]; A. Li[1]; M. Wang[1]; L. Jia[1]

1. Shanghai University, School of Materials Science and Engineering, China

The deposition rate of boron nitride (BN) from boron trichloride (BCl_3) and ammonia (NH_3) by chemical vapor deposition (CVD) was studied at different deposition temperature and residence time, using $BCl_3/NH_3/H_2/N_2$ mixture gases at a volume ratio of 1:3:1:6 with a total pressure of 4.5kPa. The deposition rates defined by mass increment as a function of reactor length were investigated at different deposition temperatures and residence times. The results demonstrated that BN was not deposited from BCl_3 and NH_3 directly. During the deposition intermediate products such as Cl_2BNH_2 were absorbed on the surface with a high probability and subsequently broke down that resulted in the surface reactions following the BN products. Hence, the deposition rate is a result of the competition between the consumption in gas-phase reaction and absorption on surface, which caused a maximum appeared at a deposition temperature of 650ºC and a residence time of 0.24 s. Then the BN coatings heat-treated at different temperatures were characterized by SEM, FT-IR, XRD, XPS and TEM. The crystallization of hexagonal boron nitride (h-BN) was improved with increasing heat-treated temperature. According to TGA and SEM of disbanding BN coatings, it gave out that BN coatings can play a protective role as interface materials.

(PACRIM-P-003-2017) Modeling the Formation of Sodium and Calcium Aluminosilicate Gels at the Mesoscale Using Coarse-Grained Monte Carlo

K. Yang[1]; C. White*[1]

1. Princeton University, Civil and Environmental Engineering, USA

The structural evolution of amorphous aluminosilicates at the mesoscale (~ 1 to 100 nm) is important for a range of technological processes, including the formation of low-CO_2 cements (e.g., alkali-activated materials (AAMs)) and zeolite synthesis. However, our understanding of the mesoscale morphology of AAMs and related amorphous aluminosilicate gels is severely limited, especially the development of the three-dimensional aluminosilicate network and nanoscale porosity. This study investigates the structural changes that occur during the formation of sodium and calcium aluminosilicate gels at the mesoscale by utilizing a coarse-grained Monte Carlo (CGMC) modeling technique that exploits density functional theory (DFT) calculations. The model simulates the reaction of an aluminosilicate-rich particle in a highly alkaline solution, and therefore has the potential to elucidate the impact of chemical composition and particle morphology on the formation of the aluminosilicate-rich gels. Analysis of the CGMC simulations provides quantitative information on the particles/clusters throughout the reaction, together with pore solution chemical composition and porosity development. Hence, this simulation approach centered at the mesoscale provides crucial information inaccessible using experiments on the structural evolution of amorphous aluminosilicates.

(PACRIM-P-004-2017) Conductive Network in Complex Chalcogen-based Compounds

L. Xi*[1]; J. Yang[1]; X. Xu[2]; W. Zhang[1]; L. Chen[2]

1. Shanghai University, China
2. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Recently, we recognized that the “Phonon-glass-electron-crystal” (PGEC) paradigm can be annotated in the compounds with conductive networks. Our previous work on skutterudites and Cu_2SnSe_3 has shown that the thermoelectric (TE) performance can be improved by using the conductive networks. The high-throughput material screening was conducted from the data base of ICSD and MP. In this work, we systematically study the general conductive network in chalcogen-based compounds by first principles. Although the VBM has significant Cu anti-bonding character, our results demonstrate the close shell d^{10} configurations of monovalent Cu are relatively localized and contribute little to the group velocity and the band shape at valence band maximum. The Pisarenko relations for similar chalcogen sublattice compounds are very close. At high temperatures, the maximum power factors for different systems have similar optimal carrier concentrations. These imply that the electrical transport properties of these compounds are mainly dependent on the sublattice of chalcogen, which is the key feature of “electron crystal”. The variations on electrical transport properties of different chemical characteristic from S, Se, to Te are investigated. By using the conductive network concept, some novel TE materials, such as $Cu_{12}Sb_4Se(S)_{13}$, argyrodite-type ion conducting, are predicted and they show good TE performance.

(PACRIM-P-005-2017) Preparation of mullite whiskers reinforced SiC/Al_2O_3 composites by Microwave Sintering

B. Fan*[1]; H. Wang[1]; R. Zhang[1]; K. Guan[1]

1. Zhengzhou University, College of Material Science and Engineering, China

Mullite whiskers reinforced SiC/Al_2O_3 composites were prepared by microwave sintering in a microwave chamber with TE_{666} resonant mode. Original SiC particles were coated with SiO_2 by a sol-gel processing and mixed with Al_2O_3 particles. Mullite was introduced by the reaction between SiO_2 and Al_2O_3. The samples were sintered from 1350ºC to 1600ºC for 30 min. Physical and chemical responses were investigated by detecting changes in reflected power during the microwave sintering process. XRD, SEM techniques were carried out to characterize the samples. It was found that mullite could be formed at 1200ºC. Bridging of mullite whiskers was observed between Al_2O_3 and SiC particles due to a so-called local hot spot effect, which was the unique feature for microwave sintering. The optimized microwave sintering temperature was 1500ºC corresponding to the maximum amount of mullite whiskers within SiC/Al_2O_3 composites. The high electro-magnetic field enhanced the decomposition of mullite at higher temperatures above 1550ºC. The mechanical properties of mullite whiskers reinforced SiC/Al_2O_3 composites are much better than the SiC/Al_2O_3 composites without mullite whiskers.

(PACRIM-P-006-2017) Characteristics of $LiMn_2O_4$ synthesized by the rapid solid phase reaction using microwave for lithium ion battery

T. Hashizume[1]; A. Saiki[2]; T. Shimizu[3]; S. Miwa*[3]

1. University of Toyama, Organization for Promotion of Research, Japan
2. University of Toyama, Graduate School of Science and Engineering for Research, Japan
3. University of Toyama, Graduate School of Science and Engineering for Education, Japan

The powder of $LiMn_2O_4$ was tried to synthesize at rapid reaction using a microwave. $LiMn_2O_4$ is used for positive-electrode material for lithium ion battery. Most popular process of manufacturing $LiMn_2O_4$ powder is widely used of production method by solid phase reaction between Li_2CO_3 and MnO_2 at high temperature in air condition for several hours (example; 1073 K for 12 hr.). Therefore, the rapid solid reaction process using microwave was focused at the point of produce cost and running time. $LiMn_2O_4$ powder was fabricated by using microwave at 500 W for 5 min. Discharge capacity of lithium ion battery test cell packed into the fabricated $LiMn_2O_4$ powder was 73 $mAhg^{-1}$ at first time, and the retention capacity compared to the first time was 79% after 30 times of discharge and charge continuous test. There is a possibility that reaction time can be made very short using microwave.

(PACRIM-P-007-2017) A Novel Sol-Gel Route to Synthesize $(Sr_{0.5}Ba_{0.5})Nb_2O_6$

S. Wu*[1]; T. Chen[1]; X. Liu[1]; X. Chen[1]

1. Zhejiang University, School of Materials Science and Engineering, China

$(Sr_{0.5}Ba_{0.5})Nb_2O_6$ ultra-fine powders were synthesized by a novel sol-gel route, and the mechanism of the reaction was discussed. $SrCO_3$, $BaCO_3$, oxalate niobium and citric acid were used to initiate the sol-gel process and ethylene glycol was then added to further polymerize the cross-linking structure. The revolution of $(Sr_{0.5}Ba_{0.5})Nb_2O_6$ phase, reaction process and microstructures were investigated by XRD, Raman spectra, FTIR spectra, DSC-TG and SEM, respectively. The synthesis temperature of $(Sr_{0.5}Ba_{0.5})Nb_2O_6$ powders was as low as 600°C and the size and morphology of powders could be controlled by the synthesis temperature. By adjusting calcination temperature, the $(Sr_{0.5}Ba_{0.5})Nb_2O_6$ powders with uniform size of 20 to 500nm were obtained. Dense $(Sr_{0.5}Ba_{0.5})Nb_2O_6$ ceramics were then successfully prepared by these ultra-fine powders. An enhanced ECE value of 0.38°C was obtained at 100kV/cm.

(PACRIM-P-008-2017) Electrical Properties of SiC ceramics fabricated by spark plasma sintering

S. Jang[1]; Y. Kim*[1]; B. Jang[2]; T. Nishimura[2]

1. University of Seoul, Dept. of Materials Science & Engineering, Republic of Korea
2. National Institute for Materials Science (NIMS), Japan

Electrical properties of bulk SiC ceramics fabricated by spark plasma sintering were investigated as a function of Y_2O_3 content. The SiC specimen with no yttria and those with high Y_2O_3 content (1.0 and 5.0 wt%) showed n-type character, while those with low Y_2O_3 content (0.01 and 0.05 wt%) have p-type character. The p- and n-type SiC specimens had electrical resistivities around $10^{-2}\Omega$cm but exhibited photoluminescence spectra quite different from each other. Raman spectroscopy revealed that the SiC specimens with low Y_2O_3 content contained graphitic phase, which was insignificant for high Y_2O_3 content. The p-type character is primarily attributable to silicon vacancies (V_{Si}), while the n-type character is ascribed to nitrogen substitution in carbon sites (N_C) of the β-SiC lattice. The change in conduction type with yttria addition in the SiC specimen can be understood in terms of a competition between the densities of V_{Si} and N_C.

(PACRIM-P-009-2017) Synthesis of soluble and meltable polymer precursors with low oxygen content for ZrC/SiC/C ultra-high-temperature ceramic nanocomposites

C. Shao*[1]; J. Wang[1]; X. Long[1]

1. National University of Defense Technology, Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, China

Polymer-derived method is one of the most important ways for the synthesis of ultra-high-temperature ceramics. By reacting $Cp_2Zr(CH_2CH{=}CH_2)_2$ with low molecular weight polycarbosilane via radical polymerization method, ZrC/SiC/C ceramic precursors (PZC-PCS) with Zr:Si ratio at any proportion were synthesized. The prepared precursors can dissolve well in common solvent, and have a softening point of about 180ºC, which is benefit for the shaping of complex component. Due to the little oxygen element introduced, PZC-PCS can convert into ZrC/SiC/C ceramics at a relative low temperature of 1200ºC. ZrC/SiC/C ceramics is a kind of ceramic nanocomposites, with ZrC nanoparticles distributed uniformly in the amorphous SiC/C matrix.

(PACRIM-P-010-2017) One pot synthesis and pyrolysis of polyborosilazane to silicon boron nitride carbon

Z. Yang*[1]; Q. Chen[1]; D. Jia[1]; Y. Zhou[1]; Y. Liu[2]

1. Harbin Institute of Technology, China
2. China University of Geosciences, China

In order to avoid double synthesis and develop the polyborosilazane to have both B-C and B-N bonds, we successfully present one-pot synthesis of a preceramic polymer by reaction with dichloromethylvinylsilane, borane and boron trichloride which fulfils the above-mentioned conditions. The new route results in a high performance SiBNC ceramic material, and in a comparably high temperature resistance of the final ceramic against crystallization and oxidation resistance. Furthermore, we describe the preparation and investigation of the corresponding pre-ceramic polymer followed by a short study of the thermal polymer-to-ceramic conversion into a new amorphous material. Various characterization techniques such as X-ray photoelectron spectroscopy, fourier-transformed infrared spectroscopy, X-ray diffraction (XRD), scanning electron microscopy an transmission electron microscopy (TEM) were used to characterize different properties of the synthesized SiBNC powder.

(PACRIM-P-011-2017) Fabrication of oxide-dispersion-strengthened FeCrAl alloy and its application to nuclear fuel cladding

D. Park*[1]; J. Park[1]; Y. Jung[1]; B. Choi[1]; H. Kim[1]; J. Yang[1]; Y. Koo[1]

1. Korea Atomic Energy Research Institute, Republic of Korea

To improve the high-temperature strength of FeCrAl alloy, which has excellent oxidation resistance at high temperature, oxide-dispersion-strengthened alloy was fabricated. The laser beam scanning process is introduced as new oxide dispersion strengthened alloy manufacturing method. The oxide powders were dispersed on the surface of the FeCrAl alloy was coated on the surface, and then the laser beam was scanned to penetrate and disperse the oxides into the metal matrix. The effects of the various powder materials on the mechanical properties of FeCrAl Alloy were examined. In addition, we investigated the heat-affected zone formation characteristics and the behavior of fine oxide dispersion behavior by varying the laser output conditions and obtained optimal manufacturing process conditions. Microstructure of dispersed oxides was investigated by scanning electron microscope and transmission electron microscopy to identify the mechanism of oxide dispersion during laser beam scanning process. The change of high temperature mechanical properties due to strengthening of oxide dispersion was evaluated and it was observed that the high temperature strength of oxide dispersion strengthened FeCrAl alloy was improved compared to the conventional alloy.

(PACRIM-P-012-2017) Thermal diffusivity of Cu-Cu/RGO Composites

H. Lee*[1]

1. KITECH, Republic of Korea

It was investigated that thermal diffusivity of Cu-Cu/RGO composites was varied with a volume fraction of Cu/RGO powders. The Cu/GO powders, which were dispersed by graphene oxide on copper powder, were prepared by mechanical alloying and spark plasma sintering processes. And then, the Cu/RGO was obtained by a hydrogen reduction process. It could be convinced from these results that the heat flow path for increasing a thermal diffusivity was supplied by the graphene dispersed composite powers after sintering, and the thermal diffusivity of Cu-Cu/RGO composites showed higher values than that of pure copper. It could be mentioned that the dispersion of graphene in the copper matrix was main role of providing the heat flow path in Cu-Cu/RGO composites, which let the thermal diffusivity increased.

(PACRIM-P-013-2017) Study of Size Separation of Sub-Millimeter Granular Material Using Vibro-Fluidization

J. Gowda[1]; J. Wollmershauser[1]; S. D. Johnson*[1]

1. Naval Research Laboratory, USA

Granular materials have many industrial and research uses and the need for narrow size distributions is important. Granular convection is a phenomenon whereby larger particles rise to the top of a vertically shaken container. This work focuses on the separation of comparably sized sub-millimeter diameter particles under the influence of vertical shaking to better understand the dynamics involved in granular separation at sub-millimeter sizes. We mixed volumetric ratios of 4:8 and 6:6 mL of 70 μm tungsten carbide and 50 μm yttria stabilized zirconia milling media and placed the mixtures in 1” dia. glass tubes to undergo vibro-fluidization. We imaged the vibration in real-time and analyzed the time to separate for several shaking amplitudes. We find that the separation process can be modeled by a simple exponential decay function with parameters that can be used to gauge the physical separation process. In addition to measuring the dynamics of separation, we measured the purity of the resultant materials by iteratively vibrating and removing the separated powder. Purity was quantified by x-ray diffraction and scanning electron microscopy imaging of the separated media. We find that after separation the resulting material is 95% pure. This high-purity is remarkable considering the closeness of the particle sizes involved.

(PACRIM-P-014-2017) Polycrystalline nanosialon material with low thermal conductivity

Z. Pedzich*[1]; W. Wierzba[1]; P. Putyra[2]; P. Rutkowski[1]; M. M. Bucko[1]

1. AGH University of Science and Technology, Department of Ceramics and Refractory Materials, Poland
2. Institute of Advanced Manufacturing Techniques, Poland

Paper describes procedure of manufacturing of polycrystalline sialon bodies without open porosity utilizing powders derived from Self-propagation High-temperature Synthesis (SHS) process. These powders were densified by Spark Plasma Sintering (SPS) procedure. Finally, homogeneous, nanocrystalline microstructure of material was assured. The apparent density of sintered samples was about 90% of theoretical one. Measurements of the thermal properties confirm that closed nanopores, uniformly dispersed in the material, decreased its thermal conductivity about three times when compared to a typical value for sialon material. Acknowledgements: The work was supported by the Polish State Ministry of Science and Higher Education under AGH University work no. 11.11.160.637 and by the Polish Ceramic Society.

(PACRIM-P-015-2017) Application a high-pressure for superconducting materials synthesis

A. Sklyarova*[1]; S. Shinoda[1]; T. Nagumo[1]; H. Suematsu[1]

1. Extreme Energy-Density Research Institute, Nagaoka University of Technology, Japan

Solid-state reaction synthesis is the most applicable route for obtaining of polycrystalline copper-based superconductors. Although this synthesis route is easiest and popular, some of the phases are not possible to obtain using the simple powder (or pellet) annealing. High-pressure synthesis is used in cases when necessary to obtain superconducting phases which are unstable or contain a lot of impurity after a solid-state synthesis. For copper-oxide superconductors the firing of a sample mixture under a high pressure leads to improving of the diffusion process during the synthesis and provides satisfied oxygen pressure that is important for superconductivity properties appearing.

(PACRIM-P-016-2017) Relation between the applied pulse and current fluctuation cycle and morphology of YSZ thin films fabricated by the electrochemical deposition method

A. Saiki*[1]; T. Hashizume[2]; T. Fujita[1]

1. University of Toyama, Materials Science and Engineering, Faculty of Engineering, Japan
2. University of Toyama, Collaboration and Promotion Center for Industry and Academia, Japan

Thin films of YSZ (yittria stabilized zirconia) were used as buffer layer in electro devices becouse of their chemical stability and insulation property. In this study, by applying the pulsed electrical fields during the electrochemical deposition, the morphology control of deposititted YSZ films was examined. Mixture of $ZrO(NO_3)_4$, $Y(NO_3)_3$ $-6H_2O$ were dissolved into water and then they were controlled nearly pH3 by adding NH_3(aq) to make the precursor solution. The thin film was deposited on the glass substrate near the minus electrode by applying the electrical field of 3.0 V for 20 min. In addition, another pulsed electrical field of 0 to 10 Hz was applied to the perdicular direction to the film deposition direction. After annealing at 723 K for 6 h in air, the YSZ films were crystallized. In the limited condition, the pinstripe patterns of YSZ films according to the frequency of the applied pulsed electrical field were observed. It was expected that ions movements in a precursor solution were controlled by the standing wave due to the applied pulsed electrical field and therefore deposition area were limited. There was a correlation also between pinstripes distance and current fluctuation cycle period.

(PACRIM-P-017-2017) Microstructure and grain size distributions in magnesia-alumina spinel ceramics prepared by spark plasma sintering

T. Uhlirova[1]; V. Necina[1]; W. Pabst*[1]

1. University of Chemistry and Technology, Prague, Department of Glass and Ceramics, Czech Republic

Magnesia-alumina spinel (MAS) is one of the favorite materials for preparing transparent ceramics for impact-resistant optical windows. Therefore both optical and mechanical properties are important for these ceramics. Apart from highest density and the absence of pores, which can both be achieved by spark plasma sintering (SPS), the grain size is the main parameter that can be optimized. On the other hand, from the theoretical point of view, MAS prepared by SPS is an ideal system to study inconstrained grain growth. This contribution presents a systematic approach for the microstructural characterization of MSA ceramics (Baikowski, France) prepared by SPS (FCT Systems, Germany). Based on scanning electron microscopic images, obtained from thermally etched planar sections, the grain boundary density and the mean curvature integral density are determined via stereology-based image analysis, including standard errors and confidence intervals, and from them the corresponding size measures (mean chord length, Jeffries size) and grain size numbers (linear and planar) are calculated. Further, it is shown how grain size distributions can be obtained from area-equivalent grain section diameter distributions using appropriate corrections for the random section problem. Finally the proximity of the grain size distribution to a Rayleigh distribution is investigated.

(PACRIM-P-018-2017) Numerical modeling of elastic moduli and conductivity of porous alumina – effects of pore shape and pore size distribution

W. Pabst*[1]; E. Gregorova[1]; T. Uhlirova[1]

1. University of Chemistry and Technology, Prague, Department of Glass and Ceramics, Czech Republic

The porosity dependence of elastic moduli and conductivity is a long-standing problem of materials science. After decades of research it has become clear that there is no a single model relation that can predict the porosity dependence of these properties. In particular there is no analytical relation that can be used to predict these properties for isotropic porous materials with random microstructure. However, efficient software packages are available today that allow numerical predictions, so that the effective properties of porous materials can now be studied in a systematic way for arbitrary digital microstructures. In this work we study the elastic moduli and thermal conductivity of porous alumina with convex isometric pores (initially spherical pores, isolated or overlapping, in simple cubic, body-centered cubic, face-centered cubic and random arrangement), concave isometric pores (simulating the partial sintering of initially spherical grains, isolated or overlapping, in simple cubic, body-centered cubic, face-centered cubic and random arrangement), randomly arranged and oriented anisometric pores (prolate or oblate spheroids) as well as alumina foams (open-cell and closed-cell Kelvin foams and random foams). Moreover, the influence of the pore size distribution is investigated for monodisperse, extremely bidiperse and uniform size distribution.

(PACRIM-P-019-2017) High-performance γ-alumina porous green bodies with hierarchical heterogeneities

A. Kocjan*[1]; T. Konegger[2]; A. Dakskobler[3]

1. Jozef Stefan Institute, Slovenia
2. Vienna University of Technology, Austria
3. VALL-CER d.o.o., Slovenia

High-performance γ-alumina porous green bodies with hierarchical heterogeneities were fabricated by consolidation of the AlN-powder-hydrolysis-derived mesoporous γ-alumina (MA) powder. The MA consists of nanocrystalline, yet micron-sized, hierarchically self-assembled, aggregated mesostructured lamellas with surface areas exceeding 220 m^2/g, also exhibiting a monomodal mesoporosity; whereas a single lamellae is presumably an iso-crystal composed of several nanometer-sized primary crystallites. In the present paper it will be shown that depending on the consolidation pressure it was possible to manipulate the pore size distribution from being bimodal, i.e., hierarchical heterogeneities – meso- versus macro-porosity, to being monomodal around the original narrowly distributed meso-pores within the MA precursor powder. Such MA porous green bodies, with no additional calcination or sintering step, exhibited high gas permeability in combination with high elasticity, flexural and compressive strengths, as a result of the homogeneous packing of the primary crystallites, also contributing to the lowered thermal conductivities. In this way we retained the intrinsic properties of the MA that can further influence the active materials in contact, aiming at an application related to catalysis, separation, filtration, sensing and thermal insulation.

(PACRIM-P-020-2017) Effect of microstructures of gelation freezing derived porous ceramics on thermal conductivity

C. Matsunaga*[1]; H. Hyuga[1]; Y. Yoshizawa[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Structural Materials Research Institute, Japan

Refractory ceramics fibers (RCF) with good thermal insulation properties and low cost have been widely utilized in various industrial furnaces at elevated temperature. However, RCF and ceramic fibers are categorized as Group 2B (a possible human carcinogen) as stipulated by World Health Organization. Thus, the fibrous insulators have to be carefully reviewed. In these applications, low thermal conductivity is the most essential factor as thermal insulation. Thus, it is necessary to fabricate porous ceramics with high porosity because the thermal conductivity can decrease with increasing the porosity. Gelation freezing method has some possibility to make ultrahighly porous ceramics. In this study, we try to develop alternatives RCF used at approximately 1000°C using gelation freezing method, in which natural diatomite powder has been used as one of candidates as a raw material. The relationship between porosity, thermal conductivity and microstructure of obtained samples will be discussed.

(PACRIM-P-022-2017) Microstructural characterization of three-dimensionally networked porous carbon material using X-ray CT and FIB-Technique

R. Inoue*[1]; G. Li[1]; E. Kojo[1]; M. Nakajima[1]; Y. Kubota[2]; Y. Kogo[1]

1. Tokyo University of Science, Japan
2. Japan Aerospace Exploration Agency, Japan

Recently, we developed new type of porous carbon materials with three-dimensionally networked structure. Performance of our developments as thermal protection system is superior to conventional carbon-based porous materials and fiber foams. In addition, these materials have excellent mechanical properties. It is believed that unique microstructural characteristics attribute to mechanical properties, however, microstructure of them is not still visualized because of their complicated microstructure and experimental difficulty. In the present study, we prepared three-dimensionally networked porous carbons (TNPCs) with equal porosity for all pore sizes, namely, 4.5, 4.9, and 9.8 μm. Then, complicated microstructure was visualized in three-dimensions using multi-slice images obtained using X-ray computed tomography and focused ion beam (FIB)-scanning electron microscopy. Microstructural characteristics of TNPCs, i.e., dimensions of strut and shape of pore, were successfully understood. In this presentation, effectiveness of these experimental techniques (X-ray CT and FIB-SEM) for understanding of microstructural characteristic of TNPCs will be presented.

(PACRIM-P-023-2017) Piezoceramic cellular foams

F. Eichhorn[1]; J. Biggemann[1]; S. Kellermann[1]; A. Kawai[2]; K. Kato[2]; K. Kakimoto[2]; T. Fey*[1]

1. Friedrich-Alexander University Erlangen-Nürnberg, Department Material Science and Engineering, Germany
2. Nagoya Institute of Technology, Department of Materials Science and Engineering, Graduate School of Engineering, Japan

Cellular and porous materials offer a wide spectrum of applications such as catalyst support structures, lightweight materials and energy adsorptions. Porous piezoceramics are used for sensor and ultrasonic applications. Piezoceramic foams with a high porosity (P> 75 vol%) were manufactured of PZT and LNKN by replica method. Characterization was carried out on microstructure, mechanical and piezoelectric properties regarding to given pore sizes. Pore size distribution and strut thickness as well as pore network and orientations were determined by X-ray micro tomography. Fracture strengths σ_b (compression) between 0.29 and 1.52 MPa (PZT) and

0.04 and 0.07 MPa (LNKN) were compared to Gibson and Ashby's model of open- and closed-cell foams. The longitudinal and transversal coupling coefficients d_{33} and d_{31} decreased in a range of 38 to 178 pCN^{-1} or -13 to -184 pCN^{-1} compared to dense PZT and LNKN material. With decreasing pore size similar effect to mechanical behaviour (increase in strength) an improvement of piezoelectric values was determined also for relative permittivity (8 – 102).

(PACRIM-P-024-2017) Micro-Meso Porous Alkali Bonded Ceramics as Solid Adsorbent for CO_2 capture

V. Medri*[1]; E. Papa[1]; E. Landi[1]; F. Miccio[1]; M. Minelli[2]; F. Doghieri[2]

1. National Research Council of Italy, ISTEC, Italy
2. University of Bologna, Department of Civil, Chemical Environmental and Materials Engineering (DICAM), Italy

Alkali bonded ceramics are synthetic and amorphous alkali aluminosilicates, currently known as geopolymers. They are chemically consolidated in alkali aqueous solutions under mild thermal treatment (<100°C). Since alkali bonded ceramics can be regarded as the amorphous counterpart of zeolites, their application can be potentially extended in the chemical sector of molecular sieves. In this research, alkali bonded ceramics have been prepared in monolith porous form, in order to investigate the adsorptive performances of CO_2 and light gases (CH_4 and N_2) by means of a volumetric method in the sub-atmospheric pressure range. The analysis of the gas adsorption properties showed a quite good capacity for CO_2, remarkably higher than those of CH_4 and N_2, pointing out the significant ability in the selective capture of CO_2. The values of selectivity in capacity obtained from the adsorption measurements, up to 200 and 100 for CO_2/N_2 and CO_2/CH_4 separation, respectively, are considerably higher than those of most of the adsorbent materials commonly accounted for in such applications.

(PACRIM-P-025-2017) Thermally insulating mullite foams prepared with wheat flour – from preparation to tomography

E. Gregorova*[1]; T. Uhlirova[1]; W. Pabst[1]

1. UCT Prague, Department of Glass and Ceramics, Czech Republic

Mullite ceramics are highly refractory materials that can be used for high-temperature thermal insulation purposes. In order to improve the thermal insulation performance at low and moderately high temperatures the introduction of pores is advantageous. Since the thermal conductivity is uniquely determined by the microstructure, a detailed characterization of the latter is a precondition for successful heat transfer predictions. In this work highly porous mullite ceramic foams have been fabricated by a recently developed generic proces based on the foaming of mullite suspensions with wheat flour. Commercial mullite powder has been used to prepare aqueous suspensions with 65 wt.% mullite and 20 vol.% wheat flour. The suspension was ball-milled for 6 h on a shaker, cast into metal molds and heated to 80 °C for 4 h. After demolding the samples were dried and fired at 1600 °C. The as-fired samples were characterized via the Archimedes technique, scanning electron microscopy, mercury porosimetry and X-ray computed microtomography. Stereology-based image analysis of planar sections is used to extract the complete set of global metric descriptors (porosity, interface density, mean curvature integral density), including the corresponding size measures (mean chord length, Jeffries size) while spatial images are used to extract the Euler characteristic.

(PACRIM-P-026-2017) Temperature dependence of Young's modulus of silicate ceramics from the magnesia-alumina-silica system

E. Gregorova*[1]; T. Smolikova[1]; W. Pabst[1]

1. UCT Prague, Department of Glass and Ceramics, Czech Republic

Silicate ceramics based on the magnesia-alumina-silica system, including steatite ceramics for electrotechnical applications and cordierite ceramics for automotive catalyst supports, are among the most widely used engineering ceramics. In this contribution the temperature dependence of the Young's modulus, i.e. a basic input parameters for thermal shock parameter calculations, is investigated in a systematic way with changing composition, achieved by mixing two raw materials (kaolin and talc). After characterization via X-ray diffraction, thermal analysis and laser diffraction the raw materials were mixed to achieve kaolin-talc weight ratios of 10:0, 8:2, 6:4, 4:6, 2:8 and 0:10, ball-milled in water, dried, crushed, uniaxially pressed at 40 MPa and sintered at 1280 °C (2 °C/min, 2 h). The samples were characterized by X-ray diffraction and Archimedes measurements and their Young's modulus was measured via impulse excitation, from room temperature up to 1000 °C. The results indicate that all materials contain cristobalite and exhibit its typical elastic anomaly. The elastic hysteresis that is well known for materials containing cordierite is suppressed in materials that contain also mullite beside cordierite. The Young's modulus of compositions made with kaolin-talc ratios 10:0, 8:2 and 0:10 is almost independent of temperature.

(PACRIM-P-027-2017) Recycled glass foam for microwave absorber application

R. Benzerga*[1]; R. Lebullenger[2]; V. Laur[3]; L. Le Gendre[1]; Y. Lamri[1];
A. Sharaiha[1]; P. Queffelec[3]

1. IETR - University Rennes 1, France
2. ISCR - University Rennes 1, France
3. Lab-STICC UBO, France

Absorber materials resulting from the combination of a dielectric matrix filled with lossy particles (carbone, ferrite, conductive polymers) are of interest in the microwave field. Currently, most commercially available composites absorbers are based on organic polymers. In this work, we present the performance of an eco-designed and polyfunctional inorganic foamed composite. This structure is obtained from recycled waste glass products. Two types of waste (soda-lime glasses and Cathode Ray Tubes / CRT) were combined with various foaming agents (C, SiC, AlN). The dielectric characterization was done between 8 and 12 GHz (X-band) by using a rectangular waveguide. The results show that the density of the foamed material and the type of the foaming agent greatly influence the dielectric properties. The use of carbon particles as foaming agent leads to lossy materials. A pyramid structure (21.6 × 68.8 × 9.4 mm) has been implemented from carbon loaded glass foam and inserted into a shorted rectangular waveguide. The measurement of reflection loss of the device was conducted to estimate the absorption capacity of the foam. This reflection loss was greater than 19.6 dB in the studied frequency range and reaches 42.2 dB at 10.56 GHz. The high losses associated with the thermal stability of inorganic foams position these "green" materials as potential high power load at microwave frequencies.

(PACRIM-P-028-2017) Metamaterial for microwave absorption improvement of pyramidal absorbers

L. Pometcu[1]; A. Sharaiha[1]; R. Benzerga*[1]; P. Poliguen[2]

1. IETR - University Rennes 1, France
2. DGA/DS, France

This paper addresses the combination of artificial materials with natural absorber materials in order to enhance their absorption properties and compactness. We proposed and demonstrated a method to increase the absorption properties of conventional pyramidal microwave absorbing materials by the use of two different unit cells of metamaterials. Two different design of Microwave Material Absorbers (MMA), consisting on the combination of two resonant cells, are used for this work. The first combination is composed of asymmetrical metamaterial cells while, the second combination is composed of symmetrical metamaterial cells. The MMA are printed on one side of the Arlon 880 substrate ($\varepsilon_r = 2.2$) where the other side is metallized and considered as a ground plane. Simulations, using the commercial CST electromagnetic software, are done for the hybrid absorber materials. MMA are placed on the back of the rectangular base of the pyramidal absorber to form the hybrid absorber.

The natural absorbers are made of commercial carbon loaded polyurethane foam material. The measurement results of these hybrid materials show a significantly decrease of the reflection loss. We obtain an improvement of the absorption in normal incidence as well as in oblique incidence (30° and 45°) comparing to a classical pyramid absorber. The hybrid absorber made with the symmetrical MMA show a broadband optimization between 2 and 18 GHz.

(PACRIM-P-029-2017) Evaluation of Ceramic/Ceramic (Al_2O_3/ Al_2O_3) Joint Interface Prepared via Brazing

M. Leylaz Mehrabadi*[1]

1. University of Tehran, School of Metallurgy and Materials Eng, Islamic Republic of Iran

Recent investigations show that ceramic/ceramic joints have high potential for applications in industry. Cost and difficulty in manufacturing complex components, either in one-step or by joining of ceramic-metal and ceramic-ceramic, have inhibited more widespread use. It is very important to know how to join components without any problem. The main aim of preparing this paper has been investigating of joining two ceramics with metal fillers (Al_2O_3 to Al_2O_3), the interface of Al_2O_3/ Al_2O_3 with the same metal interlayer (Ag-Cu-Ti) and the effects on properties. The results showed that the optimum joining of Al_2O_3/Al_2O_3 was obtained by applying a metal layer of Ag-Cu as well as an active metal of Ti-6Al-4V. The second filler was used to increase wet ability and improve strength. Microscopic investigations revealed penetration and activation of elements from the interface to bulk of ceramic body and it was the major reaction in the joints. Both joints showed the deepest penetration of Ti atoms from interface into the ceramics. According to the XRD results, TiO and V_2O_5 were the most important phases in the Al_2O_3/Al_2O_3 interface. The strength of both joints increased until an optimum time and temperature condition and decreased after that by forming of other phases, which inhibited the formation of a stronger interface. The optimum time and temperature is suggested to be 900°C and 60 min for Al_2O_3/ Al_2O_3.

(PACRIM-P-030-2017) New Applications of Graphene in GaN Based optoelectronics and Its Thermal Stability Study

C. Leiming*[1]

1. Zhengzhou University of Aeronautics, China

A novel device consisting of graphene and GaN is demonstrated in this report. Chen et al. reported a GaN-metal Schottky diode for ultraviolet detecting. However, the transmittance of the semi-transparent metal film is very low. Besides, metal has a fixed work function, and thus it is hard to increase the Schottky barrier which is very important to improve the detectivity. Graphene is not only very transparent and conductive, but also work function tunable. An ultraviolet detector made of graphene and GaN is introduced in this report with super low leakage current density 2.8e-8 A/cm^2 at -8 V, which is much lower than metal-GaN Schottky diode 5e-7 A/cm^2 at -5 V. Its responsivity reaches up to 0.18 A/W under about 360 nm ultraviolet light illumination and the open circuit voltage is increased 150 mV by $AuCl_3$ doping. The result represents one of the very few reports on GaN-graphene ultraviolet detectors, which is an important electronic application of GaN Schottky devices.

(PACRIM-P-031-2017) Microwave-assisted construct Ag/ZnO/g-C_3N_4 ternary micro/nano composites with enhanced photocatalytic activity under visible light irradiation

H. Lu*[1]; X. Li[1]; Z. Zhang[1]; R. Zhang[1]

1. Zhengzhou University, Materials Science and Engineering, China

Ag/ZnO/g-C_3N_4 ternary micro/nano composites were successfully synthesized by a simple and convenient microwave-assisted route. Graphite-like C_3N_4 sheets were obtained by exfoliating the prepared g-C_3N_4 powders. Phase structure, valance state, morphology, thermal and optical properties of the products were characterized by XRD, XPS, SEM, TG, UV-vis DRS, FI-IR and PL, respectively. Photocatalytic performance of Ag/ZnO/g-C_3N_4 was evaluated by studying the degradation of methylene blue (MB) dye in aqueous solution under visible light irradiation. The results show that well crystallized Ag/ZnO/g-C_3N_4 ternary micro/nano composites were achieved under microwave radiation power of 240 W for 15 min. The Ag/ZnO/g-C_3N_4 photocatalysts exhibited an enhanced photocatalytic performance as compared to monolithic or dual structure materials. The Ag/ZnO/g-C_3N_4 photocatalyst with 5.0mol% silver exhibited obviously the best photocatalytic activity among the Ag doped samples under degradation condition. The apparent reaction rate constant (k, 0.0083min^{-1}) of 5.0 mol%Ag/ZnO/g-C_3N_4 is 7.5 times higher than that of monolithic ZnO (k, 0.0011min^{-1}) and 2.37 times higher than that of ZnO/g-C_3N_4(k, 0.0035min^{-1}). The possible photocatalytic mechanism of Ag/ZnO/g-C_3N_4 during the degradation process was also discussed.

(PACRIM-P-032-2017) Nano-glass ceramic cathodes for Li^+/Na^+ mixed-ion batteries

W. He*[1]; Y. Yue[2]

1. Qilu University of Technology, Shandong Key Laboratory of Glass and Functional Ceramics, China
2. Aalborg University, Section of Chemistry, Denmark

Electrode materials can display superior electrochemical performances and behavior via the nanoscale design. Here, the low-temperature synthesis of nano-glass ceramics (NGCs) is based on inheriting the network structure of yeast polyphosphate metabolism. The NGCs-3 sample synthesized with a molar ratio of Fe/V=7:6 is composed of nano-domains of semiconducting oxide glass (Li_2O-Na_2O-Fe_2O_3-V_2O_5-P_2O_5, LNFVP), nanocrystalline particles ($Li_9Fe_3P_8O_{29}$, $Li_{0.6}V_{1.67}O_{3.67}$ and $VOPO_4$), and nanopores connected by interfaces. We have clarified the mixing ion transport mechanism and the electrochemical reactions, and the influences of molar ratio of Fe/V on the structure and electrochemical properties of NGCs. The coexistence of V^{4+}/V^{3+} and Fe^{3+}/Fe^{2+} redox couples can exchange multiple electrons between different nanoparticles. This nanoscale design offers a new possibility improved the electrochemical performances of Li^+/Na^+ mixed-ion batteries (LNMIBs). The NGCs-3 electrode exhibits a higher discharge capacity (145 mAh g^{-1}) and energy storage density (525 Wh kg^{-1}) at 5C, and the capacity retention reaches 70% after 1000 cycles. More importantly, we have established a direct relationship between the electrochemical kinetics and nanostructure of NGC electrode materials.

(PACRIM-P-033-2017) Controlled Synthesis of Various Copper Oxide Nanostructures as Functional Material for Gas Sensor

Y. Oh*[1]

1. Korea Institute of Science and Technology, Opto-Electronics Materials Devices Research Center, Republic of Korea

Copper oxide (CuO/Cu_2O) nanoparticles were prepared by alcothermal or hydrothermal method. The average size of the nanoparticles ranged from 10 to 60nm. The particle size decreases with increasing reducing agent concentration and relative concentration of capping molecules. Even after 60 days of storing, it shows the same percentage of copper to oxygen elements as after synthesis. Copper oxide nanoparticles were integrated into sensor structure for HCN detection providing fast response and recovery time. Importantly, the Copper oxide NPs can be recycled many times. These nanowires(25~45nm in dia) prepared by hydrothermal synthesis have high flexibility and transmittance. CuO NWs were used to make a simple gas sensor. The CuO NWs sensor performs stabile selectivity level for benzene. The response and recovery time to 1ppm acetone is around 98s and 21s. Fabrication method of CuO[Cu] (copper nanoparticles with copper oxide shell around) in an ethylene glycol solution are reported. This facile method take place through the chemical reduction of copper nitrate and copper sulfate in ethylene glycol within the presence of a polymer surfactant (Polyvinylpyrrolidone), which was added to preclude aggregation and give dispersion stability to the final colloidal nanoparticles. The size of the hybrid nanoparticles can be controlled from 50 to 120nm by varying the synthesis parameters.

(PACRIM-P-034-2017) Active metal brazing substrates superior in thermal fatigue resistance obtained by highly-thermal conductive silicon nitrides with high toughness

H. Miyazaki*[1]; Y. Zhou[1]; S. Iwakiri[2]; H. Hirotsuru[2]; K. Hirao[1]; S. Fukuda[1]; N. Izu[1]; H. Hyuga[1]

1. National Institute of AIST, Advanced Manufacturing Research Institute, Japan
2. Denka. Co, Ceramic Research Dept., Japan

A newly-developed active metal brazing (AMB) substrates made of silicon nitride ceramics with both high thermal conductivity and superior fracture toughness were tested under thermal cycling from -40 to 250ºC and its resistance to the copper delamination from ceramic substrate was investigated. No peeling off of Cu layers was observed even after 1k cycles for the highly-thermal conductive and tough Si_3N_4 AMB substrate, whereas other AMB substrates with lower fracture toughness exhibited spalling of Cu layer at an early stage of temperature cycling. Acoustic scanning microscopy observation of the substrates after 1k cycles hardly revealed cracks in the newly-developed Si_3N_4 AMB substrate. The decrease in the flexural strength after thermal cycling was negligible for the highly-thermal conductive Si_3N_4 AMB substrates, whereas those of others dropped rapidly with the thermal cycles. Thus, excellent mechanical reliability under harsh thermal environments was confirmed for the developed Si_3N_4 AMB substrate. This work was supported by the Council for Science, Technology and Innovation (CSTI), the Cross-ministerial Strategic Innovation Promotion Program (SIP), "Next-generation power electronics/Consistent R&D of next-generation SiC power electronics" (funding agency: the New Energy and Industrial Technology Development Organization (NEDO)).

(PACRIM-P-035-2017) International Standards for Properties and Performance of Advanced Ceramics – Over 30 Years of ASTM Committee C28 Standards

M. G. Jenkins*[1]; J. Salem[2]; G. D. Quinn[3]; J. Helfinstine[4]; S. T. Gonczy[5]

1. Bothell Engineering and Science Technologies, USA
2. NASA Glenn Research Center, USA
3. NIST, USA
4. Corning Incorporated, USA
5. Gateway Materials Technology, USA

Mechanical and physical properties/performance of brittle bodies (e.g., advanced ceramics and glasses) can be difficult to measure correctly unless the proper techniques are used. For over three decades, ASTM Committee C28 on Advanced Ceramics, has developed numerous full-consensus standards (e.g., test methods, practices, guides, terminology) to measure various properties and performance of monolithic and composite ceramics and coatings that, in some cases, may be applicable to glasses. These standards give the "low-down" for determining many mechanical, physical, and thermal properties and performance thereby provideing accurate, reliable, repeatable and complete data. Involvement in ASTM Committee C28 includes users, producers, researchers, designers, academicians, etc. who write, continually update, and validate through round robin test programmes, nearly 50 standards over the three decades since the Committee's inception in 1986. Included in this poster is a pictogram of the ASTM Committee C28 standards and how to obtain them either as i) individual copies (physical or digital) with full details or ii) a complete collection in one volume. A listing of other ASTM committees of interest is included. In addition, some examples of the tangible benefits of standards for advanced ceramics demonstrate their practical applications.

(PACRIM-P-036-2017) Adhesion measurement of thin silicate coatings on LAS glass substrates

M. Jeon*[1]; J. Lee[1]; Y. Han[2]; S. Lee[3]

1. Korea Testing Laboratory, Materials & Components Technology Center, Republic of Korea
2. Korea Institute of Ceramic Engineering and Technology, Republic of Korea
3. KC Glass & Materials, Republic of Korea

The prepared thin silicate coatings are used for decorative films on LAS substrates. The silicate coatings should have low coefficient of thermal expansion comparable to the LAS substrate for high temperature applications an good adhesion with the substrates. The silicate coatings have a typically brittle properties and, therefore, it is very difficult to find adhesion by conventional pull test. Scratch testing is one of fast and effective methods to obtain the critical loads that are related to adhesion properties of coatings. Critical load is known to be a function of coating-substrate adhesion, thickness, hardness, stylus tip condition, loading rate, coating stress, roughness, and friction. The glass pastes were prepared with boro-silicate glass frit having low thermal expansion coefficient and ceramic coloring pigment. Thin silicate films were coated on LAS glass substrate by screen printing method and heat-treated at 750-800ºC with quartz tube furnace. Adhesion of thin silicate coatings on LAS glass substrates were measured using a scratch tester. Each silicate coatings were scratched by a diamond stylus and various critical loads required to peel off the coatings were determined together with image analysis of scratch tracks and change of friction coefficient. The effect of the coating composition and thickness on adhesion measurement are discussed in terms of coating failure and damage features.

(PACRIM-P-037-2017) Preparation of separative-phase fancy glaze derived from iron ore slag

X. Wang*[1]

1. Shaanxi University of Science & Technology, China

With the rapid development of iron metallurgical industry, it has caused a huge amount of iron ore slag. Dumping or disposal of such great quantities of tailing causes damage to the ecological environment. The iron ore slag contains iron, silica, alumina, calcium oxide etc., indicating that it is a valuable resource for ceramic glaze colorants. In this work, to overcome the shortcomings of the conventional technologies. We attempted to utilize iron ore slag as the ceramic glaze colorant to prepare the phase separation fancy glaze. The separative-phase fancy glaze was successfully prepared with the addition of 25 wt% iron ore slag. Effects of the firing temperature on the chromaticity, precipitated phase and microstructure of separative-phase fancy glaze were investigated. A possible coloring mechanism was proposed to explain the variation of glaze colors and patterns with the increasing of firing temperature. The results indicated that with increasing the firing temperature, the content of whitlockite decreased while the size of phase separation droplets in glazes increased. The residual whitlockite weakened coloring of Fe_2O_3 and formed glaze patterns. In addition, the increased size of phase separation droplets weakened the structural color, which increased the L* and b* value of glazes. Therefore, the color of separative-phase fancy glaze got more yellow and brown gradually.

(PACRIM-P-038-2017) Ball indentation test after thermal fatigue of plasma sprayed E/TBC

K. Lee*[1]; Y. Chae[1]; J. Park[2]

1. Kookmin University, School of Mechanical Systems Engineering, Republic of Korea
2. Korea Atomic Energy Research Institute, Republic of Korea

Environmental barrier coatings are indispensable for protecting Si-based material such as Si_3N_4 and SiC from oxidation and corrosion. However, highly insurable layer such as thermal barrier coatings is also needed to increase operation temperature such as 1600ºC class of high-efficient gas turbine system. Therefore, E/TBC double layers are maybe a solution to protect the composite both high temperature condition and hot vapour condition. High mechanical endurance against damages by foreign objects is also required for the coatings. In this study YSZ/mullite+Yb_2SiO_5 coatings and YSZ/ Yb_2SiO_5 coatings of E/TBC are deposited by an air plasma spray on the SiC_f-SiC substrates to prevent high temperature oxidation and water vapour corrosion for gas turbine hot parts. Thermal fatigue tests are then conducted to test thermal durability of E/TBC under 1200ºC of top part and 900ºC of bottom part. The cycles are conducted to 4000 and 5000cycles. Ball indentation tests are conducted before and after thermal fatigue of YSZ/ mullite+Yb_2SiO_5 and YSZ/ Yb_2SiO_5 E/TBC. Tungsten carbide ball with a radius of 3.18mm is used for obtaining indentation load-displacement curves. Relative hardness and stiffness changes will be discussed from load-displacement curves. The results indicates that the E/TBC double layers have good thermal durability and desirable for high temperature gas turbine system.

(PACRIM-P-039-2017) Rare earth ions doped fluorophosphate glass-fluoride crystal composites: The preparation and spectral properties

J. Fan*[1]; S. Chen[1]; L. Zhang[1]

1. Shanghai Institute of Optics and Fine Mechanics, China

Crystal-glass composites are very promising laser materials due to the combined properties of their crystal and glass components, such as the ability to be produced in large size and efficient luminescence. Conventionally, crystal –glass composites can be produce by heat treating method, in which, however, the sorts of precipitated crystals are limited by the compositions of the glass matrices and the size of the crystals has to be confined in less than 20 nm to avoid Rayleigh scattering. Recently, we developed a new method to prepare this kind of composites. In this method, fluoride crystals are directly introduced into fluorophosphates glass matrix by co-firing powder mixtures of fluoride crystals powders and fluorophosphate glass powders followed by quenching. The refractive index of fluorophosphate glass can be adjusted to match that of fluoride crystals to minimize light scattering and break size limitation of the crystal components. Er^{3+} doped CaF_2 and SrF_2 crystals have been successfully incorporated into fluorophosphates glass matrix. The crystals in the composites were micrometers in size. The in-line transmittance of the composites was higher than 75% near 800nm due to the matching of the refractive indices. Mid-infrared luminescence was observed in the composite. The successful fabrication of the composites indicates that this method is very promising.

(PACRIM-P-040-2017) The Cu matrix composites reinforced by TiN/TiB_2 particulates synthesized via self-propagating high temperature synthesis

J. Yin*[1]; Y. Zeng[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Cu matrix composites reinforced by different molar ratios of TiN/ TiB_2 particulates (Cu/TiB_2/TiN composites) have been prepared by powder metallurgy method. Cu/TiB_2/TiN composite powder was fabricated successfully utilizing the self-propagating high-temperature synthesis (SHS) reactions of Cu–Ti–BN systems. X-ray diffraction (XRD) results revealed that the exothermic reactions of the Cu–Ti–BN systems proceed in such a way that Ti reacted with BN to form TiB_2 and TiN. The microstructure observed by Scanning electron microscope (SEM) showed that most of the TiB_2 grains had the clubbed structures, and the TiN grains were near-spherical structure. The TiN/TiB_2 ceramics and the residual BN were adhered to the molten Cu particles randomly. Hot-press sintering was carried out at different temperature to obtain the densified Cu/TiB_2/ TiN composites using the Cu/TiB_2/TiN composite powder as the raw materials. Mechanical and wear properties of the composites were test in this work. The results indicated that both hardness and bending strength of composites were significantly increased by the TiN/TiB_2 additions. The Cu/TiB_2/TiN composites had better wear resistance than the pure Cu. And the coefficient of friction of Cu/ TiB_2/TiN composites was slightly lower due to the combined effect of the hard TiN/TiB_2 ceramics and the BN lubricant films.

(PACRIM-P-041-2017) Formation of nanostructure AlTiN coating layer on WC tool material

K. Kim*[1]; Y. Kim[1]; Y. Lee[1]; J. Lee[2]

1. Sejong University, Republic of Korea
2. Kong Ju National University, Republic of Korea

In order to improve the properties of the tool materials, it is necessary to improve the corrosion and oxidation resistance at the high temperature area. Generally, it is well understood that the microstructural control of coating layer on the WC tools has an strong influence to control corrosion and oxidation resistance. In this study, we focus on finding the relationship between the microstructural length-scale and the primary physical properties of the AlTiN coating layer on the WC tools. Especially, the formation of the AlTiN layer is very effective to enhance the oxidation resistance at the high temperature. Furthermore, the nanostructured AlTiN phase controlled by deposition parameters plays critical role to reveal the novel physical properties of the AlTiN coating layer on WC tools, thus resulting in significant improvement of the reliability of the WC tools.

(PACRIM-P-042-2017) Boron nitride/Silicon nitride composites with high properties prepared by gas pressure sintering

L. Zhao*[1]; S. Lee[1]

1. Korea Institute of Materials Science, Republic of Korea

BN_p/Si_3N_4 and BN_w/Si_3N_4 composites were prepared by gas pressure sintering. The influences of composition and preparation process on the dielectric properties, mechanical properties, phase composition and microstructure of composites were investigated. The dielectric and mechanical properties of BN_p/Si_3N_4 composites with different volume content of BN particles were investigated, and the phase composition and microstructure of the composites were analyzed. BN particles could improve the dielectric properties of BN_p/Si_3N_4 composites, but the mechanical properties decreased. When the volume content of BN particles was 10vol.%, the dielectric constant and dielectric loss tangent were 4.03 and 8.36×10^{-3} respectively, and the bending strength and fracture toughness still reached 198.9MPa and 3.06 $MPam^{1/2}$. The principal crystal phases of the composites were h-BN and β-Si_3N_4. The effects of BN whiskers on the dielectric and mechanical properties of BN_w/Si_3N_4 composites were also investigated. When the volume content of BN whiskers was 10vol.%, the dielectric constant and dielectric loss tangent were 3.8 and 5.00×10^{-3} respectively, and the bending strength and fracture toughness still reached 215MPa and 3.23 $MPam^{1/2}$ respectively. The interlocked microstructure of BN whiskers and rod-like β-Si_3N_4 was responsible for the relatively good mechanical properties of BN_w/Si_3N_4 composites.

(PACRIM-P-043-2017) Elasticity and Structure of Silicate Glasses under in-situ Static and Shock-Wave Presssures

M. Manghnani*[1]; A. Hushur[2]; T. Sekine[5]; Q. Williams[4]

1. University of Hawaii, Hawaii Institute of Geophysics & Planetology, USA
2. Xinjiang University, China
4. University of Californa, Santa Cruz, USA
5. Center for High Pressure Science and Technology Advanced Research (HPSTAR), China

We review the current status regarding the compression behavior (volumetric strain) and structural changes (i.e., Si-O-Si, B-O-B, B-O-Si, Si-O-Ti bonds) in sillica, borosilicate, and SiO2-TiO2 glasses under in-situ static pressures up to 70GPa using multidisciplinary techniques: ultrasonic interferometry, Brillouin and Raman scattering, and X-ray diffraction. Excellent agreement between the high-pressure ultrasonic and Brillouin results enables detailed examination and interpretation of the anomalous behavior (increasing compressibility with pressure) that occurs within these glasses at ~ 2 GPa. The reversibility (at lower pressures) and irreversibility (above certain higher threshold pressure) in the compression behavior of these glasses is precisely revealed from the in-situ high-pressure ultrasonic and Raman data. The static pressure results are discussed in terms of the compositional and structural differences in these glasses. The results from the static experiments are compared with the shock-wave data for these glasses. In general, there is inherent lack of full agreement between the densification curves obtained for these glasses under the static and dynamic studies. The implications are discussed in light of the elastic and structural data obtained from a few shock-quenched borosilicate and SiO2-TiO2 glasses.

(PACRIM-P-044-2017) Crystal structure of the defect pyrochlore potassium tantalate on ion-exchanging dipped in sodium aqueous solution by Rietveld analysis

T. Hashizume*[1]; A. Saiki[2]; S. Miwa[3]

1. University of Toyama, Organization for Promotion of Research, Japan
2. University of Toyama, Graduate School of Science and Engineering for Research, Japan
3. University of Toyama, Graduate School of Science and Engineering for Education, Japan

Potassium tantalate synthesized on tantalum plate by hydrothermal synthesis method. The potassium tantalate was defect pyrochlore crystal structure by X-ray diffraction analysis. The tantalate can be reported exchanged at A site cation in alkaline solution was reported in previous conference (PACRIM11). The defect pyrochlore tantalate was considered as $K_2Ta_2O_5(OH)_{1.6}H_2O$ by Reitveld analysis using XRD patterns of this tantalate on assumption that the space group was Fd-3m with hydroxy ion and/or crystal water. When the defect potassium tantalate dipped in 6M sodium aqueous solution for 512min, 293K, the tantalate was calculated to the ratio of K:Na = 1:9, and crystal structure was though as $K_{0.1}Na_{0.9}Ta_2O_5(OH)_{1.6}H_2O$ by Reitveld fitting curves from XRD pattern. The crystal parameters of the potassium and ion-exchanged tantalate were calculated to 1.0620(1) nm and 1.0535(1) nm respectively. Ion-exchange of K+ and Na+ might be occurred that K+ or Na+ ion through the tunnel structure between TaO6$^-$ octahedron.

(PACRIM-P-045-2017) A new AlB_{12} based composite with aluminum matrix

V. Kartuzov*[1]; P. Mazur[1]; O. Vasiliev[1]; V. Muratov[1]; Y. Kartuzov[1]

1. Institut for Problems of Materials Sciences NAS of Ukraine, Ukraine

The aim of the present work is to demonstrate the possibility of Al-AlB_{12} composite preparation and assess its prospects from technological point of view. Sample specimens of Al-AlB_{12} composites were prepared by impregnation of AlB_{12} powder (produced at IPMS NAS of Ukraine) by molten aluminum at 1100, 1200 and 1300 °C keeping the system at respective maximum temperatures for 15 min. At 1100 °C the structure is a continuous fine grained even distribution of at least two phases. We suggest from the analysis of Al-B phase diagram, that those phases are crystalline aluminum dodecaboride and solid solution of AlB_{12} in Al, but its real and precise constitution is the matter of further study. Conducting the impregnation at 1200 °C leads to a remarkable growth of the phase which we associate with the solid solution. At 1300 °C this phase forms continuous network. Wetting of AlB_{12} by molten aluminum has technologically appropriate level, which is in contrast with the case of B_4C where wetting is poor and complex techniques must be employed to obtain composite with high boron content. Thus, Al-AlB_{12} composites are promising for the replacement of current boron carbide based composites in, for example, neutron absorbing applications. Specific operational properties of the composites are presently studied.

(PACRIM-P-046-2017) Influence of Grain Size on the Mechanical Properties and Sputtering Resistance of h-BN Ceramics

X. Duan*[1]; D. Jia[1]; Z. Wang[1]; Z. Yang[1]; Y. Zhou[1]

1. Harbin Institute of Technology, China

Hexagonal boron nitride (h-BN) matrix composite ceramics exhibit versatile and good properties, and they have potential important applications in the field of aerospace, electronics, metallurgy, machinery, nuclear energy, etc. In this presentation, h-BN powders were ball-milled, then hot-pressing sintered with different conditions to control ceramics with different grain sizes. The results show that h-BN ceramic grain size increases gradually with the sintering temperature increasing from 1600°C to 1900°C and holding time extending from 0.5h to 4h. The h-BN ceramics with average grain size from 0.5μm to 8μm are obtained. With the increase of h-BN ceramic grain size, the bending strength decrease, and the relationship between bending strength and grain size conform to the Hall-Petch formula. The h-BN ceramic with the grain size of 0.5μm has the best elastic modulus, bending strength and fracture toughness, as 50.1 GPa, 163.5 MPa and 2.85 MPa×m$^{1/2}$. The Xe ion sputtering resistance properties of h-BN ceramic material gradually decreased with the increase of grain size. The reasons of h-BN grains damage by Xe ions sputtering are B-N bond broken and BN layers delaminated. While the surface loss of composite ceramics are because of h-BN grains damage, mullite phase damage and some h-BN grains detached from surfaces.

(PACRIM-P-047-2017) Aerosol Deposition of MgB_2 as a novel processing method for superconducting tapes

D. Hanft*[1]; T. Stöcker[1]; P. Glosse[2]; S. Denneler[2]; T. Berthold[2]; M. Oomen[2]; S. Kauffmann-Weiss[3]; E. Günther[3]; F. Weis[4]; M. Weiss[4]; W. Häßler[5]; B. Holzapfel[3]; R. Moos[1]

1. University of Bayreuth, Functional Materials, Germany
2. Siemens AG, Germany
3. Karlsruhe Institute of Technology, Germany
4. Palas GmbH, Germany
5. Leibniz Institute for Solid State and Materials Research, Germany

For more economic energy harvesting from wind power an improvement of the power to weight ratio of the generator is essential. As a starting point this can be achieved by replacing rotor coils of heavy copper by superconducting tape coils. MgB_2 is a material that shows a good superconducting behavior also as polycrystalline film. A relative high working temperature of about 20 K below the critical temperature of 39 K and a low density makes it suitable for large-scale applications. An important feature for further processing to coils is a flexible architecture of such conductors. For the already commercialized powder in tube technique, the good performance of filaments is counteracted by the costly process. The Aerosol Deposition Method (ADM) could be a solution to manufacture cost efficient μm-thick tape superconductors. Although MgB_2 is an intermediate phase, it shows brittle ceramic-like mechanical behavior and can be deposited by ADM. We achieved superconducting films of several micron thickness on different substrates, like glass or bendable nickel-base alloys (Hastelloy) with a transition temperature T_{C0} of 18 K and current density of $J_C \approx 5$ kA/cm^2 (at 4 K, 0 T). In this work, we studied the influence of deposition parameters, such as carrier gas type and carrier gas flow as well as the role of powder morphologies and found a correlation to the film morphology of the MgB_2 films.

(PACRIM-P-048-2017) Two-Stage Sintering of Nano-sized Yttria Stabilized Zirconia

E. Gorzkowski*[1]; J. Drazin[2]; S. Wimmer[1]

1. Naval Research Lab, USA
2. ASEE, USA

It is known that defects, such as grain boundaries and solute cations reduce the lattice thermal conductivity of materials by scattering phonons. However, these defects have little influence on the radiative component of thermal conductivity. To reduce this component, one must consider photonic mechanisms where differences in the refractive index (due to pores) are most successful in reflecting radiation. However, the size and shape of the pores must be tailored in order to maintain mechanical integrity. One method to create this desirable microstructure (i.e., small grain size with large pores) would be to control the pore size through a polymer sphere burnout followed by a two stage sintering process, i.e., short dwell at high temperature followed by quickly quenching to a lower temperature for a longer dwell. The processing steps needed to make the microstructure will be discussed, as well as, the resultant thermal conductivity.

(PACRIM-P-049-2017) Dielectric Thick Film Produced via Aerosol Deposition

E. Gorzkowski*[1]; E. Patterson[2]; S. D. Johnson[1]

1. Naval Research Lab, USA
2. ASEE, USA

Aerosol deposition (AD) is a thick-film deposition process that can produce layers up to several hundred micrometers thick with densities greater than 95% of the bulk. The primary advantage of AD is that the deposition takes place entirely at ambient temperature; thereby enabling film growth in material systems with disparate melting temperatures. The bonding and densification of the film and film/substrate interface are thought to be facilitated by local temperature rise, high pressure, and chemical bonding during deposition, which leads to a dense nano-grained microstructure. In this talk we present results on the deposition of dielectric and ferroelectric materials deposited by aerosol deposition including the effect of processing parameters on the resultant material properties.

(PACRIM-P-050-2017) Plasma Emission during the Collision of Ceramic Particles on Aerosol Deposition

J. Akedo*[1]; T. Saeki[1]

1. ACT, AIST, Japan

Aerosol Deposition (AD) method is a unique approach for metal and ceramic coating, where solid state submicron metal and ceramics particles are accelerated by gas flow up to 100 - 500 m/s and then impacted onto a substrate. During collision of fine particles and interaction with substrate, these ceramic particles formed thick, dense and hard ceramic layers at room temperature. No additional heating for solidification of ceramic powder was required. We named this phenomenon “Room Temperature Impact Consolidation (R.T.I.C)”. In this RTIC of ceramic powder, if He gas was used with high gas follow ratio over 10L/min, the plasma emission was observed during the collision of particles and the color of ceramic layer became black. These emission spectrum lines had good coincidence with the He spectrum lines induced by electrical excitation. But there are no explanation about the change of layer color. In this presentation, we would like to discuss about the relationship between this plasma emission and formation of the layer structuring.

(PACRIM-P-051-2017) Hybrid aerosol deposition towards delight design

K. Shinoda*[1]; T. Saeki[1]; M. Mori[1]; J. Akedo[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Advanced Coating Technology Research Center, Japan

Ceramic coatings onto three-dimensional objects that are consisting of metals, ceramics, and polymers will provide us a new tool for supporting additive manufacturing and enable us new design for lightweight components and heat resistant components. Aerosol deposition (AD) technology is a relatively new method that can fabricate dense ceramic coatings that adhere strongly to substrates without thermal damage. Therefore, it will be a good candidate technology for this purpose. In this background, we have been developing a hybrid aerosol deposition (HAD) process, which showed some feasibilities to satisfy these requirements. The HAD process is basically a hybrid technology of aerosol deposition and plasma spray, which compensates disadvantage of aerosol deposition (AD) such as low deposition rate by plasma spray. We also try to expand its applicability to a delight design tool for consumer products, by which we can give delight to users. We will present our recent challenge on the development of HAD process and its applicability to a delight design tool. This work was supported in part by NEDO SIP, Innovative Design /Manufacturing Technologies, High-Value Added Ceramic Products Manufacturing Technologies.

(PACRIM-P-052-2017) Utilization of Al Scrap Waste and Fabrications of Advanced Ceramics

M. Shahien*[1]; E. M. Ewais[1]

1. Central Metallurgical Research & Development Institute, CMRDI, Refractory & Ceramic Materials Division, Advanced Materials Department, Egypt

Ceramic engineering and industry is facing several challenges including, expensive raw materials and prerequisites of sevier experimental conditions, such as high temperatures and pressures of the synthesis process. On the other hand, the wastes of several industries are serious challenge, regarding its harmful environmental effects. Recently, an interesting trend in the ceramic industry of utilization and recycling these waste materials into valuable ceramic materials is growing. This study is dealing with the aluminum scarp (Al scrap), thus huge amounts are produced annually. Basically, the main amount of this scrap is recovered through recycling. In this study, we are finding an alternative technological approach to utilize the Al scrap chemically to synthesis one of the most important ceramic materials (aluminum oxide or alumina: Al_2O_3), with low cost. Furthermore, the feasibility of utilization this synthesized Al_2O_3 powder for sintering as well as the fabrication of its yttrium aluminum garnet composites were investigated.

(PACRIM-P-053-2017) Thermal Sprayed AlN Coatings from Deposition to Properties

M. Shahien*[1]; M. Shahien[2]; M. Yamada[1]; M. Fukumoto[1]

1. Toyohashi University of Technology, Mechanical Engineering, Japan
2. Central Metallurgical Research & Development Institute, CMRDI, Advanced Materials, Egypt

The high thermal conductivity, high electric resistivity and chemical stability of aluminum nitride (AlN) ceramics are receiving wide attention in a diverse range of applications. Aluminum nitride ceramics are successfully developed in the form of powders, sintered compacts and thin films. Several techniques are used to deposit the AlN thin films, basically vapor deposition techniques including chemical vapor deposition (CVD), physical vapor deposition (PVD). However, it was difficult to fabricate thick AlN films (more than 100 μm) with these techniques, due to their low deposition rates. For thick ceramic films deposition, thermal spray process had been widely used. The process involves heating of the powder material to a molten or semi-molten (softened) state. The heat source is typically a flame or an electric arc, which uses the gas to propel the material to the targeted substrate. However, it was difficult to deposit the AlN particles in thermal spray process due to the decomposition of AlN particles under high temperatures without melting state. Recently, we successfully deposited the AlN thermal sprayed coating by using the reactivity of the thermal plasma and the chemical reaction between a molten feedstock material and the nitriding plasma species. In this paper, we will present our recent achievements to fabricate thick AlN coatings from deposition to fabrication of high thermal conductivity coatings.

(PACRIM-P-054-2017) New Challenge on Suspension Plasma Spraying of Fine Ceramics

M. Shahien*[1]; M. Shahien[2]; M. Suzuki[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Advanced Coating Technology Research Center, Japan
2. Central Metallurgical Research and Development Institute, CMRDI, Advanced Materials, Egypt

Plasma spray is a generic term for a group of commonly used processes for depositing ceramic coatings. It is defined as the method of coating application by the deposition of molten or semi-molten (softened) particles propelling onto a substrate. The material in form of powder with average particle size of about 20-100 μm and good flowability is injected into very high temperature plasma. Then the hot materials impacts on the substrate surface and rapidly cools forming the coatings. However, it was difficult to spray the fine particles (submicron or nano-sized) directly in the plasma, due to the easy agglomeration of the fine particles and, therefore, the rapid clogging of the feeding path. Suspension plasma spraying (SPS) is a relatively new process which enables spraying of the submicron or nano-sized particles in the form of suspensions. This study will discuss a new challenge on suspension plasma spraying of fine ceramic particles, with using the axial injection of feedstock materials, gas consumption and relatively low power.

(PACRIM-P-055-2017) Tribological characteristics of conventional and spark plasma sintered TiCN based cermets

V. Verma[1]; B. Kumar*[1]

1. IIT Roorkee, India

In the present work, densified TiCN-WC-Ni/Co cermets with or without TaC were processed via conventional sintering at 1550°C for 2h at 100 MPa and spark plasma sintering (SPS) at 1400°C for 3 min at 70 MPa. Sliding wear behavior against steel, cemented carbide (WC-Co) and silicon carbide (SiC) ball was studied on processed cermets in unlubricated conditions at 5, 10 or 20N load. The coefficient of friction (COF) varied from 0.25 to 1.1 and wear rate from 10^{-6} to 10^{-7} mm^3/Nm with the change in load and counterbody. In general, the investigated cermets exhibited less friction and wear against steel ball whereas high friction and wear obtained against cemented carbide and silicon carbide ball. The worn surfaces of cermets are characterized by fracture, grain pull-out and tribolayer formation. Against steel, the increased material transfer and formation of iron oxide-rich tribochemical layer were responsible for the reduction in friction and wear for Ti(CN)-5WC-10Ni-10Co-5TaC cermet. Against cemented carbide (WC-Co) and silicon carbide (SiC) high contact temperature caused depletion of tribolayer from the cermet surface and resulted in high wear. Among all the investigated cermets the addition of TaC and Co in TiCN-Ni-WC cermet resulted in minimum COF and wear rate. The refined size and least fraction of adjacent ceramic phase attributed for reduced wear in TaC added TiCN-WC-Ni/Co cermet.

(PACRIM-P-056-2017) The friction properties of Zr-Cu-Si-N coatings synthesized by magnetron sputtering process with single alloying targets

K. Moon[1]; H. Lee[1]; T. Kim[1]; G. Bang[1]; S. Shin*[1]

1. KITECH, Heat Treatment Technology R&BD Group, Republic of Korea

In automobile engine moving parts industry DLC are well traditional as a common solution in order to overcome wear problems. The friction reduction properties of DLC are well known in dry and lubrication conditions. But DLC coating is not compatibility in automotive engine oil environment for friction reduction. The reason is that currently the additives in automotive engine oil are show poor compatibility with DLC coatings. Recently, nitride nanocomposite films such as nc-ZrN/Cu and nc-MoN/Cu coatings have been introduced with high hardness and low friction properties which are expected to be substituted for DLC coating. In this study, Zr-Cu-Si based single alloying targets were prepared by arc melting. Zr-Cu-Si-N coatings were coated on the automobile engine moving parts by magnetron sputtering process with single alloying targets, and the friction and wear properties of the coatings were investigated. Friction properties were tested with high frequency reciprocating test machine at 100°C for 1 hrs with 75 N of load conditions. The Zr-Cu-Si-N coatings showed as much as 24% of friction reduction compared with DLC coating and wear of the nanocomposite coatings was not observed.

(PACRIM-P-057-2017) The mechanical properties of Ti-Si based coating synthesized by magnetron sputtering process with single alloying targets

K. Moon[1]; H. Lee[1]; T. Kim[1]; G. Bang[1]; S. Shin*[1]

1. KITECH, Heat Treatment Technology R&BD Group, Republic of Korea

TiN coatings were used widely in cutting tools, dies and wear resistant parts, because of their high hardness tools and wear resistance, as well as the satisfactory combination of strength and fracture toughness. Also recently to improve the mechanical properties of TiN coating, binary elements addition such as Si has been popularly tried. The addition of Si to TiN and structurally well manipulation led to the formation of coating of TiN and Si_3N_4 phases. This resulted in the super-hardness over 30 GPa and the increase of the oxidation temperature over 1000°C. However, it is not easy to add Si to the TiN by a proper PVD system. In this study, Ti-Si based single alloying targets were prepared by arc melting. The investigation on the alloying targets showed that their were dendrite, inter-dendrite structure and had a high toughness. Ti-Si-N coatings were deposited by magntron sputtering method with the prepared targets. Their structures and mechanical properties were investigated by SEM&EDS, Nano-indentor etc. Also, the effect of the Si element contents on the mechanical properties of the Ti based coatings were reviewed in this study.

(PACRIM-P-058-2017) Selective Design of Graphene and Graphene Oxide Quantum dots for biolabelling application

S. Mhin*[1]; S. Kang[3]; H. Han[2]

1. Korea Institute of Industrial Technology, Heat treatment R&D group, Republic of Korea
2. Korea Institute of Industrial Technology, Republic of Korea
3. Hanyang University, Materials Science and Engineering, Republic of Korea

Graphene and Graphene oxide quantum dots (GQDs & GOQDs) have attractive properties and potential applications. However, their various applications are limited by a current synthetic method which requires long processing time. In this study, we present a facile and remarkably rapid method for production of GQDs exhibiting excellent optoelectronic properties. We employed the pulsed laser ablation (PLA) technique to exfoliate GQDs from multi-wall carbon nanotube (MWCNTs), which can be referred to as a pulsed laser exfoliation (PLE) process. We could selectively produce either GQDs or graphene oxide quantum dots (GOQDs) by simply changing the organic solvents utilized in the PLE processing. The synthesized GQDs show distinct blue photoluminescence (PL) with excellent quantum yield (QY) up to 12% as well as sufficient brightness and resolution to be suitable for biolabelling applications.

(PACRIM-P-059-2017) Low frictional coating of Ti contained nanocomposite and a-C:H layers for automobile components by the plasma enhanced chemical vapor deposition

Y. Cho*[1]; Y. Choi[1]; J. Sle[1]; K. Moon[1]

1. KITECH, Republic of Korea

The diamond like carbon (DLC) films have excellent properties of high hardness, chemical stability, and low friction that prevail applied on the automobile components. This research focused on the development of chemical vapor deposition process for functional intermediate layer and hydrocarbon layer with plasma technology.

Those were systematically deposited on the nitrocarburized SCM415 steel using the tetra-dimethyl-amino-titanium (TDMAT) of metal organic precursor and acetylene gas. In order to enhancing adhesion, the Ti contained functional layer firstly deposited on substrate with pulsed DC plasma (150 kHz, -600 V) at pressure of 1 Pa and temperature of 350 °C. The a-C:H coating carried out on Ti intermediate layer with Ar and C_2H_2 mixed gases at the same plasma condition and pressure after then heat off. The hardness of films measured by the micro-indenter and friction coefficient was surveyed by the ball-on-disk tribometer. Chemical bonding states was analyzed by the Raman and the XPS. The films had high hardness as 21 GPa, however, films showed low lubrication properties as friction coefficient of 0.06. The responsibility of protective coatings for automobile components was evaluated by the motoring rig operation system (Lambda 3.3) for tappets, which supported real-time operations in automobile engine.

(PACRIM-P-060-2017) ‘Peeled-wire’ like CNT-SiO_2 core-shell structure with self-exposed end caps

Y. Jeong*[1]; W. Han[2]

1. Korea Institute of Industrial Technology, Republic of Korea
2. Seoul Womens University, Department of Chemistry, Republic of Korea

The CNT-SiO2 core-shell structure is particularly appealing because the insulating SiO2 layer wraps around the CNTs, functioning as a gate dielectric. However, it is still a challenge to expose both end-caps of the structure for enabling them to serve as electrodes, which additionally requires complicated post processes. Here, we present a unique CNTs-SiO2 core-shell structure where both ends are uncovered with SiO2 in a “peeled-wire” structure. In this structure, SiO2 particles partially encapsulate the CNTs during the synthesis, resulting in both end-caps of the nanotube being self-exposed and electrically conductive. The field-effect transistor build-up with this structure exhibits p-type characteristics with a linear conductance behavior on Id-Vd output performance. This approach for making self-formed electrodes in the CNT-SiO2 core-shell structure provides a simple and efficient way for applying them to future nanodevices in terms of process simplicity and cost effectiveness.

(PACRIM-P-061-2017) Porous geopolymer insulating filling for basalt reinforced CMC

A. Natali Murri[1]; E. Landi[1]; V. Medri*[1]; L. Laghi[2]; C. Mingazzini[3]

1. CNR ISTEC, Italy
2. CertiMaC ScarL, Italy
3. ENEA, TEMAF, Italy

Ashes derived from combined vegetal and animal biomass are mainly based on calcium phosphate and secondly on aluminosilicate compounds: they still represent almost an unexplored secondary raw material, although they are partially reactive fillers for alkali-activated materials. Mixed biomass ashes were used in combination with metakaolin and potassium di-silicate aqueous solution to obtain by direct foaming porous geopolymers to be used as insulating core with basalt reinforced Ceramic Matrix Composites (CMC) skins. The formulations were finalized to maximize the amount of ashes disposed. Microstructural, chemical-physical and thermal characterization were performed. This study was developed in the frame of the project EEE-CFCC (www.eee-cfcc-it), POR FESR of E-R Region, Italy.

(PACRIM-P-128-2017) Preparation and Structure of Geopolymer-based Alkali-activated CFB Ash Composite for Removing Ni^{2+} from Wastewater

W. Mozgawa*[1]; M. Krol[1]

1. AGH University of Science and Technology, Faculty of Materials Science and Ceramic, Poland

Disposal in landfills is the most common means of handling ash generated in circulating fluidized bed (CFB) boiler power plants. Cement and concrete technology have been identified as one of the major uses for ashes. However it was found that CFB ash cannot be used as a cement replacement in concrete due to its unacceptably high sulfur content. Therefore other uses of ash should be investigated, which can provide more cost-effective ash management. A novel free-sintering inorganic material for wastewater treatment was fabricated in this study. This material was synthesized using ash and sodium hydroxide solution at relatively low temperature (80°C). The effects of reaction systems composition (NaOH concentration) on the phase composition of resulting products have been determined. In particular, the structures of materials were examined using FT-IR spectroscopy in the middle infrared range. The results were compared to the XRD measurements as well as SEM observations. It was found that synthesis of material with satisfactory functional properties is possible using 0.8 ml of 5 M NaOH solution per 1 g ash. Results showed that the resulting geopolymers efficiently removes Ni^{2+} ions from aqueous solutions wastewater and may have potential application in removing heavy metals from wastewater.

(PACRIM-P-062-2017) Sintering behavior of Ag-Ni electrode powder with core-shell structure

K. Kim[1]; J. Koo[1]; J. Choi*[1]; Y. Han[1]

1. Korea Institute of Ceramic Engineering and Technology (KICET), Engineering Ceramic Center, Republic of Korea

Expensive silver powder is used to form electrodes in most IT equipment, and recently, many attempts have been made to lower manufacturing costs by developing powders with Ag-Ni or Ag-Cu core-shell structures. This study examined the sintering behavior of Ag-Ni electrode powder with a core-shell structure for silicon solar cell with high-energy efficiency. The electrode powder was found to have a surface similar to pure Ag powder, and cross-sectional analysis revealed that Ag was uniformly coated on Ni powder. Each electrode was formed by sintering in the range of 500 to 800 degrees Celsius, and the specimen sintered at 600 degrees Celsius had the lowest sheet resistance of 5.5 mΩ/square, which is about two times greater than that of pure Ag. The microstructures of electrodes formed at varying sintering temperatures were examined to determine why sheet resistance showed a minimum value at 600 degrees Celsius. The electrode formed at 600 degrees Celsius had the best Ag connectivity, and thus provided a better path for the flow of electrons.

(PACRIM-P-063-2017) Functional bulk MgB_2 – based superconductors for application in fault current limiters

T. Prikhna*[1]; V. Sokolovsky[2]; V. Meerovich[2]; V. Moshchil[1]; V. Sverdun[1]; A. Kozyrev[1]

1. Institute for Superhard Materials of the National Academy of Sciences of Ukraine, Ukraine
2. Ben-Gurion University of the Negev, Israel, Israel

Bulk MgB_2–based superconductors are promising for application in fault current limiters (FCL) which can provide a definite rate of response to a fault event resulting in the SC – normal state reversible transition. The main characteristics determining the material suitability are the critical current density, j_c, thermal conductivity and thermal capacity. The bulk MgB_2 samples were produced under 30 MPa (hot pressing) and 2 GPa (quasihydrostatic pressing) at 800–1050ºC from Mg and B or MgB_2 with and without additions. It has been shown that the SC properties depend on the distribution of admixture oxygen, boron- and oxygen-enriched nanosized inhomogenities in MgB_2 matrix, connectivity between SC grains, and material porosity. The transformer method gives the j_c $1.6\bullet10^4 - 6.3\bullet10^4$ A/cm^2 at 4.2 K while magnetometer measurements showed the $j_c=2.24\bullet10^5 - 5.1\bullet10^5$ A/cm^2 at 10 K in self-magnetic fields, which can be explained by the instability of the SC state of MgB_2 in a variable magnetic field. Using the transformer method AC losses per a cycle before quenching for the best materials were estimated around 0.75-1 J/cm^3 and the powers of losses was 200 W. The FCL model with rings cut out from SC MgB_2 materials prepared using various technologies demonstrating that MgB_2 is a promising material for application in inductive FCLs.

(PACRIM-P-064-2017) $LaRNiMnO_6$ (R=Pr, Nd, Sm) Double Perovskite Ceramics as New Candidates for Multiferroic Materials

X. Chen*[1]; H. Lin[1]; X. Shi[1]

1. Zhejiang University, School of Materials Science and Engineering, China

In the present work, $LaRNiMnO_6$ (R=Pr, Nd, Sm) double perovskite ceramics were designed and synthesized, and characterized as new candidates for multiferroic materials. The crystal structure was determined as monoclinic in space group $P2_1/n$, and the dense ceramics could be obtained by a solid state reaction process. A ferromagnetic transition similar to that in La_2NiMnO_6 occurred in the present ceramics and the T_C point decreased with decreasing ionic radius of R. The significantly enhanced magnetodielectric effect was determined in the present ceramics, and the maximum magnetodielectric coefficient up to -7.7% was obtained in $LaSmNiMnO_6$. Moreover, a dielectric anomaly around the magnetic T_C was detected for the present ceramics which also indicated the magnetodielectric coupling.

(PACRIM-P-065-2017) Direct Fabrication of $BaTaO_2N$ film on Tantalum substrate by ammonothermal method

Y. Maruyama*[1]; T. Watanabe[1]

1. Meiji University, Japan

$BaTaO_2N$ are attracting attention as a water splitting photocatalyst that can ultilize a long wavelength light. In generally, $BaTaO_2N$ photoelectrode is fabricated by using $BaTaO_2N$ powder. There is no report that $BaTaO_2N$ film is directly fabricated on a conductive substrate. Therefore, we attempted to fabricate $BaTaO_2N$ film on Tantalum substrate by ammonothermal method. Ammonotermal method is a method for nitridation under supercritical ammonia. In the present study, we investigated the effect of reaction temperature on the product. As a results, we successfully directly fabricated $BaTaO_2N$ film on Tantalum substrate by ammonothermal method at 700°C for 5 h. The XRD pattern of the product agreed with the pattern for $BaTaO_2N$. $BaTaO_2N$ film and Tantalum substrate were observed in the product by scanning electron microscope. The film thickness of $BaTaO_2N$ was 1-5μm. The product showed a photoresponse and an anode photocurrent by photoelectrochemical measurement under visible light irradiation.

(PACRIM-P-066-2017) Optical and Electrical Properties of MSO/ Ag/ MSO/ SiO_2 Hybrid Film Deposited on PET Film

G. Jang*[1]

1. Chungbuk National University, Materials Engineering, Republic of Korea

A hybrid structure of Mn doped SnO_2 (MSO)/Ag/ Mn doped SnO_2 (MSO)/SiO_2 was deposited on PET substrate by sequential RF/DC magnetron sputtering at room temperature. Optical and electrical properties were systematically investigated as a function of MSO thickness and oxygen partial pressure. In order to estimate the optical characteristics and compare them with experimental results in advance, the simulation program named EMP (Essential Macleod Program) was adopted. EMP simulation results suggested that a multilayered film of MSO (40 nm)/Ag (10 nm)/MSO (40 nm))/SiO_2 (10 nm) exhibited the highest visible transmittance of 87.1 % at 550 nm, whereas experimentally measured transmittance showed 85.1 %, somewhat lower than simulation data. X-ray diffraction patterns of the prepared SnO_2 multi-layered films were found to have a typical amorphous phase. Measured film thickness was about 110 nm. The lowest R_s was about 9 Ω/sq, acquired at the multi-layers with the structure of MSO (40 nm)/Ag (10 nm)/ MSO (40 nm)/ SiO_2 (10 nm). In addition, the sheet resistance and resistivity of MSO/Ag/MSO/SiO_2 multi layer films increased systematically with increasing the thickness of MSO layer from 40 to 55 nm. It was shown that the Φ_{TC} values of MSO/Ag/MSO/SiO_2 multi layer film were in the range of $18.9 – 32.4 \times 10^{-3}\Omega^{-}$

(PACRIM-P-067-2017) Fabrication and Study of Bi_2O_3-SiO_2 based Glass-ceramics

J. Xie*[1]; F. Zhang[1]; D. Lin[1]; T. Wang[1]; L. Zhang[1]; Y. Shi[1]

1. Optoelectronic Materials and Device Research Centre, Department of Electronics and Information Materials, School of Materials Science and Engineering, China

In this paper, silica crucible containing the mixture was put in an electrically heated muffle furnace and the temperature was raised slowly to a temperature about 900-1100°C depending on the composition of $(1-x)Bi_2O_3$-$3/2SiO_2$-xAl_2O_3. The matrix glasses of based Bi_2O_3-SiO_2 system were prepared by melting method and glass-ceramics were obtained by heat treatment at characteristic temperatures determined by the Differential Scanning Calorimetry (DSC). The results show that the kinds of glasses with x=0-0.1 in all prepared $(1-x)Bi_2O_3$-$3/2SiO_2$-xAl_2O_3 matrix glasses can develop into transparent or translucent glass-ceramics after proper heat treatment and their crystalline phases are mainly $Bi_4Si_3O_{12}$ and $Bi_{12}SiO_{20}$ respectively. The crystals in all glass-ceramics observed under scanning electron microscope show granular in shape and their sizes are within the range of 0.5-2.0um. The density and hardness of glass-ceramics after heat treatment are higher than that of untreated glasses in the Bi_2O_3-SiO_2 system. The Bi_2O_3-SiO_2 based glass-ceramics maintain similar optical property as that of $Bi_4Si_3O_{12}$ single crystal which has the emission spectra located in 350–650nm wavelength, and their optical intensities are almost proportional to the crystalline volume fraction. The optical transmission of these glass-ceramic samples is above 65% at the range of 450-700nm.

(PACRIM-P-068-2017) Fracture threshold of radius of curvature of a silver nanowires electrode for highly flexible devices

S. Kim*[1]; D. Kim[1]; J. Ahn[2]

1. Korea Institute of Science and Technology, Clean Energy Research Center, Republic of Korea
2. Korea Institute of Science and Technology(KIST), Advanced Analysis Center, Republic of Korea

In a next-generation transparent electrode based on silver nanowires (Ag NWs), in-depth studies of mechanical characteristics of individual Ag NWs is an important issue for providing a critical strain failure criterion. In-situ tensile and buckling tests of five-fold twinned Ag NWs were performed for evaluating failure of conductive electrodes with radius of curvature (ROC) of highly flexible devices (FDs). We demonstrated that the mechanical and electrical failure of conductive electrodes entirely depends on the lattice strain of Ag NWs, which has a linear relationship with the ROC and substrate thickness of electrodes. The NWs with a diameter greater than ~40 nm at lattice strains beyond the elastic limits exhibit brittle failure without plastic deformation under tensile loading, leading to a rapid increase in sheet resistance for flexible electrodes. In-situ buckling loading–unloading tests clearly show that the brittle NWs under negative compressive strain can endure the lattice strain that is much higher than those under positive tensile strain, resulting in the enhancement of failure resistance of flexible electrodes. Thus, the elastic strain of brittle Ag NWs provides a mechanical and electrical failure criterion of FDs because the decrease in failure resistance limits figure of merit of FDs.

(PACRIM-P-069-2017) High strength and transparent micro capillary ceramics via insert ceramic injection molding technology

S. Kim*[1]; D. Kim[1]; G. Choi[1]; J. Park[2]; G. Kim[3]

1. Korea Institute of Science and Technology, Clean Energy Research Center, Republic of Korea
2. MID Co., Ltd., Ceramic R&D Center, Republic of Korea
3. Kosma Co., Ltd., R&D Center, Republic of Korea

Transparent polycrystalline alumina ceramics have been widely used in the areas of sensor domes, windows, in particular, small precision parts such as micro-capillaries and ceramic discharge metal-halide lamp envelopes due to its transparency, mechanical strength, gas impermeability, corrosion resistance, and cost-effectiveness. For the fabrication of small component parts, micro ceramic injection molding (μ-CIM) is a prospective technology because of its high economic potential for large series production. In spite of the merit, μ-CIM technology at present lacks processes suitable for high-strength ceramics as well as large-scale manufacture. To fabricate high-strength capillary ceramic parts with a micro hole, more elaborate μ-CIM technology is needed to be implemented for defect-free fabrication. For a high strength and transparent capillary ceramics, light scattering centers such as residual pores, grain boundaries, secondary phases, and rough surfaces are also to be controlled. In our study, we newly developed insert μ-CIM technology for fabricating small precision capillary molded parts with a micro hole. We also achieved high strength and transparent micro capillary ceramics through a homogeneous grain microstructure control by preventing abnormal grain growth and an enhanced densification by a delicate hot isostatic press sintering.

(PACRIM-P-070-2017) Ultrahigh Transparency Ce:GAGG Ceramic Prepared by Hot Isostatic Pressing Process

X. Chen*[1]; Y. Wu[1]

1. Alfred University, Kazuo Inamori School of Engineering, USA

Highly transparent Ce:GAGG ceramics have been prepared via oxygen sintering, followed by hot isostatic pressing (HIPing). The highest transmittance measured at the Ce^{3+} emission wavelength of 558nm was 81.5%. The relationships between transmittance, oxygen sintering and hot isostatic pressing have been intensively studied. It was determined that grain size could be well controlled by optimizing the temperature and dwell time of the pre-sintering step, and the parameters of the HIPing process. Porosity was almost entirely eliminated after HIPing. Samples developed a brown coloration during HIPing, which was attributed to the presence of color centers. At short dwell times, post-HIPing annealing in air initially improved transmittance, but prolonged annealing times resulted in translucent samples.

(PACRIM-P-071-2017) Erbium oxyorthosilicate films prepared by sol-gel spin-coating

L. Fan[1]; Y. Wu*[1]; Y. Shi[2]

1. Alfred University, Materials Science, USA
2. Shanghai University, School of Materials Science and Engineering, USA

Er_2SiO_5 films were fabricated through the Pechini sol-gel process. XRD measurements of the films annealed at 950-1200°C for 2h show that the films are highly crystalline, and can be matched to a standard Er_2SiO_5 PDF card (ICSD #89622), with no second phases observed. As calcining temperature was increased from 950 to 1200°C, no phase transformation was observed. The effect of coating rotation speed on the microstructure of the films was investigated over a speed range of 2000-8000 rpm. It was determined that the microstructure of the films depends on the relative ratio between the centrifugal force and the viscous force between the sol and silicon substrate at a certain speed. At spin speeds lower than 6000 rpm, the centrifugal force is lower than the viscous force, and the sol cannot disperse uniformly on the substrate. At spin speeds higher than 6000 rpm, the centrifugal force is much higher than the viscous force between the sol and silicon substrate, which results in the film being torn apart. It was determined that the optimal spin speed to fabricate films using this specific sol is ~6000 rpm, which results in smooth and crack-free Er_2SiO_5 films.

(PACRIM-P-072-2017) Investigation of cerium-modified barium titanate ceramics prepared by the sol-gel method

C. A. Stanciu*[1]; A. Ianculescu[1]; B. Vasile[1]; R. Trusca[1]; M. Cernea[2]; I. Pintilie[2]

1. Politechnica University of Bucharest, Department of Oxide Materials Science & Engineering, Romania
2. National Institute of Materials Physics, Romania

Pure and cerium-doped barium titanate nanopowders described by the formula $Ba_{1-x}Ce_xTiO_3$ and $Ba_{1-x}Ce_xTi_{1-x/4}O_3$ for (x=0.05 and 0.005) were prepared by the sol-gel method. After annealing at 900°C/2h, the non-stoichiometric powders with built-in Ti vacancies show single phase compositions for both samples, while the stoichiometric powders show small amounts of secondary phases. SEM investigations of the ceramics sintered at 1300°C/4h indicate significant changes of the microstructural features as a function of dopant content and stoichiometry. Thereby, an obvious decrease of the average grain size was observed as the Ce^{3+} content decreases from x=0.05 to x=0.005, irrespective of the presence or absence of Ti vacancies. More homogeneous and denser microstructures were observed for the ceramics with built-in titanium vacancies than in the case of the ceramics free of compensating defects. A sharp ferroelectric-paraelectric transition is obtained for all the ceramics but the values of the Curie temperatures (T_C) are very different. For the higher content of Ce, T_C is close to room temperature, while for the smaller Ce^{3+} content, the T_C is closer to the values obtained for pure $BaTiO_3$. Due to the proximity of the paraelectric–ferroelectric phase transition, the ceramics with x=0.05 present at room temperature higher dielectric permittivity values than the samples with lower Ce^{3+} content (x=0.005).

(PACRIM-P-073-2017) Microstructure of ZnO thin films by Raman spectroscopy

E. Burov*[1]; O. Majerus[2]; S. Grachev[1]; Y. Le Du[2]

1. Saint-Gobain, Laboartoire Mixte Saint-Gobain/CNRS, France
2. Ecole Nationale Supérieure de Chimie de Paris, LCMCP (Chimie ParisTech), France

Zinc oxide is used as one of the layers in glass coatings for a number of applications. For this reason, over the last ten years many technics have been developed and adapted to characterize these films. The most popular approach to observe the microstructure is still X-ray diffraction (XRD) [Conchon, 2010]. It gives a good vision on the average state of the microstructure of the sample and its crystallinity. However, XRD is insensitive to local structure modifications, amorphous and disordered media (close to grain-boundaries, for example) and to the defects at the surface. In this study we propose an original approach for the ZnO thin film characterization based on the coupling of the confocal Raman spectroscopy and non-negative matrix factor spectra deconvolution [Woelffel, 2015]. ZnO thin films with thickness from 10 to 150 nm have been prepared by the radio frequency magnetron sputtering. The microstructure has been verified by XRD. The cartography of the sample surface was carried out in order to study the surface structure, its homogeneity and modification due to deposition conditions and post treatment (stress, annealing temperature, etc.). We also investigated the substrate optical properties (absorption, reflection, etc.) impact on the Raman response of the film.

(PACRIM-P-074-2017) Concentration-dependent Cytotoxicity of Sub-micron Oxide Particles in Prostate Cancer Cells

J. G. Fisher*[1]; U. Farooq[1]; E. Hwang[5]; U. Thuan[4]; Y. Jung[4]; J. Lee[3]; V. Lakshmanan[2]

1. Chonnam National University, Materials Science and Engineering, Republic of Korea
2. Chonnam National University Medical School, Biomedical Sciences, Republic of Korea
3. Chonnam National University Hwasun Hospital, Research Center for Cancer Immunotherapy, Republic of Korea
4. Chonnam National University Medical School, Biochemistry, Republic of Korea
5. Chonnam National University Hwasun Hospital, Urology, Republic of Korea

Prostate cancer is globally the second most common cancer type and the fifth leading cause of cancer-related death in men. Much research is being carried out on oxide nanopowders as carriers for therapeutic drugs, imaging agents and tumor-specific targeting agents. Recent work has shown that cerium oxide nanoparticles selectively attack PC-3 prostate cancer cells, leading to the possibility of the use of oxide nanoparticles in the treatment of prostate cancer. In this work, we study the cytotoxicity of submicron-sized $KNbO_3$ and $(K_{0.5}Bi_{0.5})TiO_3$ particles to normal and prostate cancer cell lines. $KNbO_3$ and $(K_{0.5}Bi_{0.5})TiO_3$ powders are prepared by the mixed oxide method. Particle size analysis is carried out using dynamic light scattering. The structure of the powders is examined using X-ray diffraction, Fourier transform infra-red and Raman scattering spectroscopy. The microstructure of the powders is examined using scanning electron microscopy. Cell viability analysis is carried out by MTT assay using EAHY926, PC-3 and DU-145 cell lines. Cell uptake studies are carried out using Rhodamine 123 and DAPI coated particles.

(PACRIM-P-075-2017) Usage of layered silicates for observation on photophysical interaction between dye molecules and metal nanoparticles

M. Eguchi*[1]

1. National Institute for Materials Science (NIMS), Japan

The goal of this study is the microscopic observation of exciton-polaritons which are composed of coherent interaction between localized surface plasmon resonance (LSPR) induced at the surface of metal nanoparticles and electronic motion in molecules. In this study, microscopic study on exciton-polaritons has been aimed by controlling nano-structure of monomeric dye molecules at the surface of metal nanoparticles. In particular, porphyrin molecules and cubic Ag nanoparticles were adopted to form the exciton-polaritons. In order to combine porphyrin molecules and cubic Ag nanoparticles, layered silicates were utilized since we have been revealed that the layered silicates adsorb some porphyrin molecules monomerically and modify surfaces of cubic metal nanoparticles. Furthermore, for effective coupling, Ag nanoparticles and porphyrin molecules were chosen whose peaks positions at maximum extinction are approximate each other. Herewith, when the detuning of each peak position was small enough, the complex showed a peak split in UV-visible extinction spectra which indicates formation of exciton-polaritons between LSPR and porphyrin molecules, whereas the extinction spectra of complexes with larger detuning was reproduced by superposition of the spectra of metal nanoparticles and porphyrin molecules.

(PACRIM-P-076-2017) New wide-gap, p-type conductive oxide, $Sn_2M_2O_7$ (M=Nb and Ta) pyroclore

N. Kikuchi*[1]; K. Nishio[2]; Y. Aiura[1]; S. Akane[2]; S. Ikeda[2]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan
2. Tokyo University of Science, Japan

p-type transparent conductive oxides (TCOs) has been attract attention of material scientists and engineers. However it is difficult to realize p-type TCOs because of localized valence band maximum (VBM) composed by O 2p orbital. Hybridization of the localized O 2p and metal d orbital or chalcogen p orbital has been carried out to modify the VBM, however the p-type TCOs explored so far were insufficient for practical transparent electronic devices because of low mobility, durability and productivity. In this paper, new wide-gap, p-type conductive oxide, $Sn_2M_2O_7$ (M=Nb and Ta) pyroclore was reported. Since the VBM of $Sn_2M_2O_7$ was composed of hybridized band of Sn 5s and O 2p, delocalized and isotropic nature of the VBM is expected to realize high mobility. Band gap was estimated to 2.4 eV for $Sn_2Nb_2O_7$ and 3.0 eV for $Sn_2Ta_2O_7$, indicating high transparency in visible range. A positive sign of the Hall coefficient and Seebeck constant of $Sn_2M_2O_7$ indicated p-type conductivity. ^{119}Sn Mössbauer absorption spectra exhibited that Sn^{4+} in $Sn_2M_2O_7$ plays an important role for p-type carrier generation.

(PACRIM-P-077-2017) Innovative Copper-containing Ceria-based Anodes for Intermediate Temperature Solid Oxide Fuel Cells

A. Iannaci*[1]; V. De Marco[2]; V. M. Sglavo[2]

1. Istituto nazionale scienza e tecnologia dei materiali INSTM, Italy
2. University of Study of Trento, Italy

One of the major barriers to the widespread diffusion of SOFC is related to the employment of nickel at the anodic side. Although such metal is a highly effective hydrogen oxidating catalyst, it is toxic and its activity is decreased by a variety of poisoning substances contained or generated by cheaper fuels like CH_4. Latest efforts to replace nickel have driven the research towards composite anodes based on copper and gadolinia doped ceria (GDC). Such cermets are characterized by high electronic conductivity, provided by Cu, and excellent catalytic activity towards oxidation reactions provided by ceria. The aim of the present work was to produce and analyze the behavior of CuO/GDC-based SOFC. The anode (Li_2O-doped GDC and CuO) and the electrolyte (made by Li_2O-doped GDC) were realized by aqueous tape casting. Different cells were produced by thermal compression of a certain number of anode layers and one electrolyte layer. LSCF-based cathode was applied by screen printing before final co-sintering. The realized cells were tested at 650°C using H_2 and mixed CH_4/CO_2 fuels and very interesting and promising performances were recorded. Co-funded by Caritro foundation (Trento, Italy)

(PACRIM-P-078-2017) Synthesis of lanthanum silicate apatite type from the basic catalysis reaction of sodium silicate

C. Yamagata*[1]; F. S. Silva[1]; V. Ribas de Morais[1]

1. Nuclear and Energy Research Institute, Department of Material Science and Engineering, Brazil

Lanthanum silicate is considered as a promising material to be used as electrolyte in IT-SOFC (Intermediate Temperature Solid Oxide Fuel Cell) due to its superior Ionic conductivity, at temperatures around 600° C. The conventional method of solid state mixture is usually used in the synthesis of lanthanum silicate. This process requires high temperatures, as well as development of undesirable secondary crystalline phases that diminish considerably the Ionic conductivity of the material. In this work, lanthanum silicate was synthesized by a modified sol-gel method from basic catalysis reaction, using Na_2SiO_3 as a source of silica. The relevance of the proposed method is the use of Na_2SiO_2 and the basic Catalysis reaction, instead of TEOS and acid catalysis, respectively, as it is usually practiced. The obtained powder was characterized by XRD and scanning electron microscopy (SEM). The single crystalline apatite phase of lanthanum silicate was reached by calcination of the precursor at 900° C, this temperature is much lower than other conventional methods of synthesis.

(PACRIM-P-079-2017) Measurement of the fracture energy of glass/steel joints in planar solid oxide cell stacks

K. Agersted*[1]; H. Abdoli[2]; P. Alizadeh[3]; B. F. Sørensen[4]; H. L. Frandsen[1]; D. Boccaccini[1]

1. Technical University of Denmark, DTU Energy, Denmark
2. Science and Research Branch, Islamic Azad University, Department of Materials Engineering, Islamic Republic of Iran
3. Tarbiat Modares University, Department of Materials Science and Engineering, Islamic Republic of Iran
4. Technical University of Denmark, DTU Wind Energy, Denmark

Glass-steel couples used for sealing in planar solid oxide cell stacks are subjected to a variety of mixed fracture modes as a consequence of local thermomechanical mismatch (mode I) and more global thermomechanical mismatch between components (mode II). A method for measuring fracture energy under mixed modity of glass/steel joints, using a glass ceramic sealant together with a steel, Crofer 22APU, employs a 3-layer sandwich of steel/glass/steel, which allows for stable crack growth and a special test fixture to create uneven bending moments. This double-cantilever specimen is loaded within a range of uneven bending moments expressed as a phase angle and the crack tip stress state can be varied from pure mode I (0°) to pure mode II (90°). Two types of failure were identified for crack growth patterns: The crack kinking out from the interface and running into the glass matrix parallel to the interfaces, relating to phase angles <30°, or the fracture path running along one of the interfaces between glass and steel, relating to phase angles >68°. Depending on the mode mixity, fracture energies between 7.1 and 69.8 J/m^2 were obtained for phase angles between 0° and 90 °. Hence, mechanical robustness depends markedly on the fracture mode.

(PACRIM-P-080-2017) Optimisation of sealing process and interfaces between glass-ceramic sealing and SOC stack components

K. Agersted*[1]; F. Smeacetto[2]; A. Gianfranco[2]; I. Ritucci[1]; R. Kiebach[1]

1. Technical University of Denmark, DTU Energy, Denmark
2. Politecnico di Torino, Department of Applied Science and Technology, Italy

A glass-ceramic sealing material in the alkaline earth aluminosilicate system with smaller additions of zirconia, sodium and boron oxides have been investigated together with three other candidates for sealing behaviour together with typical SOC stack materials, the zirconia electrolyte, coated and non-coated interconnect steel, Crofer APU. At sealing temperatures between 800ºC and 850ºC, sufficient compliancy and strong adhesion was obtained for this glass-ceramic, while extended heat treatment at SOC operating conditions facilitated partial crystallisation of nepheline and a Ca-Mg-Al silicate (augite) to yield stable CTE at ~12 10^{-6} K^{-1}, thus providing an excellent match of thermomechanical properties to neighbour components. Long-time behaviour and interface chemistry was investigated in detail.

(PACRIM-P-081-2017) The effect of carbon nanostructured materials on the hydrogen release of light metal-borohydrides

A. Nale[1]; F. Pendolino[1]; A. Maddalena[1]; P. Colombo*[1]

1. University of Padova, Industrial Engineering, Italy

Carbon allotropes and derivates show novel behavior in a framework of promising technologies. Among them, nanohorns attracted attention as an alternative to graphene because of their reactivity, the prospective to trap molecules and their biocompatibility. A modification of the nanohorn surface provides reactive sites in order to engineer advanced composite materials for energy storage application with hydrogen content materials. A suitable strategy consists in oxidizing and reducing the nanohorns; oxidation was carried out with a novel synthetic method, comprising of 4-steps chemical synthesis at low temperature. Reduced nanohorns oxide (rNHO) were prepared by clean thermal treatment in hydrogen atmosphere. Light metal borohydrides are good candidate materials for hydrogen storage but they are limited by their excessive stability. The effect of rNHO on lithium boronhydride (LiBH4) have been investigated with thermal programmed desorption volumetric analysis, to test the gas release in presence of different modifications of carbon nanomaterials. A decrease of gas release temperature and a different profile compared to pure LiBH4 are observed. rNHO show the most pronounced impact on the gas release performance of LiBH4 even without metal additives with catalytic properties.

(PACRIM-P-082-2017) Analysis of property and application of LSCF–SCDC composite cathode materials

Y. Wu*[1]; C. Li[1]

1. National Taipei University of Technology, Institute of Material Science and Engineering, Taiwan

In this study, the anode (60 wt% Ni – 40 wt% $Sm_{0.2}Ce_{0.8}O_{1.9}$), electrolytes ($Ce_{0.8}Sm_{0.15}Ca_{0.05}O_{1.875}$), cathode ($La_{0.6}Sr_{0.4}Co_{0.\ 2}Fe_{0.8}O_{3-\delta}$), three composite cathodes (90 wt% $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ – 10 wt% $Ce_{0.8}Sm_{0.15}Ca_{0.05}O_{1.875}$, 80 wt% $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ – 20 wt% $Ce_{0.8}Sm_{0.15}Ca_{0.05}O_{1.875}$, 70 wt% $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ – 30 wt% $Ce_{0.8}Sm_{0.15}Ca_{0.05}O_{1.875}$) and the buffer layer ($Ce_{0.8}Sm_{0.15}Ca_{0.05}O_{1.875}$, $La_{0.4}Ce_{0.6}O_{1.8}$, $La_{0.85}Sr_{0.15}Ga_{0.8}Mg_{0.2}O_{2.825}$) were prepared by solid state reaction method. The electrolyte-supported solid oxide fuel cell, symmetrical cell and three-electrode cell were also prepared in the study. The symmetrical cell were measured by AC impedance analyzer to analyze the polarization resistance of cathode. In the meantime the exchange current density and activation energy of composite cathodes will also be obtained. The three-electrode cell were measured by CV and AC impedance analyzer, and the overpotential values are obtained. The crystal structure, surface morphology, electrical property of the cathodes were analyzed by XRD, SEM, electrochemical instrument and AC impedance analyzer.

(PACRIM-P-083-2017) Crystal structure and low-temperature thermoelectric properties of metastable cubic $Ge_2Sb_2Te_5$ bulk material

T. Omoto[1]; I. Yamada[2]; Y. Kubota[1]; A. Kosuga*[1]

1. Osaka Prefecture University, Department of Physical Science, Graduate School of Science, Japan
2. Osaka Prefecture University, Nanoscience and Nanotechnology Research Center, Research Organization for the 21st Century, Japan

Recently metastable $Ge_2Sb_2Te_5$ (GST) with cubic structure was suggested as a potential low-temperature thermoelectric material by ab-initio calculation study. In this study, we prepared metastable cubic GST bulk material by combination of melt spinning technique and room-temperature high-pressure (RTHP) pressing. Rietveld analysis clarified that the melt spun GST powder contained more than 90 wt% of the metastable cubic phase, demonstrating effectiveness for preparing GST-cubic powder by melt spinning. The RTHP pressing made it possible to prepare high density of the GST bulk sample with ca. 95 % of the theoretical density without transformation of the metastable cubic to the stable hexagonal GST phase. After RTHP pressing, the X-ray diffraction peaks of GST-cubic structure became broadened, which was attributed to the introduction of defects. Our samples exhibited high Seebeck coefficient of ca. 200 μVK^{-1} with high electrical conductivity at room temperature, which is characteristics feature of the metastable GST material. We predicted the relationship between the introduced defects and transport properties using ab-initio calculation in order to tune the transport properties of the metastable cubic GST bulk material.

(PACRIM-P-084-2017) Evolution of herringbone structures in GeTe-based thermoelectric materials with adding elements

H. Lee*[1]; S. Kim[1]; S. Lee[1]; S. Lee[1]; J. Jo[1]

1. Kyungpook National University, Materials Science and Engineering, Republic of Korea

GeTe-based thermoelectric materials show a very high ZT value of about 1.8, an extremely low thermal conductivity of 0.3-1.0 W/mK and a large carrier mobility of 100-200 cm^2/Vs. To improve a ZT value, researches on adding a suitable metal component to GeTe have been carried out. It is well known that if metal elements like Ag, Sb, Bi, and Pb were added in GeTe, ZT values are improved because the metallic atoms added scattered acoustic phonons, leading to low thermal conductivity. Recently, twin boundaries and phase separation in thermoelectric materials are emerging as an important issue. The effects of doping and phase separation depend strongly on the microstructure of a material. However, only a few studies on the microstructure of GeTe-based thermoelectric materials have been carried out. In this work, we examined the microstructure of GeTe-based thermoelectric materials by using transmission electron microscopy. We analyzed the evolution of herringbone structures in GeTe-based thermoelectric materials with adding elements.

(PACRIM-P-085-2017) Preparation and properties of $Bi_2Se_xTe_{3-x}$ Bulk Materials

J. Zheng[1]; S. Chen[1]; K. Cai*[1]

1. Tongji University, School of Materials Science & Engineering, China

Bi_2Te_3 and Bi_2Se_3 nanoplates were prepared by a microwave-assisted wet chemical method, then $Bi_2Se_xTe_{3-x}$ bulk nanocomposites with various x values were prepared by hot pressing the Bi_2Te_3 and Bi_2Se_3 nanoplates at 80 MPa and 723 K in vacuum. The phase composition and microstructures of the bulk samples were characterized by powder x-ray diffraction and field-emission scanning electron microscopy. The electrical conductivity of the $Bi_2Se_xTe_{3-x}$ bulk nanocomposites increases with increasing Se content, and the Seebeck coefficient value is negative, showing n-type conduction, and its absolute value decreases with increasing Se content. The highest power factor among the studied samples, 24.5 $\mu Wcm^{-1}K^{-2}$, is achieved at 369 K from the sample with x = 1.

(PACRIM-P-086-2017) Synthesis and thermoelectric characterization of silicon and metal silicides nanocomposites

K. Kurosaki*[1]; S. Tanusilp[1]; Y. Ohishi[1]; H. Muta[1]; S. Yamanaka[1]

1. Osaka University, Japan

Thermoelectrics (TEs) can convert heat gradients into electricity and vice versa, making them important to the future of power generation from waste heat. Conventional TE materials such as Bi_2Te_3 and PbTe contain highly toxic and/or rare elements, though, limiting their application. Thus, many wish to develop a high-performance TE material made from inexpensive, environmentally friendly, and Earth-abundant elements. Si and metal silicides nanocomposites would be a good candidate for such materials. It can be expected that metal silicides dispersed into the Si matrix in nanoscale scatter heat carrying phonons effectively, leading to the enhancement in the TE performance of Si. In the present study, we focus on a melt spinning method to synthesize such nanocomposites, in which the size and the distribution states of the metal silicides can be controlled by changing the cooling rate. We synthesized the nanocomposites composed of Si and various metal silicides (e.g. VSi_2, Mg_2Si, $NiSi_2$, …) and characterized their microstructures and the TE properties. This work was supported in part by JSPS KAKENHI Grant Number 252890 and JST, PRESTO. Additional support was provided in 2014 by the Program for Creating Future Wisdom, Osaka University.

(PACRIM-P-087-2017) Weak chemical bonds contributing to the intrinsically low thermal conductivity in α-MgAgSb thermoelectric materials

T. Zhu*[1]; X. Zhao[1]

1. Zhejiang University, Materials Science and Engineering, China

Understanding the lattice dynamics and phonon transport from the perspective of chemical bonds is essential for improving and finding high efficiency thermoelectric materials and for many other applications. Here we elucidate the coexistence of global and local weak chemical bonds as the origin of the intrinsically low lattice thermal conductivity of non-caged structure Nowotny-Juza compound, a-MgAgSb, which was identified as a new type of promising thermoelectric material in the temperature of 300-550K. The global weak bonds of the compound lead to a low sound velocity. The unique three-centered Mg-Ag-Sb bonds in a-MgAgSb vibrate locally, and induce low frequency optical phonons, resulting in "rattling-like" thermal damping to further reduce the lattice thermal conductivity. The hierarchical chemical bonds originate from the low valence electron count of a-MgAgSb, with the feature shared by Nowotny-Juza compounds. Low lattice thermal conductivities are therefore highly possible in this series of compounds, which is verified by our phonon and bulk modulus calculations on some of the compositions.

(PACRIM-P-088-2017) Growth behavior of Bi_2Te_3 and Sb_2Te_3 thin films on graphene substrate grown by plasma-enhanced chemical vapor deposition

C. Lee[1]; G. Kim[1]; Y. Lee*[1]

1. Korea Research Institute of Chemical Technology, Advanced Materials Division, Republic of Korea

Among the various chalcogenide materials, Bi_2Te_3 and Sb_2Te_3 have attracted considerable attentions as near room temperature thermoelectric materials because of having the highest figure of merit coefficient ($ZT \approx 1$) at room temperature. For enhanced thermoelectricity, highly oriented thermoelectric thin films with superlattice structure should be required because microstructure of the thin film can play a significant role of electric carrier transport and phonon scattering center. A comparative study of the substrate effect on growth mechanism of the chalcogenide Bi_2Te_3 and Sb_2Te_3 thin films was carried out. The obvious microstructural discrepancy in both of the deposited Bi_2Te_3 and Sb_2Te_3 thin films was observed according to graphene or SiO_2/Si substrate. Bi_2Te_3 and Sb_2Te_3 thin films deposited on the graphene substrate were observed to have more flat and highly oriented crystallographic structure compared to that of SiO_2/Si substrate. Based on the experimental results of this study, the initial adsorption site of graphene substrate during chemical vapor deposition process which has been discussed only through the simulation method could be demonstrated.

(PACRIM-P-089-2017) Optical, electrical and magnetic properties of SiC ceramics and related composites

Z. Huang*[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Our advanced carbide ceramics group are one of the biggest and most energetic ones in SICCAS. SiC-based ceramics/composites, as a class of strategic engineering materials, are shining their new brightness recently. Traditionally, SiC ceramic and its related composites are used as structural ceramic materials; however, during the last decade, our group dedicated ourselves to making SiC promising advanced materials, focusing find potential applications in several amazing research fields of optical, electrical and magnetic aspects. Owing to our continuous researches, high-performance SiC ceramic/composite materials are developed through compositional designing and microstructural tailoring. The relationships between these functional properties as well as optimized microstructures response to several fundamental problems scientifically, ranging from sintering theory, additive strengthening to grain boundary engineering, et al.

(PACRIM-P-090-2017) A facile process to prepare n-type carbon buckypapers and their enhanced thermoelectric performance

Y. Yoo*[1]

1. Korea Research Institute of Chemical Technology, Republic of Korea

In this study, we investigated the thermoelectric materials and their performance excluding the conducting polymers. We prepared a thermoelectric device with p-type organic thermoelectric hybrid film and n-type buckypaper. Both the film and buckypaper are made of a hybrid filler of graphite nanoplatelets (GNPs) and single-walled carbon nanotubes (SWNTs). The p-type thermoelectric hybrid film has a free-standing form and enhanced thermoelectric performance owing to a polyvinylidene fluoride/carbon hybrid film purified with an acid solution, which successfully eliminates amorphous carbon, additives, and impurities. The n-type thermoelectric buckypaper was made with a filtration method with GNPs and SWNTs to the membrane filter. To convert this to an n-type thermoelectric property, a polyethyleneimine solution was also added during filtration process. In addition, adding sodium dodecyl benzene sulfonate during carbon dispersion enhanced thermoelectric performance, which was confirmed by measuring the electrical conductivity and Seebeck coefficient. A thermoelectric device using silver electrodes was produced with the thermoelectric composite film and buckypaper to verify its thermoelectric voltage and generating power.

(PACRIM-P-091-2017) Novel semi-transparent inorganic thin film solar cells based on ultrathin Sb_2S_3 films prepared by atomic layer deposition

D. Kim*[1]; S. Sung[1]; S. Lee[1]; S. Park[1]; K. Yang[1]; J. Kang[1]

1. Daegu Gyeongbuk Institute of Science and Technology, Convergence Research Center for Solar Energy, Republic of Korea

Semi-transparent (ST) solar cell is one of the most interesting topic in photovoltaic researches due to various applications, such as building-integrated PV (BIPV), device-integrated PV (DIPV), and so on. Most of recent ST solar cell researches are based on organic systems, such as DSSC and OPV. However, organic-based ST solar cells are suffered from stability problems, which is a significant obstacle for commercialization. In order to overcome the troublesome stability problem of organic-based ST solar cells, we have proposed a novel inorganic-based ST solar cell. Inorganic semiconductor antimony sulfide (Sb_2S_3) is a representative absorber material for inorganic-organic hybrid solar cells. Because of higher absorption coefficient and wide bandgap, ultrathin Sb_2S_3 films would be appropriate for the absorber materials of ST solar cells. In our work, we have prepared ultrathin Sb_2S_3 films and used them as absorber layers for ST solar cells. In order to deposit uniform and high-quality Sb_2S_3 ultrathin films, Sb_2S_3 films were deposited by atomic layer deposition (ALD) system. Through the optimization of the deposition condition and the thickness of Sb_2S_3 films, Sb_2S_3 film showed 30% transparency and ST-Sb_2S_3 solar cell with 3% efficiency was successfully fabricated, which showed excellent device stability in ambient condition.

(PACRIM-P-092-2017) Electrical and Optical Properties of In-Zn-Sn-O Thin Films

H. Y. Lee*[1]; M. Putri[1]

1. Yeungnam University, Materials Science and Engineering, Republic of Korea

Electrical and optical properties of In-Zn-Sn-O ternary oxide thin films will be presented. The choice of chemical composition is beyond the solubility limit of ZnO and SnO_2 in In_2O_3 ceramics and films. We have found a range of cost-competitive transparent conductive oxide (TCO) films with low indium content and oxide films suitable for thin film transistor applications. Sample preparation as well as characterization methods will also be described, together with electrical and optical property data.

(PACRIM-P-093-2017) Prodigiosin pigment as natural sensitizer for TiO_2 films and its potential use as photovoltaic material in solar cells

P. Hernández-Velasco[1]; M. Rodríguez-Delgado[2]; J. Villarreal-Chiu*[1]

1. Universidad Autónoma de Nuevo León, Facultad de Ciencias Químicas, Laboratorio de Biotecnología, Mexico
2. Tecnológico de Monterrey, Laboratorio de Nanotecnología Ambiental, Centro del Agua para América Latina y el Caribe, Mexico

In this work, we report for the first time, the use of prodigiosin as potential photosensitizer for TiO2 P25-based films. Prodigiosin is a natural pigment, produced as secondary metabolite by the non-photosynthetic bacteria Serratia marcescens. The extracts were obtained from late cultures of the S. marcescens grown on peanut oil broth using chloroform. Prodigiosin purity was analysed by FTIR and H-NMR spectroscopy; their optical characteristics were studied, as well, showing appreciable absorption in the visible region. TiO_2 nanoparticles were modified with SDS in order to enhance its amphiphilic character, improving the absorption of the pigment on TiO_2 surface. A suspension of the modified- TiO_2 was deposited on a conductive glass and the film formed was sensitized by direct adsorption. The electrode was immersed in a prodigiosin solution (in a concentration of 10 mg/mL). The resulting material was characterized by UV-Vis, diffuse reflectance spectroscopy and SEM. From the J-V curves, the essential photoelectrochemical parameters related to the solar cell performance were determined; reaching a conversion efficiency of 0.04% by the photovoltaic material. While more experiments are required, the results obtained constitute a first approach that suggests that this dye-sensitized material could be use in solar energy conversion systems.

(PACRIM-P-094-2017) Fabrication of $CuSbS_2$ compound films by metal stack sulfurization for photovoltaic applications

S. Sung*[1]; D. Kim[1]; S. Park[1]; S. Lee[1]; K. Yang[1]; J. Kang[1]

1. Daegu Gyeongbuk Institute of Science and Technology, Convergence Research Center for Solar Energy, Republic of Korea

A ternary I-V-VI_2 chalcogenide, copper antimony sulfide ($CuSbS_2$), as an alternative absorber to Cu(In,Ga)$(Se,S)_2$ and CdTe has recently become one of the most interesting materials for use as a solar cell absorber layer because of non-toxic and low-cost elements. Recently theoretical studies have predicted that $CuSbS_2$ compound film has direct band gap energy of about ~1.5 eV and an optical absorption coefficient of around 10^4 cm^{-1}, which means the potential of $CuSbS_2$ as photovoltaic materials. Various deposition methods for fabricating $CuSbS_2$ compound films such as co-sputtering, chemical bath deposition, spray pyrolysis, and electro deposition have been reported. In this work, we have tried to utilize metal stack prepared by vacuum deposition process as a precursor for the fabrication of $CuSbS_2$ compound films. We prepared Cu and Sb metal stack by evaporator or sputter system, which was then sulfurized at high temperature for the crystallization of $CuSbS_2$ compound films. Various conditions of metal stack precursor, such as the thickness of metal stack, chemical composition of metal stack, and the temperature of pre-annealing, were investigated to achieve high quality $CuSbS_2$ compound films. Photovoltaic properties of thin film solar cells using $CuSbS_2$ compound films as absorber materials were also investigated in order to evaluate the possibility of photovoltaic application of $CuSbS_2$.

(PACRIM-P-095-2017) Effect of Lead and Tellurium Oxides on Contact Formation of Silicon Solar Cells

M. Naylor*[1]; R. Mayberry[1]; M. Hoerteis[1]

1. Heraeus Precious Metals North America, LLC, Photovoltaics Global Business Unit, USA

This study is focused on a comparison between crystalline and glass additives to screen printed silver pastes on silicon solar cells and the resulting interfacial microstructures and electrical performance. The first series of pastes with crystalline additives contain mixtures of PbO and TeO2 from 0 to 100 mol% PbO. The second series of pastes contain glasses in the Al2O3-PbO-TeO2 ternary system where the PbO/TeO2 ratio matches those in the pastes from the first series. The pastes were fast fired at 800-950 °C after screen printing on p-type mono-crystalline silicon wafers with a Si_3N_4 anti-reflective coating. Electrical performance was assessed using the dual diode model after collecting I-V curves from the printed and fired wafers in addition to actual measurements of contact resistance compensating for finger line widths. Interfacial microstructure and reactions with Ag, Si_3N_4, and Si are assessed via SEM/EDS to compare the two series of pastes. Conclusions relating high cell efficiency to ideal interfacial microstructures and reactions with the PbO/TeO2 based crystalline and glass additives are made using I-V data, contact resistance, and SEM data.

(PACRIM-P-128-2017) Nanostructures of Thin films for photoelectrochemical water splitting

P. Zhang*[1]; L. Gao[1]; X. Song[1]

1. Shanghai Jiao Tong University, School of Materials Science and Engineering, China

Photoelectrochemical (PEC) hydrogen production has aroused great interests to meet the demand for clean and renewable energy. Nanostructures have been designed and implemented to adjust the optical absorption, charge-transport path, surface area, and charge separation to improve the PEC performance of the thin film photoelectrodes. Photoelectrodes with various materials, morphologies, film thickness, and/or composite structures have been prepared and their performance-structure-composition relationships will be discussed.

(PACRIM-P-096-2017) Effects of (Fe+He) Irradiation on Ti_3AlC_2: characterization of defects and microstructure evolution

L. Pang*[1]

1. Institute of Modern Physics, Chinese Academy of Sciences, China

Ti_3AlC_2 is a representative material of MAX phase family which belongs among high-performance ceramic materials. This material combines benefits of metal and ceramics. As its high resistance to creep, crack propagation and high mechanical damage performance, and low neutron activation[1], Ti_3AlC_2 is considered to be a very promising new candidate material for future advanced nuclear device. In this work, we investigate varieties of microstructure of ion-irradiated Ti_3AlC_2, particularly on the formation of He related defects and their evolution under the environment of a large of displacement damage. Firstly, the Ti_3AlC_2 were irradiated by 3.5 MeV Fe-ion at the fluences of 1×10^{16} ions/cm^2, to produce enough amount of vacancy defects in advance. Next, these samples were implanted with 500 keV He-ion at the fluences in the range of 1×10^{16}-1×10^{17} ions/cm^2, respectively. The irradiated samples were characterized with grazing incident X-ray diffraction and TEM. Comparing with the results of single-beam (He-ion or Fe-ion) irradiation, we found that the case of (Fe+He) irradiation causes more remarkable deformation in materials. The results of TEM revealed that deposited He concentration plays an important role on the size of cavities.

(PACRIM-P-097-2017) Oxygen potential, oxygen diffusion, electrical conductivity and defect equilibria in PuO_{2-x}

M. Watanabe*[1]; M. Kato[1]

1. Japan Atomic Energy Agency, Japan

Plutonium dioxide (PuO_2) is a basic element constituting nuclear oxide fuels. PuO_2 having fluorite structure is non-stoichiometric compounds. Therefore, various properties of PuO_2 have been investigated as function of Oxygen to Metal (O/M) ratio. The properties of non-stoichiometric oxides have been evaluated based on defect chemistry, because variation of point defect concentration are closely related to properties including oxygen potential, oxygen diffusion and electrical conductivity. The oxygen potential of PuO_{2-x} was evaluated with Brouwer diagram. Formation energies of point defect were determined by ab-initio calculation and Brouwer diagram. The relationship among oxygen potential, oxygen diffusion and electrical conductivity were described as function of O/M ratio and temperature.

(PACRIM-P-098-2017) Materials for radioactive ion beam sources: From glassy carbon to lanthanum hexaboride

S. Rothe*[1]

1. CERN, Engineering Department, Switzerland

The radioactive ion beam facility ISOLDE at CERN delivers radioactive isotopes of 74 different chemical elements requested by its users. The isotopes are generated in through nuclear reactions induced by impinging 1.4 GeV protons a thick target. The reaction products are extracted as singly charged ions from an ion source and distributed throughout the facility. To ensure an efficient ionization while maintaining a minimum amount of contamination by other elements, beams of each elements are created by different combinations of target materials and ion source configurations. We will present an overview of the ion source materials and highlight ongoing studies of a glassy carbon as ion source material which could enable ion beam purification through a gating technique. We will illustrate how the thermal stress was mitigated through mechanical engineering and show the limits of the current design. To perform long-term stability and reliability tests in the future, we envisage the construction of a dedicated test-stand, which can run undisturbed for extended periods. This setup will also enable us to perform compatibility studies with a high throughput. The first candidate for these investigations is the low-work function material lanthanum hexaboride has shown incompatibilities in the past. We will conclude with an outlook to these ongoing developments.

(PACRIM-P-099-2017) Low-cost preparation method for anti-dirt coating on concrete block using titanium oxide photocatalytic powder

S. Ono*[1]; N. Kishikawa[1]; S. Kawase[1]; T. Hayashi[1]; N. Asano[1]

1. Nagoya Municipal Industrial Research Institute, Japan

We established a low-cost preparation method for anti-dirt coating on concrete block using titanium oxide photocatalytic powder. Titanium oxide photocatalytic powder was prepared from titanium tetraisopropoxide, ethanol and water. The photocatalytic activity was evaluated by the methylene blue decomposition test. The anti-dirt property was also estimated by stained degree by methylene blue in the coated film after the test. We examined photocatalytic activity of titanium oxide powders prepared in various volume ratios of water to ethanol. In the result, we found out that the volume ratio of water to ethanol in hydrolysis was an important factor in preparing powder of high photocatalytic activity. The optimum volume ratio of water to ethanol was 1.4. The prepared titanium oxide powder has about 70% photocatalytic activity of Aeroxide® P25. Concrete blocks were coated by titanium oxide powder in various compositions, mixed with cement and methyltriethoxysilane binder. Addition of cement to binder was useful for giving anti-dirt property to the film surface. The coated concrete block showed good photocatalytic activity with anti-dirt property, in the film composition of 30 mass% titanium oxide powder, 30 mass% cement and 40 mass% binder.

(PACRIM-P-101-2017) Adaptation of the Chevron-Notch Beam Fracture Toughness Method to Large Specimens Harvested from Diesel Particulate Filters

A. Wereszczak[1]; O. Jadaan[2]; M. Modugno[1]; G. W. Hatala[2]; M. Lance*[1]

1. Oak Ridge National Lab, USA
2. University of Mount Union, USA

The apparent fracture toughness of a porous cordierite ceramic was estimated using a large specimen whose geometry was inspired by the ASTM-C1421-standardized chevron-notch beam. The specimens had nominal dimensions of 20 x 40 x 160 mm, were harvested out of unaged and aged diesel particulate filters, and were tested in three-point bending. Using the same combination of experiment and analysis used to develop the standardized chevron-notch test for small, monolithic ceramic bend bars, an apparent fracture toughness of 0.6 MPa√m was estimated for the unaged cordierite diesel particulate filter whereas there was a 50% increase (0.9 MPa√m) after it had been aged with 20% biodiesel fuel containing 14 ppm Na. The effectiveness, simplicity, and robustness of this adapted specimen geometry and test method lends itself to potential standardization and evaluation of (macroscopic) apparent fracture toughness of an entire porous-ceramic, diesel particulate filter structure. This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

(PACRIM-P-102-2017) Parasitic Reactions in Nano-sized Silicon Anodes for Lithium-ion Batteries

H. Gao*[1]; Y. Ren[2]; X. Zuo[2]; G. Xu[1]; L. Xiao[3]; I. Plümel[3]; H. Wiggers[3]; K. Amine[1]; Z. Chen[1]

1. Argonne National Lab, Chemical Science and Engineering Division, USA
2. Argonne National Laboratory, X-ray Science Division, Advanced Photon Source, USA
3. University of Duisburg-Essen, Institute for Combustion and Gas Dynamics–Reactive Fluids (IVG), Germany

When designing nano-Si electrodes for lithium-ion batteries, the detrimental effect of the c-$Li_{15}Si_4$ phase formed upon full lithiation is often a concern. In this study, Si nanoparticles with controlled particle sizes and morphology were synthesized and the parasitic reactions of the metastable c-$Li_{15}Si_4$ phase with the non-aqueous electrolyte was investigated. The use of smaller Si nanoparticles (~ 60 nm) as well as the addition of fluoroethylene carbonate additive played decisive roles in the parasitic reaction such that the c-$Li_{15}Si_4$ phase could disappear at the end of lithiation. This suppression of c-$Li_{15}Si_4$ improved cycle life of the nano-Si electrodes but with a little loss of its specific capacity. In addition the characteristic c-$Li_{15}Si_4$ peak in the dQ/dV plots can be used as an early-stage indicator to the cell capacity fade during cycling. Our findings can contribute to the design guidelines of Si electrodes and allow us to quantify another factor to the performance of the Si electrodes.

(PACRIM-P-103-2017) Conditioning the safety index of Ni-rich cathode oxides for lithium ion batteries

J. Gim*[1]; B. T. Yonemoto[1]; J. Liu[1]; H. Gao[1]; G. Xu[1]; K. Amine[1]; Z. Chen[1]

1. Argonne National Lab, CSE, USA

Ni-rich cathode materials with high energy density has degradation issue of electrochemical performance due to the significant side reaction between electrolyte and cathode. To solve this, a Full Concentration Gradient (FCG) materials consisting of a high-Ni core and a relatively high-Mn outer layer was designed to provide improved stability as well as cycle life characteristic. However, a Ni-rich core still has some possibilities to be contact with electrolyte, especially if the particle in the core part is unexpectedly porous. We found the strategy to tune the particle porosity by controlling a feed rate of transition metal sulfate solutions and ammonium hydroxide solution during co-precipitation synthesis using Continuous Stirred Tank Reactor (CSTR). Additionally, the effect of surfactant was studied in the standpoint of the electrode stability. The structural characteristics was compared for the materials obtained by different feed rate with analysis of by X-ray diffraction, electron microscopy and dynamic light scattering. The interfacial kinetic reaction between the delithiated Ni-rich cathode and a nonaqueous electrolyte was investigated by our home-built high-precision leakage current measurement system. The result of this study indicated a different reaction phenomenon and further implies that the safety of Ni-rich cathode by co-precipitation could be controlled.

(PACRIM-P-104-2017) Study on Performance Enhancement Mechanism of Hydrogenated $Li_4Ti_5O_{12}$ using Ptychography

J. Eom*[1]

1. Korea Automotive Technology Institute (KATECH), Clean & Energy Materials R&D Center, Republic of Korea

In this work, we suggest a facile method to achieve the improved electrochemical performance of micro-sized LTO ($Li_4Ti_5O_{12}$) particles for high-power Li-ion batteries. The electrochemical performances of the micro-sized LTO particles were significantly improved by hydrogenation. There are several reports about hydrogenation of LTO, which led to the enhancement of electrochemical performance. However, in-depth studies about the hydrogenation effect have not been reported. Herein, by combination of spectroscopic and microscopic tools with different length scale of observation, the surface nature of hydrogenated LTO was carefully investigated. We found that the surface of LTO was decomposed into crystalline Li_2TiO_3 and amorphous H_xTiO_2 by hydrogenation, thereby high charge conduction as well as chemical stability can be enabled in the LTO. Our work provides the best working LTO ever reported with the commercially available particle level, while unveiling the detailed hydrogenation mechanism about the hydrogenated LTO for the first time. We believe that our work offers insight about how the hydrogenation affects the microstructure of electrode materials and their electrochemical properties.

(PACRIM-P-105-2017) Case Studies on Non-Aqueous Zn Ion Systems to Develop Multivalent Ion Batteries

S. Han*[1]; P. Senguttuvan[1]; S. Kim[1]; A. L. Lipson[1]; S. Tepavcevic[1]; B. Ingram[1]; T. Fister[1]; C. Johnson[1]; J. Vaughey[1]

1. Argonne National Lab, USA

In this study, the intercalation chemistry on a variety of cathodes materials (e.g., V_2O_5 and Mn_2O_4) and reversible deposition/dendritic growth issues on a Zn metal anode have been investigated in various non-aqueous Zn electrolytes. Among various Zn metal cells, a hydrated Zn/nanostructured bilayered V_2O_5 cell with an acetonitrile(AN)-Zn$(TFSI)_2$ electrolyte demonstrates good reversibility and stability for 120+ cycles with nearly 100% Coulombic efficiency and ~170 $mAhg^{-1}$ of gravimetric capacity, albeit operating at a cell voltage of 0.7 V vs. Zn/Zn^{2+}. A Zn/nanostructured δ-MnO_2 cell with an AN-Zn$(TFSI)_2$ electrolyte also shows good reversibility (~100% Coulombic efficiency) and stability for 50+ cycles with ~100 $mAhg^{-1}$ capacity and relatively higher operating voltage of 1.2 V vs. Zn/Zn^{2+}. On the other hand, Zn dendrite growth studies on a Zn metal anode in non-aqueous Zn electrolytes have been conducted under various conditions, including various current densities and time. The cycled Zn metal anodes were characterized using SEM-EDX and X-ray tomography to analyze morphological changes and dendritic growth in both selected regions and overall samples. Results from all these extensive research effort devoted to non-aqueous Zn systems provide an opportunity to delve into the mechanisms in multivalent-ion cell chemistry and solve the present issues in multivalent cell design and prototyping.

(PACRIM-P-106-2017) Advancing automotive Li-ion batteries with Aerosol-based synthesis of high-voltage cathode materials

D. Zarvalis[1]; G. Gkanas[1]; G. Kastrinaki[1]; S. Lorentzou*[1]; A. G. Konstandopoulos[1]

1. CERTH, Aerosol & Particle Technology Laboratory, APTL, Greece

Rapid advancement of technologies for next-generation Li-ion batteries production will be critical to address the requirements for clean, efficient and safe transportation by Electric Vehicles. The challenge of bringing high-voltage (5V) cells into the market calls for advancements in the employed cathode materials. Current work discusses the synthesis of spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) by aerosol spray pyrolysis. Synthesis was performed in both lab and pilot scale reactors where the effect of precursor solution chemistry and concentration, synthesis temperature and calcination profiles on the particle nanostructure was studied. The precursor solution chemistry and reactor operating conditions were adjusted in order to obtain the LNMO structure while the calcination profile conditions (700°C-900°C) determined whether the ordered ($P4_332$) or the disordered (Fd-3m) spinel crystal phase was obtained. Temperatures over 800ºC led to the Fd-3m phase where larger crystallite sizes were observed. Higher aerosol concentration led to different particle morphology due to lower evaporation rate. A near-spherical particle morphology was observed with various porosity formations depending on the calcination profile. Finally, doping of the LNMO structure with metals (Mg, Fe, Al) was performed, exhibiting improved electrochemical performance in terms of specific capacity and cycle life.

(PACRIM-P-107-2017) Li_2ZrO_3 -coated Overlithiated Layered Oxides for the High Performance Cathode Material in Lithium Ion Batteries

J. Park[1]; Y. Kwon[1]; H. Kim[1]; Y. Lee[1]; W. Choi*[1]

1. Korea Institute of Science and Technology, Center for Energy Convergence, Republic of Korea

Recently, high energy density lithium ion batteries (LIBs) play an important role in the field of portable and electronic devices and electrical vehicles. Current $LiCoO_2$ is around 160 $mAhg^{-1}$ with lithium utilization in the structure less than 50%. Moreover, their cost and safety requirement are still problems for the adoption of lithium ion technology for these large-battery application. To overcome this problem, Over-lithiated Layered Oxide (OLO) materials have been considered one of the promising cathode materials for the next generation of cathode materials. Among them, $0.5Li_2MnO_3$-$0.5LiNi_{0.5}Mn_{0.5}O_2$ which is known as high capability (250 $mAhg^{-1}$) has excellent electrochemical performance and stability at higher cut-off voltage beyond 4.8 V. However, its severe capacity fading during high current rates is generally related to the unstable structure and the side reaction with electrolytes. Herein, we reports Li_2ZrO_3 -coated $Li_{1.2}Ni_{0.2}Mn_{0.8}O_2$ for high performance cathode material in lithium ion batteries. The concept is both to decrease the interface resistance by crystallization of the surface layer and cover the particles with Li_2ZrO_3 that would suppress the particles against side reactions with the electrolyte.

(PACRIM-P-108-2017) Hollow MoS2-carbon anode materials synthesized with a space-confined reaction for high performance lithium ion batteries

X. Song*[1]; Z. Sun[1]; P. Zhang[1]; L. Gao[1]

1. Shanghai Jiao Tong University, China

For commercial rechargeable lithium ion batteries, graphite-based materials are widely used as the traditional anode materials by virtue of its low cost, low electrochemical potential etc. Nevertheless, it is suffered from two main disadvantages, including the limited storage capacity (372 mAh g^{-1}) and the poor rate performance induced by low Li diffusion constant. To circumvent these issues, hollow/porous carbon based materials have attracted considerable attention, because they can provide the following characteristics: 1) the large surface area leads to sufficient electrode-electrolyte interface to absorb Li^+ ions, promoting rapid charge-transfer reaction; 2) the ultrathin shell can reduce the transport length of Li^+ ions, while the nanopores on their surface facilitate Li^+ ions transfer via enormous channels; 3) the hollow interior can buffer against the structure strain associated with the local volume change. Herein, a kind of novel MoS_2-carbon hollow anode materials was elaborated with space confined reaction methods, which shows high reversible capacity and excellent rate performance with good cycle life. For instance, MoS_2-carbon hybrid hollow spheres delivered high specific capacity (831 mAh g^{-1} at 1A g^{-1} up to 200 cycles) and excellent rate capability (831, 738.6, 675.7, 612.8 and 562.9 mAh g^{-1} at 1, 3, 5, 8 and 10A g^{-1}, respectively).

(PACRIM-P-109-2017) Synthesis and Electrochemical properties of Li_2CO_3-coated Nanocrystalline Fe_2O_3 anodes for Li-ion Batteries

Y. Liu*[1]; Y. Yang[1]; M. Gao[1]; H. Pan[1]

1. Zhejiang University, School of Materials Science and Engineering, China

Rechargeable Li ion batteries with high energy density and long cycle life are critical for addressing the ever-increasing need of energy storage in various technological applications. Transition metal oxides (MxOy) have great potential as alternative anodic materials for next-generation LIBs, because of their high specific capacity, natural abundance, good safety, low cost and environmental friendliness. However, fast capacity fading, low initial Coulombic efficiency, and poor rate capability have retarded their practical applications. Herein we demonstrate an amorphous Li2CO3-coated nanocrystalline α-Fe2O3 hierarchical structure prepared by a facile one-step room-temperature mechanochemical process. The conformal coating and hierarchical structure significantly increase the cycling durability and rate capability. Typically, a 1–3-nm-thick amorphous Li_2CO_3 layer is conformally coated on Fe_2O_3 nanocrystallines (~10 nm in size) that form hierarchically aggregated particles 400–800 nm in size by ball milling α-Fe_2O_3 with LiH in CO_2. The prepared Li_2CO_3-coated nanocrystalline α-Fe_2O_3 exhibits highly stable long-term cyclability as it delivers a reversible capacity of 975 mAh g^{-1} with 99% of retention after 400 cycles at 100 mA g^{-1}. At a high rate of 3000 mA g^{-1}, its reversible capacity still remains at 537 mAh g^{-1}, superior to the uncoated counterpart (311 mAh g^{-1}).

(PACRIM-P-110-2017) Carbon-sphere-intercalated holey graphene electrode for high energy density electrochemical capacitors

S. Wu[2]; K. Hui[3]; K. Hui*[1]

1. University of Macau, Institute of Applied Physics and Materials Engineering, Macao
2. Pusan National University, School of Materials Science and Engineering, Republic of Korea
3. University of East Anglia, Faculty of Science, United Kingdom

Desirable porous structure and huge ion-accessible surface area are crucial for rapid electronic and ionic pathway electrodes in high-performance graphene-based electrochemical capacitors. However, graphene nanosheets tend to aggregate and restack because of van der Waals interaction among graphene sheets, resulting in the loss of ionaccessible surface area and unsatisfactory electrochemical performance. To resolve this daunting challenge, a novel approach is developed for the self-assembly of holey graphene sheets intercalated with carbon spheres (H-GCS) with freestanding electrodes by using a simple vacuum filtration approach and a subsequent KOH activation process. Through the introduction of carbon spheres as spacers, the restacking of reduced graphene oxide (rGO) sheets during the filtration process is mitigated efficiently. Micro-scaled holes on rGO sheets produced by subsequent KOH activation also provide rapid ionic diffusion kinetics and high ionaccessible electrochemical surface area, both of which favor the formation of electric double-layer capacitance. The H-GCS electrode exhibits specific capacitance 207.1 F g^{-1} at 1 A g^{-1} in 6 M KOH aqueous electrolyte. Moreover, the symmetric electrochemical capacitor assembled with H-GCS electrodes and organic electrolyte is capable of yielding a maximum energy density of 29.5 Wh kg^{-1} with a power density of 22.6 kW kg^{-1}.

(PACRIM-P-111-2017) Directing the lithium-sulfur reaction pathway via sparingly solvating electrolytes for high energy density batteries

C. Lee*[1]; Q. Pang[4]; S. Ha[2]; L. Cheng[3]; L. Nazar[4]; K. G. Gallagher[2]; M. Balasubramanian[1]

1. Argonne National Lab, XSD, USA
2. Argonne National Lab, CSE, USA
3. Argonne National Lab, MSD, USA
4. University of Waterloo, Canada

DOE's energy storage hub (JCESR) is exploring "beyond lithium-ion" solutions that can attain important metrics (pack level energy density of 400 Wh/L, cost of $100/kWh) relevant to transportation applications. The Li-S battery has long been seen as a potential next generation battery chemistry for electric vehicles owing to the high theoretical specific energy and low cost of sulfur. However, even state-of-the-art Li-S batteries suffer from short lifetimes due to the migration of highly soluble polysulfide (PS) and exhibit less than desired energy density. The use of sparingly solvating electrolytes in lithium-sulfur batteries is a promising approach to decouple electrolyte quantity from reaction mechanism, thus creating a pathway towards high energy density. Herein, we demonstrate that sparingly solvating electrolytes can fundamentally redirect the Li-S reaction pathway by inhibiting the traditional mechanism. The sparingly solvating electrolytes promote intermediate and short-chain PS during the first third of discharge, before disproportionation results in crystalline Li2S and a restricted fraction of soluble PS which are further reduced during the remaining discharge. Moreover, operation at intermediate temperatures allows for minimal overpotentials and high utilization of sulfur at practical rates. The results of this study will be presented in the meeting.

(PACRIM-P-112-2017) Millimete-Wave Heating of Lossy Ceramics for Beamed Energy Applications

B. Jawdat*[1]; B. W. Hoff[1]; M. Hilario[2]; F. Dynys[3]

1. Air Force Research Lab, USA
2. University of Southern California, USA
3. NASA Glenn Research Center, USA

Far-field wireless energy transmission could enable transformative technologies including remote power-beaming and beamed-energy propulsion. Millimeter-waves are readily available from high power sources, allow for smaller transmitting antennas compared to larger wavelengths, and exist in an atmospheric window with reduced water absorption. Critical to this technology is the development of a robust mm-wave heat-exchanger which will convert incoming mm-waves into heat. Materials which are not too reflective, have a high loss tangent, and are mechanically and chemically stable at very high temperatures must be developed. In this work, candidate heat-exchanger materials are selected by extracting the dielectric constants ε' and ε" of a range of materials from measurements of s-parameters obtained using a high-temperature free-space VNA measurement setup. A low-power mm-wave heating apparatus is developed to test heat-exchangers using promising materials; the apparatus consists of a 100 W extended-interaction klystron (EIK) which outputs mm-waves at 95 GHz into a vacuum chamber which contains a heat-exchanger with two channels for fluid flow. The temperatures of the heat-exchanger and fluids are monitored to study the coupled mm-wave absorption and heat-transfer characteristics of these heat-exchangers. The results of this experiment will be used to design heat-exchangers for a high-power 100-kW experiment.

(PACRIM-P-113-2017) Effects of Electron Beam Irradiation on the Electrical Properties of ZnO Thin Film Transistor

B. Jun*[1]; J. Choi[1]; I. Cho[1]; C. Kim[1]

1. Korea Atomic Energy Research Institute, Neutron Utilization Technology Division, Republic of Korea

ZnO is an n-type wide and direct bandgap semiconductor and it shows superior electrical properties even in amorphous phase. The effects of 250°C heat-treatment after an electron beam irradiation process on the chemical bonding, electrical properties, and bandgap structure of ZnO thin films prepared using a sol-gel process were examined. The irradiation energy of the electron beam was 0.1 MeV and the irradiated electron dose was varied from 7.5E15 cm^{-2} to 1.5E17 cm^{-2}. An XPS analysis showed that the electron beam irradiation decreased the concentration of metal-oxygen bonding and increased the OH^- bonding. The electron beam irradiation resulted in an increase in the carrier concentration in ZnO films. In addition, the on/off ratio was maintained at $\sim10^5$, and the V_{th} values shifted negatively from 11 to 1 V. As the irradiation time increased from 0 to 300 s, the subthreshold swing (SS) values of ZnO TFTs increased from 1.03 to 3.69 V/decade. The electrical properties of the samples heat-treated at 250°C after irradiation were better when compared to the sample heat-treated at 400°C without irradiation representing an on/off ratio of $\sim10^2$ and SS value of 10.4 V/decade. Additionally, the band gap energy was investigated using XPS and a spectroscopy ellipsometer, and the band gap energy increased from 3.16 to 4.0 eV with an increasing electron beam irradiation dose.

(PACRIM-P-114-2017) Development of High Reliability Glass-Polymer Laminates

M. Lanagan*[1]; M. Sarkarat[2]; M. Yuan[2]; R. Rajagopalan[2]; Z. Shihai[3]

1. Pennsylvania State University, Dept. of Engineering Science and Mechanics, USA
2. Pennsylvania State University, Materials Research Institute, USA
3. PolyK Technologies LLC, USA

Dielectric breakdown is the key parameter in governing capacitor energy density and insulation reliability. Recent results have shown that alkali free glass has excellent dielectric breakdown strength at high temperature, with values approaching 700 V/μm at 200°C. The study of dielectric failure in polymer and ceramics is a fertile area of theoretical and experimental research and the specific breakdown mechanism depends upon external factors such as temperature and time. Polymer-glass laminates were fabricated by dip coating or casting polymer solutions on glass substrates. In this work, coatings of polyurethane and fluorene polyester with thickness range between 100 nm and 2 micrometers were deposited on glass ribbons that were between 10 and 50 micrometers thick. Dielectric constant, dielectric loss, leakage current, and breakdown field were performed on the laminates up to temperatures of 400°C. It was found that the polymer coatings significantly improved both the dielectric breakdown and mechanical breakdown properties of the glass which is attributed to control of local electric field and mechanical stress distributions in glass.

(PACRIM-P-116-2017) Biodeterioration of Ancient Glasses and Implications to the Long-term Modeling of Glass Alteration

J. L. Weaver*[1]; C. Pearce[1]; P. DePriest[2]; R. Koestler[2]; R. Sjoblom[3]; D. Peeler[1]; A. A. Kruger[4]

1. Pacific Northwest National Laboratory, USA
2. Smithsonian, Museum Conservation Institute, USA
3. Lulea University of Technology, Sweden
4. Department of Energy, Office of River Protection, USA

The alteration of glass under natural conditions can occur by many avenues including through exposure to an altering solution, such as groundwater or seawater, or by biodeterioration. Biodeterioration is the deterioration of a substance by agents of a microbiological origin. This degradation can occur either directly through

colonization of the glass surface by microbial species, or indirectly through the interaction of metabolic byproducts with the glass surface. A review of the alteration of a selection of glass artifacts by fungi and bacteria, ranging from ancient Swedish Hillfort glasses to medieval stained glass windows is presented. The formation of bio-crusts and bio-films, along with the possible causes of biopitting will be discussed. The result of this review will be placed into context with modern glass corrosion mechanisms, and the development of a holistic long-term model for glass alteration.

(PACRIM-P-117-2017) Alteration of glass fiber vs. glass powder: Reducing uncertainty in rate measurement

B. Parruzot*[1]; A. A. Kruger[2]; J. Ryan[1]

1. Pacific Northwest National Lab, Energy and Environment Directorate, USA
2. Department of Energy, Office of River Protection, USA

Single-Pass Flow-through (SPFT) and Product Consistency Tests (PCT) are common methods used to measure glass alteration rates and characterize secondary alteration products, which are then used to parameterize alteration models. Currently, to accelerate the reaction progress, glass is crushed and sieved into a high surface area powder and then washed. Particle size is controlled to an extent by the sieve sizes, but the size distribution within this fraction varies from batch to batch. Furthermore, despite washing, low amounts of fines may remain and increase the surface of glass due to their high specific surface area. Also, particle geometry is often approximated as spherical, but their irregular shape makes initial aspect ratios of more than 2.5 common, with highly variable evolutions throughout alteration depending on the actual particle shape. All these disparities contribute significant error to the measured alteration rate. By using glass fiber instead, the diameter can be controlled to tight tolerances and a regular shaped material produced with no further preparation needed. Parallel SPFT and PCT experiments were performed at various temperatures/flows but constant surface area-volume ratios with nuclear waste glass simulant powder and fiber materials (annealed or not). ICP-OES, optical and electron microscope results are compared and surface area effects and evolution are discussed.

(PACRIM-P-118-2017) Thermal and Radiation Stability of Magnesium Potassium Phosphate Cements for Waste Encapsulation

L. J. Gardner*[1]; C. L. Corkhill[1]; S. A. Bernal[2]; J. Provis[1]; N. C. Hyatt[1]

1. The University of Sheffield, Materials Science and Engineering, United Kingdom
2. The University of Sheffield, Civil and Structural Engineering, United Kingdom

Magnesium potassium phosphate cements (MKPC) are near-neutral pH, low water demand and high early-compressive strength cementitious systems produced via an acid-base reaction. MKPCs are under consideration as encapsulants for certain nuclear wastes (e.g. reactive metals, such as Al, Mg and U in the UK) that may otherwise corrode in the high pH and/or the high free water availability in PC based encapsulants. For this application, MKPCs are required to be radiation tolerant and withstand the effects of a thermal incident (i.e. a fire) without the loss of containment. In this study, the radiation tolerance of blended MKPC binders (with slag and fly ash) was investigated using a Co-60 source up to an adsorbed dose of 10 MGy, whilst the fire performance of these materials was assessed in-line with the fire-resistance requirements for UK nuclear waste encapsulants. The results indicated that MKPC are tolerant to gamma radiation as no phase assemblage changes were observed, whilst the fire performance revealed considerable changes in the microstructure and phase assemblage, resulting in the formation of well-understood mineral phases whilst retaining dimensional stability. Overall, this study demonstrates that MKPCs meet the encapsulant design (radiation tolerance) and fire performance requirements for UK intermediate level waste, associated with transport and geological disposal.

(PACRIM-P-119-2017) Synthesis and characterization of simulant corium materials produced from meltdown of the Chernobyl reactor Unit 4

N. C. Hyatt*[1]; S. T. Barlow[1]; D. Bailey[1]; A. J. Fisher[1]; C. L. Corkhill[1]; M. C. Stennett[1]

1. The University of Sheffield, Materials Science & Engineering, United Kingdom

A preliminary investigation of the synthesis and characterization of simulant 'lava-like' fuel containing materials (LFCM), as low active analogues of the LFCM produced by melt down of Chernobyl Unit 4, produced materials of comparable microstructure and phase assemblage. Simulant materials were synthesised by melting batched reagents in a tube furnace at 1500ºC, under reducing atmosphere with controlled cooling to room temperature, to simulate conditions of lava formation. Characterisation using XRD and SEM-EDX identified several crystalline phases including ZrO_2 and UO_x, and solid solutions, with spherical metal particles, encapsulated by a glassy matrix. The UO_X and ZrO_2 phase morphology was very diverse comprising of fused crystals to dendritic crystallites from the crystallisation of uranium initially dissolved in the glass phase. This project aims to develop simulant LFCM to assess the durability of Chernobyl lavas and to determine the rate of dissolution, behaviour and evolution of these materials under shelter conditions.

(PACRIM-P-120-2017) Multicomponent diffusion and crystallization in borosilicate glass melt

H. Pablo[1]; S. Schuller*[1]; M. Roskosz[2]; M. Toplis[3]; E. Gouillart[4]; T. Charpentier[5]

1. CEA, DTCD, France
2. MNHN, France
3. IRAP, France
4. Saint-Gobain Recherche, France
5. CEA, DSM, France

In France, High Level radioactive Waste (HLW) resulting from nuclear spent fuel reprocessing is incorporated in a complex sodium borosilicate glass. Today, the understanding of the phenomena that occur during vitrification is of major interest for improving the final glass homogeneity and for finding new matrix compositions. Among the phenomena that must be taken into account, chemical diffusion is particularly interesting as it is the driving force for many physico-chemical properties of the melt like its redox, viscosity, electrical conductivity or its trend to precipitate/dissolve crystalline phases. It is also a powerful tool for describing the mobility of atoms and their kinetics. In this work, an experimental approach has been developed for getting information on chemical diffusion mechanisms in simplified borosilicate glasses between their glass transition temperature and 1100°C. In this kind of systems, considered as multicomponent systems, the study of diffusion requires the use of Fick's second law transposed in matrix notation. The diffusion coefficients calculated with this law constitute a matrix whose properties allow the determination of diffusive exchanges and their rates. These results have been used for better understanding crystallization phenomena that may occur in the glasses and NMR analyses have been performed in order to follow the structural evolutions along diffusion profiles.

(PACRIM-P-121-2017) Applications of ellipsometry to the analysis of corroded glass surfaces

T. Kaspar*[1]; J. Ryan[2]; J. Reiser[3]

1. Pacific Northwest National Lab, Physical and Computational Sciences Directorate, USA
2. Pacific Northwest National Lab, Energy and Environment Directorate, USA
3. Washington State University, USA

Characterization of the alteration layers that form on glass surfaces during corrosion processes is imperative to understand both the mechanism and rate of glass alteration. In recent years, state-of-the-art materials and surface characterization techniques such as secondary ion mass spectrometry (SIMS) depth profiles and cross-sectional SIMS mapping, various forms of transmission electron microscopy (TEM), atom probe tomography (APT), and solid-state nuclear magnetic resonance (NMR) have been employed to study various aspects of the alteration layers that result from corrosion. In most cases, these techniques are destructive and thus can only be employed at the end of the corrosion experiment. In contrast, here we present the results of alteration layers investigated by non-destructive spectroscopic ellipsometry (SE). SE provides pertinent information on alteration layer thickness, morphology, and, through correlation of the index of refraction, composition. SE measurements are compared to cross-sectional SIMS mapping and cross-sectional secondary electron microscopy with electron-dispersive spectroscopy (SEM-EDS) line profiles. Reasonable correlations are found, opening the possibility of non-destructive measurements as corrosion experiments progress. In the future, in-situ measurements in a liquid cell may be possible.

(PACRIM-P-122-2017) Effects of processing parameters on microstructure and crystallization behaviour of sol-gel SiO_2-P_2O_5-CaO bioglass

S. Mollazadeh*[1]

1. Ferdowsi University of Mashhad, Engineering, Islamic Republic of Iran

For synthesizing an in-situ glass, tetraethyl orthosilicate (TEOS) hydrolysis is favored by nitric acid catalysis in ethanol. Triethyl phosphate and dissolved calcium nitrate were added to TEOS, then pH of solution brought to appropriate value. In the other method (ex-situ), tetraethyl orthosilicate and triethyl phosphate were hydrolyzed separately and calcium nitrate was added to the hydrolyzed triethyl phosphate. Two solutions were mixed together. obtained sols from each method were gelled and then dried with a suitable process. According to the DTA analyses, samples were heat treated at the different temperatures. The sample's features were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy. The results indicated that synthesis process had effects on arrangement and type of the final crystalline phases. hydroxyapatite was the major crystalline phase which were crystallized in in-situ samples while ex-situ samples showed wellastonite and tri calcium phosphate as its main crystalline phase. In each sample, the SEM results demonstrated identical spherical morphology but the size and amount of the crystalline phases varied. FTIR results showed that there were chemical bond between characteristic group of in-situ synthesised bioglass. MTT assey showed all in-situ and ex-situ bio-glass were biocompatible.

(PACRIM-P-123-2017) Thermal stability of Si-hydroxyapatite synthesised by solution combustion methode

S. Mollazadeh*[1]

1. Ferdowsi University of Mashhad, Engineering, Islamic Republic of Iran

In this study, Si precursor was synthesized by sol-gel method and added to the solution with different ratios during the process of Calcium Phosphate powder by solution combustion synthesis. For this purpose, tetraethyl Orthosilicate were used as row material. The effects of Si^{4+} substitution on morphology and thermal stability of hydroxyapatite were investigated. Calcium Nitrate Tetrahydrate and Ammonium dihydrogen phosphate were also used as starting materials. Glycine, Urea and acid citric were used as fuels. Two different Heat treatments were operated at different temperatures. The results revealed that Si^{4+} ratios and fuel factor increase thermal stability of hydroxyapatite powders. Synthesised powders had different morphology based on the kind and amount of fuels. XRD and TEM results revealed that hydroxyapatite and calcium phosphate were the nano sized. BET results showed that hydroxyapatite were porous. Substituting and increasing the amount of Si^{4+} decreased the amount of porosity. the kind of fuels had a great effect on the purity of synthesised powders in a way that acid citric led to the purest powders and urea resulted in less purifed synthesied powders.

(PACRIM-P-124-2017) Machinability and Cellular Responses of (Y,Nb)-TZP for Dental Implants

Y. Jo[1]; D. Kim*[2]; J. Han[3]

1. Seoul National University, Dental Research Institute, Republic of Korea
2. Sejong University, Department of Advanced Materials Engineering, Republic of Korea
3. Seoul National University, Department of Prosthodontics, School of Dentistry, Republic of Korea

Main drawback of zirconia implants manufactured by using 3Y-TZP in clinical applications is its poor machinability, which hinders angulation of one-body implants after placement and surface modification for improved osseointegration. (Y,Nb)-TZP having modified cation coordination with oxygen ions in tetragonal structure demonstrated enhanced machinability supported by low Vickers and scratch hardness values and high fracture toughness in addition to resistance to the low temperature degradation. As a consequence, the average roughness of 0.93±0.05 μm for (Y,Nb)-TZP was much higher than that of 3Y-TZP, 0.62±0.05 μm, after sandblasting with 50 μm alumina for 1 min at 2 bars. Pre-osteoblast and human gingival fibroblast cells were attached well and spread widely on (Y,Nb)-TZP. The gene expression patterns of bone-related proteins using real-time pcr during osteoblast differentiation on (Y,Nb)-TZP showed that collagen synthesis, ALP activity, and bone mineralization were achieved at appropriate level, confirming that (Y,Nb)-TZP is non-toxic, biocompatible, and highly osseointegrative.

(PACRIM-P-125-2017) In vitro and in vivo study of a novel zirconia/tantalum biocermet for hard tissue implants

J. F. Bartolomé*[1]; A. Smirnov[1]; J. Moya[1]; R. Couceiro[2]; F. Guitian[3]; A. Martínez-Insua[3]

1. Instituto de Ciencia de Materiales de Madrid (ICMM) - Consejo Superior de Investigaciones Científicas (CSIC), Spain
2. Translational Medical Oncology; Health Research Institute of Santiago (IDIS); Fundacion Ramon Dominguez, SERGAS, Spain
3. Instituto de Cerámica de Galicia, Universidad de Santiago de Compostela (USC), Spain

New multifunctional composite materials containing wear resistance and hardness ceramics (3Y-TZP) reinforced by non-toxic metal with low magnetic susceptibility (Tantalum) were fabricated by wet mixing of powders and spark plasma sintering. These materials showed excellent mechanical properties under static and cyclic loading accompanied by a tribological performance, resistance towards low-temperature degradation, EDM machinability and negligible MRI artefacts. The aim of this study was to investigate the biological tolerance of these new zirconia/Ta biocermets implants with both in vitro and in vivo approaches. In vitro (mesenquimal cells), the biocermets showed no deleterious effect on cell proliferation, extra-cellular matrix production or on cell morphology. Cylinders of biocermets, as well as commercially Ta and zirconia rods were implanted in the tibiae of New Zealand white rabbits. All the animals were euthanatized after 6 months. A newly formed bone was observed in close contact with material surfaces. No inflamed or multinucleated cells were present. In vitro studies and in vivo studies revealed that 3Y-TZP/Ta biocermets appeared to be biocompatible. This opens the possibility to produce novel biomaterials with a optimal combination of properties (mechanical, tribological and biological) to make implants for a variety of different hard tissue replacement applications.

(PACRIM-P-126-2017) Co-electrospray of Mesemchymal Stem Cells and Gene with Non-viral Vector in Hydrogel Microspheres for Enhanced Stem Cell-based Therapy

Q. Zhao[1]; H. Sun[1]; M. Wang*[1]

1. The University of Hong Kong, Department of Mechanical Engineering, Hong Kong

Stem cell-based therapies are promising for treating human tissue loss. Mesenchymal stem cells (MSCs) are increasingly used. After delivery to target, MSCs need to have a suitable environment for differentiation and their fate should be appropriately directed. One approach is to modify MSCs first via gene delivery and then encapsulate genetically engineered MSCs in a carrier for subsequent use, e.g., in tissue engineering. In this study, a one-step co-electrospray process was established for simultaneously encapsulating MSCs and gene with a vector in hydrogel microspheres, providing an environment for localized and high-efficiency gene delivery. Poly(ethylenimine)-poly(sorbate) (PEI-PS) conjugate was synthesized as vector and plasmid DNA encoding enhanced green fluorescence protein (pEGFP) was model gene. PEI-PS/pEGFP complexes at 5:1~15:1 were prepared. Co-electrospray of MSCs and PEI-PS/pEGFP complexes was conducted via coaxial electrospray: inner capillary of coaxial spinneret was fed by a MSC suspension with PEI-PS/pEGFP complexes and outer capillary was fed by a Na-alginate aqueous solution, which led to formation of hydrogel microspheres with PEI-PS/pEGFP complexes and MSCs in the liquid core. Various experiments were conducted subsequently. The gene transfection efficiency was found to be enhanced inside the microsphere environment.

(PACRIM-P-127-2017) Polymer-metal Hybrid Nanoparticles as a Novel Gene Vector for Cancer Imaging and Therapy

Q. Guan[1]; M. Wang*[1]

1. The University of Hong Kong, Department of Mechanical Engineering, Hong Kong

Gene therapy uses exogenous genes for therapeutic functions and is promising for treating cancer. Therapeutic genes are delivered into cells and must overcome various barriers before reaching the target. Due to problems with viral vectors, non-viral vectors are developed for gene delivery. Nanoparticles (NPs) such as gold NPs are potential nanovectors owing to their various advantages. In this study, hybrid NPs with an Au-Ag bimetallic core and a folic acid-chitosan shell (Au-Ag@CS-FA), which can provide cancer targeting and imaging functions, were investigated as a new nanovector. Highly branched Au-Ag NPs were synthesized as core and FA-conjugated CS formed the shell in Ag@CS-FA NPs. Tests showed sufficient FA molecules in the CS-FA shell, which would provide the ability for targeting folate receptor overexpressed cancer cells. For cancer detection, rhodamine B was embedded in Au-Ag@CS-FA NPs, which would emit SERS signals. Plasmid DNA encoding enhanced green fluorescent protein with a CMV promoter (pEGFP) was used as model gene. NP/pEGFP complexes at different ratios were prepared to investigate effects of incubation time and pH on the binding ability of Au-Ag@CS-FA NPs with pEGFP. Results showed Au-Ag@CS-FA NPs were stable, had good biocompatibility and possessed strong DNA binding ability in the acidic environment. SERS signals given by Ag@CS-FA NPs enabled cancel cell imaging.

Wednesday, May 24, 2017

GOMD Award Lectures

Stookey Lecture of Discovery

Room: Kona 5

8:35 AM

(GOMD-PL-002-2017) In Pursuit of Perfect Glass: Fifty Years and Still At It (Invited)

P. C. Schultz*[1]

1. Peter Schultz Consulting, LLC., Virgin Islands (U.S.)

Armed with a new PhD degree in glass science from Rutgers University, I joined Corning's exploratory research team in the summer of 1967 and soon began what became a life-long professional relationship with the perfect glass: fused silica. I will describe my early research on the preparation of unique doped fused silica glasses by flame hydrolysis and their unusual properties, and how this led to the successful development (with co-workers Bob Maurer and Don Keck) of the first low loss optical fibers for telecommunications in 1970. Our invention of methods and materials still used today to manufacture virtually all telecom fiber will be discussed. My transition from scientist to a key business executive of the world's largest supplier of optical grade fused silicas (1984 to "retirement" in 2000) and subsequent career and challenges (2001 to present) as technical advisor and Board member to several global companies (including building and operating an all-fiber network in the US Virgin Islands) will be described.

GOMD Symposium 1: Fundamentals of the Glassy State

Glass Formation and Relaxation I

Room: Kona 4

Session Chairs: Ellyn King, Corning Incorporated; Pierre Lucas, Univ of Arizona

9:45 AM

(GOMD-S1-048-2017) Link between Elasticity and Viscosity of Glass-forming Systems (Invited)

L. Huang*[1]; S. Jaccani[1]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA

For most liquids, the temperature dependence of viscosity is super-Arrhenius, i.e., viscosity increases more dramatically upon cooling than expected from the Arrhenius law. Despite the technological and geological importance, the structural origin of this non-Arrhenius temperature dependence of viscosity, remains elusive to date and constitutes an important but unsolved problem in the condensed matter physics. This is mainly due to the lack of in-situ analysis of the microscopic events during the viscous flow process. Our study has shown that high temperature elasticity can help understand the structural developments above the glass transition temperature (T_g) and the fragility of glass-forming liquids, thus providing a mechanistic understanding of the non-Arrhenius temperature dependence of viscosity at the atomic scale. A modified elastic model for viscosity was proposed to predict equilibrium viscosity of liquid and non-equilibrium viscosity of glass based on the temperature-dependent elasticity.

10:10 AM

(GOMD-S1-049-2017) Structure, Dynamics and Glass Formation – New Insight from Metallic Glass-Forming Liquids (Invited)

K. F. Kelton*[1]

1. Washington University, Physics, USA

The correlation between structural ordering, liquid dynamics and the glass transition is an outstanding question in all glass-forming systems. However, it is difficult to examine experimentally. The liquid viscosity changes by orders of magnitude with essentially negligible changes in the structure factor or pair correlation function of the liquid. Recent experimental evidence for this correlation in metallic liquids will be discussed. A crossover in the viscosity at T_A (which according to molecular dynamics studies marks the onset of cooperative shear flow) corresponds to ordering beyond nearest neighbors. Independent of their fragility, the viscosities of all metallic liquids studied fall on a universal scaled curve of $\log(\eta/\eta_o)$ and T_A/T, where η_o is the extrapolated viscosity infinite temperature. The fragility and the reduced glass transition temperature, T_{rg}, generally correlate with glass formability in metallic liquids. Both can be predicted from liquid viscosity measurements made near T_A. Finally, a new model for viscosity that gives a universal fit for polymer, silicate and metallic liquids with a single fitting parameter is presented and discussed. Research was partially supported by the National Science Foundation (DMR 1506553) and NASA (NNX16AB52G).

10:35 AM

(GOMD-S1-050-2017) Revisiting the Stretched Exponential Relaxation of Glasses

O. Gulbiten*[1]; J. C. Mauro[1]

1. Corning Incorporated, Science & Technology Division, USA

The non-exponential behavior of relaxation processes in glassy materials has been known for many decades. A stretched exponential relaxation function has been used to define the evolution of first order thermodynamic properties and macroscopic physical properties. Recently, several authors demonstrated evidence for the existence of the dynamic heterogeneities that govern the non-monotonic relaxation of second order thermodynamic properties. Development of high accuracy in-situ property measurements during relaxation processes motivated us to revisit one of these longstanding questions in glass physics. In this study we present comprehensive experimental results that may elucidate the underlying nature of the stretched exponential relaxation function.

10:50 AM

(GOMD-S1-051-2017) Activation Enthalpy of Anelastic Relaxation in Ionomer Glasses using Impulse Excitation Technique

A. K. Swarnakar[1]; A. Stamboulis[2]; O. Van der Biest*[1]

1. K U Leuven, Materials Engineering, Belgium
2. University of Birmingham, School of Metallurgy and Materials, United Kingdom

The present work reports the anelastic behaviour of ionomer glasses with general composition $4.5SiO_2$-$3Al_2O_3$-$1.5P_2O_5$-3MO-$2MF_2$ where M is one of the alkaline earth metals (M = Mg, Ca, Sr and Ba) using internal friction measurements. An anelastic relaxation peak was observed below the glass transition temperature for each composition except for Mg glass. For the first time, the activation enthalpies of the relaxation peaks were determined by the Impulse Excitation Technique (IET) in these ionomer glasses. An Arrhenius plot of resonance frequencies against temperature was used for activation enthalpy calculation. The mechanism gives rise to these peaks is thermally activated. The origin of the relaxation peaks is associated with the nonbridging oxygen motion on the glass network sites.

11:05 AM

(GOMD-S1-052-2017) Importance of liquid fragility for energy applications of ionic liquids

S. Krohns*[1]; P. Sippel[1]; P. Lunkenheimer[1]; A. Loidl[1]

1. University of Augsburg, Experimental Physics V, Germany

Ionic liquids are salts that are liquid below 100 °C and offer outstanding properties (e.g., low volatility and high electrochemical stability). For this reason they bear a high potential for new applications, e.g., as electrolytes in energy-storage devices such as supercapacitors or batteries. In addition the ionic conductivity is an essential figure of merit for these applications. However, often ionic liquids exhibit a rather low conductivity hampering their applicability. Most ILs show dynamic properties typical for glassy matter, which dominate many of their physical properties. An important method to study these dynamical glass-properties is dielectric spectroscopy that can access relaxation times of dynamic processes and the conductivity in a broad frequency and temperature range. First, we present results on a large variety of pure ionic liquids showing that the conductivity of these ILs depends in a systematic way not only on their glass temperature but also on the so-called fragility, characterizing the non-canonical super-Arrhenius temperature dependence of their ionic mobility. Second, we address the questions if the conductivity can be optimized by mixing pure ILs. For this, we analyzed for two mixing series results of glass temperatures derived by differential scanning calorimetry and fragilities deduced from frequency and temperature dependent measurement of the dielectric properties.

11:20 AM

(GOMD-S1-053-2017) Influence of Equilibrium and Nonequilibrium Viscosities on Delayed Elasticity

Z. Zheng*[1]; J. C. Mauro[1]; D. C. Allan[1]; X. Guo[1]; O. Gulbiten[1]

1. Corning Incorporated, USA

"Delayed elasticity" has been proposed to explain the non-exponential relaxation in glassy solids and is believed to be closely related to the stretching exponent of the stretched exponential decay function. We have developed and implemented a Finite Element Method (FEM) model simulating a beam-bending setup, using the generalized Maxwell model and considering both stress and structural relaxation effects using the Mauro-Allan-Potuzak (MAP) viscosity equation. The influence of the equilibrium and nonequilibrium viscosities on the delayed elasticity is investigated using the model.

11:35 AM

(GOMD-S1-054-2017) Enthalpy Relaxation and its Correlation to the Medium-Range Structural Evolution in a Hyperquenched SiO_2–Al_2O_3 System

Y. Zhang*[1]; D. Zhao[2]; Y. Yue[3]

1. Qilu University of Technology, China
2. Unifrax I LLC, USA
3. Aalborg University, Denmark

We study the sub-T_g enthalpy relaxation in an extremely unstable binary SiO_2–Al_2O_3 (SA) glass and its correlation to the change of the medium-range structure. The DSC results show that the energy release peak for the hyperquenched SA glass over temperature is not symmetric, and a long tail is observed at the lower temperature starting from the onset temperature of the enthalpy release. With increasing annealing, the long tail gradually evolves into a peak and the peak becomes broader. This phenomenon is quite different from that of many other hyperqenched glass systems, in which the long tail gradually disappears with increasing annealing. Using NMR, we find that the contents of both the 5- and 6- fold coordinated Al species in the hyperquenched SA glass decrease with sub-T_g annealing, while the 4-fold coordinated Al species increases. This leads to the formation of the oxygen triclusters which can act as the mullite nucleation sites. This is confirmed by the ordered structural domains at nano-scale as shown in the HRTEM images. The extremely unstable behavior of the studied glass against crystallization is attributed to both the higher content of the 5- fold coordinated Al (~ 63%) and the easily formed oxygen triclusters in the hyperquenched glass during sub-T_g annealing. The triclusters also indicate the structural heterogeneity of the supercooled liquid.

11:50 AM

(GOMD-S1-055-2017) Correlation between Fragility and Configurational Heat Capacity in Calcium Aluminosilicate Glasses

T. K. Bechgaard*[1]; J. C. Mauro[2]; M. Bauchy[3]; Y. Yue[1]; L. R. Jensen[1]; M. M. Smedskjaer[1]

1. Aalborg University, Denmark
2. Corning Incorporated, USA
3. University of California, Los Angeles, USA

Enabling accurate prediction of the properties of aluminosilicate glasses and glass-forming liquids is important for the development of new glass compositions for high-tech applications. In this study, we use a combined topological and thermodynamic approach to connect the configurational heat capacity ($C_{p,conf}$) with the liquid fragility (m) and glass transition temperature (T_g) of calcium aluminosilicate glasses. To obtain glasses with different structural and dynamical features, we study two glass series; one at the tectosilicate join with varying SiO_2 content and one with constant CaO content but varying Al_2O_3/SiO_2 ratio. $C_{p,conf}$ is determined using differential scanning calorimetry (DSC), while m and T_g are determined through both DSC and direct viscosity measurements. The $C_{p,conf}$ model is found to generally predict the measured data well, but deviations between modelled and measured $C_{p,conf}$ values appear for the strongest glasses in the tectosilicate series and for the most peraluminous glasses in the constant CaO series. We discuss the origins of these model-data discrepancies based on the structural evolution in the glasses as determined through Raman spectroscopy measurements.

GOMD Symposium 3: Optical and Electronic Materials and Devices: Fundamentals and Applications

Photon and glass interaction

Room: Kona 3
Session Chairs: Matt Dejneka, Corning Incorporated; Xiaoju Guo, Corning Incorporated

9:45 AM

(GOMD-S3-037-2017) Femtosecond Laser-Matter Interactions in Ternary Zinc Phosphate Glasses (Invited)

D. Krol*[1]

1. University of California, Davis, Materials Science and Engineering, USA

Femtosecond (fs)-laser writing of optical waveguides inside glass substrates ideally requires permanent modification of the glass structure resulting in a positive refractive index change as is, for example, the case for fused silica. Phosphate glasses, which are of interest as host materials for active devices since they allow incorporation of high concentrations of rare earth ions, typically produce negative refractive index changes in the laser-exposed regions. We have recently found that good quality waveguides can be fabricated in zinc polyphosphate glass compositions with a [O]/[P] ratio close to 3.25. For practical applications multi-component glasses offer more robust stability as well as better corrosion resistance. In order to determine if an [O]/[P] ratio of 3.25 is also required in such glasses we have –in collaboration with Prof. Brow's group at MS&T-systematically investigated femtosecond laser-matter interactions in a series of zinc aluminum and zinc magnesium phosphate glasses with [O]/[P] ratios varying between 3.00 and 3.50. In this talk I will discuss fs-laser processing experiments in these glasses, both in bulk and at the surface, as well as results on optical and structural characterization of the laser-modified materials.

10:15 AM

(GOMD-S3-038-2017) Ultrafast Laser Modification of Optical Glasses

D. K. Dobesh*[1]; S. T. Locker[1]; S. K. Sundaram[1]

1. Alfred University, Glass Science, USA

We are working on ultrafast laser modification of optical glasses. The modifications can increase the versatility of the new generation of glasses by creating a high contrast refractive index alterations. Using the low repetition rate regime of femtosecond laser pulses, we can change the refractive index of the glasses locally and significantly below the glass transition temperature. Using new commercially available titanium based optical glasses along with heavy metal dopants and fluorides, we will vary the laser parameters (depth of focus, fluence, and energy density) to investigate the mechanism that causes the increase in the refractive index. We will use density measurement, differential scanning calorimetry (DSC), x-ray diffraction (XRD), and Raman spectroscopy before and after laser irradiations of glasses to support the mechanism. We will use neutron diffraction for detailed glass structure characterization. We will present our results and progress made on the glass structure - laser-induced refractive index change correlation.

10:30 AM

(GOMD-S3-039-2017) Thermal and Structural Analysis of Ultrafast Laser Irradiated Oxide Glasses

S. T. Locker*[1]; P. Tumurugoti[2]; S. K. Sundaram[2]

1. Alfred University, Glass Science, USA
2. Alfred University, USA

Preliminary results have shown us that ultrafast irradiation of multiple oxide glasses can cause a measurable increase in surface hardness without influencing surface chemistry, elemental concentration or inducing stress fields significantly. We have undertaken a systematic detailed study the effect of ultrafast laser radiation on the glass structure and mechanical properties. We will use both low- and high-repetition femtosecond laser pulses with various pulse energies, counts, and energy densities. After laser irradiation, densification will be calculated for each pulse energy to maximize glass surface strength. We will use differential scanning calorimetry (DSC), Raman spectroscopy, extended X-ray absorption fine structure (EXAFS), and X-ray absorption near edge structure (XANES) to characterize the glass structure before and after laser irradiation. We will report a case study of the laser fluence's effect on glass densification as well as perform thermal and structural analysis of the ultrafast irradiated samples.

10:45 AM

(GOMD-S3-040-2017) Formation of Nanoscale Surface Deformation in Fused Silica by CO_2 Laser Pulses

B. Nayak*[1]

1. Corning Incorporated, USA

Due to their strong absorption, CO2 lasers are the laser of choice for micro/nano machining of silica. Focused CO2 laser pulses, when incident on surface of silica, typically produce holes whose depths are in the range of microns. These holes are predominantly formed by surface evaporation, surface melting and flow. Increase in fluence and multiple pulses result in producing deeper holes where multiple reflections become important hole formation mechanism to be considered. However, on decrease in incident fluence, it is observed that below certain critical fluence, nanoscale surface deformations are observed on silica surfaces. For fluence in the range of 1.5 J/cm2 to 5 J/cm2, nanoscale deformations are formed where the depth of nanoscale structures are in the range of 100s of

nanometers. However, when laser fluence is reduced to <1.5 J/cm2, depth of nanoscale deformation in the range of 10s of nanometers are observed. Beyond 5 J/cm2, hole depths increases to the order of microns. In this work we explore the possible mechanism behind such nanoscale structure formation. Post thermal annealing and Raman characterizations on laser irradiated spots are carried out to understand whether the nanoscale structure formation is due to material removal or mere deformation caused by incidence of laser.

11:00 AM

(GOMD-S3-041-2017) Compositional trends and energy dependence of photoinduced effects in spin-coated chalcogenide glass thin films

A. Kovalskiy*[1]; M. White[1]; J. Allen[1]; J. Bunton[1]; J. R. Oelgoetz[1]; R. Golovchak[1]; P. Xiong-Skiba[1]; M. Vlcek[2]

1. Austin Peay State University, Department of Physics and Astronomy, USA
2. University of Pardubice, Center of Materials and Nanotechnologies, Faculty of Chemical Technology, Czech Republic

In-situ studies of photoinduced optical effects in spin-coated chalcogenide glass thin films under exposure to band gap and super-bangap LED light of different intensities are presented. It is shown that arsenic sulphide glasses are photostable at the exposure to the band gap light of 90 mW power whereas irradiation with the UV light of the same intensity leads to stable and repeatable photodarkening with very minor irreversible component. The photodarkening effect is much faster in S-rich compositions comparatively to stoichiometric one. Little different behavior is observed for the spin coated arsenic selenide thin films which reveal photosensitivity at the same irradiation conditions for both UV and band gap light exposure. However, slower kinetics of the photoinduced changes of optical transmittance should be noticed. The described effects are detected in both vacuum and ambient conditions. The prolonged irradiation in air leads to surface oxidation accompanied by slight photobleaching. The kinetics of photoinduced optical changes are compared with similar effects for thermally evaporated chalcogenide glass thin films.

11:15 AM

(GOMD-S3-042-2017) Chalcogenide glasses – their micro/nanostructuring, examples of applications

M. Vlcek*[1]; L. Loghina[1]; S. Slang[1]; J. Buzek[3]; K. Palka[3]; A. Kovalskiy[2]

1. FCHT University of Pardubice, Center of Materials and Nanotechnologies, Czech Republic
2. Austin Peay State University, Department of Physics and Astronomy, USA
3. FCHT University of Pardubice, Department of General and Inorganic Chemistry, Czech Republic

Chalcogenide glasses (CHGs) are very promising materials for many photonic applications due to their unique properties and functionalities. They posess for example wide IR transmission window, high non-linearity of optical properties, high refractive index and many of them are sensitive to bandgap or UV light, or electron and ion beams. In adition their composition can be locally modified by exploiting radiation induced diffusion and dissolution of suitable metals (e. g. Ag, Zn). In this paper we present results giving evidence that all these structural/compositional changes result in selective wet or dry etching which allows ChGs surface structuring on micro and/or even nanoscale. Lower rigidity and lower softening temperatures in comparison with classical oxide glasses allow their surface to be corrugated by direct laser writing method or by embossing. We review methods of CHGs micro and nanostructuring and demonstrate applications of CHGs thin films prepared by vacuum based or solution based deposition techniques (such as spin-coating) in high-resolution UV and electron lithography and as materials for fabrication of diffractive elements for VIS and IR spectral region.

11:30 AM

(GOMD-S3-043-2017) Tellurite glass film for enhanced emission and collection efficiency of NV center in nanodiamond

X. Pan*[1]; J. Zhao[1]; Y. Ruan[1]; H. Ebendorff-Heidepriem[1]

1. ARC Centre of Excellence for Nanoscale BioPhotonics, Institute for Photonics and Advanced Sensing and School of Physical Sciences, the University of Adelaide, Australia

The nanodiamond (ND) particle with a single nitrogen vacancy (NV) centre has been a promising single photon source, which is an indispensable component for quantum cryptography and quantum computing. To promote ND (refractive index n ~ 2.4) towards a robust single photon emitter, the transparent high refractive index materials around ND is highly expected, as the increased surrounding refractive index enhances both the emission rate and collection efficiency of ND. Here, we investigated the use of tellurite glass film (80TeO2-10ZnO-10Na2O, TZN, refractive index n ~ 2.0) to enhance the performance of ND as a single photon emitter. By advancing the non-hydrolytic sol-gel method and establishing the spin coating protocols, thin layers of TZN sol-gel with thicknesses between 60 nm and 100 nm were achieved to fully coat ND particles (size ~ 45nm). The subsequent annealing process successfully transformed TZN sol-gel coating into TZN glass film. The high transparency of TZN glass film is secured by optimizing the annealing conditions (temperature, duration and atmosphere) for minimal crystallization and metallic Te formation. The emitted photon counts of identical ND particles before and after TZN glass film were recorded, which shows the improvement of NV centre emission due to high refractive index TZN glass film.

Optical Fibers

Room: Waikoloa 3
Session Chair: Bruno Bureau, University of Rennes 1

9:45 AM

(GOMD-S3-044-2017) Fluoride Glass Fibers (Invited)

M. Saad*[1]

1. Thorlabs, R&D, USA

Discovered 40 years ago at Rennes University, fluoride glasses have experienced intensive development during the first two decades. The glass formation in halide systems has been quite a surprise. In fact, glass formation rules established for oxide glasses can't be used to predict glass formation in halide systems. Hundreds of compositions have been reported in different glass family systems. This is a huge advantage, since glass composition can be tailored for each application requirements. Initially, most research programs focused on telecommunication applications. This is due to theoretical ultralow loss of fluoride glass fibers, which are two orders of magnitude lower than those of silica glass fibers. Even if the ultimate goal was not reached, the intensive development has made the technology fairly mature to produce high quality optical fibers for short and medium length applications. Furthermore, fluoride glasses are good host for rare earth ions. They are then good candidate for active applications such as fiber lasers and amplifiers. Current commercial fibers have optical loss ranging from 10 to 100 dB/km and mechanical strength ranging from 50 to 100 kpsi. More recently, we have introduced Indium fluoride glass fibers, multimode and single mode, with transmission window from 0.3 um up to 5.5 um. The presentation will report the latest development of fluoride fiber technology and their applications.

10:15 AM

(GOMD-S3-045-2017) Development of all-solid chalcogenide microstructured optical fibers

J. Troles*[1]; C. Caillaud[1]; G. Renversez[2]; T. Jouan[1]; L. Brilland[3]

1. University of Rennes 1, France
2. Institut Fresnel, UMR 7249, France
3. SelenOptics, France

Chalcogenide fibers are well known for their infrared transparency until 12 μm, depending on the composition. An original way to obtain single-mode fibers is to design microstructured optical fibers (MOFs). These fibers present unique optical properties thanks to the high degree of freedom in the design of their geometrical structure. In this study, all-solid microstructured optical fibers based on chalcogenide glasses have been achieved and characterized. The first fibers present $As_{40}S_{60}$ low refractive index inclusions (n = 2.4) embedded in an $As_{38}Se_{62}$ glass matrix (n = 2.8). The second type of fibers are made in the same $As_{38}Se_{62}$ matrix, with high index inclusions based on $Te_{20}As_{30}Se_{50}$ glass (n = 2.9). The single mode regime of the fibers was demonstrated theoretically and experimentally by near field measurements in infrared.

10:30 AM

(GOMD-S3-046-2017) Molten Core Fabrication of Intrinsically Low Nonlinearity Glass Optical Fibers

M. Cavillon*[1]; J. Ballato[1]; P. Dragic[2]; C. Kucera[1]; T. Hawkins[1]

1. Clemson University, Materials Science and Engineering, USA
2. University of Illinois at Urbana-Champaign, Department of Electrical and Computer Engineering, USA

Optical nonlinearities serve as limitations for power scaling in high energy laser (HEL) systems. Paramount amongst these parasitic phenomena are stimulated Brillouin scattering (SBS), stimulated Raman scattering (SRS), nonlinear refractive index, n_2-related wave-mixing phenomena (e.g., SPM, FWM), as well as thermal effects such as transverse mode instability (TMI). In this work, material solutions to novel glass optical fibers that exhibit intrinsically low nonlinearities were investigated. Specifically, silica-clad fibers possessing core compositions in the alkaline earth fluoride (AEF_2) – alumina (Al_2O_3) – silica (SiO_2) system will be presented. Alkaline earths and Al_2O_3, when added to silica, participate in the formation of intrinsically low Brillouin and Raman materials. Further, the incorporation of fluorine (in this case through AEF_2) lessens the linear and nonlinear refractive indices, as well as the thermo-optic coefficient, thus rendering the fiber single mode and reducing TMI. The fibers are fabricated using the molten core technique since it is an effective way to produce fibers having wide compositional (quantitatively and qualitatively) range, which could not be otherwise achieved using conventional techniques.

10:45 AM

(GOMD-S3-047-2017) Tellurium based fibers for far infrared

C. Boussard-Pledel*[1]; S. Cui[1]; B. Bureau[1]; J. Lucas[1]

1. University of Rennes, France

Among chalcogenide glasses, the Te-rich glasses, thanks to an optical transmission window extending until 30 μm, are good candidates for the detection of chemical or biological species in the mid or far-infrared range. First, tellurium based fibers have been developed in the frame of large-scale projects such the DARWIN mission. The goal is to find signs of life on earth-like planets thanks to an interferometer operating from 6 to 20 μm. The main issue is to elaborate single mode fibers able to detect CO_2 at 15 μm. After the development of many Te-rich compositions in the Te-Ge-Ga, Te-Ge-I, Te-Ge-Ga-I systems, we focused our activity on the synthesis of Te-Ge-Se glasses, containing no more than 3% of Se but stable enough to draw fibers transmitting light until 16 μm. Then, single mode fibers have been successfully fabricated thanks to a new preform molding process. This method has been implemented to avoid crystallization induced by the traditional rod in tube method. On the other hand, the growing need for sensors able to detect diseases in the medical domain or polluting molecules in the environmental area led us to the discover of very stable Te-Ge-AgI glasses and low loss fibers have been obtained thanks to purification and polishing methods. These fibers have been implemented in Fiber Evanescent Wave Spectroscopy permitting detection of molecules from 2 to 16 μm.

GOMD Symposium 4: Glass Technology and Crosscutting Topics

Glass Corrosion III: Novel Interrogation Methods

Room: Kona 2
Session Chairs: John McCloy, Washington State University;
Mike Harrison, National Nuclear Laboratory

9:45 AM

(GOMD-S4-026-2017) Mechanistic Studies of Ancient Glass Corrosion

J. Ryan*[1]

1. Pacific Northwest National Lab, USA

A very unique Roman-era glass specimen from the sunken vessel the Iulia Felix has been analyzed with respect to corrosion mechanisms. The unique geometry of this artifact prevented unintended damage of some of its corrosion layers during nearly two thousand years of corrosion and the process of its recovery. Analysis of this undisturbed location with electron microscopy has revealed a 500 μm thick series of alteration layers consisting of ~1600 to 1800 lamella. This appears to correlate with the number of years that the sample was altered, suggesting a possible annual cycle of glass dissolution and mineral precipitation. Furthermore, by measuring the thickness of each of layer, we see a pattern of alteration that mimics the known regional temperature variations in Southern Europe over the past two millennia as predicted by a modern climate change model. Additionally, bulk portions of these materials were examined for their propensity for ion exchange diffusion. The solid state diffusion profiles from both laboratory experiments and the ancient corroded surfaces are compared. The results from both the lamella and the ion exchange work are presented in terms of the current theories of glass corrosion.

10:00 AM

(GOMD-S4-027-2017) Unique Insight into Glass Corrosion Dynamics by In Situ Hyperspectral Raman Imaging

L. Dohmen*[2]; C. Lenting[1]; T. Geisler[1]

1. University of Bonn, Germany
2. Schott AG, Germany

Information about the mechanism(s) of glass corrosion is usually obtained by analysing the reaction products after quenching the experiments to room temperature, drying, and mechanical sectioning so that it is often difficult to gain information about the dynamics of the alteration process. To overcome such drawbacks, we have applied, for the first time, in situ and real-time hyperspectral Raman spectroscopic imaging to investigate glass corrosion. Hyperspectral imaging enabled us to observe the dynamic evolution of the corrosion rim while it is forming. Three in situ experiments were carried out in home-made reaction cells. Two of the experiments were run with a simple ternary borosilicate glass that shows a high reaction rate and has only one stable phase in the system (silica gel). The second glass was a more complex, refractory glass containing Ba and Ca as additional network modifiers. All glasses were corroded in a 0.5 M $NaHCO_3$ solution at 90°C, which enabled us to monitor the pH value (on μm scale) during the experiment using the integrated intensity of the $\nu_5(HCO_3^-)$ and $\nu_1(CO_3^{2-})$ bands. It was possible to determine the kinetics of the reaction(s) with a high spatiotemporal resolution, the precipitation of secondary phases, and the intriguing formation of a pH gradient within the reaction rim as well as in a fluid boundary layer at the glass surface after calcite started to precipitate.

10:15 AM

(GOMD-S4-028-2017) Glass Alteration In-Situ Monitoring using Raman Spectroscopy

B. Parruzot*[1]; A. Lines[1]; C. D. Lukins[1]; J. Ryan[1]

1. Pacific Northwest National Lab, Energy and Environment Directorate, USA

Real-time continuous monitoring of glass corrosion could help to better determine Stage III glass corrosion behavior and the corresponding triggering and sustaining mechanisms through pH and solution speciation monitoring. A custom-built in-situ Raman system was used. A 671 nm laser is connected through a splitter and optical fibers to probes equipped with a sapphire window. Each probe is continuously immersed in the leachate directly in the alteration vessels. Signal from each probe is then collected by a 10-channel Raman spectrometer. Boron speciation remains simple over the range of pH and temperature relevant for glass corrosion. Two main species present two distinct Raman signals: $B(OH)_3$ predominates up to pH $\approx$ 9, whereas $B(OH)_4^-$ predominates at higher pH values. Quantification of both boron species in solution allows to recalculate the pH over the range of interest for stage II and early stage III. The extent of glass alteration is determined from the total amount of B released. Simulated high-level and low-activity waste glasses were altered up to 160 days at 23°C, 70°C and 90°C. The Raman signal obtained from these tests was processed and normalized using reference solutions and compared to ICP-OES analysis of the leachate. The results will be discussed in terms of existing terminology of glass behavior as well as computational corrosion models.

10:30 AM

(GOMD-S4-029-2017) Nanoscale and Multi-Isotope Tracer Observations at the Borosilicate Glass Corrosion Interface

C. Lenting*[1]; M. Kilburn[2]; M. Klinkenberg[3]; O. Plümper[4]; T. Geisler[1]

1. Uni Bonn, Steinmann-Institut, Germany
2. The University of Western Australia, Centre for Microscopy, Characterisation and Analysis, Austria
3. Forschungszentrum Juelich, Institut für Energie- und Klimaforschung, Germany
4. Universiteit Utrecht, Earth Sciences, Netherlands

Borosilicate glasses are currently the standard material for the immobilization of highly radioactive waste. To predict their long-term stability of borosilicate glasses in a geological repository in the case of groundwater contact, it is important to have a thorough understanding of the alteration mechanism and the rate-limiting steps. To advance that knowledge, we conducted a series of corrosion experiments on the International Simple Glass and a ternary borosilicate glass in silica-rich solutions with five isotope tracers (D, ^{18}O, ^{10}B, ^{30}Si, ^{44}Ca) to follow the exchange between solution, reaction rim, and pristine glass. The run products were analyzed by NanoSIMS and TEM, and sample surfaces development was further investigated by Raman and AFM. Since each tracer plays a different role in the glass structure and reaction behavior, the tracer distribution in the reaction rim delivers new insights to the long-time discussed reaction mechanism. The results clearly show a decoupling of the isotope tracers and their distribution within the reaction rim and across the glass interface. Furthermore, new arguments for a water-rich layer are given by deuterium enrichment at the corrosion interface.

10:45 AM

(GOMD-S4-030-2017) About the relevance of ion beam irradiations to simulate the radiation aging of nuclear glass

S. Peuget[1]; A. Mir*[2]; S. Miro[1]; C. Jegou[1]

1. CEA, France
2. University of Huddersfield, School of Computing and Engineering, United Kingdom

So as to ensure the long term structural integrity of the materials subjected to simultaneous irradiations with many particles, it is important to understand if multi particle irradiation scenarios can alter the mechanisms of the damage formation from the one inferred from the single particle irradiations. To that purpose, mono, sequential and simultaneous beam irradiations from Alpha particles and Au ions were carried out to understand the impact of the inelastic and elastic energy losses interactions on the damage formation in a borosilicate glass, named ISG. Final material damage state was observed to depend on the irradiation sequence of the ions. Gold irradiation always generates damage. However, alpha irradiation of the gold pre-irradiated samples can result in damage recovery at high gold pre-damage fraction. Simultaneous double beam irradiations induced an intermediate damaged state between the two sequential scenarios. In parallel, alpha decays self-irradiation effects of an ISG glass doped with ^{244}Cm were studied by NMR spectroscopy. It was shown that the damage state induced by the alpha decays irradiation is lower than the one induced by Au irradiation, confirming the existence of a recovery process associated to Alpha particle. These results demonstrate that a partial self-healing of the damage occurs in the nuclear waste glass matrices.

11:00 AM

(GOMD-S4-031-2017) Influence of Irradiation on the Structure and Corrosion of Borosilicate Glasses

N. Krishnan[1]; M. Wang[1]; B. Wang*[1]; J. C. Mauro[2]; G. Sant[1]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA
2. Corning Incorporated, USA

Borosilicate glasses are commonly used to chemically immobilize high-level radioactive wastes. Although they are usually considered to be “self healing” upon irradiation, the detailed effect of irradiation on their atomic structure remains largely unknown. However, elucidating irradiation-induced long-term structural changes is of primary importance since, in turn, glasses’ structure can affect their dissolution rate. Here, using molecular dynamics simulations, we show that the atomic networks of borosilicate glasses undergo notable changes under irradiation. In particular, short-range (coordination numbers, bond angles) and medium-range defects (ring statistics) are observed. In addition, we show that the intrinsic resistance to irradiation of borosilicate glasses strongly depends on their composition and structure. Finally, based on a previously established topological model of dissolution, we quantify the positive or negative effect of irradiation on the dissolution rate of various borosilicate glasses.

11:15 AM

(GOMD-S4-032-2017) Chemical durability of iron phosphate waste forms containing 40 wt% of a high MoO_3 Collins-CLT waste with different cooling rates

J. Hsu*[1]; J. Bai[1]; R. Brow[1]; C. Kim[2]; J. Szabo[2]; A. Zervos[2]

1. Missouri S&T, USA
2. MO-SCI Corporation, USA

The secondary waste stream produced by a uranium extraction process includes high concentrations of MoO_3, ZrO_2, lanthanide oxides, and noble metals that have low solubilities in borosilicate glasses, but greater solubilities in iron phosphate glasses. The chemical durability of partially crystallized iron phosphate waste forms containing up to 40 wt% of a high MoO_3 Collins-CLT waste simulant, quenched from melts at different rates (water quenched, as-cast and canister centerline cooling, CCC), was determined in water at 90°C using the product consistency test (PCT). The waste form created at the faster cooling rate has a better chemical durability than waste forms cooled more slowly. Surface topology measurements by optical microscopy indicate that the corrosion rate of the residual glass is faster than that of the crystalline phases and that the residual glass in the quenched waste form is more chemically stable than that in the CCC sample. Iron phosphate crystals in the slowly-cooled (CCC) waste forms deplete the iron content and increase the phosphate content of the residual glass, making it less durable in water.

11:30 AM

(GOMD-S4-033-2017) High Alumina Borosilicate Glass Development for High-Level Waste, Part I: Toxic Leaching Characteristic Procedure and Product Consistency Test

Y. Chou*[1]; M. J. Schweiger[1]; J. Vienna[1]; J. B. Lang[1]; V. Gervasio[1]; N. L. Canfield[1]; L. P. Darnell[1]; R. L. Russell[1]; B. McCarthy[1]; G. Piepel[1]; S. K. Cooley[1]; K. M. Fox[2]; T. Edwards[2]; A. A. Kruger[3]

1. Pacific Northwest National Lab, USA
2. Savannah River National Lab, USA
3. US DOE, USA

Pacific Northwest National Laboratory has led the efforts to develop glass composition-property models for HLW at Hanford Site, WA. In the first phase a matrix was statistically designed to efficiently augment existing high-alumina HLW glasses with 46 additional compositions containing Al_2O_3 up to 30 wt%. In the first part of this series of work glass leaching and durability properties by Toxicity Characteristic Leaching Procedure (TCLP) and Product Consistency Test (PCT) were reported and compared to the requirements of waste treatment plant under construction at Hanford Site. For TCLP and PCT both quenched (Q) and simulated canister-centerline cooled (CCC) samples were tested. In addition, crystallinity of CCC samples was characterized. The results show that PCT Na, Li, and B responses are largely congruent as are the Cd and B releases by TCLP for most glasses. Composition effects on these responses are described and compared to previous studies focused on lower-alumina Hanford HLW glasses. The impacts of some crystalline phases were found to significantly impact both PCT and TCLP results. Existing models for TCLP (Cd) and PCT will be tested with current data and discussed. Preliminary analyses of the composition regions prone to the formation of these crystalline phases and their impacts on PCT and TCLP are presented

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium I

Room: Kona 5
Session Chairs: Himanshu Jain, Lehigh University; Ralf Müller, Bundesanstalt für Materialforschung und -prüfung (BAM)

10:00 AM

(GOMD-S6-001-2017) Design and Control of Crystallization in Oxide Glasses (Invited)

T. Komatsu*[1]

1. Nagaoka University of Technology, Japan

There has been a great progress in the design and control of crystallization in oxide glasses, e.g., the relationship between glass composition and crystalline phase/morphology. We reviewed the basic scenario for glass crystallization, typical types of glass crystallization, and features of laser-induced crystallization by using some examples such as nonlinear optical nano-crystallization in tellurite- and borate-based glasses. In the laser crystal patterning, not only highly oriented crystal lines with bending, spiral, and two-dimensional planar morphologies were designed, but also the self-organized homo-epitaxial crystal growth in crossing lines was demonstrated, proposing a new crystal growth science and technology beyond the law of nature in glasses. The crystallization processing of glasses is becoming more and more important as a novel technique for the development of new functional glass/crystal hybrid materials and also as an approach for a deep understanding of the nano-scale heterogeneous structure in glasses.

10:45 AM

(GOMD-S6-002-2017) Fortunate Period and Experience in Komatsu Lab (Invited)

T. Fujiwara*[1]

1. Tohoku University, Applied Physics, Japan

Several challenges of research work in related with glass materials and photonic devices performed in Komatsu lab. from 2000 to 2006 will be introduced. It is a lot of years or not, however, it's one of the most impressive and favorite time in my research experience. Second-order optical nonlinearity in glass is, especially, the main topic. Novel developed perfect surface crystallized glass with strong orientation to the crystalline axis and the laser-induced technique for position localized crystallization in glass are the key issues for creating the electro-optical "active" fiber-form devices in advanced communication networks.

11:15 AM

(GOMD-S6-003-2017) Diffusion processes controlling viscous flow and crystallization in silicate liquids (Invited)

E. D. Zanotto*[1]; F. Tiemi[1]; R. Lancelotti[1]; D. R. Cassar[1]; A. M. Rodrigues[1]; R. Nuernberg[1]; M. L. Nascimento[2]

1. UFSCar, DEMa, Brazil
2. Universidade Federal da Bahia, Faculty of Sciences, Brazil

In this talk we critically review selected literature data and also include a plethora of new (unpublished) data on the diffusion processes controlling important dynamic phenomena in silicate glass-forming liquids, such as viscous flow and crystal growth. We cover an extensive range of diffusivities (~10^{-7} to 10^{-22} m^2/s) for the following systems: SiO_2 (Q^4), $Li_2O.2SiO_2$ (mostly Q^3), $Na_2O.2SiO_2$ (mostly Q^3) and $PbO.SiO_2$ (mostly Q^2), in the liquid, supercooled liquid, and glassy states of each system. We compare the diffusivities calculated from the viscosity curves with those estimated from the crystal growth kinetics, and with measured self-diffusion coefficients of the glass forming ions (Si^{+4} and O^{-2}) and the "modifier" cations (Li^{+1}, Na^{+1} and Pb^{+2} or Pb^{+4}). The possible diffusion mechanisms are fully discussed.

PACRIM Symposium 07: Porous Ceramics: Innovative Processing and Advanced Applications

Mechanical Properties of Porous Ceramics

Room: King's 2
Session Chairs: Günter Motz, University of Bayreuth; Yuki Kubota, Japan Aerospace Exploration Agency

8:30 AM

(PACRIM-S7-029-2017) Comparison of 4 point bending and compression test on porous ceramics (Invited)

M. Stumpf[1]; B. Zierath[1]; T. Fey*[1]

1. Friedrich-Alexander University Erlangen-Nürnberg, Department Material Science and Engineering, Germany

Porous ceramics as foams are used for various applications such as catalyst support structures, filters, lightweight materials, energy adsorption, band gap material or energy storage materials or for solar thermal transceivers. Due to their high porosity they exhibit a high permeability and depending on cell type and size excellent isolation properties. Most common ceramics foam manufactured by industry obtain cell sizes between 10 and 20 ppi. Mechanical properties are mostly tested in compression and less in bending. In the absence of compaction during compression a more detailed analysis of mechanical properties even at lower strength values is possible. Alumina ceramic reticulated foams with 30, 45 und 60 ppi initial cell size were processed and test in compression and 4-point bending at room temperature with an instron testing equipment. FEM-simulations on μCT models depending on real structures were used to identify fracture source and behaviour inside the structure to reveal a fracture path different in testing methods. The difference in 4-point bending (2,05 MPa) and compression test (2,82 MPa) for e.g. 45 ppi foams was determined and is caused by different strut fracture behaviour.

9:00 AM

(PACRIM-S7-030-2017) Experimental investigation and analysis of mechanical properties of three-dimensionally networked porous carbon material

R. Inoue*[1]; L. Geng[1]; E. Kojo[1]; M. Nakajima[1]; Y. Kubota[2]; Y. Kogo[1]

1. Tokyo University of Science, Japan
2. Japan Aerospace Exploration Agency, Japan

Three-dimensionally networked porous carbon (TNPCs) are expected to apply thermal protection system for space craft. Our previous works showed TNPCs have excellent mechanical properties compared with conventional carbon foams with similar porosity. We believe that their unique microstructural characteristics attribute to their excellent mechanical properties, however, reasonable explanation is not proposed. The objective of this study is to link between microstructural features of TNPCs and their macroscopic mechanical properties. We fabricated TNPCs using porous phenolic resin precursor with different pore size. Three kinds of TNPC with same porosity for all pore sizes, namely, 4.5, 4.9, and 9.8 μm was prepared. Then, microstructure in three-dimensions was characterized using multi-slice images obtained using X-ray CT and FIB-SEM. Various mechanical properties of TNPCs, i.e., tensile strength, bending strength and fracture toughness, were also evaluated. In this presentation, the major factor contributing to macroscopic mechanical properties of TNPCs will be presented.

9:20 AM

(PACRIM-S7-031-2017) Are minimum solid area models useful?

W. Pabst*[1]; E. Gregorova[1]

1. University of Chemistry and Technology, Prague, Department of Glass and Ceramics, Czech Republic

Minimum solid area (MSA) models have arisen as an attempt to develop analytical models for describing the porosity dependence of effective properties of porous materials with concave pore surfaces. Due to the absence of a viable alternative, MSA models have been frequently invoked to describe the properties of partially sintered ceramics. Here we show, using numerical modeling, that the results of MSA models are wrong even for the simplest geometries (e.g. those based on the simple cubic packing of monosized spherical particles). It is demonstrated that MSA models de facto replace the microstructure of porous materials by a parallel model representing an upper bound which can be realized only by anisotropic, but not by isotropic, materials. Therefore the mere existence of non-trivial cross-property relations contradicts the predictions of MSA models. It is shown that MSA models also contradict experimental data for real-world materials (e.g. partially sintered alumina and zirconia). Further, it is recalled that for materials with random microstructures MSA fractions are not even well defined, since they contradict the Delesse-Rosiwal law of stereology. Therefore MSA models cannot be used for isotropic random materials, and even a special case for which MSA models would be correct does not exist. Thus it may be concluded that MSA models are not only wrong, but also useless. First steps towards alternative analytical models are indicated.

Novel Engineering Applications of Porous Ceramics II

Room: King's 2
Session Chairs: Tobias Fey, Friedrich-Alexander University Erlangen-Nürnberg; Ryo Inoue, Tokyo University of Science

10:15 AM

(PACRIM-S7-032-2017) Gas Flow Sputtered Thermal Barrier Coatings for Turbine Components

N. Rösemann*[2]; K. Ortner[1]; M. Bäker[2]; J. Petersen[1]; G. Bräuer[3]; J. Rösler[2]

1. Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany
2. TU Braunschweig, Institute for Materials, Germany
3. TU Braunschweig, Institute for Surface Technology, Germany

Porous thermal barrier coatings (TBC) reduce the thermal load of gas turbine components. State-of-the-art TBCs consist of partially yttria stabilized zirconia (PSZ) and are deposited by thermal spray techniques or electron beam physical vapor deposition. This talk investigates an alternative, innovative deposition technique (gas flow sputtering - GFS) and discusses the influence of process parameters on the microstructure and the suitability of GFS coatings as TBCs. PSZ coatings were deposited on polished FeCrAlY-Alloy substrates, varying the substrate temperature and oxygen flow rate, and described utilizing WDX, SEM, FIB and XRD. The substrate temperature is the crucial parameter. Between 500 and 800 °C, four types of columnar microstructures are found based on XRD pattern and morphology. The growth direction of the columns changes from <111> to <100>, accompanied by a change in shape from triangular to four-sided. The principal shape of the columns is explained using a growth model. Varying the oxygen flow rate at a given substrate temperature alters the microstructure defined by the substrate temperature. While oxygen flow rates above a certain level do not have an effect, low oxygen flow rates lead to further densification and compressive stresses, rendering these conditions unsuitable for TBC manufacturing. In conclusion, promising microstructures are presented accompanied by guidelines for process parameters.

10:35 AM

(PACRIM-S7-033-2017) Microstructure characterization of porous ceramics via Minkowski functionals

W. Pabst*[1]; T. Uhlirova[1]; E. Gregorova[1]

1. University of Chemistry and Technology, Prague, Department of Glass and Ceramics, Czech Republic

The effective properties of porous materials depend on the porosity and all other details of the microstructure. A complete quantification of these details is not possible, but there is a systematic way towards a more comprehensive desription: the Minkowski functional approach. According to a mathematical theorem from integral geometry (Hadwiger's characterization theorem) a wide class of microstructures is completely determined by four Minkowski functionals, which are closely related to four independent global microstructural descriptors: volume fraction (porosity), interface density (surface density), mean curvature integral density (or 2D Euler characteristic) and total curvature integral density (or 3D Euler characteristic). In this contribution we show how these four descriptors and derived pore size measures (mean chord length, Jeffries size) can be obtained in practice for porous ceramics. It is shown that stereology-based image analysis using the point counting technique is the method of choice for obtaining the metric descriptors, including estimated standard errors and confidence intervals. Using binarized sections from tomographic images, the disector probe is applied to evaluate the 3D Euler characteristic. Case studies presented include porous alumina foams prepared via biological foaming with yeast and porous mullite-based ceramic foams prepared by foaming with wheat flour.

10:55 AM

(PACRIM-S7-034-2017) Thermal Conductivity of Foam Glasses Prepared using High Pressure Sintering

M. B. Østergaard*[1]; R. R. Petersen[1]; J. Konig[2]; M. Bockowski[3]; Y. Yue[1]

1. Aalborg University, Chemistry and Bioscience, Denmark
2. Jozef Stefan Institute, Advanced Materials Department, Slovenia
3. Polish Academy of Sciences, Institute of High Pressure Physics, Poland

The increasing focus on better building insulation is important to lower energy consumption. Development of new and improved insulation materials can contribute to solving this problem. Foam glass has a good insulating effect due to its large gas volume (porosity >90 %). It can be produced with open or closed pores. If only open pores exist, air is the dominating medium for the insulating effect. However, closed pores make it possible to trap gases inside the foam. The gas can be introduced either chemically, through foaming agents, or physically, by gas compression-decompression at high temperatures. By introducing the gas physically it is possible to control composition of both the gas phase and the solid phase of the foam glass. In this work we have prepared foam glasses by physical foaming. Panel glass powder from obsolete televisions was first sintered under a gas pressure of 5-25 MPa using helium, nitrogen, or argon. The sintering result in closed-porous body with high pressure bubbles. Subsequent reheating above the glass transition temperature resulted in an expansion of the bubbles. The entrapped gas composition was analysed by gas chromatography. Furthermore, we investigated how the thermal conductivity varies with gas composition. This allows us to determine the contribution of the gas and solid phase to the total thermal conductivity of a foam glass.

PACRIM Symposium 10: Multifunctional Nanomaterials and Their Heterostructures for Energy and Sensing Devices

Nano- and Heterostructures for Solar Energy Capture and Conversion (PV, Solar Fuels, Catalysis) I

Room: Queen's 5

Session Chair: Sanjay Mathur, University of Cologne

8:30 AM

(PACRIM-S10-001-2017) On the Effects of Design, Interfacial Electronic Structure and Dimensions on the Performance & Stability of Photoelectrodes for Solar Water Splitting (Invited)

L. Vayssieres*[1]

1. Xian Jiaotong University, IRCRE, School of Energy & Power Engineering, China

A quantitative description of the multi-scale fabrication design of novel purpose-built advanced low-cost photoelectrodes for solar water splitting will be presented. This will involve the direct effects of dimensions (including size, shape, aspect ratio, orientation and confinement) as well as aqueous surface chemistry, interfacial electronic structure (probed at synchrotron radiation facilities), and in-situ electrical properties on the performance and atomic-scale origin of long-term stability of heteronanostructures for cost-effective and efficient solar (sea)water oxidation and overall (sea) water splitting for hydrogen generation. Examples will be given on low-cost, earth-abundant and non-toxic transition metal oxides as well as on nitrides. Finally, the latest advances in efficient single-junction photoelectrodes that do not require any transparent conductive substrates (TCOs) will be presented and discussed.

8:55 AM

(PACRIM-S10-002-2017) Reducing charge recombination of hematite electrodes for solar water oxidation by controlling grain boundary effect (Invited)

A. M. de Freitas[1]; F. L. de Souza*[1]

1. Federal University of ABC, Center of Natural Science and Humanity, Brazil

This work describes the combined effect of nitrogen atmosphere and chemical addition of Sn on the hematite surface electrode and its implication on the photoelectrochemical performance (PEC). For comparison, undoped [Air or N_2-Fe_2O_3] and Sn-modified [Air or N_2-Sn-Fe_2O_3] hematite electrodes were prepared by a microwave-assisted hydrothermal method varying the synthesis time from 1 to 5 hours and subjected to additional thermal treatment at 750 °C for 30 min in air and nitrogen (N_2) atmosphere. Electrodes obtained after 4 h of synthesis exhibited the highest performance showing photocurrent density around 0.45 to 0.65 $mA.cm^{-2}$ at 1,23 VRHE for Air and N_2-Fe_2O_3. Whereas the Air or N_2-Sn-Fe_2O_3 electrodes showed photocurrent density from 0.5 to 1.0 $mA.cm^{-2}$ at 1,23 VRHE. Top-view scanning electron microscopy (SEM) was conducted showing no significant changes on the undoped electrodes morphology in contrast of a drastic reduction in grain size observed on Sn-modified. By impedance spectroscopy (Nyquist plot) was observed that the combination of N2 atmosphere with chemical addition of Sn significant reduce the electrical resistance increasing it performance for water oxidation assisted by light. This effect can be related to the reduction of grain boundary energy and creation of O2 vacancies favoring a more efficient charge transport decreasing the recombination rate.

Nano- and Heterostructures for Solar Energy Capture and Conversion (PV, Solar Fuels, Catalysis) II

Room: Queen’s 5
Session Chair: Sanjay Mathur, University of Cologne

10:00 AM

(PACRIM-S10-003-2017) Visible Light-driven Water Splitting on Semiconductor Metal Oxide Photoanodes (Invited)

J. Augustynski*[1]

1. Centre for New Technologies, Warsaw University, Poland

Efficient solar light absorption combined with long-term stability are the critical issues that condition implementation of semiconductor materials in photo-electrochemical water splitting devices. These are the reasons why the choice of the semiconductors intended to operate as water oxidation photo-anodes is actually restricted to a few metal oxides. However, none among those materials, able to absorb a significant portion of solar light, exhibits band-edge energy levels that match those of hydrogen and oxygen evolution reactions. Neither tungsten trioxide (WO_3), nor bismuth vanadate ($BiVO_4$) and still less hematite ferric oxide (Fe_2O_3) have the positions of the conduction band edges more negative than the hydrogen evolution potential, a condition necessary to perform unassisted water splitting. Consequently, continuing efforts are devoted to minimize the bias voltage required to perform visible light-driven photo-oxidation of water in tandem device. These efforts include, among others, development of new water oxidation electrocatalysts and incorporation into photo-anodes of plasmonic metal nanostructures to improve light capture and charge photogeneration. Recent advances regarding the largely investigated photo-anode material WO_3 (E_g = 2.5 eV) will be discussed.

10:30 AM

(PACRIM-S10-004-2017) Design and constructing of Fe_3O_4/Graphene super-paramagnetic nano-architecture for photo-catalytic hydrogen Evolution driven by visible light

W. Zhang*[1]; G. Lu[1]

1. Lanzhou Institute of Chemical Physics, Chinese Academy of Science, State Key Laboratory for Oxo Synthesis and Selective Oxidation, China

Magnetic nano-materials have also received much attention at present. Because of their sensitive response to external magnetic field, functionalized magnetic nano-materials have shown wide application for the drug delivery, dual imaging, recoverable catalyst, bio-sensors, and selective recovery of metal ions or molecules. In this work, we report a Fe_3O_4/Graphene composite nano-architecture which was designed and constructed, and applied in the field of photo-catalytic hydrogen evolution (HER) driven by visible light. Owning to the synergistic effect of each component in the nano-architecture, it exhibited high photo-catalytic activity, robust stability and favorable convenience for photo-catalytic HER reaction. For one thing, the super-paramagnetic component endowed the nano-architecture with sensitive response to outside magnetic field, thus it could be separated conveniently from reactive system and re-dispersed into the photo-catalytic reactive system for reuse. For another, the graphene sheets not only improved the transfer of photo-electrons in large scale, but had surface-repair ability for the super-paramagnetic component. Besides, Pt nano-crystals were induced to expose their high-energy (111) facets in the nano-architecture, and those high-energy facets effectively promoted the photo-catalytic HER further.

10:45 AM

(PACRIM-S10-005-2017) The enhancement of carrier conductivity and charge mobility by iodine doping on graphene oxide and their roles on solar hydrogen generation

G. Lu*[1]

1. Lanzhou Institute of Chemical Physics, China

The conductivity, carrier concentration, and mobility of iodinated graphene oxide (I-GO) were significantly increased about five orders of magnitude compared with pristine graphene oxide (GO). Such enhancement mainly attributed to I_3^- and I_5^- implanted into the surface of GO, which led to a larger Rashba spin–orbit coupling induced by heavy adatoms with active electrons living in p orbitals. The tunneling of an electron between two carbon atoms through the polyiodides p orbitals opened additional channels for hopping in I-GO, which gave rise to the superior charge transfer performance. Based on these properties of I-GO, a highly active H_2 evolution I-GO/Pt system was prepared by an in situ chemical deposition method. I-GO/Pt catalyst exhibited higher activity of hydrogen generation and quantum efficiency when Eosin Y (EY) was used as a photosensitizer under visible light irradiation. I-GO not only provided a large area and two-dimensional substrate for the confined growth of uniformly sized Pt particles but also greatly enhanced the transfer of photoelectrons from excited EY to the Pt catalyst because of its promotion of charge separation, leading to the significant enhancement of photocatalytic hydrogen evolution.

11:00 AM

(PACRIM-S10-006-2017) From precursors to functional materials: Nanostructured thin-films for energy harvesting, storage and conversion (Invited)

Y. Gönüllü*[1]; A. Möllmann[1]; J. Leduc[1]; M. Pyeon[1]; D. Bialuschewski[1]; S. Öz[1]; E. Jung[1]; T. Fischer[1]; S. Mathur[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany

The energy transition from fossil to renewable energy carriers demands constant innovation throughout the value chain starting from functional materials and processes over components and devices up to whole system integration regarding energy harvesting, conversion, storage, utilization and recovery. Scalable synthesis and processing of defined materials, with tailored functions and properties are the foundation of a sustainable future energy cycle. The availability of suitable precursor systems with defined composition, volatility and decomposition profile forms the basis of a thorough understanding and control of deposition processes, which is usually the bottle neck for further advances in materials processing using either solution or vapor phase techniques. Especially the industrial uptake of new precursor systems requires a scalable and cost competitive precursor supply with adequate shelf-life and industrially manageable toxicity and reactivity profiles. This presentation will highlight the advances of precursor derived nanostructured materials in energy harvesting (perovskite solar cell), storage (Li-ion batteries) and conversion (solar hydrogen) with the focus on the underlying process control using tailor made precursor systems and alternative processing techniques.

PACRIM Symposium 11: Engineering Ceramics: Processing and Characterizations

Mechanical Properties III

Room: King's 1

Session Chairs: Jingyang Wang, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences; Tohru Suzuki, National Institute for Materials Science

8:30 AM

(PACRIM-S11-035-2017) Capability of plastic deformation in $RE_2Si_2O_7$ disilicates (Invited)

J. Wang*[1]

1. Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, High-performance Ceramics Division, China

Weak interfacial phase between fiber and matrix enhances the toughness of ceramic matrix composite (CMC) through interface debonding and fiber pullout. Compared with typical BN and graphite phases, oxidation resistant weak interfacial phases are crucial important for the optimal long-term stability of CMCs in harsh environments. Rare earth disilicates are promising candidate of novel interfacial phase in SiC/SiC CMCs due to their damage tolerance, good high temperature stability, and compatible thermal expansion coefficients with SiC. Recent progresses suggested good capability of room temperature plastic deformation in some $RE_2Si_2O_7$ disilicates. Deformation modes were observed as deformation twinning, dislocation gliding, and slip bands at room temperature. Mechanisms of plastic deformation could be explained based on analysis of heterogeneous chemical bonding, theoretical shear deformation resistance, and possible twinning modes. The present presentation provides a fundamental understanding of the plastic deformation in RE disilicates and will guide materials selection of oxidation resistant weak interfacial phases in SiC/SiC CMCs.

9:00 AM

(PACRIM-S11-036-2017) Mechanical properties of textured alumina prepared by colloidal processing in a magnetic field

T. S. Suzuki*[1]; T. Uchikoshi[1]; B. Kim[1]; K. Morita[1]

1. National Institute for Materials Science, Japan

Designed microstructure is useful for improvement of mechanical and functional properties in bulk materials. Crystallographic orientation is one of the effective microstructure control in ceramics as well as metals. We already reported that crystalline orientation can be controlled by a magnetic field even in diamagnetic ceramics. Ceramics particles with asymmetric crystal lattice structure show anisometric magnetic susceptibility. When a strong magnetic field is applied to alumina particles in a stable suspension, the particles were rotated to an angle minimizing the system energy by a magnetic torque generated from the interaction between the magnetic anisotropy and the applied magnetic field. After consolidation of alumina slurry in a magnetic field, the compact bodies are sintered by electric furnace or SPS without a magnetic field. The c-axis of alumina was aligned parallel to the magnetic field. The bending strength of textured alumina was higher than that of random alumina at room temperature and high temperature. High temperature deformation of alumina depends on the orientation direction and enhanced to the direction at 45-degree angle to the crystallographic orientation.

9:15 AM

(PACRIM-S11-037-2017) Microstructural Effects on Glass-Ceramic Mechanical Response and Slow Crack Growth Behavior

K. T. Strong*[1]; S. Dai[2]; D. Bencoe[3]; T. Diebold[1]; K. Ewsuk[3]

1. Sandia National Laboratories, Material Mechanics and Tribology, USA
2. Sandia National Laboratories, Microsystem Packaging and Polymer Processing, USA
3. Sandia National Laboratories, Electrical, Optical, & Nano Materials, USA

The average linear coefficient of thermal expansion (CTE) of lithium aluminosilicate glass-ceramic (GC) can be tailored by systematically modifying the thermal profile used to crystallize the starting amorphous material. This tunability is useful for applications such as designing and fabricating a matched expansion glass-ceramic (GC) to metal seal. In addition to producing GCs with different thermophysical properties, modifications to the thermal profile will produce GCs with drastically different microstructures. The objective of this study was to correlate the effects of microstructure on GC mechanical properties, and on slow crack growth (SCG) behavior in particular. Image processing analysis is used to quantify GC microstructures, as well as relationships between GC microstructure and mechanical response including fracture toughness, hardness, and strength. The SCG behavior was characterized by measuring the fracture strength at varying stressing rates. Finally, the use of the SCG parameters obtained from dynamic measurements to calculate the lifetime of GC materials under static stress conditions will be discussed. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:30 AM

(PACRIM-S11-038-2017) Synthesis, characterization and properties of a glass-ceramic material based on the system $BaO-TiO_2-Ta_2O_5-B_2O_3-Al_2O_3$

A. I. Sánchez-Vázquez*[1]; J. J. Ruiz-Valdés[1]; A. Álvarez-Méndez[1]; J. Ibarra-Rodríguez[1]

1. Universidad Autónoma de Nuevo León, Facultad de Ciencias Químicas, Mexico

Through several different compositions based on the system $BaO-TiO_2-Ta_2O_5-B_2O_3-Al_2O_3$ it was possible to obtain a glassy material stable to spontaneous crystallization and with relatively low melting temperature (1450°C). Through X-ray diffraction analysis the characteristic vitreous phase of the glassy state was determined. The glass transition temperature was determined using differential thermal analysis, for a value of 620°C. The methodology and parameters for casting and annealing were decisive to obtain the stable glass. A study of crystallization kinetic was performed, these values corresponded to: E_a=50.5 kJ/mol; $v=7.4 \times 10^{33}$ min^{-1}; n=1.5. SEM analysis shows the presence of a barium-tantalium-titanium phases, as a flake kind structure. Mechanic properties tests were performed, HV=894 kg/mm^2 and compression test (539 MPa). Chemist attack was tested in acid, basic and aqueous medium, showing a high resistance to the aqueous attack (2.8% loss in weigh), following by the basic attack (9.5% loss in weigh) and the most significance loss in weigh was by the acid attack (29.5%). The dielectric properties show a dielectric constant higher than the commercial materials (resistivity, ε_r=147.1), making this glass ceramics a good competition for current materials.

9:45 AM

(PACRIM-S11-039-2017) Toughening mechanisms in the ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ ternary system

S. Heinze*[1]; C. Levi[1]

1. UC Santa Barbara, Materials, USA

Although the ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ ternary system contains several single phases exhibiting one or more properties that are useful in thermal barrier coating applications, e.g. low thermal conductivity, considerable toughness, and reactivity with molten silicates, none of the single phases alone displays an appropriate balance of the requisite attributes. The potential to blend the material response of the various phases together to achieve exceptional combinations of properties motivates investigation into the behavior of multiphase compositions. This study explores the trends in toughness as a function of phase content in the three-phase field containing the tetragonal zirconia solid solution, fluorite, and yttrium tantalate and connects the observed response to the microstructural aspects of fracture. Indentation results suggest that the high toughness of the tetragonal phase diminishes rapidly with the addition of either second phase. Analysis of fracture surfaces and indentation cracks indicates that the mode of fracture and crack propagation pathways varies between each phase and plays a critical role in understanding the active toughening mechanisms. Ongoing TEM microscopy and STEM in-situ pillar compression tests aim to verify both ferroelastic switching as a toughening mechanism in the tetragonal zirconia phase as well as domain boundary motion as a toughening mechanism in twinned monoclinic yttrium tantalate.

Mechanical Properties IV

Room: King's 1
Session Chair: Rajan Tandon, Sandia National Laboratories

10:15 AM

(PACRIM-S11-040-2017) Failure Modes and Mechanics of Fracture in Co-Fired Engineering Ceramics (Invited)

R. Tandon*[1]; A. Thom[2]

1. Sandia National Laboratories, USA
2. Medtronic Inc, USA

Co-fired engineering ceramics can provide integration of multiple functions in one package, and lead to device miniaturization. Co-fired metals have thermal and elastic mismatches with the ceramic, producing local residual stresses which severely impact the fracture behavior and reliability. Observations and fracture analysis of a commercial low temp co-fired ceramic with gold vias show that while strength is reduced by as much as 60%, the susceptibility to sub-critical crack growth (SCG) is not lowered. A circumferential cracking mode around the vias has been observed in this system. Fracture mechanics solutions are derived to describe this failure mode, and correlated with fracture observations of crack kinking. In in vivo simulations of a commercial high temperature co-fired alumina ceramic-platinum via system, circumferential cracking is observed, but only at the slowest stressing rates. Processing changes made to these materials, which ultimately led to strength and SCG characteristics that were undistinguishable from the base materials, are described. Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

10:45 AM

(PACRIM-S11-041-2017) Charcterization and Modeling of Microstructural level Stresses in Brittle Materials

M. Teague*[1]; S. Grutzik[1]; T. Buchheit[1]

1. Sandia National Laboratories, USA

Brittle failure is often influenced by difficult to measure and variable microstructure scale residual stresses. Recent advances in photoluminescence (PL) spectroscopy, including improved confocal laser measurement and rapid data collection spectroscopic data have established the potential to map residual stress variating with microscale spatial resolution (<2 microns) To investigate the limits of PL spectroscopy as a microscale stress mapping tool, results from the mapping stress generated in bonded, mis-oriented bi-crystals an polycrystalline alumina. These results will compared to microstructure models generated from electron backscatter diffraction (EBSD) to highlight the advances and limits of currently modeling capability to predict stresses within complex microstructures.

11:00 AM

(PACRIM-S11-042-2017) Anisotropic heterogeneities for improved fracture toughness – using mica as a model system

M. T. Johnson*[1]; T. Ekeh[1]; N. R. Brodnik[1]; K. Faber[1]

1. California Institute of Technology, Applied Physics and Materials Science, USA

Ceramic materials have long been of interest due to a unique set of elastic, thermal, and physical properties; however, the use of these materials can be significantly limited due to their brittle nature and tendency to fail catastrophically. Recent modeling efforts have explored the inclusion of microstructural heterogeneities which have been shown to have a positive influence on fracture toughness. While additive methods are currently expanding the options available for microstructural design, simpler analogs are available to evaluate these model predictions. In the current work, we adapt Obriemoff's mica splitting experiments to include designed heterogeneities, specifically controlled mica thickness variations, and monitor the force required to cleave mica sheets through these thickness changes. The force required to propagate a crack through a change of thickness is observed to be significantly higher (on the order of 5x for geometries tested) than the force required to propagate through a uniform thickness. This heterogeneity-induced toughening is attributed to changes in flexural rigidity and is expected to occur in similar brittle systems.

11:15 AM

(PACRIM-S11-043-2017) Fracture of Wet Particulate Materials: Effect of Saturation on the Toughness

M. L. Sesso*[1]; G. Franks[1]

1. The University of Melbourne, Department of Chemical and Biomolecular Engineering, Australia

For ceramic materials produced via the colloidal or wet approach, the mechanical properties of the final product are related to the pre-processing steps. The transition from a wet fully saturated part to a dry green body is accompanied by a significant change in mechanical integrity. Although there exists a fundamental understanding of the various drying stages of wet ceramics and their relationship to the formation of cracks, there are few studies that quantify the fracture toughness of these wet bodies particularly at various levels of saturation. In this work, we present a method for measuring the fracture toughness of wet and dry particulate materials. The fracture surfaces of the green bodies at various levels of saturation reveal the presence of plastic deformation of the particle network. The relationship between saturation and the fracture toughness is presented. The role of the size of the plastically deformed zone is related to the degree of saturation and the fracture toughness.

11:30 AM

(PACRIM-S11-044-2017) Sense-Dependent Fracture Toughness in Additively Manufactured Composites with Anisotropic Heterogeneities

N. R. Brodnik*[1]; C. Hsueh[2]; K. Bhattacharya[1]; G. Ravichandran[2]; K. Faber[1]

1. California Institute of Technology, Materials Science, USA
2. California Institute of Technology, Mechanical Engineering, USA

Ceramics have long been of interest as engineering materials because of their high stiffness and good thermal and chemical stability. However, their effectiveness has historically been limited by their low fracture toughness. To improve the toughness of these brittle materials, we have developed additively manufactured composites that use anisotropic heterogeneities to both increase and directionally tailor fracture toughness. These composites are produced using stereolithography and are designed as thin structures whose heterogeneities are uniformly spaced parallel channels with asymmetrical cross-sectional areas. A thin structure allows for study of the systems in a two-dimensional stress state, and the directional alignment of the channels produces fracture toughness values that vary based on how the asymmetrical cross-section is oriented with respect to the direction of crack propagation. Methods for evaluation of fracture toughness have been established through simulation as well as through experiment on a model brittle photopolymer system, and these methods are expected to function analogously on ceramics produced through similar processes. Based on these evaluations, increases in toughness of 50% or more can be achieved for a given composite when compared to its homogeneous matrix material.

11:45 AM

(PACRIM-S11-045-2017) Sintering, structure and properties of AlB_{12}–based ceramics

T. Prikhna*[1]; P. Barvitskiy[1]; V. Sverdun[1]; R. A. Haber[2]; V. Muratov[3]; V. Domnich[2]; S. Dub[1]; M. Karpets[3]; V. Kovylaev[4]

1. Institute for Superhard Materials of the National Academy of Sciences of Ukraine, Ukraine
2. Rutgers University, The State University of New Jersey, Department of Materials Science and Engineering, USA
3. Institute for Problems in Material Science of the National Academy of Sciences of Ukraine, Ukraine
4. “Proton-21” Electrodynamics Laboratory (EDL), Ukraine

The paper presents the results of the study on sintering of AlB_{12}–based ceramics at 30 MPa and 2 GPa pressure-temperature conditions from submicron α-AlB_{12} (without and with C and TiC) and $AlB_{12}C_2$ powders, their structure and mechanical properties. The light materials are developed for armor plates and other products of the spectrum of application for shock-resistant ceramic. Materials sintered from α-AlB_{12} powder at 30 MPa, 2080-1950ºC contained 94-98% of α-AlB_{12} (ρ=2.58 g/cm^3) and their mechanical characteristics were rather similar: H_V(49N)=24.1 GPa hardness, K_{1c}(49 N)=4.9 MPa•m$^{0.5}$ fracture toughness, R_{bs}=336 MPa bending and R_{cs}=378 MPa compressing strengths. The 2 GPa pressure allowed us to obtain dense α-AlB_{12} at 1200ºC. Additions of 17% C to the α-AlB_{12} powder changed the phase composition of the material sintered at 30 MPa, 1950°C for 86% $AlB_{12}C_2$ and 14% AlN with ρ=2.7 g/cm^3 and lead to the increase of K_{1c}(49 N) to 5.9 MPa•m^{0,5} and R_{cs} to 423 MPa. The material sintered from $AlB_{12}C_2$ powder under the same conditions contained almost 100% of $AlB_{12}C_2$ (r=2.57 g/cm^3) and demonstrated K_{1c}(49 N)=3.4 MPa•m$^{0.5}$, H_V(49N)=27.9 GPa, R_{bs} 311 MPa, R_{cs}=1461 MPa. The material sintered from a-AlB_{12} powder with 20% TiC at 30 MPa and 1950°C contained 74% $AlB_{12}C_2$, 22% TiB_2, 4% Al_2O_3, had high mechanical characteristics H_V(49N)=28.9 GPa, K_{1c}(49 N)=5.2 MPa•m$^{0.5}$, R_{bs}=633 MPa and R_{cs}=640 MPa, but its density increased to ρ=3.2 g/cm^3.

PACRIM Symposium 12: Design, Development, and Applications of Ceramic-Matrix Composites

CMC I

Room: Kohala 3
Session Chair: Walter Krenkel, University of Bayreuth

8:30 AM

(PACRIM-S12-002-2017) SiC_f/SiC Ceramic Matrix Composites’ Durability Dependence on Mechanical and Thermal Loading Histories (Invited)

A. S. Almansour*[1]; J. D. Kiser[1]; C. Smith[1]; R. Bhatt[2]

1. NASA Glenn Research Center, Ceramic and Polymer Composites Branch, USA
2. Ohio Aerospace Institute at NASA GRC, Ceramic and Polymer Composites Branch, USA

Silicon Carbide based Ceramic Matrix Composites (CMCs) are attractive materials for use in high-temperature structural applications in the aerospace and nuclear industries. Under high stresses and temperatures, creep degradation is the dominant damage mechanism in CMCs. Consequently, chemical vapor infiltration (CVI) SiC_f/SiC ceramic matrix composites (CMC) incorporating Sylramic^{TM}-iBN SiC fibers coated with boron nitride (BN) interphase and CVI-SiC matrix were tested to examine creep behavior in air at a range of elevated temperatures of (2200 - 2700°F). Samples that survived creep tests were evaluated via RT fast fracture tensile tests to determine residual properties, with the use of acoustic emission (AE) to assess stress dependent damage initiation and progression. Microscopy of regions within the gage section of the tested specimens was performed. Observed material degradation mechanisms are discussed.

8:55 AM

(PACRIM-S12-003-2017) Determination of material properties for short fiber reinforced ceramic matrix composite under bending load

Y. Shi*[1]; D. Koch[1]

1. DLR - German Aerospace Center, Institute of Structures and Design, Ceramic Composites and Structures, Germany

For continuous fiber reinforced ceramic matrix composites (CMC), there is an extensive knowledge of the influence of coupon geometry on the failure mode and the determined resistance in bending tests. In contrast, there are few studies on this topic for short fiber reinforced CMC and no geometry standard for bending tests for such materials exists. In this work, the influence of different sample numbers, coupon geometry and test conditions on the calculated mean and variance of flexural strength has been investigated. Two different short fiber CMCs were examined under four point bending mode. It is shown that a number of five coupons is sufficient for getting reliable data. Furthermore it is shown that below a certain specimen cross-section a decrease of the determined strength was observed. The standard deviation and the distribution of rupture stress strongly depended on the specimen geometry size, the fiber length and the loading span width. The correlation of the fiber orientation in the loaded area, of the region of failure initiation and of the measured flexural strength were investigated by high resolution X-ray computer tomography and SEM in order to obtain further insight into the causes of strength scatter in these materials. The presented results will be proposed to a future standard for the bending test of short fiber reinforced CMC materials.

9:10 AM

(PACRIM-S12-004-2017) Preparation of interphase in C/SiC composites and the effect on mechanical properties

Y. Zhu*[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, Structural Ceramics Engineering Research Center, China

C/SiC composites were fabricated by polymer infiltration and pyrolysis, using C fiber as reinforcement. A layer of pyrocarbon (PyC) and a layer of SiC coatings were first deposited on the fiber surface. The effect of thickness of SiC interphase on microstructure and mechanical properties of the fabricated composites was investigated to extend the application of such C fiber to ceramic matrix composites. As the thickness of deposited SiC increased, the density of the composite gradually increased. Simultaneously, the bending strength and proportional limit stress were also improved. When the thickness of SiC interphase reached about 1 μm, the ultimate bending strength and proportional limit stress of the composites were enhanced sharply. The fracture behavior of the fabricated composites was totally changed after PyC/SiC deposition. Long fiber pullout dominated the fracture surface for composite with PyC/SiC interphase, while for the one without the interphase no fiber pullout was observed.

9:25 AM

(PACRIM-S12-005-2017) Al_2O_3-based ceramic with high density prepared under high temperature gradient direction solidification (Invited)

K. Gao*[1]; X. Guo[1]; R. Zhang[1]

1. Zhengzhou University of Aeronautics, Henan Key Laboratory of Aeronautical Material and Application Technology, China

To obtain the excellent high density Al_2O_3-based oxide ceramic material, $Al_2O_3/YAG/ZrO_2$ ternary eutectic ceramics were prepared by high temperature gradient direction solidification (laser floating zone melting). Effects of directional solidification rate (10 μm/s, 20 μm/s and 30 μm/s) on microstructure morphologies and fracture toughness of oxide eutectic ceramics have been investigated. Its microstructure were all performed on full regular eutectic lamellar microstructure included Al_2O_3 phase, YAG phase and ZrO_2 phase at different solidification rates. These phases were formed interpenetrating network by coupled growth, in which Al_2O_3 phase and YAG phase were continuously connected to each other on three-dimensions space and ZrO_2 phase was filled in them. With solidification rate decreasing, the average lamellar spacing of eutectic was obviously decreased to nearly 2.6 μm. Moreover, The microstructure of Al_2O_3-based oxide ceramic was rapidly refined and its densification was improved. Due to fine microstructure, the crack arrest and crack propagation path deflected, the maximum fracture toughness of Al_2O_3-based oxide ceramic was improved to 3.6 $MPa.m^{1/2}$ as solidification rate decreasing. The experimental results showed that the high density and high toughness Al_2O_3-based oxide ceramic material could be well achieved under high temperature gradient direction solidification.

10:05 AM

(PACRIM-S12-006-2017) Oxidation behaviors of SiC_f/SiC composite ablated by Kerosene-Oxygen flame (Invited)

J. Park*[1]; B. Lim[2]; H. Moon[3]; H. Lee[1]; D. Kim[1]; W. Kim[1]

1. Korea Atomic Energy Research Institute, Nuclear Materials Development Division, Republic of Korea
2. Dai Yang Ind. Co., Republic of Korea
3. SeWon Hardfacing, Co., Republic of Korea

SiC_f/SiC composites are known to have excellent properties in terms of their oxidation resistance, high strength, and chemical stability at higher temperatures. Therefore, it is a promising material for structural applications at high temperature, such as jet engine components, nozzle, and scram jet. During exposure to an oxidizing atmosphere at higher temperatures, degradation of the properties through the oxidation of non-oxides restricts the application of non-oxide components at higher temperatures. In this study, SiC_f/SiC composites were prepared through EPD and HP process. Two-dimensionally woven Tyranno-SA3^{TM} SiC fabric was used as a reinforcement. Commercial β-SiC with 10 wt.% of Al_2O_3–Sc_2O_3 and 10 wt.% of Al_2O_3–Y_2O_3 sintering additives were used as the matrix phases, respectively. The HP was applied at 1750ºC for 1 h in an Ar atmosphere with a pressure of 20 MPa. The EBC coated specimens were also prepared using Yb_2SiO_5 and LGZ. The ablation tests were carried out under a kerosene-oxygen flame in a temperature range of 1500 to 1700ºC. The angle between the flame and SiC_f/SiC composite was 90º. The oxidation behaviors will be discussed based on an analysis of the microstructures, weight, and phase changes of the specimens before and after ablation. The microstructure and chemical composition were observed using SEM with EDS. The phase analysis was conducted through X-ray diffraction and XPS.

10:30 AM

(PACRIM-S12-007-2017) Materials & Processing, Design & Analysis, Testing & Data Review in Support of CMH-17 for CMCS in Aero Applications An Overview and Progress to Date

M. G. Jenkins*[1]; J. E. Gallego[1]

1. Bothell Engineering and Science Technologies, USA

Composite Materials Handbook-17 (CMH-17) evolved from MilHdbk-17 and provides information and guidance needed to design and fabricate components from all classes of composite materials (i.e., polymer, metal and ceramic matrix composites). Currently supported by the FAA, its primary purpose is the standardization of engineering data development methodologies related to testing, data reduction, and data reporting of property data for current and emerging composite materials. CMH-17 includes composite materials properties that meet specific data requirements. In particular, the CMC portion of the handbook is the primary and authoritative source for characterization and statistically-based property and performance data of current and emerging advanced CMCs. It reflects the best available data and methodologies for characterization, testing, analysis and design, and includes data development and usage guidelines in support of design methodologies for CMC components. This paper provides an overview and progress to date of the CMC of CMH-17.

10:45 AM

(PACRIM-S12-008-2017) The mechanical properties of CMCs torque tube

X. Liu*[1]; L. Cheng[1]

1. Northwestern Polytechnical University, China

CMCs(Ceramic matrix composites) torque tubes are considered as prospective alternatives for actuator due to their light weight, high modulus and high performance in various extreme environments. For such applications, torque tubes experience significant bending and/or torsion loading during the installation and operation phases. The mechanical characteristics of torque tubes with different ply angles are tested and determined. Long fiber reinforced torque tubes have high performance than that of the short fiber reinforced ones. And found that SiC/SiC torque tube had overwhelming mechanical performance than C/SiC torque tube.

11:00 AM

(PACRIM-S12-009-2017) Mechanical behavior of C/SiC composite under atomic oxygen environment

D. Wang*[1]; X. Liu[1]

1. Northwestern Polytechnical University, School of Materials Science and Engineering, China

The C/SiC specimens were exposed in a simulated atomic oxygen (AO) environment to evaluate their stability in low Earth orbit. The

tensile property of C/SiC was tested and found that AO bombardment can greatly affect tensile strength of uncoated C/SiC, while it has less influence on the SiC coated C/SiC. The microscopic observation found C/SiC degradation is mainly attributed to carbon fiber's dissipation by AO via SiC matrix cracks.

11:15 AM

(PACRIM-S12-010-2017) Microstructure, mechanical properties and oxidation resistance of SiC_f/SiC composites incorporated with boron nitride nanotubes

G. Zhu*[1]; S. Dong[1]; D. Ni[1]; C. Xu[2]; D. Wang[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, CMCs Laboratory, China
2. Florida State University, USA

SiC_f/BNNTs-SiC hierarchical composites were fabricated via firstly in situ growth of boron nitride nanotubes (BNNTs) on the surface of silicon carbide (SiC) fibers using boron powder as raw material and subsequently matrix densification by chemical vapor infiltration (CVI) and polymer impregnation/pyrolysis (PIP) methods. With the incorporation of BNNTs, energy dissipation mechanisms at nanoscale triggered by BNNTs such as pullout, debonding, crack deflection and crack bridging are observed. But the positive effect of BNNTs on mechanical properties has not been raised due to the offset from the negative effect of pores in composites. Additionally, the residual boron powder results in an improved oxidation resistance and parabolic oxidation kinetics of SiC_f/SiC composites at 900°C, thanks to the protective effect of B_2O_3 glassy phase formed by oxidation of boron. Consequently, a better strength retention after oxidation is obtained. Moreover, it is believed that the remained strengthening and toughening mechanisms aroused by BNNTs surviving after oxidation probably also make a contribution to the better strength retention.

PACRIM Symposium 14: Novel Spray Coatings

Fine Particle Spray Technology

Room: King's 3
Session Chairs: Jun Akedo, AIST; Sanjay Sampath, Stony Brook University

8:30 AM

(PACRIM-S14-001-2017) Development of Anti-scratch and Highly Transparent Alumina Coating using Aerosol Deposition (Invited)

J. Park*[1]

1. IONES, Republic of Korea

Surface treatment techniques have developed to enhance mechanical, optical and chemical characteristics in the industry of semiconductor, display, equipment and automobile. Recently, powder spray based techniques such as aerosol deposition (AD), cold spray (CS), warm spray (WS) and suspension plasma spray (SPS) were regarded as relatively low temperature process or highly dense layer coating. Especially, AD is greatly attractive technique because it is able to form highly dense coating layer by just physical impact of powders without any binders, cracks and micro-voids, in addition, it is possible to proceed at room temperature. These advantages have resulted in more outstanding surface properties from micro and nanometer scales, including the morphology, chemistry, crystal structure, physical, and mechanical properties. In this study, we tried to fabricate the highly transparent and anti-scratch alumina coated tempered glass by AD in order to apply for mobile cover glass as protecting layer from external damage. In the results, we have fabricated highly transparent and anti-scratch alumina coating on tempered glass using AD. Then, transmittance of the alumina coated glass was about 90% at visible range and surface damage was not occurred in scratch test Furthermore, it was verified that AD-Alumina layer has nano-sized grain with pure alpha-alumina phase by TEM & XRD.

9:00 AM

(PACRIM-S14-002-2017) Deposition of Transparent Alpha-Alumina on Glass by Granule Spray in Vacuum

D. Park*[1]; S. D. Johnson[2]; B. Hahn[1]; J. Ryu[1]; W. Yoon[1]; J. Choi[1]; J. Kim[1]

1. Korea Institute of Materials Science, Republic of Korea
2. Naval Research Laboratory, USA

Transparent alpha-alumina films were deposited by spraying spherical granules made of alpha alumina particles. Dry air was supplied in two inlets; carrier air inlet and supplemental air inlet. Carrier air passed through the granule chamber and carried the granules while supplemental air did not pass through the granule chamber. The two airs merged just before the nozzle. So, the supplemental air can be accelerated the granules by increasing the pressure difference at the nozzle throat.. The pressure difference increased as the air flow rate was increased. The pressure difference can increase also by decreasing width of the nozzle throat The film growth rate expressed in film thickness/granule consumption term increased as the air flow rate was increased. However, the film growth rate was lower for the narrow throat nozzle than for the wider throat nozzle. The film growth rates were partially explained in terms of the velocity distributions of the granules at the nozzle throat. The microsturctures of alumina films were affected by the air flow rates and closely related to the optical transmittance.

9:15 AM

(PACRIM-S14-003-2017) Uniform and dense Al_2O_3 coating fabricated from fine particles by low power rf induction plasma

T. Saeki*[1]; K. Shinoda[1]; M. Mori[2]; J. Akedo[1]

1. National Institute of Advanced Industrial Science and Technology(AIST), Advanced Coating Technology Research Center (ACT-RC), Japan
2. (Ryukoku University), National Institute of Advanced Industrial Science and Technology (AIST), Japan

The realization of environmental-friendly process is one of the important issues in manufacturing and coating technologies of ceramics. In this aspect, the formation of dense, uniform, and homogeneous coatings by the use of fine powder as raw material attracts attention in the recent spray coating technologies. Thermal spray is one of the popular process. On the other hand aerosol deposition (AD) method is also gaining the attention because this method can form very dense ceramic coatings without thermal heating. However, the AD method is inferior to thermal spray method in terms of deposition efficiency of raw material and deposition rate. Therefore, we made a study of a boundary between thermal plasma spray and aerosol deposition and have developed a new coating process named a hybrid aerosol deposition (HAD) method. The HAD process utilizes rf induction plasma with a lower power input (~a few kW level) compared to conventional plasma spray and improves the weak points of the AD method mentioned above with keeping the advantage of the AD method. Thus, a very dense and uniform coating was obtained by HAD process. As a case study, the formation of Al_2O_3 coatings having high density and uniformity by using HAD process will be shown. This work was supported in part by NEDO SIP, Innovative Design /Manufacturing Technologies, High-Value Added Ceramic Products Manufacturing Technologies.

9:30 AM

(PACRIM-S14-004-2017) Fine Ceramic Coating Deposition by 4 kW Plasma Spraying System

M. Shahien*[1]; M. Shahien[2]; M. Suzuki[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Advanced Coating Technology Research Center, Japan
2. Central Metallurgical Research and Development Institute, CMRDI, Advanced Materials, Egypt

Thermal spray technology is well-known surface coating technology with wide applicability and high deposition rates. Thermal spraying has several advantages such as wide flexibility of spraying material; metals, inter-metallic compounds, ceramics, plastics and their compounds. Furthermore, thermal spraying process vary according the heat source, spray velocity and materials, to wide variations of spraying process including; plasma spray, flame spray, arc spray, warm spraying, cold spraying, and aerosol deposition). In thermal spray field plasma spray is widely used technology for ceramic coatings depositions with high application speed and relatively low cost. It is based on spraying of micron-sized feedstock powders (20-100 μm) into high temperature plasma jet, where it is rapidly heated and accelerated with a high velocity to the substrate material. In this study, we will present our recent challenge to deposit the fine ceramic particles in submicron-sized directly by a newly developed plasma spraying system with low input power of about 4 kW.

9:45 AM

(PACRIM-S14-005-2017) Thermal sprayed dense ceramic coating fabricated by using fine particle

K. Sato*[1]

1. Fujimi Incorporated, Thermal Spray Dept., Japan

Plasma sprayed ceramic coatings have been widely used in industries to attain valuable properties, such as high hardness, anti-wear, anti-corrosion, barrier of thermal conduction, controlled friction and so on. In industry, APS ceramic coating using more than 30 μm particles is conventional technology. Recently, denser coatings fabricated by conventional technology have been required by several applications. In our study, it is achieved that denser coatings were fabricated by HVOF, APS and SPS by using fine particle. Those coatings were same level in porosity, however, hardness, XRD pattern and electrical property were different according to the thermal spray process.

Process Improvement of Aerosol Deposition

Room: King's 3
Session Chairs: Kentaro Shinoda, National Institute of Advanced Industrial Science and Technology (AIST); Balu Balachandran, Argonne National Laboratory

10:15 AM

(PACRIM-S14-006-2017) An Empirical Growth Dynamics Model for Aerosol Deposited Films (Invited)

S. D. Johnson*[1]; D. Park[2]

1. Naval Research Laboratory, USA
2. Korea Institute of Materials Science, Republic of Korea

Aerosol deposition is a technique that can create dense polycrystalline films at room temperature at a very high growth rate of up to several microns per minute. The rate of growth of these films and the mechanisms of the deposition process can depend on many parameters including, the quality of the aerosol, pumping speed, carrier gas flow rate, relative pressures, and the properties of the constituent particles and substrate. The influence of these parameters on the film growth process is poorly understood. The goal of this work is to develop a better understanding of the control parameters used in the aerosol deposition process. We deposited barium hexaferrite powder with varying starting quantities from 5 g to 100 g onto glass slides for fixed deposition times from 2 minutes up to 32 minutes. The resulting film thicknesses were measured and tabulated. We find that for a fixed value of time the thickness of the films is proportional to the starting powder mass in the aerosol chamber. Within this linear range, we fit the data to an analytical growth dynamics model that predicts the film thickness based on the deposition time and starting powder quantity. Using this model we can gain insight into the instantaneous film deposition rate and the maximum achievable film thickness for a given powder quantity.

10:45 AM

(PACRIM-S14-007-2017) Some novel aspects when manufacturing alumina films by the Aerosol Deposition Method (ADM)

R. Moos*[1]; M. Schubert[1]; J. Exner[1]; M. Hahn[1]; N. Leupold[1]; J. Kita[1]

1. University of Bayreuth, Dept. of Functional Materials, Germany

With the Aerosol Deposition Method (ADM) dense ceramic films can be produced at room temperature directly from a ceramic raw powder. Many novel applications are possible using electrically insulating alumina films that are processed without high temperature sintering steps. In the first part, this contribution reports on the high temperature electrical insulation behavior of alumina ADM-deposited films. This is determined by a setup in accordance to ASTM D257 or IEC 60093. It will be shown that the processed films perform better than conventional alumina substrates as they are commercially available for thick-film technology. This may open up new applications. The second part reports on some observations that occur when substrate hardness and substrate roughness are systematically varied. Ductile substrates can be expected to give strong film anchoring, whereas high hardness substrates might require higher particle velocities to form adherent layers. In this study, four ceramic substrates (two types of Al_2O_3, sapphire, and LTCC) with different hardness and surface roughness were alumina coated in order to study the formation of an anchoring layer and their effect on the deposition rate. As a result, and in contrast to some literature observations, a much smaller anchoring layer compared to that found on metallic substrates was found on the hard ceramic substrates.

11:00 AM

(PACRIM-S14-008-2017) Study on Improving Deposition Efficiency of Aerosol Deposition Method (Invited)

K. Naoe*[1]; M. Nishiki[1]

1. Hitachi, Ltd., Research & Development Group, Japan

The aerosol deposition method (ADM) has been attracting attentions as a new method for formation of ceramic films. Dense ceramic films with thickness of 1 ~ 100 mm can be formed directly on a substrate by impacting fine ceramic particles with around 1 mm or sub-micrometer in diameter. The most distinguishing feature of this method is that the process temperature can be room temperature. It has been reported that a wide variety of ceramic films, such as Al_2O_3, $Pb(Zr, Ti)O_3$, AlN, and MgB_2, can be obtained by ADM. To use ADM industrially, it is necessary to improve the deposition efficiency, which is the ratio of film weight to consumed particle weight, because high deposition efficiency leads to cost reduction of ceramic films formed by ADM. Therefore, we had systematically investigated the dependency of the deposition efficiency on various deposition conditions. As the conditions, the process for producing ceramic particles, the impact velocity, and the substrate temperature were chosen in this study. Moreover, we tried to develop a novel apparatus of ADM based on the results. The apparatus was equipped with the cyclical use system of ceramic particles, which enabled us to repeatedly use the ceramic particles that were not deposited on substrates.

11:30 AM

(PACRIM-S14-009-2017) Mechanism Investigation of Ceramic Thick Film Coating on Plastic/Resin Layer by Aerosol Deposition Method

H. Noda*[1]; J. Akedo[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Advanced Coating Technology Research Center, Japan

The Aerosol deposition (AD) method in one of the advanced coating process for ceramic materials on various type of substrate, such as glass substrate, SUS substrate. Many type of conventional ceramic coating process required high temperature firing or substrate heating to make dense ceramic layer, In contrast of this, the AD method has advantages, especially, the AD method process is allowed room temperature coating of ceramics. It means that there are large potential opportunities for coating on various kinds of substrate which could not apply high temperature firing such as plastic/resin substrate. This article shows the challenges and there mechanisms to apply ceramic coating on plastic/resin layer, and how to overcome these challenges. From mechanism view point, stress and adhesion mechanism between substrate and ceramic layer at AD process has investigated. One of the important factors is how to make anchoring layer between ceramic and plastic/resin layer. In order to make anchoring layer, This article shows that viscoelasticity property of plastic/resin layer is one of the predominant factors.

11:45 AM

(PACRIM-S14-010-2017) High temperature water vapor stability of thermal reflection coating formed by aerosol deposition

M. Tanaka*[1]; S. Hori[2]; S. Kitaoka[1]; M. Yoshida[2]; O. Sakurada[2]; K. Nishioka[3]; Y. Kagawa[3]

1. Japan Fine Ceramics Center, Japan
2. Gifu University, Japan
3. The University of Tokyo, Japan

SiC fiber reinforced SiC matrix composites (SiC/SiC) have been expected to use the hot and high-pressure section components of the next generation gas turbine engines. However, SiC/SiC suffers from oxidation and volatilization in high temperature combustion gas environments, so environmental barrier coatings (EBCs) are essential to overcome these limitations. If EBCs could effectively reflect the thermal energy radiated from a high temperature heat source, the resulting decrease in surface temperatures will inhibit the diffusion of oxidant species through the EBCs, thereby drastically reducing the oxidation of the underlying SiC/SiC. We have previously proposed the EBCs with thermal reflection. These EBCs have a periodic layered structure composed of Al-doped $Y_2Ti_2O_7$ (AYT) and Al_2O_3 with large refractive index difference. To maintain the performance of environmental barrier and thermal reflection in high temperature, at least it is essential to form the dense layers to keep a designed difference of refractive index and to inhibit the cracking by sintering shrinkage in high temperature. Aerosol deposition (AD) technique will be expected to form such dense layers, so it can be expected to solve these problems. In this study, the AYT/Al_2O_3 multi-layered coating was formed by AD, and the structural stability of the coating was investigated in high temperature water vapor environment.

PACRIM Symposium 16: Geopolymers: Low-Energy and Environmentally-Friendly Ceramics

Geopolymers I

Room: Queen's 6
Session Chair: Claire White, Princeton University

8:30 AM

(PACRIM-S16-001-2017) Mechanical characterization of fly-ash/borosilicate based geopolymers (Invited)

G. Taveri*[1]; I. Dlouhy[1]

1. Institute of Physics of Materials, Czech Republic

Portland cement is responsible for approximately 8% of annual greenhouse gas emission, causing the climate to change. The Geopolymers are a green alternative to concretes. These are aluminosilicate polymers, made through a chemical process known as polycondensation. Incorporating waste geopolymers were produced in order to decrease the cost of production. Fly-ash, a thermal power plant byproduct, and waste glasses were employed as primary sources in the geopolymers production. Borosilicate glasses, wastes from dismantled pharmaceutical vials, were effective from the microstructural standpoint, since boron actively participates to the polycondensation. The effects of this improvement were mechanically tested by compression and bending testing and chevron notch test (fracture toughness). The fracture surface was then examined by confocal and SEM microscopies. Compression and bending tests showed an improvement compared to normal fly-ash/waste glass based geopolymers (25% more in compression). Whereas, fracture toughness was low, meaning brittleness and low resistance to crack propagation. SEM micrographies corroborated the brittleness, showing a ragged surface, along with several cracks, due to the presence of significant porosity and impurities. The fracture surface 3D pattern (confocal spectroscopy) evidenced an irregular crack propagation, whose proclivity was mainly, but not always, to follow the porosity.

9:00 AM

(PACRIM-S16-002-2017) Crystal engineering and reaction kinetics of functional metakaoline-based geopolymers (Invited)

M. Pernechele*[1]; T. Troczynski[1]; M. Ho[1]; R. Grutze[1]; M. Pawlik[1]

1. University of British Columbia, Material Engineering, Canada

The crystal engineering of geopolymers allows control, in particular directing and maximizing, of the nucleation and growth of zeolites from the amorphous gel. The control over geopolymer reactions and crystallization is a necessary step to expand the geopolymer applications from mere construction materials to functional advanced ceramic materials. Using a full factorial design we have determined the factors affecting the setting of metakaoline-based geopolymers, the reaction kinetics, and the crystallization products including the zeolite types and yields. The studied parameters were: curing time and temperature, system chemistry in terms of Na/Al, H_2O/solid, and presence of seeding additives, including colloidal nanofaujasite and sodium waterglass. Geopolymerization rate and extent were obtained from decomposition of the FTIR spectra, while the nucleation and growth of the zeolites from the amorphous gels were examined by quantitative XRD with internal standard. SEM imaging on selected samples supported the findings. It was found that the reaction kinetics and extent strongly depend on the curing conditions, and the system chemistry. By tailoring the composition and using the seeding additives we were able to control the crystallizing zeolite type and yield. It is concluded that it is possible to engineer the geopolymers crystal structure to customize their properties and application.

9:30 AM

(PACRIM-S16-003-2017) Characterizing the role of water on the structure and mechanical properties of aluminosilicate geopolymers (Invited)

M. R. Sadat[2]; K. Muralidharan*[1]; L. Zhang[2]

1. University of Arizona, Materials Science and Engineering, USA
2. University of Arizona, Civil Engineering and Engineering Mechanics, USA

Using molecular dynamics simulations, the evolution of the structure and mechanical properties of sodium aluminosilicate geopolymer binders as a function of water content has been investigated in this study. The elastic constants and ultimate tensile strength of the geopolymer binder was calculated as a function of water content and Si/Al ratio, which showed that increasing the Si/Al ratio from 1-3 increased the ultimate tensile strength and elastic stiffness of the binder systematically. On the other hand increasing the water content decreased the strength and stiffness of the binder. An examination of the diffusivity of the alkali cations showed that the alkali cations' mobility was greatly enhanced by the presence of water and as a consequence, destabilized the structural stability of alumina tetrahedra, leading to subsequent failure of the geopolymers. Further, the diffusion behavior of alkali cations and water molecules were found to be anomalous clearly showing different regimes of diffusion. This study provides new insight into possible failure mechanisms in geopolymers underlined by structural instability of alumina tetrahedra in the presence of water molecules.

Geopolymers II

Room: Queen's 6

Session Chair: Krishna Muralidharan, University of Arizona

10:15 AM

(PACRIM-S16-004-2017) The material properties of cellulose nanofiber (CNF) reinforced metakaolin based geopolymer composites (Invited)

S. Cho*[1]

1. Hyundai Motor Group, Republic of Korea

The cellulose nanofiber is the next generation fibers which have higher mechanical properties than carbon nanofibers, especially elongation. Incorporating small amount of CNF into metakaolin based geopolymers would significantly increase their strength and elongation, which is not possbile in traditional fiber reinforced geopolymer composites. The microstructure, mechanical and thermal properties of CNF reinforced geopolymer composites were investigated in this work.

10:45 AM

(PACRIM-S16-005-2017) Role of magnesium and amorphous calcium carbonate in reducing the extent of carbonation degradation in silicate-activated slag pastes (Invited)

E. McCaslin[1]; C. White*[1]

1. Princeton University, Chemical and Biological Engineering, USA

Chemically-activated materials for concrete applications are being explored due to their lower CO_2 emissions compared to Portland cement-based systems and utilization of industrial byproducts. However, these systems based on calcium-rich precursors (byproducts) are seen to suffer from carbonation-induced degradation, where CO_2 infiltrates the pore network and chemically attacks the binder phases. Preliminary research has revealed that at extremely high CO_2 concentrations, magnesium in the slag precursor can act as a phase stabilizer, leading to the existence of an amorphous calcium carbonate (ACC) phase combined with a lower extent of binder gel decalcification. Here we will present a parametric study of the influence of CO_2 concentration, magnesium content, sample age and relative humidity on the formation of ACC in slag-based pastes. The pastes have been characterized using thermal analysis, ^{13}C nuclear magnetic resonance, X-ray diffraction and Fourier transform infrared spectroscopy. From the results we are able to pin-point at which conditions ACC is stable in this system, and to elucidate the chemical mechanisms controlling this intricate carbonation process.

PACRIM Symposium 17: Advanced Functional Ceramics and Critical Materials Perspective

Advanced Functional Ceramics and Critical Materials Perspective IV

Room: Kohala 2

Session Chairs: Kazuyoshi Ogasawara, Kwansei Gakuin University; Yuji Noguchi, The University of Tokyo

9:45 AM

(PACRIM-S17-032-2017) Diagram Approach to the Inverse Problem to Find Novel Mn^{4+}-Doped Red Phosphors (Invited)

K. Ogasawara*[1]

1. Kwansei Gakuin University, Department of Chemistry, Japan

Thanks to the recent advances in fast computers and electronic structure calculation programs, it is getting easier to obtain the energy levels and wave functions by solving the Schrödinger equation for a given system. However, in the development of novel functional materials, what we really want to do is to know the structures or materials which possess the desired properties. In other words, we need to solve the inverse problem of the electronic structure calculation. For example, in the case of red phosphor for the white LEDs, emission wavelength of 630 nm is required. Recently Mn^{4+}-doped red phosphors are drawing attention as the cheaper alternative for the $(Sr,Ca)AlSiN_3$:Eu phosphor. Although oxide host is desired considering the stability against high temperature and high humidity, the emission at 630 nm has not been obtained for Mn^{4+}-doped oxides. In this work, as an approach to solve this inverse problem, we have constructed various energy diagrams of Mn^{4+} in oxides describing the relationship between the local structure and the multiplet energy levels by performing first-principles calculations using model clusters with various symmetries such as O_h, D_{4h}, D_{3d}. These diagrams are expected to be useful to find the local structures around Mn^{4+} which possess desired absorption and emission wavelengths.

10:05 AM

(PACRIM-S17-033-2017) Microstructures and their relevance to photoluminescence in Eu^{2+} doped $SrAl_2O_4$

S. Mori*[1]

1. Osaka Prefecture University, Materials Science, Japan

In order to understand unique photoluminescence effect in Eu^{2+} doped $SrAl_2O_4$, we have investgated crystal structure and its associated microstructures of the monoclinic phase with the $P2_1$ space group mainly by transmission electron microscope (TEM) experiments, combined with powder x-ray diffraction experiments. Electron diffraction experiments showed that the monoclinic phase of $Eu_{0.02}Sr_{0.98}Al_2O_4$ should be characterized as the modulated structure with the modulation vector of q=0 1/2 0, whose space group should be monoclinic $P2_1$. High-resolution TEM experiments revealed that the microstructures in the monoclinic phase can be characterized as twin structures due to the modulated structures with nanometer-sized planer defects. These defects structures should be relevant to the characteristic photoluminescence effect found in Eu^{2+} doped $SrAl_2O_4$.

10:20 AM

(PACRIM-S17-034-2017) Electromechanical coupling hysteresis curves of PZT epitaxial ferroelectric films determined by gigahertz ultrasonic method (Invited)

T. Yanagitani*[1]; T. Mori[2]; K. Wasa[3]

1. Waseda University, Japan
2. Nagoya Institute of Technology, Japan
3. Yokohama City University, Japan

High electromechanical coupling k_t and low mechanical loss in single crystal PZT is attractive for piezoelectric device applications. However, it is well-known that bulk single crystal PZT cannot be grown. The most common approach to obtain single crystal PZT is the epitaxial growth technique. Self-standing epitaxial PZT films are difficult to fabricate because general epitaxial substrate such as $SrTiO_3$ or MgO is difficult to etch away. Therefore, the resonance-antiresonance method for accurate k_t determination cannot be used. In this study, we introduce the k_t hysteresis curves obtained by an ultrasonic conversion loss (CL) of film/substrate resonator. k_t were determined by comparing the experimental CL curves with theoretical curve simulated by an equivalent circuit model. Sputter-grown PZT (1070 nm) and PT (580 nm) epitaxial films excites longitudinal wave at 1.26 GHz and 1.45 GHz, respectively. k_t of PZT and PT films at the as-grown or under -36 V bias were determined to be $k_t = 0.38$ and 0.42, respectively. Coercive electric field ($2E_c$) of the PZT and PT are determined to be 220 kV/cm and 470 kV/cm, respectively. As expected, E_c of "hard" PT are higher than that of "soft" PZT. The k_t hysteresis curve is expected to be a powerful tool for investigating the properties of ferroelectric epitaxial films without removing the substrate.

10:40 AM

(PACRIM-S17-035-2017) Enhanced piezoresponse in polar perovskite oxides: Polarization twist in (Bi,Na)TiO_3-based ferrielectrics (Invited)

Y. Noguchi*[1]; Y. Kitanaka[1]; M. Miyayama[1]

1. The University of Tokyo, Department of Applied Chemistry, Japan

The electro-mechano property of ferroelectrics governs the performance of the piezoelectric devices. It has recently been understood that a phase transition (including polarization rotaion) by applying an electric field (E) is the origin of the superior electro-mechano property. Here, we report a piezoresponse up to 1000 pm/V originating from a new mechanism in ferrielectric single crystals, termed 'polarization twist'. Single-crystal structural analysis under electric fields demonstrate that BNT–7% BT crystals exhibited an extremely high piezoelectric strain constant d_{33} up to 1000 pm/V. The structural analyses based on neutron powder diffraction and single-crystal XRD reveale that the high d_{33} originates from a polarizaiton enhancement accompanied by octahedral rotation in the P4bm ferrielectric phase. In situ X-ray diffraction (XRD) analysis using high-energy synchrotron radiation demonstrates that electric fields induce an extended polar displacement accompanied by nonpolar octahedral rotations in ferrielectric crystals, as if twisted polarization relaxes and stretches. The twisted polarization creates a large piezoresponse and finally changes to a ferroelectric polarization. Our simulations based on density functional theory and phenomenological theory show that this concept stems from a structural coupling between nonpolar octahedral rotation and polar distortion.

11:00 AM

(PACRIM-S17-036-2017) Ferroelectric and thermal Properties of x$Pb(Zn_{0.5}Te_{0.5})O_3$-(1-x)PZT Ceramics (Invited)

G. Li[1]; X. Huang*[1]; J. Zeng[1]; X. Ruan[1]; X. Shi[1]; L. Zheng[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, Functional Ceramics and Devices, China

The complex perovskite $Pb(B',B'')O_3$ compounds perform high piezoelectric and electro-mechanical properties. There are many studied on complex pervskite compositions are PMN-PT, PZN-PT, PNN-PZT. The Te^{6+}, which has the smaller ionic radius, has rarely few reported in complex perovskite compounds owing to the low melting point (733ºC) of tellurium oxides (Ti_2O_3), and lower volatile temperature (450ºC), however, the Te^{6+} substitution in B site of PZT ceramics may cause a large lattice distortion, which affects the ferroelectric and the piezoelectric properties. In this work, the x$Pb(Zn_{0.5}Te_{0.5})O_3$-(1-x)PZT (PZnTe-PZT) solid solutions with x=0, 0.02, 0.04, 0.06, 0.08 and 0.12 are prepared by solid state reaction. High density PZnTe-PZT can be sintered in an optimized sintering process: ceramics with lower x (lower than 0.12) compositions can be sintered density and grain size decreases as the Te^{6+} content increase. XRD and SEM results show that the lattice structure are changed with the Te^{6+} content increase, indicating that substion of the Te^{6+} ion in the B site of PZT ceramics, but, it is difficulty to sinter a high density as composition is x=0.12. For x lower than 0.12. It is found that PZnTe sufficiently decrease Tc than other complex perovskite. Diffuse phase transition and flat thermal expansion coefficient up to Tc are observed. The affect of Te^{6+} ion is discussed for the PZnTe-PZT compositions.

11:20 AM

(PACRIM-S17-037-2017) Enhanced energy storage density and its variation tendency in $CaZr_xTi_{1-x}O_3$ ceramcis

H. Zhou*[1]; X. Zhu[1]; X. Chen[1]

1. Zhejiang University, Materials Science and Engineering, China

The enhanced energy storage density and its variation tendency have been investigated for $CaZr_xTi_{1-x}O_3$ (x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5) solid solution ceramics. The dense ceramics with high bulk density above 97% could be obtained, and X-ray diffraction analysis confirms the orthorhombic single phase structure in all compositions. Substitution of Zr^{4+} obviously increases the densification temperature, and the homogeneous fine grain structure is obtained. With increasing x, the dielectric constant ε_r decreases from 175 to 103, while the dielectric strength E_b increases from 435kV/cm to 756kV/cm. The highest energy storage density of 2.7J/cm^3 is achieved at x=0.4, which is much higher than that of $CaTiO_3$ end-member. The energy storage density significantly improves with decreasing the thickness due to the increased dielectric strength. For x=0.5, the dielectric strength increases from 584kV/cm to 756kV/cm while the energy storage density increases from 1.6J/cm^3 to 2.6J/cm^3 when the thickness decreases from 0.50mm to 0.15mm.

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

Optical Material II

Room: Kohala 1
Session Chair: Xutang Tao, Shandong University

8:30 AM

(PACRIM-S20-028-2017) Interaction Between Localized Surface Plasmons and Yb^{3+} Doped Nonlinear Solid-State Gain Media (Invited)

L. Sanchez-García[1]; M. Ramirez[1]; P. Molina[1]; J. Carvajal[2]; M. Aguilo[2]; F. Diaz[2]; L. E. Bausa*[1]

1. Universidad Autonoma de Madrid, Fisica de Materiales, Spain
2. Universidad Rovira i Virgili, Fisica i Cristalografia de Materiales i Nanomaterials, Spain

Noble metal nanostructures offer a promising perspective for the development of new photonic devices due to their ability to manipulate light in the nano-scale. Their extraordinary capability to couple light with collective oscillations of their conduction-band electrons results in a strong confinement of the electromagnetic energy in the surroundings of the metallic nanostructures. This feature can be used to enhance the interactions between the far-field light and optical emitters placed in close proximity to the metallic nanostructures. With the aim of designing coherent sources with improved performance at nanometric scale, aggregates of silver nanostructures have been tailored to match the near infrared emission spectra of Yb^{3+} ions and deposited onto the surface of Yb^{3+}:$RbTiOPO_4$ nonlinear crystals. The role of metallic aggregates on the photoluminescence of Yb^{3+} ions, as well as on the second harmonic generation (SHG) of the $RbTiOPO_4$ nonlinear host, is analyzed. A remarkable enhancement of the Yb^{3+} photoluminescence, and of the SHG response are observed by means of the same plasmonic structures. The results constitute a promising approach for the development of coherent light sources at the nanoscale based on dielectric gain media.

9:00 AM

(PACRIM-S20-029-2017) Plasmon Enhanced SHG in Patterned Ferroelectric Crystals (Invited)

A. Gomez-Tornero[1]; P. Molina[2]; C. Tserkezis[2]; L. E. Bausa[1]; M. Ramirez*[1]

1. Universidad Autonoma de Madrid, Spain
2. Technical University of Denmark, Department of Photonics Engineering, Denmark

Nonlinear frequency conversion processes in nanosized dimensions are currently the subject of an intense activity due to their potential applications in a diversity of disciplines such as, molecular sensing, bio-imaging or integrated photon sources for quantum communication. However, at nanoscopic dimensions, the reduced interaction length of the participating waves requires of additional mechanisms to increase the nonlinear conversion efficiency. Here, we study the effects of metallic nanoparticles deposited on the domain wall surfaces of 2D ferroelectric domain structures for enhanced nonlinear optics at the nanoscale. We demonstrate that, at the immediate surroundings of the metallic nanostructures, the second harmonic generation (SHG) can be enhanced by more than two orders of magnitude with respect to the case of bare ferroelectric crystal. The larger SHG enhancement values are obtained in the near UV spectral region, which notably increase the potential applications of the system. The work represents a step towards the development of efficient frequency converter nano-devices and paves the way to the development of novel hybrid metasurfaces driven by the 2D arrangement of the inverted ferroelectric domains and the plasmonic nanostructures

9:30 AM

(PACRIM-S20-030-2017) Core-shell structure induces new ground states in ceramics of strontium titanate (Invited)

B. Hehlen*[1]; J. Kiat[2]; M. Al-Sabbagh[1]; M. Anoufa[2]; C. Bogicevic[2]; A. Al-Zein[3]

1. University of Montpellier, Physics, France
2. Ecole centrale Paris, France
3. Beirut Arab University, Lebanon

Hyper-Raman scattering (HRS) is a non-linear spectroscopy sensitive to all polar excitations, in particular the soft modes inactive in Raman. HRS has been applied to nano-ceramics of strontium titanate ($SrTiO_3$) of controlled grain size. Contrary to infrared absorption which sees an average medium, the vibrational responses of the core and the shell(s) are split in HRS, allowing thereby probing the structural and dielectric properties of the two subsystems. The resulting structural model successfully reproduces the effective dielectric permittivity measured by dielectric experiments. These results confirm the strong, but still under-exploited, potentialities of HRS for the investigation of polar materials [1]. We also demonstrate that a new ground state can be obtained by tailoring the core-shell structure of the particles. High energy X-rays at synchrotron combined to neutron diffraction and HRS revealed a lowering of the ferroelastic ground state towards a new antiferrodistortive phase, accompanied with strong shift of the critical temperature [2,3]. This new phase is discussed within the Landau theory, and the crucial competition between particle shape anisotropy, surface tension, and shear strain is analyzed as well. This shows that controlling the core-shell structure provides an easy way to stabilize new phases that cannot exist in bulk material, just like film deposition on a substrate.

10:15 AM

(PACRIM-S20-031-2017) Microstructure, compositional effects, and ionic conductivity relationship in highly conductive Nasicon glass-ceramics (Invited)

A. Martins Rodrigues*[1]; A. Cruz-Rodriguez[3]; J. Narváez-Semanate[2]; A. Muñoz Nieto[1]; J. Ortiz Mosquera[1]; R. Nuernberg[1]

1. Federal University of Sao Carlos, Materials Engineering, Brazil
2. Universidad del Cauca, Colombia
3. Institut de Ciència de Materials de Barcelona, Spain

Nasicon-structured compounds are well known for their high ionic conductivity, and therefore represent good candidates to solid electrolytes in electrochemical devices. In fact, the Nasicon structure present 3-D channels in which are located alkali ions that can move with low activation energy. Additionally, the Nasicon structure accepts a wide range of solid solutions of a large variety of compositions. This compositional versatility, and the fact that the framework of the Nasicon structure is based on a chain composed by a glass former, namely a phosphate chain, the glass ceramic route is an attractive method to the synthesis of Nasicon-based solid electrolytes. It will be discussed the glass-formability of some precursor compositions to Nasicon compounds. The temperature of heat treatment deeply influences the final Nasicon structure of some compositions. Also, Nasicon glass-ceramics may be obtained by single or double stage treatments, which leads to different microstructures and different ionic conductivities. Results on Na^+ and Li^+ glass-ceramics solid electrolytes will be discussed, focusing some microstructural effects. Compositional effects will also be highlighted, based on $A_{1+x}M'_xM''_{(2-x)}((Si,P)O_4)_3$ compositions, where A is an alkali cation, Li^+ or Na^+, M' is a trivalent cation, Al^{3+} or Cr^{3+}, and M" is Ti^{4+} or Ge^{4+}

10:45 AM

(PACRIM-S20-032-2017) Fabrication, Properties, and Solid-State NMR Investigation of a Highly Intertwined Lithium Disilicate Glass-Ceramic

S. Huang*[1]; Y. Li[1]; S. Wei[1]; Z. Zujovic[2]; Z. Huang[3]; W. Gao[1]; P. Cao[1]

1. University of Auckland, Department of Chemical and Materials Engineering, New Zealand
2. University of Auckland, Centre for NMR, School of Chemical Sciences, New Zealand
3. China University of Geosciences (Beijing), School of Materials Science and Technology, China

We developed a lithium disilicate glass-ceramic in a SiO_2–Li_2O–Al_2O_3–MgO–P_2O_5–ZrO_2 related glass system, which demonstrates a high flexural strength of 562±107 MPa. Its microstructure features highly intertwined colonies of lithium disilicate, which effectively contributes to the improvement of flexural strength. In situ XRD and SEM results indicate that minor crystalline phases of β-quartz, $MgAl_2Si_4O_{12}$, and Li_3PO_4 are formed and embedded within the $Li_2Si_2O_5$ (LS_2) crystal colonies and residual glass matrix in the glass-ceramics, which could lead to additional strengthening effect on the glass-ceramic. We will demonstrate the development process of such a novel microstructure, and discuss its possible formation mechanism. This material could be an excellent candidate for restorative dental applications up to three-unit posterior bridges, and beneficial for long-term clinical performance. In addition, we applied ^{29}Si and ^{31}P solid-state NMR spectroscopy to study the formation mechanism of lithium silicate (Li_2SiO_3: LS) phase, glass-in-glass phase separation (through ^{29}Si T_1 spin-lattice relaxation). We found that a discontinuity at 750 °C in a plot of ^{29}Si T_1 versus temperature, suggesting microstructural changes at this temperature.

The evolution of P species against temperature was proposed as per ^{31}P NMR study.

11:00 AM

(PACRIM-S20-033-2017) Translucent Mullite Ceramics with Anisotropic Grains (Invited)

A. Kocjan*[1]; M. Cesnovar[1]; D. Vengust[1]; T. Kosmac[1]; A. Dakskobler[2]

1. Jozef Stefan Institute, Slovenia
2. VALL-CER d.o.o., Slovenia

Mullite posses favorable thermal and high-temperature mechanical properties. Moreover, the optical transparency of mullite makes it a suitable for windows in high-temperatures applications. However, high sintering temperatures and pressures, also employing high-purity, synthesized precursors, are needed for fabrication. In the preset paper high-performance, translucent mullite ceramic with anisotropic grains by SPS sintering a commercial powder co-doped with silica and yttria beforehand, simply by mixing the powders was fabricated. The sintering was conducted at low temperature (1370 °C) with only contact pressure. The compositions and microstructures were inspected with XRD and SEM, while the mechanical properties in terms of bi-axial flexural strength (~420 MPa), Vickers hardness (~15 GPa) and indentation toughness (~2.5 $MPam^{1/2}$) were evaluated. Light-transmittances were recorded (~50-80 % at 1-2.5 μm) on a UV-VIS spectrometer. The combination of suitable amounts of dopants and the use of SPS sintering yielded an enhanced densification, also provoking the anisotropic grain growth, presumably due to the lowered glass viscosity during the viscous-flow sintering. Thus, we were able to meet the conflicting demands of obtaining a dense mullite at low sintering temperatures, consisting of anisotropic grains and thereby having increased mechanical properties, while at the same time retaining an excellent Vis-NIR transmittance.

PACRIM Symposium 25: Ceramics for Next Generation Nuclear Energy

Advancements in Nuclear Reactor and Fuel Development

Room: Kona 1
Session Chair: Josef Matyas, PNNL

8:30 AM

(PACRIM-S25-034-2017) Development of MA-bearing MOX fuels for Next-Generation Nuclear Energy (Invited)

M. Kato*[1]

1. Japan Atomic Energy Agency, Fast Reactor Fuel Cycle Technology Development Department, Japan

Development of Minor Actinides (MA) –bearing MOX fuels has been carried out for sodium cooled fast reactors with the aim of technology development on volume reduction and mitigation of degree of harmfulness of radioactive waste. As a part of the development, thermal properties and irradiation behaviour of MA-bearing MOX have been investigated. It was reported that Am content in MOX significantly affected various properties. Thermal properties and irradiation behaviour of MA- bearing MOX fuels were reviewed, and effect of Am content on their properties were evaluated in this work.

9:00 AM

(PACRIM-S25-035-2017) Fabrication of $(U,Ce)O_2$ and $(U,Am)O_2$ pellets with controlled porosity from oxide microspheres

L. Ramond*[1]; P. Coste[1]; M. Bataille[1]; S. Picart[1]; A. Gauthé[1]

1. CEA, France

$U_{1-x}Am_xO_{2\pm\delta}$ mixed-oxides are considered as promising compounds for americium heterogeneous transmutation in Sodium Fast Reactor. Porous microstructure is considered in order to facilitate helium release and to reduce pellet swelling during irradiation and under self-irradiation. This study focuses on determining the experimental parameters necessary to the fabrication of porous ceramic pellets with controlled porosity from mixed-oxide microspheres obtained by the Weak Acid Resin process. More precisely, U-Ce mixed-oxide microspheres were first synthesized by co-loading UO_2^{2+} and Ce^{3+} cations onto carboxylic resin beads, Ce being used as a surrogate of Am. Calcination under air followed by reduction under Ar/4vol.%H_2 led to the mineralisation of the organic matter and to the formation of $(U,Ce)_3O_8$ and $(U,Ce)O_2$ microspheres, respectively. The specific mix of these spheres permitted to obtain, after pelletization and reductive sintering, an optimized porous microstructure (88%TD, 8% open porosity). Indeed, the reduction of $(U,Ce)_3O_8$ into $(U,Ce)O_2$ during the sintering is accompanied by the formation of open porosity, mainly due to a 3% decrease of the lattice volume and to an oxygen release in the H_2O form. Parameters found for $(U,Ce)O_2$ were applied to the fabrication of the highly active $(U_{0.9}Am_{0.1})O_2$ pellets. Finally, a $(U_{0.9}Am_{0.1})O_2$ pellet with controlled porosity was fabricated.

9:15 AM

(PACRIM-S25-036-2017) Fabrication process of neutron absorber inserted oxide fuel pellet

Q. M. Mistarihi[1]; M. Yahya[1]; Y. Kim[1]; H. Ryu*[1]

1. Korea Advanced Institute of Science and Technology, Republic of Korea

A new design for burnable absorber bearing fuel was proposed by inserting lumped Gd_2O_3 inside oxide fuel pellet in order to improve the neutronic performance of nuclear fuel for pressurized light water reactors. The Gd_2O_3 particle inserted surrogate fuel pellets using 8% yttria stabilized zirconia (8YSZ) were fabricated by using cold isostatic pressing (CIP) and microwave (MW) sintering techniques. The microstructures of sintered samples were characterized by scanning electron microscopy (SEM) and X-ray diffractometry (XRD). The effects of the sintering temperature, the size and volume fraction of Gd_2O_3, and doping of Gd_2O_3 with zirconia on the sinterability of Gd_2O_3 inserted 8YSZ pellets were investigated. It was found that by doping Gd_2O_3 with zirconia to control the phase transformation during sintering, the sinterability of the Gd_2O_3 inserted pellets by MW can be improved and the interfacial crack formation owing to shrinkage difference can be reduced.

9:30 AM

(PACRIM-S25-037-2017) Feasibility Study of Zirconium Silicide as a Heavy Reflector in the Energy Multiplier Module (EM^2)

G. Jacobsen*[1]; H. Choi[1]; E. Song[1]; C. Deck[1]

1. General Atomics, Nuclear Technologies and Materials, USA

General Atomics is developing an advanced gas cooled reactor, the Energy Multiplier Module (EM^2), a long burn fuel cycle reactor that is passively safe and economically competitive with natural gas. A compact core featuring a high-efficiency reflector material is necessary for EM^2 to achieve its high net efficiency and long lifetime. A physics analysis was performed to compare zirconium silicide (Zr_3Si_2), a novel heavy reflector material, versus a more typical light reflector material like beryllium carbide (Be_2C). Zr_3Si_2 was found to reduce issues associated with power peaking that were present in Be_2C, avoiding the need for a thermal neutron filter or a complex fuel enrichment scheme at the core periphery. Based on these results a laboratory scale demonstration of Zr_3Si_2 fabrication was performed. Thermal and mechanical properties of the resulting Zr_3Si_2 monolith, including coefficient of thermal expansion, thermal conductivity, and pellet transverse rupture strength, were obtained and are compatible with the intended use as a heavy reflector. A scaled down version of an EM^2 reflector block was successfully fabricated as a proof of principle. *This work is supported by General Atomics internal funding.

9:45 AM

(PACRIM-S25-038-2017) Hot Pressing of CeO_2 as a Surrogate for $^{238}PuO_2$ Ceramic Fuel Pellets used in Radioisotope Thermoelectric Generators

D. Kramer*[1]; S. M. Goodrich[1]; C. D. Barklay[1]

1. University of Dayton, USA

$^{238}PuO_2$ ceramic pellets are used as the fuel in U.S. space nuclear power systems (Radioisotope Thermoelectric Generators - RTG). RTGs convert ^{238}Pu decay heat into electrical power via the application of thermoelectric modules. Over the last twenty years $^{238}PuO_2$ fueled RTGs have powered a variety of spacecraft such as; Cassini/Saturn, Curiosity/Mars, and New Horizons/Pluto. The fabrication of $^{238}PuO_2$ fuel pellets utilize several standard ceramic processing techniques including; ball milling, sieving, hot pressing, and sintering. Since $^{238}PuO_2$ is highly radioactive, great care needs to be taken in the performance of the ceramic forming operations to ensure personnel safety. Therefore, the application of a non-radioactive surrogate material (such as CeO_2) for processing studies would result in significantly reduced personnel exposures and a reduction in associated costs. Several ceramic processing unit operations have been used recently to fabricate sintered CeO_2 ceramic compacts as a cold surrogate for $^{238}PuO_2$. A series of hot press experiments with CeO_2 powder employing processing temperatures of up to 1700°C with pressures of up to 8000 psi (~55 MPa) have been performed. CeO_2 integral pellets have been obtained with examples being sectioned and polished for microstructural evaluation.

Development and Production of Critical Isotopes and Targets

Room: Kona 1
Session Chair: Alexander Gottberg, TRIUMF

10:15 AM

(PACRIM-S25-039-2017) Target materials for the production of radioisotopes: The importance of the microstructure (Invited)

J. Ramos*[1]

1. CERN, Engineering Department, Switzerland

At the ISOLDE facility (ISOL DEvice, where ISOL stands for Isotope Separator OnLine) at CERN - the European Organization for Nuclear Research - more than 1000 isotopes from 74 chemical elements are produced and delivered for physics studies. Radioactive ion beams (RIB) are produced with nuclear reactions resulting from the bombardment of thick targets with 1.4 GeV protons. By keeping the target at high temperatures, the thermalized isotopes diffuse to the material grains surface and effuse throughout the material porosity. After, they effuse through a transfer line to an ion source where they are ionized, creating a RIB. The target materials are mainly oxides, carbides or metals in powder, pellet or even liquid form. A total of more than 100 different materials have been tested where 23 are commonly used. Even though ISOL is 66 years old, it was only 10 years ago that microstructure engineering towards nanomaterials was considered to improve the isotope release processes. So far, out the existing 23 materials, 6 were investigated in that sense: multi wall carbon nanotubes (MWCNT), SiC, CaO, TiC-carbon black, UC_2-MWCNT, LaC_2-MWCNT and graphene is under study. In this presentation an overview of the target materials for RIB production used at ISOLDE will be done, where the main focus will be research and development towards nanomaterials and release modelling.

10:45 AM

(PACRIM-S25-040-2017) Recent developments on ISOL targets for the SPES project for nuclear physics and applications

S. Corradetti*[1]; L. Biasetto[2]; S. Carturan[2]; F. Borgna[2]; M. Ballan[3]; M. Manzolaro[1]; M. Innocentini[4]; P. Colombo[2]; A. Andrighetto[1]

1. Istituto Nazionale di Fisica Nucleare, Laboratori Nazionali di Legnaro, Italy
2. University of Padova, Italy
3. University of Ferrara, Italy
4. University of Riberão Preto, Brazil

The SPES project has the aim to develop an ISOL (Isotope Separation On-Line) facility at INFN-LNL (Istituto Nazionale di Fisica Nucleare – Laboratori Nazionali di Legnaro) for the production of neutron-rich Radioactive Ion Beams (RIBs). The facility is now under construction: the 70 MeV cyclotron, which will be used as the primary proton beam driver, has been installed and it is undergoing commissioning tests (alpha phase of SPES). The development of targets capable of producing and releasing radioactive isotopes is of extreme importance for the next two phases of the project: production of RIBs for nuclear physics (beta phase) and use of the facility for the production of medically relevant nuclides (gamma phase, in particular the ISOLPHARM project). In both cases, the design of a proper target is strictly related to the obtainment of porous refractory materials, which are capable to work under extreme conditions (temperatures up to 2000 °C in high vacuum) with a high release efficiency. For SPES beta, in most cases the target will be of uranium carbide (UCx) in which, by fission, isotopes in the 60-160 amu mass region are produced. In the case of ISOLPHARM, UCx will be used as well, but also other types of target materials are under consideration to produce a set of proton-rich nuclides. Recent results on target production and characterization for SPES beta and gamma are presented.

11:00 AM

(PACRIM-S25-041-2017) New Target Materials for Exotic Radioisotope Beams

A. Gottberg*[1]; P. Kunz[1]; L. Egoriti[1]; J. Wong[1]; P. Bricault[1]

1. TRIUMF, Targets and Ion Sources, Canada

The ISOL technique allows for production of radioisotope beams that are used for a wide range of experiments from nuclear physics, astrophysics, materials science, to preclinical medical research. Throughout the last decades a variety of complex materials and composites has been developed ranging from ceramic oxides, fluorides and carbides to higher order compounds. These materials are serving as spallation or fission targets in ISOL facilities worldwide, where mixed uranium carbide with excess graphite has become the reference material. While the nuclear production cross-section for each isotope is determined by the driver particle, its energy and the target isotopes, the final isotope beam intensity can fall as much as 8 orders of magnitude below the production yield. These losses mostly occur due to nuclear decay or chemical depletion on the isotope's path through the thick ISOL target towards the ion source. This motion is governed by diffusion inside the target material and its pores and is therefore closely related to the material's chemical and microstructural properties. Major ingredients to a high-performance target material are therefore a controlled and stable microstructure in the harsh conditions inside the target. In the past years engineered micro and nano structures with tailored grains and pores became available and promising attempts are made to translate their success towards high-power applications.

11:15 AM

(PACRIM-S25-042-2017) High-Power Ceramic Target Materials for Isotope Beam Production at ISAC-TRIUMF

L. Egoriti*[1]; A. Gottberg[1]; P. Bricault[1]; P. Kunz[1]

1. TRIUMF, Canada

As the only ISOL (Isotope Separation OnLine) facility worldwide, ISAC-TRIUMF is routinely operating ceramic fission and spallation under proton irradiation in the high-power regime to produce a variety of radioisotopes through nuclear reactions between the incoming beam and the target material. These products diffuse out of the target material and undergo an effusion path to the ionizer where are extracted in the form of radioactive ion beams. At TRIUMF, a variety of target materials which include UC_2, UO_2, ThO_2, TiC, NiO, ZrC and SiC have been developed in order to withstand not only high-temperature environments (up to 1500°C - 2000°C) with steep gradients, but also to allow fast transport processes which ultimately boost the RIB yields. This contribution summarizes the latest developments on carbide target materials carried out at TRIUMF and presents the ongoing work aimed at increasing the number of available target materials while improving their thermal, mechanical and transport properties.

11:30 AM

(PACRIM-S25-043-2017) Radium Targets for the Reactor Production of Alpha Emitting Medical Radioisotopes

R. Copping*[1]; D. Denton[1]; K. Murphy[1]; J. Wright[1]; E. Hickman[1]; C. Marcus[1]; D. W. Stracener[1]; S. Mirzadeh[1]

1. Oak Ridge National Lab, USA

Radium-226 ($t_{1/2}$ = 1600 years) can be irradiated in a reactor to produce a variety of important medical radioisotopes. These isotopes can be chemically separated and purified after irradiation and the Ra can be recycled for future use. Since radium is highly radioactive there are unique challenges with using radium as a target material. Also, the chemical properties of radium are not yet fully explored, so stable surrogate materials, such as Ba, are used to develop the process. In order to irradiate radium at the ORNL High Flux Isotope Reactor, it must be in a stable chemical form and in a safe and thoroughly certified target configuration. Recent efforts have focused on the identification and preparation of several radium compounds to be used as target material for irradiation followed by chemical processing to extract the desired product and recover the radium material. Radium in a stable chemical form can be blended into an Al pellet cermet and contained within a welded aluminum capsule. Due to the radioactive properties of radium, the material is handled in a hot cell, which required design, testing, and construction of in-cell welding and certification capability to seal and certify target capsules. The development of a suitable radium target material, pellet fabrication process, capsule welding, and target dissolution process and subsequent radium irradiation campaigns will be discussed.

11:45 AM

(PACRIM-S25-044-2017) Astatine - The rarest element on Earth: isotope production, fundamental properties and applications

S. Rothe*[1]

1. CERN, Engineering Department, Switzerland

The radioactive element astatine (At) is the rarest naturally occurring element on Earth. Certain isotopes of this enigmatic element possess decay characteristics which make them particularly suitable for cancer treatment through targeted alpha therapy. Natural astatine exists predominantly in the form of 218At, with a half-life of only two seconds. Its abundance is maintained by the radioactive decay of natural 238U, but its scarcity prohibits the use of these atoms for the study of even basic properties of the element. Instead, artificial production of astatine through nuclear reactions is required to obtain samples large enough for study of its chemistry and fundamental atomic properties. We will discuss the technical aspects of the astatine production and ion beam formation at the CERN-ISOLDE radioactive ion beam facility and present results from a continuing experiment to study the two fundamental atomic properties of astatine: the ionization potential and the electron affinity. We will highlight the application of astatine as radioactive payload in cancer therapy.

PACRIM Symposium 28: Advanced Materials and Technologies for Electrochemical Energy Storage Systems

Cell + Theory

Room: Waikoloa 2
Session Chair: Craig Arnold, Princeton University

8:30 AM

(PACRIM-S28-029-2017) Functioning of Insertion Battery Electrodes: Understanding the Correlation Between Local Phenomena and Macroscopic Output of Battery Cell (Invited)

M. Gaberscek*[1]

1. National Institute of Chemistry, Materials Chemistry, Slovenia

Typical lithium insertion electrode contains enormous number of active particles (up to 10^{14} per 1 cm^2 of substrate) and at least 3 or 4 other phases (binders, coatings, conductive additive, electrolyte) that provide its proper functioning. The mass and charge transport in such a system is inherently complex. A variety of transport-reaction processes occurring on local scale during charge and discharge of insertion electrodes have been identified and studied in great detail. However, it remains rather unclear how these local phenomena affect the actual battery output at various conditions of interest. We here present a general model that attempts to connect the state-of-the-art knowledge about nano-scale phenomena with the macroscopic electrochemical output of an insertion electrode. We verify the generality of the model not only by explaining the typical cell output but, in particular, by explaining various peculiar electrode characteristics such as i) the non-linearity of current voltage curves, ii) the so-called memory effect, iii) the apparent enhancement of kinetics using glassy particle surface decoration, iv) the variable slope of the Warburg diffusion tail during cell operation etc. Additionally, the model will be validated by showing new phenomena that have been unknown so far but are predicted by the model.

9:00 AM

(PACRIM-S28-030-2017) Coupling Mechanics and Electrochemistry in Li-ion Batteries: Strain Derivatives and Piezoelectrochemical Energy Harvesting (Invited)

C. B. Arnold*[1]

1. Princeton University, Department of Mechanical and Aerospace Engineering, USA

Because of their high energy densities and high working voltages, lithium-ion batteries are the most suitable energy storage choice for a variety of applications from large scale battery electric vehicles to small scale implantable medical devices. These systems are well-known to experience both mechanical and electrochemical phenomena and in this presentation, we discuss how the evolution of internal and external mechanical stress affects the electrochemical performance over the lifetime and how the electrochemical state of the system influences its mechanical properties. Starting with the internal stress state of the battery, we identify the dynamic nature of this quantity, fluctuating with charge/discharge and quantify its relation to charge derivative analysis for cell characterization. Taking our understanding one step further, we show how these relations lead to the ability to use off the shelf lithium ion batteries to harvest mechanical energy and describe a path toward materials optimization.

9:30 AM

(PACRIM-S28-031-2017) Computational insights into cation intercalation processes: Case studies of $Na_{2/3}Fe_{2/3}Mn_{1/3}O_2$ and Zr_2WO_8 (Invited)

J. Hart*[1]; O. Al Bahri[2]; N. Sharma[2]

1. UNSW Australia, School of Materials Science and Engineering, Australia
2. UNSW Australia, School of Chemistry, Australia

Understanding and controlling cation intercalation processes are essential for the development of high-efficiency lithium- and sodium-ion batteries with good long-term stability. Computational studies can provide detailed insights into the structural changes that occur during intercalation and hence the stability of different crystal structures. In this work, the structural transitions that occur during charging and discharging of O3-phase $Na_{2/3}Fe_{2/3}Mn_{1/3}O_2$ and Zr_2WO_8 are analyzed using both computational methods and synchrotron XRD measurements. For $Na_{2/3}Fe_{2/3}Mn_{1/3}O_2$, we show that a sequence of solid solution and two-phase transitions occurs, but the O3 structural motif is maintained throughout charging and discharging, accounting for the good structural stability. In the case of Zr_2WO_8, intercalation of sodium is shown to allow control of the thermal expansion coefficient. For both materials, computational methods are used to understand the sodium ion site occupancy and changes in lattice parameters and bond lengths caused by sodium intercalation.

Negative

Room: Waikoloa 2
Session Chair: Miran Gaberscek, National Institute of Chemistry

10:15 AM

(PACRIM-S28-032-2017) First-principles molecular-dynamics study for solid-liquid interface film (Invited)

K. Sodeyama*[1]

1. National Institute for Materials Science (NIMS), Center for Materials Research by Information Integration (cMI2), Japan

Lithium-ion batteries (LIBs) have attracted considerable attention for use in larger power sources. An important key of the stability and durability of the LIB is the solid electrolyte interphase (SEI) film formed at the negative electrode-electrolyte interface. To get insight of the formation mechanism of the film, we examine a probable scenario, referred as "surface growth mechanism," for electrolyte involving ethylene carbonate (EC) solvent and vinylene carbonate (VC) additive by using density functional theory (DFT). We first extracted stable SEI film components (SFCs) for the EC/VC electrolyte and constructed probable SFC aggregates via DFT molecular dynamics. We then examined their solubility in the EC solution, their adhesion to a graphite electrode, and the electronic properties. The results showed that the SFC aggregates are characterized by "unstable adhesion" to the graphite surface and "high electronic insulation" against the EC solution. These characteristics preclude explaining SEI growth up to a typical thickness of several tens of nanometers based on the surface growth mechanism. With the present results, we propose "near-shore aggregation" mechanism, where the SFCs formed at the electrode surface desorb into the near-shore region and form aggregates. The aggregates coalesce and SEI is formed. The present model provides a novel perspective for the long-standing problem of SEI formation.

10:45 AM

(PACRIM-S28-033-2017) Flexible elecrochemical energy storage devices based on 3D nitrogen-doped graphene foam with encapsulated germanium quantum dot (Invited)

H. Yang*[1]

1. Singapore University of Technology and Design, Singapore

Flexible batteries and supercapacitors have been identified as promising electrochemical energy storage devices, which have attracted extensive research attention. As one of the major challenges, the rational design of a novel electrode structure with a good flexibility, high capacity, fast charge-discharge rate and long cycling lifetimes remains a long-standing challenge for developing next-generation flexible energy-storage materials. In this invited talk, we are going to introduce the developing process for a facile and general approach to 3D interconnected porous nitrogen-doped graphene foam with encapsulated Ge quantum dot (Ge-QD@NG/NGF) yolk-shell nanoarchitecture for high specific reversible capacity (1220 mAh g^{-1}), long cycling capability (over 96% reversible capacity retention from the second to 1000 cycles) and ultra-high rate performance (over 800 mAh g^{-1} at 40 C). Our research open a way to develop the 3D interconnected graphene-based high-capacity electrode material systems, particularly those that suffer from huge volume expansion, for the future development of high-performance flexible energy storage systems.

11:15 AM

(PACRIM-S28-034-2017) Carbon Coated Metal Oxide Network for Lithium-Ion Battery Electrodes

H. Luo*[1]

1. New Mexico State University, USA

Lthium-ion batteries have been investigated for their promising application in hybrid electric vehicles. A great effort has been made to synthesize a variety of electrode materials to improve the energy density, rate capability, and cycling stability. Nanostructured materials have received much attention as electrodes due to the short ion transport lengths, higher electrode-electrode contact area, and better accommodation of the strain of lithium insertion/extraction. Here we report a facile polymer-assisted chemical solution method to grow carbon coated cobalt oxide, nickel oxide, bismuth oxide, and vanadium oxide network structures for lithium-ion battery anodes and cathodes. The carbon left from the decomposition of polymers is an effective binder between metal oxides and the nickel foam. As compared to the metal oxide powders prepared in a conventional way by using polymer binder and carbon black, these one-step direct growth electrodes showed much better lithium storage properties with high capacities, stable cyclability, and rate capability. For example cobalt oxides on nickel foam gave a capacity of 900 mAh/g at a current density of 1 A/g and 600 mAh/g at 4 A/g. The good performances of these electrodes could be attributed to intimate contact between the active material and the nickel foam, the porosity of the current collector, and the network structure of the active materials.

11:30 AM

(PACRIM-S28-035-2017) Investigation of battery conversion reaction kinetics in oxide in-plane nanostructures

J. Kim*[1]; T. Fister[1]; B. Lee[2]; A. Mane[3]; H. Suh[4]; J. Emery[5]; P. Nealey[4]; J. Elam[3]; P. Fenter[1]

1. Argonne National Lab, Chemical Sciences and Engineering Division, USA
2. Argonne National Lab, Advanced Photon Source, USA
3. Argonne National Lab, Energy Systems Division, USA
4. University of Chicago, Institute for Molecular Engineering, USA
5. Northwestern University, Materials Science and Engineering, USA

Conversion reactions, such as phase separation of a transition metal oxide into Li_2O and a reduced metal, are receiving attention because of their capability to provide specific capacities far beyond intercalation materials. However, these types of reactions suffer from irreversible capacity loss, poor rate, and potential hysteresis, due to substantial volume change and kinetic barriers. It is obvious that the interfacial processes play a critical role in the overall conversion reaction which enlists charge/mass transport through a complex network of metal-rich and lithia-rich domains and consequent nucleation/growth. To better understand the reaction kinetics, we have studied nanoscale model electrodes that take advantage of a geometrically well-defined, controllable and reproducible structure, which enables us to investigate more readily the correlation between electrochemical reactivity and electrode microstructure. We have examined structures containing arrays of spherical particles or periodic holes in the oxide matrix with tunable size and spacing. These electrodes were prepared by combining the rich phase-space of self-assembled block copolymers with sequential infiltration synthesis. Scanning probe methods have combined with both ex-situ and in-situ grazing incidence small angle X-ray scattering and diffraction to investigate the controlled phase separation of a conversion reaction.

11:45 AM

(PACRIM-S28-036-2017) Understanding Irradiation Effect on the Structure and Electrochemical Charge Storage Properties of TiO_2 Anode for Lithium-ion Batteries

H. Xiong*[1]; K. A. Smith[1]; A. Savva[1]; J. Wharry[2]; D. P. Butt[3]

1. Boise State University, Materials Science and Engineering, USA
2. Purdue University, USA
3. University of Utah, USA

Lithium-ion batteries are promising battery technologies to provide high energy and high power for applications such as electric vehicles or electrical grids. Recent studies have observed that lithium-ion battery electrode materials (e.g. TiO_2) containing intentional structural defects exhibit enhanced electrochemical charge storage capacity. In this work we investigate the irradiation effect on structure and electrochemical response of TiO_2 nanostructured electrodes through room-temperature and 250 °C proton and room-temperature O^{2+} irradiations, because irradiation is known to produce an excess of defects in a material. In parallel, we use TiO_2 single crystals to elucidate the effects of irradiating species and crystallographic orientation on defect production and provide a baseline to compare irradiation damage in the nanostructured TiO_2. We observed defect generation upon irradiation in both nanostructured and single crystal TiO_2 samples and changes in electrochemical response in nanostructured TiO_2 anode.

PACRIM Symposium 29: Advances in Polar, Magnetic and Semiconductor Materials: Extending Temperature Limits

High Frequency and High Temperature Materials

Room: Queen's 4
Session Chairs: Michael Lanagan, Penn State University; Paul Ohodnicki, National Energy Technology Laboratory

8:30 AM

(PACRIM-S29-025-2017) Development of Low Temperature Co-fired Alumina with a Small Quantity of Sintering Additives (Invited)

K. Shigeno*[1]; H. Fujimori[2]

1. National Institute of Technology (NIT), Ube College, Japan
2. Yamaguchi University, Japan

Alumina (Al_2O_3) has been widely used as electronic ceramics because of its high thermal conductivity, high physical strength and good dielectric characteristics. However, due to its high sintering temperature of approx. 1500 °C, it cannot be co-fired with conductors that have low electrical resistance such as Ag (m.p. of 961 °C) and Cu (m.p. of 1084 °C) to form a Low Temperature Co-fired Ceramic (LTCC). Hence, conventional LTCC materials contain a large quantity of glass (about 50 % of the total mass) for an achievement of low-temperature sintering, and the majority of such materials have a shortcoming, namely low thermal conductivity (about 2-5 W/mK). In this study, using CuO-TiO_2-Nb_2O_5-Ag_2O sintering additives, a densified alumina was obtained by firing at 860 °C, even though additives content was only 5 mass%. The thermal conductivity of the material was 18 W/mK, exceeding the values of conventional LTCC materials. Co-firing of above materials with Ag-electrodes was also examined in order to clarify the relationship between chemical compositions and their reactivities. When the content of Ag_2O in the additives was higher, any disappearance of Ag-electrodes was not found and dielectric properties were almost the same as those of conventional LTCC materials. These results indicated the obtained materials had possibility to be applied to LTCC modules having high radiation performances.

9:00 AM

(PACRIM-S29-026-2017) Development of efficient ferrite systems for operation at high temperature and high frequency (Invited)

P. Andalib[1]; Y. Chen[2]; V. G. Harris*[1]

1. Northeastern University, Electrical Engineering, USA
2. Rogers Innovation Center, USA

Power ferrites are considered essential to power conversion and conditioning functions. During the past decades, high frequency and low power loss ferrites have received much attention in efforts to reduce size, weight and temperature rise. In the present work, we investigate control of power loss and thermal management of ferrites by strategic substitution of cations and their impact upon the temperature dependence of total power loss as well as its impact on each loss component; hysteretic, eddy current, and residual. In particular, the effect of Ga on MnZn-ferrite power loss originates from a change in cation distribution; in that, Ga^{3+} ions preferably occupy the tetrahedral sites, whereas for excessive substitution, Ga ions will partially enter the octahedral sites, resulting in significant change to magnetic properties. As a result, there has been an impressive reduction of 139.5 to 22.6 kW/m^3 at 100°C and 500 kHz in the residual loss together with a modest reduction in P_e and P_h with the substitution of the optimal amount of Ga. A significant improvement in temperature coefficient of permeability and power loss over a temperature range of 40 to 110°C for optimally doped MnZn ferrites was also achieved, while retaining high permeability and Curie temperature. These results have great potential in providing a new pathway for the development of high efficiency ferrite cores.

9:30 AM

(PACRIM-S29-027-2017) Characterization of High Temperature Dielectrics at Millimeter Wavelengths (Invited)

B. W. Hoff*[1]; M. Hilario[1]; B. Jawdat[1]; D. Agrawal[2]; M. Lanagan[2]; J. Cheng[2]; F. Dynys[3]

1. Air Force Research Lab, USA
2. The Pennsylvania State University, USA
3. NASA Glenn Research Center, USA

The Air Force Research Laboratory (AFRL) Directed Energy Directorate is involved in an ongoing effort to characterize the dielectric properties of high temperature materials at millimeter wavelengths. Understanding the temperature dependence of dielectric properties of ceramics and high temperature semiconductor materials is required for development and employment of these materials in applications such as high power, high temperature millimeter-wave radomes and power beaming. AFRL's free-space measurement systems will be discussed as will be AFRL's efforts toward development of a high power millimeter wave heating and materials characterization experiment based on a 100 kW, 94 GHz, gyrotron source.

10:15 AM

(PACRIM-S29-028-2017) Elevated Temperature W-Band Dielectric Property Measurements of Alumina-Silicon Carbide and Yttria-Stabilized Zirconia Ceramic Composites

M. Hilario*[1]; B. W. Hoff[2]; B. Jawdat[2]

1. University of Southern California, USA
2. Air Force Research Lab, USA

The complex permittivity of Alumina, Silicon Carbide, and Yttria-Stabilized Zirconia ceramics are measured using free-wave transmission methods in the W-Band frequency range between 75-110 GHz and temperatures between 20-1000 C to investigate the high temperature electromagnetic properties of ceramic composites at millimeter-wave frequencies. The ceramics are fabricated with colloidal processing to obtain between 2-14 mol. percent Yttria in Zirconia and 0-40 wt. percent Silicon Carbide in an Alumina matrix. Chemical and microstructural analyses will be performed to identify mechanisms giving rise to millimeter-wave absorption and dielectric losses, and include scanning electron microscopy, electron dispersive spectroscopy, x-ray diffraction, AC impedance, mass spectroscopy, and DC conductivity measurements. The temperature profiles of the complex permittivity will be used in numerical simulations of heat exchanger wall heating and electromagnetic coupling relevant to dielectric heating applications using beamed energy. Millimeter-wave heating processes and interactions with candidate materials and heat exchanger configurations based on these dielectric property measurements will be investigated using a 100 kW gyrotron source operating at 94 GHz to study the high power millimeter-wave interactions with refractory ceramics at high temperature.

10:30 AM

(PACRIM-S29-029-2017) The codes of matter: A simple model for design of new class of materials (Invited)

X. Wang*[1]

1. University of Wollongong, Australia

This talk will present a number of new strategies we have developed for the design of new materials and properties. We will discuss how new electronic materials can be designed by shaping electronic band structures. Emphasize on a new class of materials, spin gapless semiconductors (SGSs) with exotic band structures, as well as their realization in practical compounds will be presented. It will be shown that the SGSs and Dirac SGSs are new and ideal platform for spintronics, massless spintronics, quantum anomalous Hall effect, and new electronic and spin states. Furthermore, the ultimate questions in material and property's design are raised: 1) How many new (electronic) materials or new (electronic) properties are still there? 2) What are they? 3) How to create them? A model, the codes of matter/materials based on the three ubiquitous and paramount attributes of all existing matter/materials, charge, spin, freedom of motion will be introduced. We will discuss the principles of the codes and their applications in material and property design. Many new types of exotic states and their possible experimental realizations will be discussed.

11:00 AM

(PACRIM-S29-030-2017) High thermal conductivity and high mechanical strength alumina base composites for chip type energy storage device packaging (Invited)

H. Kim*[1]; C. Kim[1]; E. Go[1]

1. Korea Institute of Ceramic Engineering and Technology (KICET), Nano Materials Convergence Center, Republic of Korea

Heat transfer in the electronic components has become an important issue due to miniaturization of the various devices, 3D integration, multifunctional design and use of higher application frequencies. Chip type super-capacitor package with ceramic substrate have many advantages such as a leakage proof, heat and humidity resistances, high volumetric efficiency, and high thermal conductivity compared with a conventional coin-type supercapacitor. In order to make a ultra-thin ceramic package for low profile chip type supercapacitor, a ceramic packaging substrate with a much stronger mechanical strength and a higher thermal conductivity is required. This work presents the thermal and mechanical properties of alumina based ceramic nano-composites containing yttria-stabilized zirconia with the co-addition of graphene oxide nanosheets and carbon nanotubes, or with the addition of boron nitride nanotubes. As a result, flexural strengths over 500MPa and thermal conductivities over 25 W/mK were achieved in the alumina composites while maintaining electrical insulation behavior. These electrically insulating ceramic nano-composite substrates with a high thermal conductivity and a mechanical strength may have a potential to be used as an ultra-thin and low-profile ceramic package materials for miniaturized energy storage device such as chip-type super capacitors.

11:30 AM

(PACRIM-S29-031-2017) Nanocomposite Soft Magnetic Materials for High Frequency and High Power Conversion Applications

P. Ohodnicki*[1]

1. National Energy Technology Laboratory, USA

Recent advances in wide bandgap based semiconductor devices open new opportunities for development of power electronics converter topologies which are simpler and demonstrate potential for higher power density, higher operational temperatures, and modularity. High frequency magnetic components are increasingly becoming a limiting factor in overall converter performance which creates new materials, device, and system level challenges that must be addressed for the most aggressive ranges of frequency, power, and temperature ratings now obtainable. This presentation will highlight key technical challenges for effective magnetic component design with an emphasis on high power, high frequency, and high teperature applications. An overview of recent successes and progress will also be described for a major funded initiative seeking to leverage wide-bandgap based semiconductor switching devices in conjunction with nanocomposite soft magnetics in an advanced power electronics converter topology for combined PV and energy storage grid integration at both commercial and utility scales.

11:45 AM

(PACRIM-S29-032-2017) Enhanced resonance magnetoelectric coupling in(1-1)connectivity composites

Z. Chu*[1]; H. Shi[1]; W. Shi[1]; J. Wu[1]; S. Dong[1]

1. Peking University, College of Engineering, China

Bulk magnetoelectric (ME) composites consisting of various piezoelectric and piezomagnetic materials with (3-0), (3-1), (2-2), and (2-1) connectivity have been proposed in a bid to realize strong ME coupling for next generation electronic device applications. Here, we report one-dimensional (1-1) connectivity ME composites consisting of a [011]-oriented $Pb(Mg,Nb)O_3$-$PbTiO_3$ (PMN-PT) single crystal fiber laminated with laser-treated amorphous FeBSi alloy (Metglas) and operating in L-T mode (longitudinally magnetized and transversely poled), which exhibits an enhanced resonant ME coupling coefficient of that is nearly 7 times higher than the best result published previously and also a superhigh magnetic sensitivity of Tesla (directly detected) at resonance at room temperature, representing a significant milestone in the progress of magnetoelectric materials. The theoretical analyses based on magnetic circuit and equivalent circuit methods shows that the enhancement in ME coupling can be attributed to the reduction in resonance loss of laser-treated Metglas alloy due to the nano-crystallization and the strong magnetic flux concentration effect in (1-1) configuration composites.

PACRIM Symposium 31: Advances in Bioceramics: Biomineralization and Bioinspired Materials

Engineering of Hard Tissues II

Room: Monarchy
Session Chairs: Hui-suk Yun, Korea Institute of Materials Science; Joanna McKittrick, UC San Diego

8:30 AM

(PACRIM-S31-030-2017) Biomimetic mineralized elastin-like scaffolds and surfaces for biomedical applications (Invited)

C. Aparicio*[1]; Y. Li[1]; J. Rodriguez-Cabello[2]

1. University of Minnesota, Minnesota Dental Research Center for Biomaterials and Biomechanics, USA
2. University of Valladolid, GIR Bioforge, Spain

The use of organic matrices as structural templates for bottom-up fabrication of hybrid nanocomposites is a powerful way to build advanced biomaterials for tissue engineering. By controlling mineral deposition in the organic matrices, predictable morphology of the mineralized nanocomposites can be obtained. We have designed and used elastin-like recombinamers (ELRs) as electrospun nanofibers, 3D hydrogels, and coatings to template mineralization of hydroxyapatite nanocrystals using biomimetic processes. Different from conventional mineralization where minerals are nucleated and grown or deposited on the surface of organic matrices, the minerals are deposited within the framework/fibril of the ELRs, attaining high mineral density, bioactive response, and mechanical properties similar to those of natural hard tissues. ELRs are recombinant polypeptides that self-assemble into twisted filaments. Amorphous precursors infiltrate into the nanocompartments between the ELR's ordered structures and then coalesce and crystallize. By designing the sequence of the ELRs and controlling the morphologies of ELRs matrices at different dimensional levels, diverse hybrid nanocomposites with optimized mechanical and biological properties can be constructed, suited for the treatment of hard tissue defects using regenerative medicine approaches.

9:00 AM

(PACRIM-S31-031-2017) From Structure and Mechanics of Bone and Teeth to Surface Designs of Orthopaedic Implants (Invited)

R. Wang*[1]

1. University of British Columbia, Materials Engineering, Canada

With an aging population, there are increasing demands for biomaterials and biomedical devices. In orthopaedics alone, about two million fracture-fixation devices and more than a million of artificial hip and knee joints are implanted every year. An ongoing challenge in orthopaedic implants has been the design of the implant surface to enhance its fixation to the surrounding bone tissue. We are seeking bioinspired approaches to address the interface issue in orthopaedic implants. Starting from fundamentals behind the structure-property relations, bone is a nanocomposite of collagen fibers and apatite mineral and possesses complicated hierarchical structures. Its mechanical properties are highly anisotropic, which in turn cause the bone-implant interfacial strength to be sensitive to bone structure at the interface. On the other hand, there are quite a few biological systems in which the interface with mineralized collagen tissues has been well-designed. One example is the enamel-cementum junctions in equine teeth. After a critical review of those biological systems and bone fracture, this presentation will also discuss new ideas of implant designs.

9:30 AM

(PACRIM-S31-032-2017) Bio-inspired adhesive coating of scaffold materials for bone regeneration (Invited)

H. Shin*[1]

1. Hanyang University, Bioengineering, Republic of Korea

Engineering bone regeneration has gained considerable interest in recent years due to various clinical issues and the limited availability of suitable bone grafts. Generally, natural bone healing is a multi-factorial process that is orchestrated by many cell types and a variety of chemicals as well as physical signals. Thus, designing scaffold materials with abilities to interact with bone forming cells and mineral-rich microenvironment is critical, and thereby, they can facilitate bone healing. In particular, diverse topographical and chemical features in the surface of scaffolds have been widely investigated as one of key factors to direct multi-facet processes in a bone microenvironment. Recently, inspired by adhesive properties of mussel proteins, dopamine has been reported to be rapidly self-polymerized under slightly basic solution, considered as a versatile coating on the surface of materials regardless of their surface chemistry. The polydopamine coating improved hydrophilicity and served as a template for ad-layer formation by bioactive molecules as well as minerals. In this presentation, the development of surface functionalized biodegradable scaffold materials by bio-inspired adhesive coating of dopamine and their effect on in vitro cellular activities including stem cells and in vivo bone regeneration will be discussed.

Bio-Inspiration for Mechanical Design

Room: Monarchy
Session Chairs: Joanna McKittrick, UC San Diego; Stephan Wolf, Friedrich-Alexander-University Erlangen-Neurnberg

10:15 AM

(PACRIM-S31-033-2017) Impact Resistant Biological Composites: Inspiration for the Next Generation of Multifunctional Materials

N. Yaraghi[1]; N. Suksangpanya[2]; L. Grunenfelder[1]; D. Restrepo Arango[2]; S. Herrera[1]; R. Wuhrer[3]; P. Zavattieri[2]; D. Kisailus*[1]

1. UC Riverside, Chemical and Environmental Engineering, USA
2. Purdue University, USA
3. Western Sydney University, Australia

Nature has evolved efficient strategies to synthesize complex mineralized structures that exhibit exceptional damage tolerance. One such example is found in the hyper-mineralized hammer-like dactyl clubs of the stomatopods, a group of highly aggressive marine crustaceans. The dactyl club consists of a multi-phase composite of oriented crystalline hydroxyapatite and amorphous carbonated calcium phosphate, in conjunction with a highly expanded helicoidal organization of the fibrillar chitinous organic matrix. We report a novel and previously unobserved architectural design, which we call "herringbone structure", that consists of a compacted and pitch-graded sinusoidal arrangement of helicoidally arranged alpha-chitin/hydroxyapatite fibers and exhibits a notable departure from the traditional helicoidal (Bouligand) structure found within most crustacean exoskeletons. This structure, which in combination with an outer dense particulate apatite layer, enhances stress redistribution under compressive loading and yields a tough and impact-resistant structure capable of delivering high-energy strikes without failure. The findings presented herein provide insight to the mineralization process and inspiration and ongoing design guidelines for the fabrication of next-generation impact-resistant composite materials.

10:30 AM

(PACRIM-S31-034-2017) Twisting cracks and other competing mechanisms in biomineralized Bouligand Structures (Invited)

N. Suksangpanya[1]; N. Guarin[1]; N. Yaraghi[2]; D. Kisailus[2]; P. Zavattieri*[1]

1. Purdue University, Lyles School of Civil Engineering, USA
2. University of California, Riverside, USA

The focus of this talk is to discuss some interesting mechanics problems that we encountered as we studied the extraordinary damage tolerance of the Bouligand structure, a naturally-occurring architecture typically found in arthropods such as the smashing Mantis Shrimp. We carry out a combined analytical, computational and experimental investigation of the structure-function relationship of two critical regions of the dactyl club of the Mantis Shrimp. The inner periodic region contains mainly a "flat" Bouligand structure (mineralized fiber layers stacked in a helicoidal arrangement); whereas the impact region reveals a sinusoidally-architectured Bouligand structure (also called Herringbone structure). This new type of architecture was found to be much more impact resistant than the flat Bouligand structure. Our investigation is mainly focused on the mechanics of these two different regions under different loading conditions. Our results revealed different mechanisms that could be incorporated in the creation of new impact resistant biomimetic composites. Our discussion will be focus the material capability to (1) filter shear stress waves (2) mitigate catastrophic failure and (3) distribute stress to better spread the damage.

11:00 AM

(PACRIM-S31-035-2017) Direct Measurement of Abrasion-Resistance in Sea Urchin Tooth (Invited)

H. Espinosa*[1]; A. Zaheri[2]

1. Northwestern University, Department of Mechanical Engineering, USA
2. Northwestern University, Theoretical and Applied Mechanics Program, USA

In this talk we present a nanoscale scratching tests methodology to directly evaluate the hypothesized self-sharpening phenomenon in sea urchin teeth. To assess the stress at the tip of the tooth, we employ contact mechanics analysis in order to shed light on the interplay between wearing and stress states. Understating the wearing mechanism as well as role of structural elements, such as mineral fibers and platelets, is achieved by pursuing microscopy characterization of the sea urchin teeth, at different length scales, after scratching. We will show that the developed methodology can be applied to study abrasion resistance of many species in the animal kingdom. Hence, we envision that such studies will provide insight for bottom-up design of bio-ceramic composite materials with similar wearing resistance.

11:30 AM

(PACRIM-S31-036-2017) Mapping performance trade-offs for biologically-inspired design: Mimicking the tail skeletons of syngnathid fishes (Invited)

M. Porter*[1]

1. Clemson University, USA

Modern prototyping methods, such as 3D-printing, provide convenient means to build reproducible physical models that mimic natural organismal designs for mechanical testing in controlled laboratory environments. Specific design modifications can be simplified or created to form idealized or hypothetical model systems with "adaptive" traits that can be individually tested and systematically compared. We use this approach to build "families" of biomimetic structures inspired by the tails of syngnathid fishes (seahorses, pipehorses, and pipefishes), which are compared to test hypotheses on the adaptive evolution of their skeletal systems. In this way, we subject the physical models to a variety of mechanical tests, quantify their response, and map their functional trade-offs. Upon comparison, it becomes clear how structural minutiae present in the tails of seahorses and related pipehorses provide them the unique ability to grasp.

12:00 PM

(PACRIM-S31-037-2017) Thermo-mechanical properties spider silks and low temperature derivation of graphitic fibers

T. Dugger[1]; H. Tang[1]; S. Correa[2]; S. Sarkar[1]; C. Hayashi[2]; D. Kisailus*[1]

1. UC Riverside, Materials Science and Engineering, USA
2. University of California Riverside, Biology, USA

Light-weight structural materials with high strength and durability and good resistance to impact are highly desirable for a number of applications. Nature has evolved efficient strategies, exemplified in the mineralized tissues of numerous species, to synthesize materials with exceptional mechanical properties. These tissues include both fibrous organic components and a mineral matrix. Spider silks are renowned as high-performance materials and compare favorably with the best manmade fibers in strength and toughness. The silk types and properties vary in their constituent proteins and can be customized for specific applications. Here, we investigate thermal annealing of silks and their effect on modulated mechanical properties (i.e., stiffness and hardness). We subsequently utilize synthetic processes to fabricate nanofibers with tuned diameter and graphitic content to mimic structural features within natural silks (e.g., crystalline domain content) that control strength and toughness.

PACRIM Young Investigators Forum: Design and Application of Next-Generation Multifunctional Materials-Addressing the New Millennium's Societal Challenges

Academics, Research, Industry, and Funding

Room: Kohala 4
Session Chairs: Surojit Gupta, University of North Dakota; Eva Hemmer, University of Ottawa; Valerie Wiesner, NASA Glenn Research Center

8:30 AM

(PACRIM-YIF-001-2017) The Impact of Materials Research and Education on Society (Invited)

L. D. Madsen*[1]

1. National Science Foundation, DMR, USA

Funding opportunities at the National Science Foundation (NSF) will be described with a focus on prospects involving the Division of Materials Research. Current supplemental funding opportunities will be included. All NSF proposals must have strong intellectual merit and broader impacts. Broader impacts may include training and education of undergraduate and graduate students and post-doctoral fellows, broadening participation to traditionally underrepresented groups and regions, outreach to K-12 and the public, and the impact of the research itself as it is subsequently reflected in new technologies. Researchers have had a tremendous impact on technological development and the quality of life – both a reflective and forward-looking perspective will be provided. Multifunctional materials are key to moving ahead.

9:00 AM

(PACRIM-YIF-002-2017) Do Not Forget the Right Characterization! (Invited)

I. Dutta*[1]; B. Wheaton[1]

1. Corning Incorporated, Characterization Sciences, USA

With the advent of the new millennium, the development of new multifunction materials is becoming increasingly important at the same time progressively challenging. The challenge is not lack of ideas or shortage of intellect or dearth of enthusiasm, the challenge is time, money and the complexity of application. The challenge is not make the best material for one function, but to make the best material with several attributes, within a shrinking budget and without the luxury of time. Thus to achieve these goals our new generation of materials scientists have to make fast-paced yet well informed decisions. Not only do we need the fundamental understanding of the materials processing and application, but also deep understanding of different materials characterization is imperative. In Corning Incorporated, we thrive on making new materials. In this talk we will show how right materials characterization has helped in developing new, advanced and multifunctional materials.

9:25 AM

(PACRIM-YIF-003-2017) Jumping... ahead? Travelling through a mixed research career between different countries....not permanent position reached yet (Invited)

A. Benayas*[1]

1. Institut National de la Recherche Scientifique, Energie Matériaux Télécommunications, Canada

One quick review to some of the circumstances navigated from M. Sc. in Photonics at Universidad Autónoma of Madrid (Spain), through international internships, PhD and Canada-based PostDoc stages, to finally arrive to a Visiting Scholar position at Stanford U (USA). Some exciting results about multifunctional NIR-emitting QDs are also included.

Next Generation High Temperature Ceramics based Materials

Room: Kohala 4
Session Chairs: Thomas Fischer, University of Cologne;
Indrajit Dutta, Corning Incorporated;
Akira Miura, Hokkaido University

10:15 AM

(PACRIM-YIF-004-2017) Polymer-derived ceramic sensors for High Temperature and Harsh Environment Applications (Invited)

G. Shao*[1]; C. Ma[1]; M. Jiang[1]; W. Zhao[1]; R. Zhang[2]; L. An[3]

1. Zhengzhou University, School of Materials Science and Engineering, China
2. Zhengzhou University of Aeronautics, China
3. University of Central Florida, Materials Science and Engineering, USA

The temperature measurement in harsh environments, such as turbine engines, coal gasfication systems, and high temperature sintering systems, is extensively important for it can provide real-time data for feedback control, system optimization and online health monitor, which can optimize system design, improve safety and reduce pollution. However, measuring temperature in these harsh environments is not straight forward. There are two critical challenges have to be addressed: firstly, the sensors must survive in the harsh environments; secondly, the sensor materials must maintain specific sensing properties in these harsh environments. Recently, several materials are under considerations for fabricating these sensors, such as Si, SiC. However, these materials have the drawbacks of limited testing temperatures and difficult to fabricate. In this presentation, a new class of materials of polymer-derived ceramics (PDCs) has been proposed for making high-temperature and harsh environment sensors. Polymer-derived ceramics are synthesized by thermal decomposition of polymeric precursors and possess excellent high temperature stability, high oxidation/corrosion resistance and high temperature semiconducting behavior. In this talk, several typical PDC sensor design, fabrication and performance are presented, including wired temperature sensors, wireless temperature and pressure sensors.

10:40 AM

(PACRIM-YIF-005-2017) High-temperature durability of oxide-oxide ceramic matrix composites exposed to engine-relevant conditions (Invited)

M. J. Walock*[1]; V. Heng[3]; A. Nieto[1]; A. Ghoshal[1]; D. Driemeyer[2]; M. Murugan[1]

1. US Army Research Laboratory, Vehicle Technology Directorate, USA
2. The Boeing Company, Extreme Environmental Materials, USA
3. The Boeing Company, USA

Future gas turbine engines will operate at significantly higher temperatures (~ 2000 °C) than current engines (~ 1400 °C) for improved efficiency and power density. As a result, the current set of metallic components (titanium-based and nickel-based superalloys) will be replaced with ceramics and ceramic matrix composites (CMCs). These materials can survive the higher operating temperatures of future engines at a significant weight savings over the current metallic components, i.e. advanced ceramic components will facilitate engines with higher operational energy. And while oxide-based CMCs may not be suitable candidates for hot-section components, they may be suitable for structural and/or exhaust components. However, a more thorough understanding of the processing-property relationships of these materials is needed. To this end, this work investigates the high temperature durability of unique oxide-oxide CMCs under an engine relevant environment. Flat oxide-oxide CMC panels were cyclically exposed to temperatures up to 1150 °C (2100 °F), within 240 m/s (~0.3 M) gas flows. The surface temperature was monitored by a pyrometer and thermocouple. An infrared camera was used to record the experiments and provide in situ monitoring of any defect formation. Flash thermography was used to elucidate defects present before and after the exposure.

11:05 AM

(PACRIM-YIF-006-2017) Developing Protective Coatings Resistant to Molten CMAS Damage to Enable Next-Generation, Efficient Aircraft Engines Utilizing CMC Components (Invited)

V. L. Wiesner*[1]

1. NASA Glenn Research Center, Materials and Structures Division, USA

In order to improve fuel efficiency in commercial aircraft, ceramic matrix composites (CMC) are widely considered a leading material system to replace metal-based turbine engine components, due to their lower density and high-temperature capabilities compared with traditional metallic structural materials. However, silicon-based CMCs are susceptible to oxidation and corrosion in the harsh combustion environment found in air-breathing turbine engines. Environmental barrier coatings (EBC) are being developed to protect and to improve the durability of CMC components in the hot-section of engines. The development of robust EBCs is threatened by sand, volcanic ash and other organic debris, which are regularly ingested by aircraft engines, especially in certain geographic regions. At target operating temperatures of future CMC-based aircraft engines (>1200°C), the ingested particulates melt, resulting in molten deposits with compositions corresponding to calcium-magnesium-aluminosilicate (CMAS). Molten CMAS behaves like a viscous glass that can infiltrate and chemically interact with protective coatings, ultimately causing premature failure of the CMC engine component. Degradation of leading candidate EBC materials by molten CMAS will be presented with a focus on work accomplished at NASA Glenn Research Center.

11:30 AM

(PACRIM-YIF-007-2017) Fabrication of translucent and fluorescent Eu doped $CaAlSiN_3$ bulk ceramics by spark plasma sintering

T. Takahashi*[1]; J. Tatami[2]; M. Iijima[2]

1. Kanagawa Academy of Science and Technology, Japan
2. Yokohama National University, Japan

High power LED have been desired for the application of lighting fixture, plant factory, medical device, and so on. However, commercial LED cannot be used to the application because it composes of phosphor powders and resin of low heat resistance. Therefore, resin free package is desired for high power application. In this work, we tried to fabricate the translucent and fluorescent Eu-doped $CaAlSiN_3$ (CASN) bulk ceramics. CASN is one of the famous red color phosphor and the properties as powder have been reported. We applied spark plasma sintering (SPS) technique to obtain dense CASN ceramics. Si_3N_4, AlN, Ca_3N_2 and Eu_2O_3 were used as raw materials. These powder were mixed by ball milling in toluene for 24h in 1 atm of N2 atmosphere. After mixing, centrifugal separation and vacuum drying were performed. Dried mixing powder was sintered at 1650, 1700 and 1750 deg C for 10 min with uniaxial pressing of 30 MPa. As a result, CASN bulk ceramics with good translucency and fluorescence were obtained. The relative density was achieved over 99%, and they showed the red fluorescent color by UV light excitation. The SEM showed that the developed Eu-doped CASN ceramics was composed of micron size grains. Grain growth was enhanced by firing at higher temperature. Internal and external quantum efficiencies in the sample at 0.8 mol% Eu were 66 and 52 mol% after sintering at 1750 deg C.

11:50 AM

(PACRIM-YIF-008-2017) On the development of novel MAXCER (MAX-Ceramics) Composites for Multifuncational Applications

J. Nelson*[1]; S. Gupta[1]

1. University of North Dakota, Mechanical Engineering, USA

$M_{n+1}AX_n$ (MAX) phases (over 60+ phases) are thermodynamically stable nanolaminates displaying unusual, and sometimes unique, properties. These phases possess a $M_{n+1}AX_n$ chemistry, where n is 1, 2, or 3, M is an early transition metal element, A is an A-group element, and X is C or N. The MAX phases are highly damage tolerant, thermal shock resistant, readily machinable, and with Vickers hardness values of 2–8 GPa, are anomalously soft for transition metal carbides and nitrides. In this presentation, we will present some of the recent studies for designing MAX phase reinforced ceramics composites.

GOMD Award Lectures

Norbert J. Kreidl Award Lecture

Room: Kona 5

12:05 PM

(GOMD-PL-003-2017) Stretched Exponential Relaxation of Glasses: Origin of the Mixed Alkali Effect (Invited)

Y. Yu*[1]; J. C. Mauro[2]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA
2. Corning Incorporated, Science and Technology Division, USA

Although it is indeed commonly believed that, as frozen supercooled liquids, glasses should continue to flow over the years (e.g., in the case of the stained-glass windows of medieval cathedrals), the dramatic increase of their viscosity below the glass transition temperature suggests, on the contrary, that their relaxation time is on the order of 10^{32} years at room temperature. However, a recent study conducted by Mauro et al. reported the intriguing dynamics of the relaxation of a commercial Corning® Gorilla Glass® at room temperature, over 1.5 years. Here, we report a novel atomistic simulation method allowing us to directly access the long-term (years) dynamics of glass relaxation at room temperature. Based on the simulation of a series of mixed alkali silicate glasses, we demonstrate that room-temperature relaxation is a direct consequence of the mixed alkali effect. Although both volume and energy feature a stretched exponential relaxation, our results reveal a bifurcation of the stretching exponents, with b = 3/5 and 3/7 for energy and volume relaxation, respectively. Relaxation is found to occur through the diffusion of local stressed structural instabilities inside the atomic network, which anneal each other when a compressed atomic unit meets one that is under tension.

GOMD Symposium 1: Fundamentals of the Glassy State

Glass Formation and Relaxation II

Room: Kona 4

Session Chairs: Ozgur Gulbiten, Corning Incorporated; Xiaoju Guo, Corning Incorporated

1:15 PM

(GOMD-S1-056-2017) Understanding the sub-T_g relaxation in mechanically excited chalcogenide glasses by comparison with hyperquenched glasses (Invited)

Y. Yue*[3]; A. Qiao[1]; H. Tao[1]

1. Wuhan University of Technology, China
3. Aalborg University, Denmark

We investigate the sub-T_g enthalpy relaxation in a milling derived, i.e., mechanically excited (ME) chalcogenide glass (Ag_3PS_4 glass) by comparing with the hyperquenched (HQ) ($>10^5$ K/s) oxide and metallic glasses. This has been done using differential scanning calorimetry (DSC). We have found that two distinct, but also correlated peaks of sub-T_g energy release with similar intensity occur in the ME glass during DSC upscanning. Such relaxation pattern is in strong contrast to the asymmetric peak observed in the HQ oxide and metallic glasses. The low-temperature relaxation peak of the ME glass is attributed to β-relaxation. β-relaxation originates from the local motion of mobile silver ions from unstable to relatively stable sites. The high-temperature peak is a result of the α-relaxation associated with the recovery of the distorted covalently bonded PS_4 units. However, for the HQ glasses, the low-temperature peak is manifested as a shoulder superimposed on the main peak. The HQ glasses lie significantly higher on potential energy landscape than the ME glass. This work implies that the ME glass is of higher structural heterogeneities than the HQ ones.

1:45 PM

(GOMD-S1-057-2017) Non-Newtonian Rheology of Glass-Forming Liquids: Observation of Universal Patterns (Invited)

S. Sen*[1]; W. Zhu[1]; B. Aitken[2]

1. UC Davis, USA
2. Corning Incorporated, USA

All families of inorganic glass-forming liquids display non-Newtonian rheological behavior in the form of shear thinning at high shear rates. Experimental evidence will be presented to demonstrate the existence of remarkable universality in this behavior, irrespective of chemical composition, structure, topology and viscosity. Different classes of glass-forming liquids are identified on the basis of the characteristic shear rates that mark the onset of shear thinning in these liquids and are related to the different length scales of the fundamental atomistic process responsible for global shear relaxation of the liquid.

2:15 PM

(GOMD-S1-058-2017) Contribution of relaxation processes in properties of glass articles obtained by rapid cooling

O. Prokhorenko*[1]

1. L.G.P. International, USA

The problem of formation of structure, and properties of glass obtained at rapid cooling has two very important aspects. One – is a correct analytical model of relaxation processes in glass being cooled at rates exceeding 50000 K/min. Another one – is a possibility of experimental validation of the model. To solve this problem more efficiently, one needs to do both parts of the work in parallel. The present paper considers theoretical aspect of the problem, namely, what are the limitation of phenomenological model of glass transition at interpretation of structural changes, which occur at rapid cooling. A new analytical solution based on the model of super-lattice deformation is offered as an alternative to existing models of relaxation in glass. To validate the new model a method of rapid-DSC working within an extended temperature range to reach the upper limit of the glass transition reached at rapid cooling (T_f>900ºC) is considered.

2:30 PM

(GOMD-S1-059-2017) Impact of Ta or Ti Additions on the Structure and Properties of AlP Silicate Glasses

R. Youngman*[1]; B. Aitken[1]

1. Corning Incorporated, Science & Technology Division, USA

Ternary glasses can be formed over a wide composition region in the Al_2O_3-P_2O_5-SiO_2 system without the incorporation of modifier cations. In general, the pronounced association between Al and P, leading to stabilization of $AlPO_4$-like tetrahedra in the network structure, results in glasses with high characteristic temperatures and other silica-like properties, such as low thermal expansion. For glasses along the 70% SiO_2 join, the ratio of Al to P determines many of their physical properties, driven by the concentration of fully networked polyhedra. In previous studies of yR_xO:(22.5-y)Al_2O_3:7.5P_2O_5:70SiO_2 glasses, where R is either an alkali or alkaline earth, we have shown that traditional modifiers typically charge balance Al for y<7.5, but preferentially associate with P for y>7.5, leading to significant network depolymerization. Here we focus on the impact of replacing Al with either Ta or Ti in an analogous series of glasses. Substitution of Ta for Al leads to a modest change in properties, along with a substantial simplification of the Al speciation, consistent with the decrease in Al:P ratio. Incorporation of Ta or Ti does not appear to change the P environment in glasses with Al>P. These results, along with evidence from crystallization experiments, suggest that, unlike the case of traditional modifiers, Ta or Ti preferentially associate with Al rather than P in AlP silicate glasses.

2:45 PM

(GOMD-S1-060-2017) Boron speciation in copper doped sodium aluminoborosilicate glasses

N. Lonnroth*[1]; R. Youngman[1]

1. Corning Incorporated, S&T, USA

Industrial glasses often are less than perfect for structural understanding due to their complexity. By careful composition design we attempt to understand the effect of each element onto the structure in these multicomponent glasses. Copper, with its ability to change oxidation state, gives an additional variable. Glasses have been designed to have a constant amount of tetrahedral boron by keeping Na_2O fixed and changing the amounts of SiO_2, Al_2O_3 and B_2O_3, where boron content ranges from 16.2 to 33mol%. NMR and Raman are used to study the structure of the glasses, with additional information provided by EPR and absorption measurements. We observe ring-type superstructures in all the glasses, even at the lowest boron content, indicating that the presence of boroxol rings is more prevalent than generally thought. Changes to the trigonal and tetrahedral boron line shapes with compositional changes, can mainly be explained by the relative amounts of each network building block. These details are used to deduce the effect of copper, how its oxidation state has changed with the compositional changes, and also what type of modifiers would be preferred by the network.

3:00 PM

(GOMD-S1-061-2017) Properties of nitrogen rich Mg-Ca-Si-O-N glasses

S. Ali*[1]; J. C. Mauro[2]

1. Linnæus University, School of Engineering, Department of Built Environment and Energy Technology, Sweden
2. Corning Incorporated, Science and Technology Division, USA

Mg-Ca-Si-O-N glasses containing high amount of nitrogen have been prepared by melting the mixture of Mg metal, Ca metal, SiO_2 and Si_3N_4 powders in nitrogen atmosphere using a radio frequency furnace. Chemical composition, surface morphology, glass transition temperature, hardness, reduced elastic modulus and refractive index of the glasses were investigated using X-ray (EDX) point analysis, scanning electron microscopy, differential thermal analysis, nanoindentation, and spectroscopic ellipsometry. Mg was substituted for Ca in these glasses. The obtained glasses were found to be homogenous, and most of them were not transparent in the visible region. These glasses show high values of glass transition temperature (1020°C), and crystallization temperatures (1150°C). The hardness and reduced elastic modulus increases upon substitution by Mg, up to 13 GPa and 150 GPa respectively. The refractive index of the glasses was found to decrease upon increasing substitution by Mg.

3:15 PM

(GOMD-S1-062-2017) Structure and crystallization properties of Zn aluminosilicate glasses

L. Cormier*[1]; J. Brahamcha-Marin[1]; V. Montouillout[2]

1. UPMC - CNRS, Institut of Mineralogy, Material Sciences and Cosmochimie, France
2. CNRS, CEMHTI, France

The ZnO-Al_2O_3-SiO_2 (ZAS) system is an important glass-ceramic ternary diagram due to transparency and high use temperature. There is thus a wide concern to clarify the glass structure and to understand the structure-properties relationships, in order to optimize the crystallization routes towards the formation of glass-ceramics. In glasses, Zn^{2+} ions are usually considered as being exclusively in tetrahedral environments. This is markedly different to other divalent cations in aluminosilicate glasses, such as Mg^{2+} and Ca^{2+}. As a result of this four-fold coordination, Zn is localized in a network-forming position, requiring the charge compensation by other cations. In the ZAS system, this should be provided by high-coordinated Al and, thereby, Zn content could greatly influence the coordination of Al. The structure of these glasses has been investigated using several experimental techniques: ^{27}Al high-resolution NMR, neutron and X-ray diffraction. The structural information is coupled with crystallization properties been determined by coupling DSC and in situ X-ray diffraction experiments.

3:45 PM

(GOMD-S1-063-2017) Atomic-scale in-situ observation of phase coarsening process in glass

K. Nakazawa*[1]; S. Amma[2]; T. Miyata[1]; T. Mizoguchi[1]

1. University of Tokyo, Institute of Industrial Science, Japan
2. Asahi Glass, Japan

Phase separation in glass materials is a well-known phenomenon, and it is known that its behavior largely influences to mechanical and optical properties of glass materials. Thus, the phase separation phenomenon in glass materials has extensively been investigated. However, since a direct observation of the phase separation with high spatial resolution under controlling temperature has accompanied difficulties, basic knowledges for the phase separation in the glass materials, such as nucleation and growth behaviors, are still under controversy. Here, we prepared CaO-Al2O3-SiO2 glasses with a composition of an immiscibility region by melt-quenching method. The phase separation and growth behaviors are investigated using an atomic resolution aberration corrected scanning transmission electron microscopy (STEM), electron energy loss spectroscopy(EELS), and in-situ heating experiment. We successfuly visualize the nano-meter size phase separation in the glass, and track its growth behavior at high temperature. The details will be discussed in our presentations.

4:00 PM

(GOMD-S1-064-2017) Redox processes in silicate melts

D. R. Neuville*[1]; M. Cicconi[2]

1. IPGP-CNRS-USPC, Géomatériaux, France
2. Universität Erlangen-Nürnberg, Department Werkstoffwissenschaften, Lehrstuhl für Glas und Keramik, Germany

Redox of glasses and melts is one of the most important key points in Material and Earth Sciences. Redox plays an important role during melts elaboration in furnace: for instance, viscosity properties can change as a function of redox, and also for the final product redox can affect optical properties, durability, density… But several issues are still in suspend : -i) does the same redox mechanisms occur at high and low temperature? –ii) what are the driving forces of the redox mechanisms? –iii) what is the change around the redox elements occurs during redox change? –iv) what is the change in the glass structure during redox change? To answer, at all these questions, several experiments have been made by Raman spectroscopy, X-Ray Absorption spectroscopy, viscosity measurements, and show very interesting behavior on the iron, but also on the alkali or earth-alkaline element during redox changes. During the presentation, we plan to present and discuss these results.

4:15 PM

(GOMD-S1-065-2017) Transrotational Solid State Order Discovered by TEM in Crystallizing Amorphous Films and New Model of Amorphous State Based on Curved Lattice Clusters

V. Y. Kolosov*[1]

1. Ural Federal University, Institute of Natural Sciences, Russian Federation

Exotic thin crystals with unexpected transrotational microstructure are discovered by transmission electron microscopy (TEM) for crystal growth in thin amorphous films of different chemical nature prepared by various methods. The unusual phenomenon can be traced in situ in TEM column: dislocation independent regular internal bending of crystal lattice planes in a growing crystal. Unit cell translation is complicated by small rotation realized round an axis lying in the film plane (up to 300°/μm) for different geometries: cylindrical, ellipsoidal, toroidal, saddle, etc. Transrotational microcrystal resembles ideal single crystal enclosed in a curved space. Complex skyrmion-like lattice orientation texture can be formed. Transrotational micro crystals have been eventually recognized by other authors in some vital thin film materials, i.e. PCMs for memory devices. Atomic model and possible mechanism of the phenomenon are discussed. New nanocrystalline models of amorphous state are proposed: fine-grained structures with lattice curvature (like transrotation) in grains/clusters. Thus the great variety of different transrotational lattice geometries inside fine crystal grains corresponds to different amorphous structures hardly distinguished by usual methods but inevitably resulting in distinct physical properties.

4:30 PM

(GOMD-S1-066-2017) Universality in the Non-Newtonian Shear Thinning Behavior of Simple Binary Chalcogenide Liquids in the Systems As-Se and Ge-Se

W. Zhu*[1]; M. A. Marple[1]; B. Aitken[2]; S. Sen[1]

1. UC Davis, Materials Science Engineering, USA
2. Corning Incorporated, USA

The shear rate dependence of the viscosity of As_xSe_{1-x} ($5\leq x\leq 40$) and Ge_xSe_{1-x} ($10\leq x\leq 25$) liquids is studied using capillary rheometry. All liquids display non-Newtonian rheological behavior in the form of shear thinning. The onset of such behavior is characterized by shear rates that are nearly four orders of magnitude slower than the average rate of structural relaxation. Proper normalization of the viscosity vs. shear rate data demonstrates a remarkable universality in this behavior, irrespective of chemical composition, structure, topology and temperature. The existence of such universality suggests an underlying commonality in the fundamental atomistic mechanism of shear thinning in these chalcogenide liquids. On the other hand, it questions the validity of the conventional wisdom of shear thinning arising from topological modifications of the melt structure at high shear rates, in the form of alignment of structural units facilitating viscous flow. An explanation of this intriguing behavior of glass forming liquids will be sought within the framework of the mode-coupling theory.

4:45 PM

(GOMD-S1-116-2017) Structural Changes in Lead Phosphate Glasses doped with Vanadyl

C. Churya*[1]

1. Jawaharalal Nehru Technological University Hyderabad, Tirumala Engineering College, India

A series of lead phosphate glasses doped with vanadyl were prepared by a single -step process from PbO and $NH_4H_2PO_4$. In these glasses the transmission metal ion as vanadyl VO^{2+} ion derived from $VOSO_45H_2O$ referred as VO^{2+} (VS) doped and the another vanadyl ion VO^{2+} derived from vanadium pentoxide, V_2O_5 referred as VO^{2+}(VP) is used as another dopant. A thorough Knowledge of optical properties of these transparent glasses will enable successful utilization of glasses for optical applications such as windows, filters and lasers. The optical absorption spectra of these glasses in the ultra-violet region have been recorded. The results obtained in the present work on the electronic absorption spectra observed to d-d bands. The VO^{2+} ions along with the double-bonded oxygen exist in a molecular complex which is identified as VO_5 polyhedra in lead phosphate glass network. As the PbO content in the glass increases, structural changes take's place in the network. The IR Spectra of these glass samples were recorded and presented with the results. The changes in the IR band frequencies are expected to reflect the structural changes in the glass system.

5:00 PM

(GOMD-S1-117-2017) Heterogeneous Nucleation Measurements by Differential Thermal Analysis

K. S. Ranasinghe*[1]; D. E. Day[2]; C. Ray[2]; G. Humble[3]

1. Kennesaw State University, Physics, USA
2. Missouri University of Science & Technology, USA
3. South Paulding High School, Physics and Physical Science Department, USA

The effect of concentration of platinum particles on heterogeneous nucleation was investigated in a lithium disilicate glass. The heterogeneous nucleation rate at 440C, 450C, and 470C was measured numerically using the DTA method for the lithium disilicate glass containing 0.001 and 0.005 wt% platinum along with the quenching number of nuclei for each concentrations

Glass and Entropy

Room: Kona 3
Session Chair: Lothar Wondraczek, University of Jena

1:15 PM

(GOMD-S1-068-2017) The very different ways in which “excess” entropy develops above T_g in “fragile” vs “strong” liquid systems (Invited)

C. A. Angell*[1]

1. Arizona State University, School of Molecular Sciences, USA

The rate at which entropy in a glassformer, in excess of the vibrational entropy, increases as temperature rises above T_g, is given by $dS = \int_{T_g}^{T} dC_p d\ln T$, and varies enormously because dC_p varies enormously. It is typically small for tetrahedral network liquids like BeF_2, and SiO_2 (and vitreous water), and large for unstructured liquids. Furthermore dC_p of each group then tends to change in opposite ways as temperature rises above T_g. Invoking the Adam-Gibbs equation, this is enough to explain the existence of a “strong/fragile” pattern of relaxation times in glassformers. However, it leaves quite unanswered the physics behind such very different dC_p behavior. To help make progress here we turn to observations on other condensed matter systems that show ergodicity-breaking on cooling, and small dC_p at T_g, namely certain plastic crystals and order-disorder alloys. Each group exhibits sharp “lambda” transitions at temperatures far above T_g. Phenomenological relationships are discussed.

1:45 PM

(GOMD-S1-069-2017) Revisit of entropy issues by using the concept of spatial sampling (Invited)

A. Takada*[1]; R. Conradt[2]; P. Richet[3]

1. Asahi Glass Company, Japan
2. RWTH Aachen University, Germany
3. Institut de Physique du Globe de Paris, France

The entropy of glass is very important to understand the phenomena of relaxation, glass transition and viscous flow. One of several approaches to deepen the understanding is to extend the authors’ concept named “spatial sampling” with which entropy is defined with each passing moment even in non-equilibrium. The merits and demerits of this concept over the other methods are discussed in the cases of relaxation and glass transition. Several unsolved problems related to statistical thermodynamics are also discussed.

2:15 PM

(GOMD-S1-070-2017) Configuration entropy: A glimpse into the molecular structure of melts (Invited)

D. R. Neuville*[1]; C. Le Losq[2]

1. IPGP-CNRS-USPC, Géomatériaux, France
2. The Australian National University, Research School of Earth Sciences, Australia

The configurational properties of melts and glasses provide fundamental information needed to characterize magmatic and industrial processes. In particular, the configurational entropy of melts at temperature T, $S^{conf}(T)$, is of fundamental interest. Indeed, it is linked to the melt configurational heat capacity Cp^{conf} and viscosity η, two critical parameters that determine melt mobility and heat exchanges. For instance, the relationship between η and $S^{conf}(T)$ is of the form $\log \eta = Ae + Be/(TS^{conf})$, with Ae and Be two constants. However, a principal difficulty is to link the “macroscopic” configurational entropy with the structure of melts. Such link is possible to do with combining viscosity measurements with structural data from Nuclear Magnetic Resonance (NMR), X-ray Absorption near the Edge Structure (XANES) and Raman spectroscopy. Indeed, from viscosity measurements at low and high temperatures, $S^{conf}(T)$ can be determined. Indeed, $S^{conf}(T_g)$ directly refers to the glass configurational entropy, such that it can be related to the glass structure studied by NMR, XANES and Raman spectroscopy.

2:45 PM

(GOMD-S1-071-2017) Spin glass transition of amorphous oxides containing transition elements (Invited)

K. Tanaka*[1]

1. Kyoto University, Japan

Experimental studies have been carried out on magnetic properties of amorphous oxides containing iron or europium ions. For iron-containing oxide glasses, a cusp corresponding to the spin-freezing is observed in the temperature dependence of zero-field-cooled magnetic susceptibility. The cusp temperature shifts to the higher temperature side as the frequency of magnetic field is increased, and the frequency dependence of the spin-freezing temperature is reasonably interpreted in terms of the dynamic scaling law with a critical exponent appropriate to the spin glass transition. The aging-memory effect is also observed in the temperature dependence of zero-field-cooled dc magnetic susceptibility. The spin glass behaviour observed under a dc magnetic field for Fe^{2+}-containing glass, which is regarded as an Ising system, can be well described in terms of the droplet model. On the other hand, interestingly, thin films of amorphous oxides containing Eu^{2+} show ferromagnetic transition and subsequently spin glass transition as the temperature is decreased. Namely, the amorphous oxides exhibit the reentrant spin glass transition, which has been never observed for other amorphous oxides. The ferromagnetic transition is ascribable to the magnetic interaction between 4f spins of the Eu^{2+} ions via 5d state.

3:15 PM

(GOMD-S1-072-2017) On the relation between glass composition, local structure, and macroscopic properties

R. Conradt*[1]

1. RWTH Aachen University, GHI, Germany

Understanding the relation between the structure of a glass and its macroscopic properties has been a challenge for many decades. The static disorder of glass structure in space, i.e., the absence of a translational symmetry at the atomic scale, poses a major difficulty to such understanding. Things become, however, much easier when macroscopic properties are taken into consideration which are based on atomic vibrations or elastic waves, like: heat capacities and elastic moduli. These quantities reflect randomly distributed and distinctly directed phononic states, respectively, and thus are excellent probes to reveal local structural features of materials. At temperatures well above Debye’s temperature, heat capacities probe the short-range order, i.e., the nature of cation-anion polyhedra, whereas the elastic properties probe the linkage among such polyhedra. As concluded from expeimental data and ab-initio calculations alike, these features are close-to-identical for glasses and their isochemical crysalline low-density polymorphs. On this basis, glass properties, even of multicomponent glasses, can be predicted from the nature and constitutional relations of their crystalline counterparts. Finally, it is show how this principle can be extended to predicting viscosity.

3:45 PM

(GOMD-S1-073-2017) Collective modes and thermodynamics of the liquid state (Invited)

K. Trachenko*[1]

1. Queen Mary University of London, Physics, United Kingdom

A theory of liquid-glass transition requires understanding thermodynamic properties of liquids. This has turned out to be a long-standing problem in physics. Landau&Lifshitz textbook states that no general formulas can be derived for liquid thermodynamic functions because the interactions are both strong and system-specific. Phrased differently, liquids have no small parameter. Recent experimental and theoretical results open a new way to understand liquid thermodynamics on the basis of collective modes (phonons) as is done in the solid state theory. There are important differences between phonons in solids and liquids, and we have recently started to understand and quantify this difference. I will review collective modes in liquids including high-frequency solid-like transverse modes and will discuss how a gap in the reciprocal space emerges and develops in their spectrum. This reduces the number of phonons with temperature, consistent with the experimental decrease of constant-volume specific heat with temperature. I will discuss the implication of the above theory for the liquid-glass transition and the change of heat capacity at Tg. I will also mention how this picture can be extended above the critical point where we have recently proposed a concept of the Frenkel line on the phase diagram separating liquid-like and gas-like states.

4:15 PM

(GOMD-S1-074-2017) Pressure-Promoted Relaxation: Access to Forbidden Glassy States (Invited)

M. M. Smedskjaer*[1]; M. N. Svenson[1]

1. Aalborg University, Department of Chemistry and Bioscience, Denmark

The structure and properties of glass can be modified through compression near the glass transition temperature (T_g), but once the compressed glass undergoes annealing near T_g at ambient pressure, the modified structure and properties will relax. First, we show how the property relaxation is correlated with both the local and the medium-range structural relaxation in a sodium borate glass that has first been compressed at its T_g at 1 GPa, and then annealed at ambient pressure under different temperature-time conditions. The pressure-induced structural conversions are reversible during ambient pressure annealing near T_g, but exhibit a dependence on the annealing temperature. However, the conversions between structural units cannot account for the pressure-induced densification, and instead we suggest the packing of structural units as the main densification mechanism. Second, we also show that by first compressing an aluminosilicate glass at 1 GPa at T_g, followed by sub-T_g annealing in situ at 1 GPa, it is possible to combine the effects of hot compression and ambient pressure annealing. Through density, hardness, and heat capacity measurements, we demonstrate that the effects of hot compression and sub-T_g annealing can be combined to access a “forbidden glass” regime of high density and hardness that is inaccessible through thermal history or pressure history variation alone.

4:45 PM

(GOMD-S1-075-2017) Particle dynamics of disordered colloidal suspensions with varying interparticle attraction strength

P. Habdas[1]; Z. Brown[1]; M. Iwanicki[3]; M. Gratale[2]; X. Ma[2]; A. Yodh*[2]

1. Saint Joseph’s University, Department of Physics, USA
2. University of Pennsylvania, Department of Physics and Astronomy, USA
3. University of Pennsylvania, Department of Biochemistry and Biophysics, USA

We experimentally investigate properties of cooperative rearrangements in dense colloidal suspensions as a function of increasing inter-particle attraction. Attractive interactions between colloidal particles are induced by polymer depletion forces at fixed particle volume fraction. We vary inter-particle attraction strength and concurrently measure particle trajectories by confocal microscopy at each attraction strength. We find that inter-particle bonding causes an increasing number of particles to undergo cooperative displacements; the length scale associated with these rearrangements exhibits reentrant behavior. Other dynamical quantities such as the mean square displacement, the long-time diffusion constant, and the non-Gaussian parameter also exhibit changes as a function of attraction strength. Specifically, ergodic fluids exhibited accelerated dynamics at short times and increasingly heterogeneous dynamics over the largest length scales. Rearrangements within these samples were larger than in the repulsive glass, and heterogeneous dynamics were found across large length scales. An attractive glass was observed showing the effects of strong particle bonding exhibiting large numbers of rearranging particles qualitatively different than the repulsive glass.

5:00 PM

(GOMD-S1-076-2017) Investigation of relaxation mechanisms in glasses by combined DSC, Raman and Brillouin spectroscopies

A. Veber*[1]; M. Cicconi[1]; D. de Ligny[1]

1. Friedrich-Alexander University Erlangen-Nürnberg, Materials Science and Engineering, Germany

Recently a new experimental facility coupling DSC, Raman and Brillouin spectroscopies were implemented. Observation of thermal, elastic and structural properties simultaneously in situ is useful to study any transition, that implies several order parameters and could exhibit multiple relaxation phenomena. The technique was applied for studying relaxation mechanisms near the glass transition in phosphate, germanate and borosilicate glasses. The glasses were quenched in the DSC with different cooling rates(q_c) to obtain different fictive temperatures(T_f) and were investigated close to the glass transition temperatures (T_g) during the heating with a constant rate. Thermal properties, structure and elastic characteristics of the glasses depend on the q_c. Shift of the vibrational bands is observed. Raman and Brillouin spectroscopies data are consistent with the calorimetric measurements: the glass transition can be easily determined separately for each of the techniques. The transition temperatures, obtained from Raman and Brillouin data using a 2-state model, differ from T_g and T_f temperatures commonly determined calorimetrically. A two state model is not fully consistent with the experimental data for fast-quenched glasses evidencing additional relaxations occurring before the formal glass transition.

5:15 PM

(GOMD-S1-077-2017) Effect of water on structure and dynamics of sodium borosilicate glasses

H. Behrens*[1]; U. Bauer[1]; S. Reinsch[2]; J. Stebbins[3]; E. I. Morin[3]; P. Kiefer[4]; J. Deubener[4]

1. Leibniz University of Hannover, Institute of Mineralogy, Germany
2. BAM Federal Institute for Materials Research and Testing, Germany
3. Stanford University, USA
4. TU Clausthal, Germany

Borosilicate glass has a wide range of technical applications due to its high chemical durability and thermal-shock resistivity. Here the effect of H_2O on 16 Na_2O, 10 B_2O_3,74 SiO_2 glass is studied over a wide range of water contents from 0 to 8 wt.%. MIR spectra give evidence for the coexistence of strongly and weakly H-bonded hydrous species. Evaluation of NIR bands at 5200 cm^{-1} (molecular H_2O), 4700 cm^{-1} (B-OH), and 4500 cm^{-1} (Si-OH) reveal that OH groups dominate up to ~6 wt.% H_2O, with B-OH/Si-OH of ≈ 0.8. The incorporation of low amounts of H_2O has strong impact on structure. NMR spectra of nominally dry glasses indicate a significant fraction (12 %) of 3-coordinated boron, but almost all boron is 4-coordinated after addition of 3 wt.% H_2O. Raman spectra show that hydration results preferentially in transformation of Q^4 to Q^2 while Q^3 remain unchanged, probably stabilized by bonding to BO_4 tetrahedra. Viscosity measurements and differential thermal analysis give consistent results, confirming strong decrease of the glass transition temperature with addition of water from 849 K (dry) to 540 K (5 wt% H_2O). An additional relaxation mechanism in hydrous glasses is inferred from dynamic mechanical analysis and is assigned to cooperative processes involving hydrous species. It is postulated that this relaxation mechanism plays an important role in crack growth kinetics.

GOMD Symposium 3: Optical and Electronic Materials and Devices: Fundamentals and Applications

Quantum Processes in Glasses I

Room: Kona 2

Session Chairs: S. Sundaram, Alfred University; Jun Yang, Corning Incorporated

1:15 PM

(GOMD-S3-049-2017) Quantum Mechanical Simulations of Silicate Glasses (Invited)

A. Cormack*[1]

1. Alfred University, USA

Although classical simulations are computationally much cheaper, some processes cannot be properly modeled without the explicit inclusion of electronic structure, particularly where reactivity is concerned. The various approaches to quantum mechanical simulations will be reviewed, along with their advantages and disadvantages. Their application will be discussed and illustrated with respect to the interaction of water with silicate glasses.

1:45 PM

(GOMD-S3-050-2017) Large-Area Luminescent Solar Concentrators Fabricated by Doctor-Blade Deposition of Quantum Dots onto Window Glass (Invited)

K. Wu[1]; H. Li[1]; J. Lim[1]; V. Klimov*[1]

1. Los Alamos National Laboratory, Chemistry, USA

Luminescent solar concentrators (LSCs) are envisioned to reduce the cost of solar electricity by decreasing the usage of more expensive photovoltaic (PV) materials and diminishing the complexity of multi-cell PV modules. The LSC concept can also enable unconventional solar-energy conversion devices such as PV windows that can be especially useful in highly populated urban areas. Here we demonstrate low-loss, large-area (up to ca. 90×30 cm^2) LSCs fabricated from highly emissive core/shell quantum dots (QDs) whose optical spectra are tailored such as to minimize self-absorption of waveguided radiation. For improved compatibility with a polymer matrix and enhanced stability, QDs are encapsulated into silica shells. The QD/polymer composites are processed into devices using standard doctor-blade deposition onto window glasses. The fabricated semi-transparent devices demonstrate high optical efficiencies of more than 10% for dimensions up to tens of centimetres. The doctor-blade method presented here is highly versatile and can be applied to virtually any flat surface made of an arbitrary material. The use of this inexpensive and highly scalable technique may represent a practical route to real-life applications of QD-LSCs in both semitransparent solar windows and high-efficiency collectors of sunlight for existing PV cells.

2:15 PM

(GOMD-S3-051-2017) Glassy dynamics and a universal viscosity collapse of supercooled liquids as a consequence of the equilibrium liquid to solid transition (Invited)

Z. Nussinov*[1]

1. Washington University in Saint Louis, Physics, USA

We review the underpinning of the microcanonical ensemble and the more refined (and explicitly quantum) "Eigenstate Thermalization Hypothesis". We then find and apply a simple corollary of these to analyze the evolution of a liquid upon supercooling to form a structural glass. Simple considerations lead to predictions for general properties of supercooled liquids. Amongst other things, a collapse of the viscosity of supercooled fluids is predicted from this theory. This collapse indeed occurs over 16 decades of relaxation times for all known types of glass formers.

2:45 PM

(GOMD-S3-052-2017) Surface Passivation of Quantum Dots in Glasses (Invited)

C. Liu*[1]; M. Xia[1]; J. Han[1]; X. Zhao[1]

1. Wuhan University of Technology, China

Glasses containing semiconductor nanocrystals (Quantum Dots, QDs) have attracted a lot of attention due to the particular optical and electronic properties of QDs induced by the quantum confinement effects. In recent years, II-VI and IV-VI QDs have been fabricated in glasses, tunable photoluminescence in the visible and near-infrared wavelength spectral range has been achieved, showing great potentials towards various light sources, solar energy harvesting, information processing and etc. Glasses have been utilized as host materials for various active ions for opt-electronics applications. Incorporation of QDs into the glass can not only prevent the agglomeration, but also guarantee the chemical and thermal stability of QDs. However, as the inorganic amorphous solids, embedding the QDs inside the glass matrix prevents the further access to the surface modification. As a results, quantum efficiency of photoluminescence from QDs embedded in glasses was always found to be low. Therefore, to foster the applications of QDs, it is necessary to find the possible solution to passivate the surface of QDs. In our recent work, QDs with partial surface passivation was achieved and quantum efficiency of II-VI QDs was increased to >50%. Details on the formation, structural and optical properties of QDs doped glasses will be discussed.

Quantum Processes in Glasses II

Room: Kona 2

Session Chairs: S. Sundaram, Alfred University; Jun Yang, Corning Incorporated

3:30 PM

(GOMD-S3-053-2017) Controllable Fabrication of Novel All Solid-State Quantum Dot-doped Glass Fibers (Invited)

G. Dong*[1]; J. Qiu[1]

1. South China University of Technology, School of Materials Science and Engineering, China

PbS quantum dot (QD)-doped glass and fibers have gained great attention due to their broadband tunable near-infrared (NIR) luminescence, which are potentially applied as the gain medium of broadband amplifiers and lasers. However, due to the rapid uncontrollable growth of QDs during fiber-drawing process, it is difficult to draw high quality QD-doped glass fiber by traditional fiber-drawing methods. Just recently, a novel glass fiber-drawing method named "melt-in-tube" has been developed in our group. High-quality all solid-state PbS QD-doped glass fibers were successfully fabricated by using the "melt-in-tube" method for the first time. The precursor fibers were firstly prepared without any obvious element diffusion or crystallization by drawing the fiber preform at a heating temperature where the fiber core was already melted while the fiber cladding was softened. And then the QDs were precipitated evenly in the matrix of glass fiber core after a careful heat treatment at low temperature. From the PbS QD-doped glass fibers, intense wavelength-tunable broad NIR emission bands were observed upon an excitation. Our results suggest that PbS QD-doped glass fiber is a promising gain medium of broadband fiber amplifiers and wavelength-tunable lasers. More importantly, the "melt-in-tube" method will pave a new way for fabricating various functional QD-doped glass fibers.

4:00 PM

(GOMD-S3-055-2017) Electric Field – Assisted Formation of Quantum Dots in Glasses

B. B. Tesfamariam*[1]; H. Lee[1]; J. Wang[2]; J. Heo[1]

1. Pohang University of Science and Technology(POSTECH), Department of Materials Science and Engineering, Republic of Korea
2. Wuhan University of Technology, State Key Laboratory of Silicate Materials for Architectures, China

Semiconductor quantum dots (QDs) made of lead chalcogenide provide size dependent optical properties and tunable emission of QDs in glasses and therefore, intensively investigated optical communication fiber amplifiers and infrared laser sources etc... Diameters of QDs can be controlled through modulation of the heat treatment condition, using laser irradiation and by doping third elements. Current work reports, the infrared luminescence properties of PbSe QDs by applying an electric field as well as by changing host glass compositions. The absorption and photoluminescence bands of PbSe QDs in silicate glasses showed a red-shift as the concentration of GeO_2 and B_2O_3 increased under the same heat treatment conditions. As GeO_2 added up to 40 mol% into silicate glasses, the absorption bands shifted from 801 nm to 2593 nm and PL emission wavelength red-shifted to 2619 nm at the same heat treatment condition (470 °C/10 h). It is due to the enhanced diffusivity of ions in glasses that leads to formation of large PbSe QDs. Applying the Electric field also facilitated diffusion of ions in glasses that results the precipitation of large QDs in glasses that lead to the red-shifts in absorption and photoluminescence bands.

Glass-based Optical Devices

Room: Waikoloa 3
Session Chair: Heike Ebendorff-Heidepriem, University of Adelaide

1:15 PM

(GOMD-S3-056-2017) Side-emitting optical fiber: Fabrication routes, properties and applications in functional lighting (Invited)

L. Wondraczek*[1]

1. University of Jena, Germany

Lateral light emission from fiber waveguides has been of continuous interest for, e.g., design and interior illumination. In this talk, some of the previous applications will be reviewed, focusing on fabrication of low-cost fiber with homogeneous emission properties. From this consideration, issues will be identified which need to be overcome for future application in functional lighting, i.e., illumination tasks in which the side-emitting fiber is used to trigger photochemical or other reactions. These issues comprise mechanical strength such as required for incorporating side-emitting fiber into textile devices, and spectral emission, in particular, of UV or NIR light for applications ranging from water desinfection to biomedical purposes. An alternative type of fiber as well as techniques for controlling the scattering profile from fiber surfaces will be presented, together with examples of the above noted applications.

1:45 PM

(GOMD-S3-057-2017) New technique for direct laser writing of a low-loss waveguide in chalcogenide glasses

D. Le Coq*[1]; E. Bychkov[2]; P. Masselin[2]

1. University of Rennes 1, ISCR - Glass and Ceramic Team, France
2. University of Littoral Côte d'Opale, France

In this contribution, we report on low-loss waveguides in chalcogenide glasses written by a direct laser technique in an original configuration. The waveguides consist in a multicore-type and are composed of several channels arranged on a hexagonal lattice. Each channel is obtained by stacking voxels of refractive index variation obtained by femtosecond laser pulse burst in a static position. The distance between the channels can be varied to adapt the diameter of the waveguide, while the duration of laser burst controls the magnitude of the effective index and the propagation losses. Consequently, this process allows an independent control of the core diameter and the magnitude of the refractive index contrast between the core and the cladding. In addition, this technique leads to the lowest propagation losses never reached for a buried waveguide in a chalcogenide glass.

2:05 PM

(GOMD-S3-058-2017) Nanocomposite Melting Gels with Gold Citrate Nanospheres

S. Kallontzi*[1]; L. Fabris[1]; L. C. Klein[1]; A. Jitianu[2]

1. Rutgers University, Materials Science and Engineering, USA
2. Lehman College-CUNY, Department of Chemistry and Biochemistry, USA

Melting gels are modified silica gels that can switch from viscous to rigid, when subjected to heating followed by cooling. This cycle can be repeated many times, unless the material is heated high enough that it becomes fully cross-linked. Melting gels are prepared by sol-gel processing from functionalized siloxanes, such as methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DMDES). MTES and DMDES can be mixed in various ratios, leading to melting gels displaying different characteristics and distinctive networks. After heating to the temperature of consolidation, the material becomes permanently rigid, forming a hybrid glass-like matrix. Gold citrate nanospheres have been added to the melting gels during synthesis at different concentrations, to tune the temperature and time of consolidation. The UV-Vis spectra reveal that mondisperse gold nanoparticles undergo a size change and a plasmon shift as a consequence of their embedding in the melting gels, as also observed in consolidated hybrid glasses. Raman analysis provides information on the nature and strength of the atomic interactions among the melting gels, the nanospheres, and their interface. In addition, by varying the melting gel compositions and the concentrations of the gold nanospheres, unique nanocomposite materials are generated that can be leveraged for surface-enhanced Raman scattering applications.

2:25 PM

(GOMD-S3-059-2017) Optical properties and structure in tin silicate glasses

A. Saitoh*[1]; K. Suzuki[1]; G. Tricot[2]; Y. Hashida[1]; M. Itadani[1]; H. Takebe[1]

1. Ehime University, Materials Science and Engineering, Japan
2. LASIR UMR-CNRS 8516, Université de Lille 1, France

The optical properties of glasses with zero photoelastic constant (PEC) are particularly necessary for maintaining the polarization light direction under external stress and heat in the case of polarization or interference optical devices. One of the critical optical devices using zero-PEC glasses is required for an optical-fiber-type current sensor for use in systems that monitor the current in electrical busbars. In this study we will show low/zero PEC composition in tin silicate glass systems with some optical properties designed to the lead free fiber-type current sensors because of problems associated with the toxicity of lead element. The glasses were made by melt quenching method. In the melting environment of less than 10^{-3} atom of partial O_2 pressure were required for preventing oxidation of divalent tin ions. Disc shaped samples were provided for PEC measurement used by 632.8 nm of wavelength of light. We will mention thermal properties for reshaping and structure for understanding low PEC silicate glasses. The glass structure was analyzed by 1D ^{29}Si and ^{119}Sn nuclear magnetic resonance spectroscopy.

2:45 PM

(GOMD-S3-060-2017) Generation of Au and Au/Ag nanostructures in soda-lime silicate glasses by ArF excimer laser irradiation

M. Dubiel*[1]; M. Heinz[1]; J. Meinertz[2]; J. Ihlemann[2]; A. Hoell[3]

1. Martin Luther University Halle-Wittenberg, Institute of Physics, Germany
2. Laser-Laboratorium Göttingen e.V., Germany
3. Institute of Nanospectroscopy, HZB Berlin, Germany

Plasmonic Au/Ag nanoparticles in glass surfaces allow to create a tunable surface plasmon resonance in a wide range of wavelengths. These nanostructures enable to realize manifold applications in photonic and optoelectronic devices. Here, the Au and Au/Ag structures have been created in soda-lime silicate glasses using ArF excimer laser irradiation (193 nm) well below the ablation threshold of the glass matrix. At first, either the pure or the silver/sodium ion-exchanged float glasses have been coated by a thin Au layer and then irradiated by ArF pulses. The maximum pulse energy was 500 mJ/cm^2 and the pulse repetition rate was up to 50 Hz, at which the pulse numbers ranging up to 10 000. The optical spectroscopy demonstrated the shift of the surface plasmon resonance between 420 and 620 nm. The experiments by small angle X-ray scattering experiments (SAXS) proved the formation of pure Au or Ag particles as well as of bimetallic Au/Ag species. These results showed that such procedures allows the space selected generation of plasmonic nanostructures inside the glass surface by implantation like processes.

3:05 PM

(GOMD-S3-061-2017) Enhancing Accuracy of Refractive Index Determination of Glass Beads via Retroreflectivity Measurement

S. Shin[1]; W. Chung[2]; J. Kim[3]; S. Cho[4]; Y. Choi*[1]

1. Korea Aerospace University, Republic of Korea
2. Kongju National University, Republic of Korea
3. Korea Institute of Ceramic Engineering and Technology (KICET), Republic of Korea
4. Ewha Industrial Co. Ltd., Republic of Korea

Glass beads are a key ingredient material for use in the road marking of which retroreflection enhances the visibility during the nighttime or rainy season. As the safety-related concerns keep increasing in connection with the invisible lane marking, glass beads with refractive index tantamount to or higher than 1.9 are gathering increased attention. As for measurement of refractive index of glass that is in the form of a bead, the immersion fluid method, i.e, the Becke line method, has been conventionally employed, which necessitates the use of index-matching fluids. However, this convenient measurement technique cannot be applicable to glass beads of refractive index greater than 1.9 because index-matching fluids with such high refractive indexes are not commercially available anymore due to the toxicity issue caused by the incorporation of arsenic. On the other hand, measurement of the retroreflectivity of glass beads is quite facile and can be used to indirectly deduce their refractive index. Based on these considerations, we have aimed to enhance the accuracy of refractive index derived from the retroreflectivity measurement. Glass beads of known refractive index were tested, and the measured retroreflectivity values were calibrated with the calculated values in an effort to make thus determined refractive index more accurate and reliable.

3:40 PM

(GOMD-S3-062-2017) Pulsed Laser Deposition of Transparent Fluoride Glass

C. W. Bond*[1]; R. L. Leonard[1]; A. Petford-Long[2]; J. Johnson[1]

1. University of Tennesee, USA
2. Northwestern University, USA

Researchers have typically relied on the use of a fluorine-containing processing gas to prevent the reduction of zirconium in fluorozirconate (FZ) glasses deposited by pulsed laser deposition (PLD). The reduction of zirconium is unfavorable because it leads to the creation of absorption centers in the glass matrix and a reduction in transparency. The use of fluorine-containing processing gas has several drawbacks, however, most notably safety concerns relating to its toxicity. We have successfully deposited transparent, high-quality FZ glass on fused silica substrates by PLD, without the need for a processing gas. The ablation target was a ZLANI composition, consisting of the fluorides of zirconium, lanthanum, aluminum, sodium, and indium. It is believed that incorporation of indium into the glass matrix prevented the reduction of zirconium. The as-deposited glasses have a small amount of coloration, likely due to the presence of F-centers created during the deposition process, which is greatly diminished after heat treatment. The synthesis process and optical characterization results for these glass films will be discussed, along with some of their possible applications. This research was supported by the National Science Foundation under grant # DMR 1600783.

4:00 PM

(GOMD-S3-063-2017) Glasses for diffusion-based IR-GRIN optics

D. Gibson*[1]; S. Bayya[1]; V. Nguyen[1]; J. Sanghera[1]; C. McClain[2]; M. Kotov[3]

1. NRL, Code 5622, USA
2. University Research Foundation, USA
3. Sotera Defense Solutions, USA

Graded index (GRIN) optics offer potential for both weight savings and increased performance but have so far been limited to visible and NIR bands (wavelengths shorter than about 0.9 μm). NRL has developed IR glasses for diffusion based axial GRIN lenses compatible with all IR wavebands (SWIR, MWIR and LWIR). These new optics can be used to replace multiple refractive elements in an imaging system saving size and weight. The IR-GRIN lens technology, design space and modeling considerations will be presented in this paper.

4:20 PM

(GOMD-S3-064-2017) Durable probe for reliable in-situ measurements of high-temperature NIR absorption of molten glass

O. Prokhorenko*[1]

1. L.G.P. International, USA

Reliable methods of measurements of spectral properties of molten glass have been developed during 1990's. Relatively high cost of measurements, complexity of testing equipment and need of single-use parts made of optical grade sapphire, however, allow one not to consider these methods as prototype for development of routine testing procedures. Ideally, one should have access to simple, and reliable technique taking instruments for measurements of high-temperature absorption spectra to a level of low-cost off-the-shelf probe. The present paper describes a probe for in-situ measurements (monitoring) of absorption spectra of molten glass in NIR region within the temperature range of 1000 to 1270°C typical for major forming processes. Design, and specific features of the probe providing its long-term service inside the molten glass flow are described. Different regimes of work serving various applications are considered as well.

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium II

Room: Kona 5
Session Chairs: Yoshihiro Takahashi, Tohoku University; Jianrong Qiu, South China University of Technology

1:15 PM

(GOMD-S6-004-2017) Crystallization of silicate glasses at deep and shallow undercoolings (Invited)

J. Deubener*[1]; S. Krüger[1]

1. Clausthal Univeristy of Technology, Institute of Non-Crystalline Materials, Germany

The persistence of undercooled silicate melts and their stability against crystallization during forming and cooling processes are the foundation of the glass industry while the production of glass-ceramics relies on controlling crystallization processes during a subsequent ceramization step. With respect to the underlying kinetics of the liquid-to-crystal transformation it is frequently distinguished between the terms: “glass forming ability” (GFA) and “glass stability” (GS). The former qualifies difficulties in crystallization if cooled from above the liquidus temperature while the latter describes the same behaviour if heated from below the glass transition temperature. The concept is tested for binary model glasses. It is shown that different crystallization mechanisms are generally present, i.e. homogeneous and heterogeneous nucleation. GFA is dominated by heterogeneous nucleation at shallow undercoolings, while GS is dominated by homogeneous nucleation at deep undercoolings. The results can help to explain why previous attempts to calculate critical cooling rates from homogeneous nucleation failed by orders of magnitude. In order to improve predictions of GFA from theory data on heterogeneous nucleation at surfaces of these glasses or in contact with other materials have to be included in the calculation, which are not readily available for most glass forming melts.

1:45 PM

(GOMD-S6-005-2017) Sintering and foaming of barium silicate glass powders (Invited)

R. Müller*[1]; B. Agea-Blanco[1]; S. Reinsch[1]

1. Bundesanstalt für Materialforschung und -prüfung (BAM), Materials Engineering, Germany

The manufacture of sintered glasses and glass-ceramics, glass matrix composites and glass-bounded ceramics or pastes is often affected by gas bubble formation. Against this background, we studied sintering and foaming of barium silicate glass powders used as SOFC sealants using different powder milling scenarios. Sintering was measured by means of heating microscopy backed up by XPD, DTA, Vacuum Hot Extraction (VHE) and optical and electron microscopy. Foaming increased significantly as milling progressed. For moderately milled glass powders, subsequent storage in air could also promote foaming. Although the powder compacts were uniaxially pressed and sintered in air, the milling environment significantly affected foaming. The strength of this effect increased in the order Ar >> N_2 < air < CO_2. Conformingly, VHE studies revealed that the pores of aerated samples predominantly encapsulated CO_2, even for powders milled in Ar and N_2. Results of this study thus indicate that foaming is caused by carbonaceous species trapped on the glass powder surface. Foaming could be substantially reduced by milling in water and 10 wt% HCl.

2:15 PM

(GOMD-S6-006-2017) Pyrophosphate glass-ceramics as a cathode active material for natural abundant sodium ion batteries (Invited)

T. Honma*[1]; T. Komatsu[1]

1. Nagaoka Univeristy of Technology, Department of Materials Sciencs and Technology, Japan

Sodium ion batteries are considered to be alternative high energy density batteries because of their low cost resources. Sodium iron pyrophosphate $Na_2FeP_2O_7$ was found by our group, which exhibits good cathode properties (2.9V, 89mAh/g). In order to increase discharge voltage, $Na_2MnP_2O_7$ is more suitable. In this study, crystallization behavior and electrochemical properties of $Na_2Mn_xFe_{1-x}P_2O_7$ was examined. $Na_2MnP_2O_7$ have two type polymorph. Triclinic β-$Na_2MnP_2O_7$ is same structure of $Na_2FeP_2O_7$ and layered $Na_2MnP_2O_7$ is composed from P_2O_7 units and edge-shared MnO_6 units. By means of XRD, the diffraction patterns of crystallized sample for $Na_2MnP_2O_7$ (x=0) glass which is obtained by heat treatment at various heat treatment temperature. Primary crystallized phase confirmed as layered $Na_2MnP_2O_7$ and then layered $Na_2MnP_2O_7$ changed to β-$Na_2MnP_2O_7$ phase at higher temperature. By means of differential thermal analysis, endothermal peaks were observed around 650°C in both precursor glass and layered $Na_2MnP_2O_7$. Therefore, it is found that two different polymorphs of $Na_2MnP_2O_7$ can be obtained selectively by crystallization of precursor glass.

2:45 PM

(GOMD-S6-007-2017) Laser Irradiation of Lead and Barium Vanadate Glasses (Invited)

M. Affatigato*[1]; R. Dongol[1]; P. Dulal[1]; W. Lubberden[2]; S. Feller[1]

1. Coe College, Physics, USA
2. Central College, Physics, USA

We review our work on the effect laser irradiation on vanadate glasses, with an emphasis on structural changes induced by low power 785 nm irradiation. At these power levels, the structure appears to slowly reorganize towards more crystalline arrangements, and the effect is cumulative. Thus, prior irradiation biases the glass towards more rapid crystallization upon further exposure to the laser light. Raman characterization of lead metavanadate glasses points to growth in the band at 860 cm^{-1}, typically assigned to V-O-V ‘bridge’ vibrations, accompanied by a decrease in the 950 cm^{-1} band, usually associated with V-O stretching modes. It is thus likely that the glass begins to rearrange into longer chains, leading to the increase in V-O-V bridges, enhancing its similarity to the orthorhombic BaV phase. Commonly, a bump (caused by structural expansion) appears at these power levels. At higher laser powers, more traditional phase changes occur, alongside material ablation, and these effects are well understood by decompositions in the phase diagrams. Finally, we will discuss our writing of lines in the glass, a technique well characterized by Prof. Komatsu and coworkers. Work supported by the United States National Science Foundation under grant numbers DMR-0904615, DMR 0502051, DMR-MRI-0722682, and DMR-MRI- 0320861.

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium III

Room: Kona 5

Session Chairs: Kenji Shinozaki, AIST; Joachim Deubener, Clausthal University of Technology

3:30 PM

(GOMD-S6-008-2017) Crystallization of PbS Quantum Dots on Rare-Earth Oxide Clusters (Invited)

J. Heo*[1]

1. Pohang University of Science and Technology(POSTECH), Materials Science and Engineering, Republic of Korea

Glasses doped with PbS quantum dots (QDs) can absorb and emit light at different wavelengths by adjusting QDs' sizes. There are possible application areas including fiber-optic amplifiers. We have reported that photoluminescence located at ~ 1500nm shifts to short wavelength side as Nd2O3 content increases. Scanning transmission electron microscopy (STEM) and energy dispersive x-ray spectroscopy (EDS) show that relatively high concentrations of heavy metals such as Pb2+, Nd3+ inside QDs instead of glass matrix. Radii (r) of QDs are proportional to tx when x varies between 0.203 to 0.217 and it is considerably smaller than the value predicted by classical crystallization theory. Atom probe tomography (APT) method is used to analyze the distribution of RE3+ ions inside glass matrix and its effect on the precipitation of PbS QDs. We found Nd3+ clusters of approximately 2-4nm in diameter exist inside the glass. Extended x-ray absorption fine structure (EXAFS) analysis showed that Nd3+ ions are surrounded by ~8 oxygen ions inside the QDs and there is no evidence of forming Nd-S bonds. EDS and EELS results showed that Nd3+ ions are preferentially concentrated inside the PbS QDs rather than in the glass matrix after heat-treatment. Therefore, we believe that those Nd3+-O clusters work as nucleating sites for precipitation of PbS QDS.

4:00 PM

(GOMD-S6-009-2017) Glass and glass-ceramics for solar-pumped lasers (Invited)

S. Mizuno*[1]

1. Toyota Central R&D Labs, Inc., Japan

Solar-pumped lasers (SPLs) driven by natural sunlight enable a wide variety of applications including efficient solar photovoltaics, photosynthesis, and wireless power supply, etc. The laser medium doped with rare-earth (RE) ions is required to include co-dopants of transition metal (TM) ions as sensitizers, which absorb broadband sunlight and transfer the energy to the RE ions, because the RE ions absorb only a portion of the solar spectrum. A fiber-shaped medium is suitable from a viewpoint of high mode-matching and high cooling capacity for a low lasing threshold and stable emission. Glass and glass-ceramics are the candidate materials that satisfy all the conditions mentioned above. We have achieved laser emission using a fluoride glass fiber doped with Nd^{3+} ions under natural sunlight. However, the sensitizing effect of TM ions in glass has not yet realized because of notable multi-phonon relaxation. In this paper, the sensitizing effect of TM ions based on a new energy transfer concept in glass-ceramics is presented. The nanometer-sized TM-doped crystals embedded in the RE-doped glass matrices secure efficient nonradiative energy transfer from the TM ions to the RE ions as well as transparency.

4:30 PM

(GOMD-S6-010-2017) Development of Light-storage Glass Composites using the Frozen Sorbet Technique (Invited)

T. Nakanishi*[1]

1. Hokkaido University, Japan

The Frozen sorbet technique is used to the alumino borate glass system to prepare glass ceramics including Eu^{2+}, Dy^{3+}: $SrAl_2O_4$ microcrystals, which have light energy storage ability. The transparent glass composites with aluminoborate glass phase and the single-crystal particles have been successfully prepared. The light-energy glass composites show remarkable light-storage ability (e.g., charge-carrier trapping phenomenon) based on the natural properties of the crystals, and this provide various photo-functionalities, such as long-persistent luminescence, photo-induced conductivity, and mechano-luminescence. The preparation of transparent glass composites using the Frozen sorbet technique and their unique optical properties are presented as novel light-storage materials for energy applications.

5:00 PM

(GOMD-S6-011-2017) Tin-phosphate glass with crystal-like open structure (Invited)

A. Sakamoto*[1]; Y. Himei[5]; K. Shinozaki[4]; T. Honma[3]; T. Komatsu[3]

1. OLED Material Solutions Co., Japan
3. Nagaoka University of Technology, Japan
4. AIST, Japan
5. NEG, Japan

The local structure of 72SnO28P2O5 glass was studied by Raman scattering and Mossbauer spectra before and after crystallization. After the heat treatment at 430C for 3h in air, the glass crystallized into a mixture of Sn3(PO4)2 (75SnO25P2O5) and Sn2P2O7 (67SnO33P2O5) crystals, the tin ions in which exist as Sn2+. The Raman band positions of the crystallized sample, which were mainly assigned to Q0 and Q1 phosphate tetrahedron, were almost the same as those in the glass. The Mossbauer spectra of the glass revealed that there are two Sn2+ sites related to Sn3(PO4)2 and Sn2P2O7 structure, and the former one is the majority. This was consistent with the calculation result of packing density that shows the packing density of this glass is very close to that of Sn3(PO4)2 crystal. Such crystal-like local structure is considered to be one of the main reasons of the unique thermal conductivity, elastic modulus and Li-ion mobility of this glass.

PACRIM Symposium 08: Additive Manufacturing and 3-D Priniting Technologies

Direct Writing Technologies

Room: King's 2

Session Chair: Soshu Kirihara, Osaka University

1:15 PM

(PACRIM-S8-001-2017) Direct Write Additive Manufacturing of "Born Qualified" Ceramic Components

A. W. Cook*[1]; C. DiAntonio[1]; D. Kammler[1]; H. J. Brown-Shaklee[1]; F. Abdeljawad[1]

1. Sandia National Laboratories, USA

As ceramic additive manufacturing (AM) capabilities continue to evolve, so do the uncertainties associated with manufacturing variability and the resultant component performance and reliability. As functionality and reliability are critical factors in the development and adoption of printed ceramics, requirements to qualify materials and processes must be identified and addressed early in the development cycle. To this end, a systems engineering approach is being employed that closely couples and elicits the interdependency of materials and process research and development to mature ceramic AM technology. The formulation, compounding, and extensive characterization of a highly ceramic loaded polymer feedstock for AM will be discussed, as well as direct write platforms instrumented with a suite of feedback controls to enable spatial correlation and control of defects within a printed object. Additionally, by modeling sintering densification and coarsening mechanisms specific to ceramic materials and the manufacturing process, the capability to predict AM component performance is being developed. This work represents the inception of advanced materials and process science and technology to design, print, and process AM ceramic components that are "born qualified".

1:45 PM

(PACRIM-S8-002-2017) Additive Manufacturing Toward Turbine Engine and Electric Motor Applications

M. C. Halbig*[1]; M. Singh[2]

1. NASA Glenn Research Center, USA
2. Ohio Aerospace Institute, USA

The new capabilities offered by additive manufacturing methods allow for rapid proto-typing, expanded design envelopes, low cost processes, and final part fabrication. The methods are being applied toward innovative components for turbine engines and electric motors. Compared to conventional manufacturing, components can be more geometrically complex, compact, multi-material, innovatively cooled, integrated, and multifunctional. The materials of focus include SiC fiber reinforced/SiC ceramic matrix composites (SiC/SiC CMCs), polymer composite materials, and multi-material systems which offer high payoff in aerospace applications due to light weight, high temperature capability, optimized designs, and tailored and gradient properties. Laminated object manufacturing (LOM) and binder jetting are being used to fabricate SiC/SiC CMCs for turbine engine components. Additive processes are enabling new innovative electric motor designs which have higher power densities and/or efficiencies. Optimized rotor and stator designs are being pursed with direct printing of advanced electrically conductive coils for the stator as a major focus.

2:00 PM

(PACRIM-S8-003-2017) Silica Glass with Tailored Refractive Index Profile Using Direct-Ink-Write Additive Manufacturing

R. J. Dylla-Spears*[1]; D. T. Nguyen[1]; C. Meyers[2]; J. Destino[1]; N. Dudukovic[1]; E. Duoss[1]; J. Hughes[1]; M. A. Johnson[1]; L. R. Siegel[1]; J. E. Smay[3]; W. A. Steele[1]; C. Spadaccini[1]; T. I. Suratwala[1]; T. D. Yee[1]; C. Zhu[1]

1. Lawrence Livermore National Laboratory, USA
2. University of Minnesota, Department of Earth Sciences, USA
3. Oklahoma State University, Department of Chemical Engineering, USA

Glass optics with arbitrary composition profiles are unachievable by conventional methods, whether via layered melts, solid diffusion, or diffusion into sol gels. In this work, silica-titania composition is varied spatially across a monolithic green body (i.e. a low density form) using direct-ink-write (DIW) additive manufacturing. Rheologically tuned, silica-based DIW inks are blended inline at the print nozzle to deposit the desired material composition at the desired location within the green body. The green body is then heat treated to form a full density glass monolith containing the gradient in refractive index imparted through the silica-titania composition variation. The optic is polished to achieve the desired surface figure and surface quality. This method has been used to create a transparent, amorphous glass gradient index (GRIN) optic. The optic is probed by spectroscopic techniques to confirm that the material is amorphous as well as to examine variation in chemical composition. The refractive index change across the part has been characterized by prism refractometry as well as by interferometry. The ability of the DIW-printed glass GRIN lens to focus light is also demonstrated. *This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 within the LDRD program. LLNL-ABS-706878

2:15 PM

(PACRIM-S8-004-2017) Multi-scaled Porosity of 3-D Printed Particle Stabilised Ceramic Foams

M. L. Sesso*[1]; G. Franks[1]

1. The University of Melbourne, Department of Chemical and Biomolecular Engineering, Australia

Additive manufacturing techniques offer a way to meet today's high demand for materials to possess property-specific macro and microstructures for use in advanced applications. Current colloidal processing techniques together with the available ceramic shape forming methods enable a limited level of macro and microstructural control when producing porous ceramic components. By employing particle stabilised ceramic foams as pastes in extrusion based 3-D printing devices, ceramic parts with multi-scaled porosity can be produced. This work presents a fundamental study on the rheological properties of particle stabilised ceramic foams used as pastes for 3-D printing porous structures. In addition, we show that by controlling the inner macro structure of the printed part, functionally graded porosity can be created.

2:30 PM

(PACRIM-S8-005-2017) Robocasting of Alumina – Alginate slurries

D. Glymond*[1]; L. Vandeperre[1]

1. Imperial College, Materials, United Kingdom

Additive manufacturing is a growing set of established techniques for manufacturing conventional ceramic parts with complex geometries. In this work one of these techniques consisting of continuous extrusion of pastes, known as robocasting, is used to create dense (>98 %) alumina samples. Magnesium is a beneficial additive for alumina, promoting equiaxial grain growth in its microstructure. Alginic acid and magnesium chloride provide a slurry with the necessary rheological properties for extrusion, as well as a bespoke way of doping alumina with magnesium. Various concentrations of magnesium chloride with 45 vol % alumina were investigated. Strengths of up to 350 ± 30 MPa, dependent on composition, are observed for as printed bars.

Fused Deposition and Ink Jet Printing Technologies

Room: King's 2
Session Chair: Adam Cook, Sandia National Laboratories

2:45 PM

(PACRIM-S8-006-2017) Fundamentals of Melt Extrusion Process for 3D Additive Manufacturing

Y. Huang*[1]; P. Wang[1]; Y. Chen[1]; W. Wei[1]

1. National Taiwan University, Taiwan

A melt-extrusion (ME) module was patented (9/2014) and used to do high temperature fused deposition of metallic alloys and oxide glasses. This study investigates five active forces generated in the hot-barrel. The rheological and flowing behaviors of the melts by the melt extrusion through the heated barrel for 3D manufacturing were predominantly investigated. The ME module was designed and developed to have a temperature up to 1300 °C. The module includes a heating unit which combined with Si-based heating elements and Fe-Cr-Al wires to heat the feeding materials, a ceramic barrel (tube-type) allowing the extrusion of the feeding materials to heated sample stage, and a refractory housing consisted of three thermal insulation layers. Several related extrusion problems will be discussed, and finally get successful 3D products made by borosilicate glasses and Cu-based alloys will be presented by optimizing the processing parameters. The results show that the nozzle diameter, the viscosity of the feeding materials at operation temperature, the processing temperature of melt extrusion, and the feeding rate of source materials were significantly, and should be controlled for successful 3D printing.

3:00 PM

(PACRIM-S8-007-2017) Inexpensive thermal inkjet printing of sol-gel based YSZ layer on dense and porous substrates

C. Gadea*[1]; Q. Hanniet[1]; D. Marani[1]; S. Hojgaard[1]; V. Esposito[1]

1. DTU Energy, Denmark

Inkjet printing of functional metal oxides has in the past years been spreading in several technologies, especially using the colloidal suspension route. However, this route has limitations related to particle size, print head nozzle clogging and high temperature sintering process. An alternative particle-free route is sol-gel based inks, in which hydrolysis/condensation of a metallic precursor with water forms crystallized nano-particles at low temperature. However, a major challenge when using this type of solutions is to keep the ink stable over time to ensure durable printing. This can be achieved by inhibiting the reaction between the solvent (water) and the metallic precursor. In this study, an 8YSZ (yttria-stabilized zirconia) nano-layer has been deposited on various substrates by inexpensive thermal inkjet printing of a stable aqueous zirconium based sol-gel ink. Formulation optimization and long-term stability of the ink have been studied, and crystallinity, microstructure and electrochemical properties of the film have been characterized.

Emerging Technologies

Room: King's 2
Session Chair: Michael Halbig, NASA Glenn Research Center

3:45 PM

(PACRIM-S8-009-2017) Additive Manufacturing of Ceramics: High-Value Added Ceramic Products Manufacturing Technologies (Invited)

T. Ohji*[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

After giving brief overviews of R&D trends on additive manufacturing of metals and ceramics in Japan, this paper is focused on the R&D project "High-Value Added Ceramic Products Manufacturing Technologies", which has been conducted since 2014 under the sponsorship of the Japanese government, with target of "removing restrictions of conventional manufacturing". This project deals with two principal technologies; additive manufacturing of ceramics aimed for complex shaping and reducing lead-time, and hybrid ceramic coating on 3D polymers/metals for enhancing their reliability and functionality. The paper will introduce the objectives, research contents, research schemes as well as the latest research achievements. Particular focus is places on the R&Ds on the additive manufacturing, which contains ceramic powder layer manufacturing (powder bed fusion, or indirect selective laser sintering), slurry layer manufacturing (stereolithography) and ceramic laser sintering (direct selective laser sintering) which realizes concurrent forming and sintering. The recent R&D trends worldwide on additive manufacturing of ceramics also will be introduced. This work was conducted as a part of "High-value added ceramic products manufacturing technologies project" supported by CSTI, SIP, "Innovative design/manufacturing technologies (managed by NEDO)".

4:15 PM

(PACRIM-S8-010-2017) In operando non-destructive evaluation techniques for additive manufacturing (Invited)

A. Michaelis*[1]

1. Fraunhofer IKTS, Germany

Ceramic materials additive manufacturing (AM) offers the possibility to produce components of extremely complex geometry not achievable by conventional shaping routes. The ceramic AM-methods can be divided into powder based and suspension based techniques resulting in porous and dense components, resp. An important demand for all AM technologies is to improve reliability and performance of the manufactured components. Due to the time-consuming manufacturing processes and the layerwise building process it is necessary to control the quality of each layer for enabling the repair of a defect layer or to stop the building process for avoiding waste of time and expensive material loss. Therefore, it is important to access the quality of the printed parts as early as possible. This requires in-operando non-destructive evaluation methods. For this, we present new optical methods such as speckle laser spectroscopy and optical coherence tomography. For a further functionalization of the AM parts, 2D printing technologies can be applied. We present first results on this combination of 3D and 2D paste printing. Furthermore, examples for a combination of dense and porous structures for bio-medical applications are presented.

4:45 PM

(PACRIM-S8-011-2017) 3D printing of clays and pastes by the extrusion freeforming (EFF) method

H. Colorado*[1]

1. Universidad de Antioquia, Colombia

This research is about the additive manufacturing (AM) of kaolinite clays type following the extrusion freeforming (EFF) method. Different samples fabricated from clays were built with different water to clay ratios (W/C) and Waste contents between 0.0 and 10.0%. Cylinders for compression tests were printed, then for one day in open air at room temperature, and thereafter exposed to 1100°C for 2 hours in air atmosphere. Materials characterization was conducted with viscosity tests, scanning electron microscopy, x-ray diffraction, and other performance tests. Two different mechanisms used for printing are also presented.

5:00 PM

(PACRIM-S8-012-2017) A Modular Direct Write Additive Manufacturing Approach in the Printing of Alumina and Multi-Materials

J. M. Lavin*[1]; D. M. Keicher[1]; S. Mani[1]; M. Essien[2]; S. Whetten[1]; L. Evans[1]; A. W. Cook[1]

1. Sandia National Laboratories, USA
2. IDS, USA

Additive manufacturing and direct write printing provides an opportunity to modify the current capabilities associated with traditional ceramic processing creating a more diverse and flexible technology. We at Sandia National Laboratories have developed a modular printing platform capable of printing a range of materials using one of five platform modules: Mycrojet, syringe dispense, Sono-Tek aerosol spray, progressive cavity pump and extrusion dispense. The choice of additive manufacturing module used for a given print is dictated by material viscosity and desired feature size. This modular print platform enables the printing of ceramic and multi-materials over a range of feature size from fine to coarse. With this modular printing platform, direct write of multi-materials can be built up in a layer-by layer approach alternating from one material to another without the need to move and realign from one printing platform to another. This presentation will focus on the platform capabilities for printing alumina precursors and a range of other materials of different viscosities using the various print modules. Printed structures will be characterized to identify and understand the printing process variables and their correlation to the final printed product.

Stereolithography

Room: King's 2
Session Chair: Alexander Michaelis, Fraunhofer IKTS

5:15 PM

(PACRIM-S8-013-2017) Ceramics Additive Manufacturing: New Approach using Continuous Film Supply type Digital Light Processing

W. A. Sarwar*[1]; H. Yun[2]

1. Korea Institute of Science and Technology, Advanced Materials Engineering, Republic of Korea
2. Korea Institute of Materials Science, Engineering Ceramics, Republic of Korea

Stereolithography (SL) and Digital Light Processing (DLP) use photopolymerization to build highly accurate intricate and dense constructs hence eliminating the need for post-fabrication tooling. Conventional DLP uses vat system which uses large amount of slurry regardless of product size and reduces the printing quality due to unexpected curing because of scattering of light by ceramic particles and limits reuse of slurry. In this study, we have designed a novel DLP system which employs tape casting mechanism to formulate thin layers of ceramic slurry and DLP for layer by layer printing, and stacking onto a build stage to produce complex ceramic constructs. The thickness of each layer is controlled by doctor blade which produces fresh slurry layer through continuous film supply and unused slurry can be recovered completely unaffected. The slurry used in this study contained ceramic powder dispersed in photocurable resin consisted of photoinitiators, multifunctional oligomers, and monomers. Alumina, zirconia, and hydroxyapatite with solid loading up to 60 volume percent were printed. Our 3D printing system gives us high freedom of variable control and allows for stacking multiple materials in different layers or side by side in single layer for advanced ceramic devices.

5:30 PM

(PACRIM-S8-014-2017) Additive Manufacturing of Silica Glass by Stereolithography

C. Liu*[1]; X. Liu[1]; J. Qiu[2]; B. Qian[2]

1. Zhejiang University, Material Science and Engineering, China
2. Zhejiang University, Optical Science and Engineering, China

Additive manufacturing is an attractive technology which gives the chance to create entirely new products and manufacturing strategies. In this study, mixture of SiO_2 nanoparticles and UV curable resin with low viscosity and high solid loading was prepared by a laboratory dissolver. The green body was fabricated by a homemade 3D printing system with a 355 nm laser and followed by debonding and sintering process. The density and mechanical properties of the manufactured structure was confirmed to be the same as commercial silica glass. Er^{3+} ions were doped in the mixture and photoluminescence of Er^{3+} ions was observed in the sintered 3D printing product.

5:45 PM

(PACRIM-S8-015-2017) Stereolithographic Additive Manufacturing of Ceramic Components Using Ultra Violet Laser Dewaxing and Sintering

S. Kirihara*[1]

1. Osaka University, Joining and Welding Research Institute, Japan

Stereolithographic additive manufacturing has developed to create ceramic components directly from nanoparticles resin paste through dewaxing and sintering by using an ultra violet laser with higher irradiation power. Alumina nanoparticles of 500 nm in average diameter were dispersed in to acrylic resins at 50 % in volume fraction to obtain thixotropic slurries. The ultraviolet laser beam of 355 nm in wavelength was adjusted at 50 μm in spot diameter and scanned on the applied resin surface. Irradiation power was increased at 800 mW for cross sectional layers joining through the resin matrix dewaxing and ceramic particles sintering. By using computer aided design, manufacture and evaluation, alumina photonic crystals with micro lattice structures were fabricated to modulate electromagnetic propagations in terahertz frequency ranges. Subsequently, titania ordered porous structures with larger surface areas were created to realize effective photocatalyst performances. Moreover, calcium phosphate biological implants with natural fluctuations were fabricated to realize artificial metabolisms.

PACRIM Symposium 09: Ceramic Integration and Joining Technologies

Joining and Integration Issues

Room: Queen's 6
Session Chair: Mrityunjay Singh, Ohio Aerospace Institute

1:15 PM

(PACRIM-S9-001-2017) Joining of ceramics by brazing alloys: Thermodynamics and kinetics of interfacial interactions (Invited)

F. Hodaj*[1]

1. Grenoble Institute of Technology, Materials Science, France

Interfacial interactions - wetting and reactions at metal/ceramic interfaces are of paramount importance in many fields of materials engineering such as joining of ceramics by brazing alloys, manufacturing of metal/ceramic composites, casting of metals, etc. The purpose of this presentation is to focus on the fundamental issues of metal/ceramic interfacial interactions and to analyse the main thermodynamic and kinetic factors governing these interactions. In particular, some physicochemical aspects which can affect, or even control, the morphological evolution of the interfacial region will be discussed by using and analysing different examples of interactions between oxide or non-oxide ceramics and reactive liquid alloys. A section is devoted to discuss the effect of interfacial reactions in removing the wetting barriers. Finally, examples of differences in interfacial reactivity between sessile drop configuration and brazing configuration will be given.

1:45 PM

(PACRIM-S9-002-2017) Joining of silicon carbide for industrial applications

M. Kuhn*[1]; A. Katz[1]; R. H. Bryden[1]

1. Saint-Gobain Innovative Materials, Northboro Research & Development Center, USA

Silicon carbide (SiC) is a key ceramic material for use in structural applications at elevated temperatures due to its high strength as well as chemical, thermal shock and creep resistance. It outperforms high-temperature metallic alloys which tend to fail due to corrosion and/or creep under harsh conditions and at elevated temperatures. However, one of the limitations is the ability to join SiC components to metal or other SiC components in industrial applications. Saint-Gobain is a world-leading manufacturer of high-performance materials and produces various grades of SiC. For the manufacturability of large, complex SiC parts, we use different approaches, such as direct-bond technology, to join individual components together. The combination of direct-bonding and the use of collars allows manufacturing of tubes several meters long. Beyond these mature solutions, new joining approaches are being explored. The joints are tested for microstructural integrity, gas-tightness and mechanical strength. We will present the perspectives of a large ceramic component maker in regard of the need for reliable, scalable joining techniques to enable next generation, high efficiency, high temperature applications involving SiC components.

2:00 PM

(PACRIM-S9-003-2017) Strain and Strain Rate Matched Glass-ceramic to Metal Seals

S. Dai*[1]; B. Elisberg[2]; M. Rodriguez[2]; N. Lyon[2]

1. Sandia National Laboratories, Materials Science Center, USA
2. Sandia National Laboratories, USA

High expansion crystallizable lithium-alumina-silicate glass-ceramics were used to form matched seals to metals like stainless steel. However the thermal strain of these glass ceramics is highly nonlinear owing to the inversion in Cristobalite which is the dominant high expansion silica phase. Recently new glass-ceramics with near-linear thermal strain have been developed by crystallizing multiple high expansion silica polymorphs from the same parent glass, enabling both thermal strain and strain rate matches to the housing metals. The dynamics of multiple crystallization are analyzed to study phase stability of the near-linear glass-ceramics. Finite element stress modeling of seals using glass-ceramics with both non-linear and near-linear thermal strains are performed to reveal dependence of the interfacial stresses as well as the reliability of the seals on the linearity of the glass-ceramics. This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

2:15 PM

(PACRIM-S9-004-2017) SiC Joining Technology Using SiC-SiO_2-Al_2O_3-Y_2O_3: Microstructure and Mechanical Strength Characterization

C. P. Shih*[1]; H. Khalifa[1]; E. Song[1]

1. General Atomics, USA

Silicon carbide (SiC) and SiC continuous fiber reinforced SiC matrix (SiC-SiC) composites have huge potential for nuclear energy applications because of their unique properties including low neutron activation, stability under high radiation fluences, and high temperature strength. Joining of SiC materials to itself and to other materials is an enabling technology to the successful deployment of SiC materials in various nuclear applications. In this presentation, Joining of SiC using the transient eutectic phase (TEP) SiC-SiO_2-Al_2O_3-Y_2O_3 system is reported. Within this materials system, efforts has been put into reducing the joining temperature in order to mitigate SiC-SiC substrate strength degradation, which can occur at the very high temperatures used in traditional TEP processing. Properties of the resulting joints are found to be highly dependent on joint thickness and composition. An impermeable joint with a high apparent shear strength that results in substrate failure under double notched shear test is achieved. The effects of joint thickness and difference in coefficient of thermal expansion between the joint medium and the substrate on the shear strength and helium impermeability are discussed. *This work is supported by US DOE under contract number DE-NE0008323 and General Atomics internal funding.

2:30 PM

(PACRIM-S9-005-2017) All Silicon Carbide Tube to Plate CMC Joints and Their Use in Heat Exchangers

J. Zhang*[1]; G. Jacobsen[1]; J. Sheeder[1]; C. Deck[1]

1. General Atomics, USA

Silicon carbide (SiC) and silicon carbide fiber reinforced, silicon carbide matrix (SiC-SiC) composite components are candidate materials for extreme environments due to their retention of strength at elevated temperature and low corrosion rates. For example, SiC-SiC is currently being implemented in the areas of nuclear fuel cladding, high temperature turbine engines and high temperature heat exchangers. Challenges exist in the joining of SiC-SiC as traditional joint methods can induce thermal stresses due to CTE mismatch between the joint and substrate. The work presented here solves this issue by using an all SiC based approach for the joining of a SiC-SiC tube to a plate. Joints featuring both open ended and close ended tubes have been made. Mechanical test methods were developed to test the tube/plate architecture and test results show a joint strength similar to the SiC-SiC substrate. In order to perform helium permeability testing, novel fixturing featuring a metal to ceramic connection was developed. Results of the permeability test for the individual tube and plate coupons as well as the fully joined component showed that this technology is gas tight. Application of this work to all SiC heat exchangers, multi tube arrays, and inlet/outlet connectors will be discussed. *This work is supported by General Atomics internal funding.

PACRIM Symposium 10: Multifunctional Nanomaterials and Their Heterostructures for Energy and Sensing Devices

Nanostructures and Devices for Energy Generation, Storage and Catalysis

Room: Queen's 5
Session Chairs: Amr Helmy, University of Toronto;
Hidehiro Kamiya, Tokyo University of Agriculture and Technology

1:15 PM

(PACRIM-S10-008-2017) Conversion of Light Energy into Heat and Hot Electrons Using Hybrid Nanostructures with Plasmonic Hot Spots (Invited)

A. Govorov*[1]; L. Besteiro[1]

1. Ohio University, Department of Physics and Astronomy, USA

Metal nanocrystals exhibit strong plasmon resonances and have the ability to absorb and scatter solar light very efficiently. This study concerns special designs of plasmonic nanostructures with electromagnetic hot spots, where the energy of incident light concentrates. Overall plasmonic nanostructures with hot spots demonstrate strongly amplified energy-related effects. (1) Using such nanostructures, one can strongly enhance optical generation of heat and also confine high photo-temperatures in small volumes. (2) Plasmonic hot spots efficiently generate energetic electrons, which can be used for photochemistry and photodetection. (3) Colloidal nanocrystal assemblies with plasmon resonances allow us to strongly enhance chiral optical responses (circular dichroism) of biomolecules and drugs.

1:45 PM

(PACRIM-S10-009-2017) Hybrid 1D/2D Carbon-based composite materials with direct applications in batteries, supercapacitors and fuel cells (Invited)

D. Chua*[1]

1. National University of Singapore, Materials Science & Engineering, Singapore

Carbon-based materials have attracted much attention due to their unique properties, ranging from low dimensional effects, good structural integrity, high electrical and thermal conductivity, and chemical stability. Progress in materials fabrication technology has seen carbon-based materials changing from thin films to nanoscale dimensioned 1D carbon nanotubes and 2D graphene today. Currently, carbon based materials are the used as anode/cathode/conductive layers in various applications. In this talk, we will show that we can engineer various 1D and 2D carbon-based materials

with enhanced performance on Li batteries, supercapacitors and PEM fuel cells. We will further show and compare the fuel cell properties when engineered 1D and 2D materials are integrated. A series of in-situ tests are also performed which includes accelerated degradation test and electrochemical impedance spectroscopy to validate the effectiveness and robustness of these materials. We will mention briefly other applications for these carbon based materials.

2:15 PM

(PACRIM-S10-010-2017) Incorporation of carbon nanomaterials for the improvement of the exciton dissociation efficiency in hybrid OPV

B. Aissa*[1]

1. Institut National de la Recherche Scientifique, Energy, Materials and Telecommunications, Canada

Heliatek® has recently set a new organic photovoltaic (OPV) world record efficiency of 13.2%. Even if this threshold value is still below what is attainable by inorganic semiconductor-based counterparts, it greatly encourages its future commercial use as alternative to the silicon based technology. In these OPV devices, PV conversion is based on the separation of photogenerated charges at an interface between electron donor and acceptor materials, which imposes some constraints on the photoactive layer of the cells (diffusion length and Mobility of charges). To address this challenge, we propose to improve the conversion efficiency by incorporating highly anisotropic carbon nanomaterials (CNMs) such as carbon nanotubes (CNTs) and/or Graphene. Although CNMs have been used before in OPVs, the focus of our research is to elucidate the effect of the structural properties of the CNMs on OPV performance, which is poorly understood. Special care is taken to control the optoelectronic properties and PV characteristics of the hybrid OPV through the morphology of the CNMs and to study the improvement of the exciton dissociation efficiency at the CNMs/photosensitive polymer interface.

2:30 PM

(PACRIM-S10-011-2017) In situ Synchrotron X-ray Spectroscopy for Energy Material (Invited)

C. Dong*[1]

1. Tamkang University, Department of Physics, Taiwan

We are currently facing the problem of world's fastest-growing energy crisis. To fill the gap between energy shortage and human demand for clean energy is a big challenge. A great deal of effort has been paid to search renewable and alternative energy. In several important energy systems, such as nanostructured catalysts, smart materials, artificial photosynthesis, and energy storage systems, there are still obstacles to overcome for practical use. For example, improvement of energy conversion/generation/storage efficiency relies on advanced engineered material and well-controlled physical/chemical properties. Without comprehending the fundamental properties such as chemical states, atomic and electronic structures and how they alter near the interfacial region during the physical/chemical reaction, it is difficult to better design the material for advancing performance in an effective approach. Synchrotron x-ray spectroscopies, including x-ray absorption and x-ray emission spectroscopies are useful characterization tools to look into the local unoccupied and occupied electronic states. Exploiting the in situ characterization approach, the way to monitor the modification of atomic and electronic structures of the energy material under operational environment now becomes accessible. This presentation will report the emerging characterization tools in energy relevant materials.

3:00 PM

(PACRIM-S10-012-2017) Local Structural and Electrical Properties of VO_2/ZnO Nanostructures (Invited)

S. Han*[1]

1. Chonbuk National University, Physics Education, Republic of Korea

VO_2 is a typical metal-insulator-transition(MIT) material with the bandgap of ~05. eV and the T_c of ~ 70°C. VO_2 is transparent and dark below and above the T_c, so that it can be applicable for smart windows by controlling the temperature. VO_2 nanoparticles in a metallic phase block and scatter sunlight. The scattered sunlight by VO_2 nanoparticles can be used in solar cells. We examined the local structural and electrical properties from VO_2/ ZnO nanostructures by using the simultaneous measurements of x-ray absorption fine structure(XAFS) and resistance. The structural and electrical properties of VO_2 depend on the length of ZnO nanorods underneath VO_2. Direct comparison of simultaneously-measured resistance and XAFS from the VO_2 demonstrates that the transitions of structures, local density of the V 3d orbital states, and resistance occurred in sequence during heating, whereas the properties changed simultaneously during cooling. XAFS reveals a substantial increase of Debye-Waller factors, particularly, V-V pairs along the {111} direction in the metallic phase. XAFS results indicate that soft phonon above T_c plays a critical role in the collapse of a small band gap of VO_2. The local structural and the electrical properties of VO_2/ZnO nanorods are considerably sensitive to the interface of VO_2/ZnO as well as the length of ZnO nanorods.

3:30 PM

(PACRIM-S10-013-2017) Experimental and Theoretical Approach to Ternary Silicon Nitride-Based Phosphors

Z. Lences*[1]; I. Ibrahim[1]; P. Sajgalik[1]

1. Institute of Inorganic Chemistry, Slovak Academy of Sciences, Ceramics Department, Slovakia

Lanthanide (Ln) doped $LaSi_3N_5$ based phosphors were prepared experimentally and their electronic structure and band gaps were calculated using the screened Coulomb hybrid HSE06 functional. The synthesized $LaSi_3N_5$:Ce phosphor emits violet-blue light, $LaSi_3N_5$:Eu – green-yellow and $LaSi_3N_5$:Sm red light. The calculations showed that with increasing atomic number the band gap of Ln^{3+}-doped $LaSi_3N_5$ smoothly decreases from 4.6 eV (Ce) to 0.5 eV (Eu). The band gap of Ln^{2+}-doped $LaSi_3N_5$ increases from 0.80 eV (Ce, Pr) to 0.95 eV (Nd, Pm), 1.43 eV (Sm), and to 3.28 eV (Eu). The electronic transition in Ln^{2+}-doped LaSi3N5 has 4f-5d character. Because the Ln dopants were experimentally added mainly in a form of oxides, also the influence of N/O substitution on the band gap of $LaSi_3N_5$ was calculated. The results showed that with increasing oxygen content in the cell of $LaSi_3N_5$ the band gaps decreased by 0.2 – 0.6 eV. Some of the lanthanides were added to $LaSi_3N_5$ also in the form of fluorides and their photoluminescent properties were compared with Ln_2O_3-doped phosphors. The energy level locations were constructed from the ab initio calculated electronic structures and compared with the empirical energy level diagram. There is a good agreement between calculated and experimental data and the method can be used for phosphor material design.

*Denotes Presenter

Processing of Functional Nanomaterials and Interface-driven Functional Multi-material Heterostructures and Nanocomposites

Room: Queen's 5
Session Chairs: Alexander Govorov, Ohio University;
Sang-Wook Han, Chonbuk National University;
Daniel Chua, National University of Singapore

3:45 PM

(PACRIM-S10-014-2017) Novel Architectures for Integrated Photonic Circuits Optimized for 2D Materials (Invited)

P. Chang[1]; Y. Su[1]; C. Lin[1]; A. Helmy*[1]

1. University of Toronto, The Edward S. Rogers Sr. Department of Electrical and Computer Engineering, Canada

The advent of 2D materials brings significant opportunities and challenges to photonic circuits. Because of their thicknesses when compared to optical wavelengths in the visible and infra-red, 2D materials physically overlap with a small fraction of the guided electromagnetic modes at these wavelengths in an integrated setting. In this talk, a new approach to profit from 2D materials in integrated planar setting through the utilization of hybrid plasmonic structures and anisotropic meta-materials will be discussed. Owing to the strong field confinement, the capabilities of plasmonic modes have inspired numerous research directions with nano-scale photonic devices as focal point. Due to their dissipative nature however, there is an inherent trade-off between the propagation losses and modal confinement in plasmonic waveguides. This talk will demonstrate a new approach that utilizes hybrid plasmonic modes to alleviate the trade-off associated with their loss behavior and the modal confinement factor. This new approach holds promise to provide effective, nano-scale photonic devices using 2D materials, with losses similar to those exhibit by their dielectric counterparts such as Si. Example devices that profit from this novel architecture include optical modulators, cavities and detectors with designs specially tailored to effectively utilize 2D materials.

4:15 PM

(PACRIM-S10-015-2017) Interfacial design in dielectric nanocomposite by liquid-crystalline polymers

H. Luo*[1]; K. Zhou[1]; D. Zhang[1]

1. Central South University, State Key Laboratory of Powder Metallurgy, China

Interfacial region plays a critical role in determining the electrical properties of dielectric nanocomposites. The current state-of-the-art interfacial modification is predominantly based on utilizing flexible organic molecules which are random polymer coils and generally collapse on the surface of any modified ceramic nanoparticles, therefore the thickness and morphology of the interfacial layer cannot be finely tuned. This work focused on engineering the interfacial region between $Na_2Ti_3O_7$ nanofibers and polymer matrix, and for the first time, utilized the liquid-crystalline polymer poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrenes}(PMPCS) to modulate the interface where the main chain of the rigid polymer was forced to form a straight conformation. Owing to the rigidity, orientation and strong spatial effects of PMPCS, a series of core-shell structured $Na_2Ti_3O_7$@PMPCS nanofibers with finely tuned shell thickness were prepared. The prepared $Na_2Ti_3O_7$@PMPCS/P(VDF-HFP) nanocomposites showed significantly different permittivity from 19.1 to 143.4 at the same condition with the gradient thicknesses of PMPCS shell. This work provided an important foundation to further investigate the interface effect in dielectric composite.

4:30 PM

(PACRIM-S10-016-2017) Organic Ligands Structure Design for Concentrated TiO_2 Nanoparticle Dispersions in various organic solvents and polymer (Invited)

H. Kamiya*[1]; Y. Okada[1]

1. Tokyo University of Agriculture and Technology, Institute of Engineering, Japan

In our previous study, TiO_2 nanoparticles modified with a commercial phosphoric acid surfactant can be dispersed in both polar and less-polar organic solvents and polymers. However, the relationship between molecular structure and colloidal stability is not clear and the structure is not optimized for better dispersion. In this study, we designed and synthesized a series of novel amphiphilic organic ligands with various molecular structure and used them to modify TiO_2 nanoparticles. We designed the amphiphilic organic ligands with different lengths of alkyl and ethylene glycol chains and a phosphoric acid group for TiO_2. A series of the ligands were synthesized in 3 steps from commercially available alkyl bromides. The modified nanoparticles were aggregated in the aqueous solution, which were then collected by centrifugation and washed with water to remove free ligands and dried in vacuum. The resulting modified TiO_2 nanoparticles were then dispersed in several organic solvents to study the relationship molecular structure and colloidal stability. We discovered the optimum lengths of alkyl and ethylene glycol chains to disperse TiO_2 nanoparticles into various polar and nonpolar organic solvents using sonication. Furthermore, this optimum ligand modified TiO_2 nanoparticles were able to be uniformly dispersed into polymer.in high concentration.

5:00 PM

(PACRIM-S10-017-2017) Flexible and individually addressable vertical nanotube crossbar arrays on graphene layers

Y. Tchoe*[1]; Y. Song[1]; J. Park[1]; H. Kim[1]; K. Lee[1]; J. Yoon[1]; J. Park[1]; H. Oh[1]; H. Yoon[1]; T. Lee[1]; G. Yi[1]

1. Seoul National University, Department of Physics and Astronomy, Republic of Korea

1-D nanostructures (NS; nanorods, nanotubes, and nanowires) have gained tremendous attention over the past decades, due to their excellent crystal quality and novel physical properties. For these reasons, numerous novel devices based on the 1-D NS have been extensively studied and reported over the past decades. In particular, the 1-D NS have been expected to be the key elements for the future electronic and optoelectronic devices with ultimate resolution. In spite of all these advantages that the 1-D NS devices have, however, because of the difficulties in preparing the NS and nanodevices in a well-controlled and ordered manner, it has long been very challenging to monolithically integrate many numbers of single 1-D NS devices into a small space in a well-organized manner. To overcome this issue, here, we report the fabrication and characteristics of vertical ZnO nanotube (NT) crossbar arrays grown on graphene layers. To make the ZnO NT crossbar arrays, position- and morphology-controlled ZnO NT were grown on CVD graphene layers/SiO_2/Si substrate. Polyimide layer were formed on the sample and these entire layers were peeled off from the substrate. Top and bottom electrode lines were formed in a highly aligned manner with each ZnO NT, forming individually addressable ZnO NT crossbar array. The interesting electrical characteristics of these devices and their flexibility were demonstrated.

5:15 PM

(PACRIM-S10-018-2017) Fabrication of low-dimensional carbon and titania nanotube composites via solution chemical process and their electrical properties

S. Eom*[1]; S. Cho[2]; T. Goto[2]; T. Sekino[2]

1. Osaka University, Division of Materials and Manufacturing Science Graduate School of Engineering, Japan
2. Osaka University, The Institute of Scientific and Industrial Research (ISIR), Japan

Low dimensional structures have attracted tremendous attention in recent years. Titania nanotubes (TNTs) have received many attention in wide range of application due to their properties. However, it has rather low electrical conductivity so that enhancing the conductivity is necessary if they can be used for various devices such as sensor material. We have thus investigated a synthesis of low-dimension carbon and TNT composite via solution chemical process. The low-dimensional carbons such as carbon nanotube (CNT) and graphene oxide (GO) are widely known as 1- and 2-dimensional carbon materials. At first CNT/TNT(1d/1d) composite have been synthesized via the solution chemical route. The product had a unique core-shell nanotubular structure, where CNT core was surrounded by rolled shell form of TNT. Meanwhile, GO/TNT(2d/1d) composite had sheet structure, in which TNT decorated on the 2-d carbon sheet. Electrical resistivity of synthesized 1d/1d and 2d/1d composites were measured in a powdery form by the 4-probe resistivity test at room temperature. The larger amount of carbon exhibited lower resistivity, but small amount of carbon (around 1wt.%) also showed a good powder electrical conductivity of approximately $10^5\Omega$cm. Detailed nanostructural features and electrical properties will be discussed.

5:30 PM

(PACRIM-S10-019-2017) Shape-Controlled Barium Titanate: From nanorods array to ordered nanosheets array and nanospheres

L. Yao*[1]; J. Zhai[2]; H. Chen[1]

1. University of Macau, Faculty of Science and Technology, Macao
2. Tongji University, Functional Materials Research Laboratory, China

The well-ordered ferroelectric oxides array appears shape-dependent properties that could exhibit superior performance in piezoelectric, mechanical, optical and electrical aspects, especially in the energy harvesting and energy storage. In this study, an intriguing strategy by a 3-step hydrothermal reaction was proposed to synthesize ordered barium titanate array on a transparent conductive substrate using the alkali-treated titanium oxides nanorod array as the template. Through controlling the concentration of Ba^{2+}, the temperature, the PH value and the solvent solution, a variety ordered morphologies have been successfully prepared, exhibiting either nanorod array, nanosheets array and nanospheres. The orientation and dispersibility of the obtained barium titanate could be further determined by the ionic strength of the solution.

5:45 PM

(PACRIM-S10-020-2017) The origin of ferroelectricity in strained $CaTiO_3/SrTiO_3$ superlattices

R. Engel-Herbert*[1]

1. The Pennsylvania State University, Materials Science and Engineering, USA

Complex perovskite oxide superlattices have received considerable attention as these artificial structures can possess properties that are beyond the bulk counterparts of the constituting layers. Interface phenomena can become dominant if a high interface density is achieved, leading to the emergence of otherwise unattainable functionalities. Excellent thin film synthesis control with precision down to the atomic layer are a mandatory requirement to ensure high quality interfaces to understand these emerging phenomena. In this talk the role of stoichiometry on stabilizing the ferroelectric ground state in strained $CaTiO_3$ and $SrTiO_3$ thin films as well as $(CaTiO_3)_n(SrTiO_3)_n$ superlattices is discussed. While $CaTiO_3$ and $SrTiO_3$ were both ferroelectric when epitaxially strained, the analysis of a series of superlattices with layering thicknesses from n=1 to 10 unit cells revealed that the ferroelectric properties were dependent on the layer thickness and interface roughness. Superlattices with layer thickness n larger than 5 revealed ferroelectricity, while for n<5 no ferroelectricity was found if the interfaces were atomically abrupt. Synchrotron-based X-ray diffraction experiments in conjunction with scanning transmission electron microscopy revealed that the ferroelectricity for the n<5 superlattices can be infused if rougher interfaces were formed resulting in a intermixing of the layers at the interface.

6:00 PM

(PACRIM-S10-021-2017) Development of Miniature Generator Combined with Magnetic Ceramic Material and Silicon Micro Air Turbine

K. Mishima*[1]; K. Kudo[1]; M. Takato[1]; K. Saito[1]; F. Uchikoba[1]

1. Nihon University, Japan

This paper proposes a 5mm scale electromagnetic induction type generator. The developed generator is constructed by combining a multilayer ceramic magnetic circuit and a MEMS (Micro Electro Mechanical Systems) air turbine structure. In the miniature electromagnetic induction type generator, the miniature three-dimensional magnetic circuit with a magnetic material and miniature structure are required. Using multilayer ceramic technology, a three-dimensional coil and a magnetic core are simultaneously introduced. However, this technology is difficult to fabricate a microstructure like the turbine blades. In contrast, the MEMS technology has advantage in microfabrication. However, it is based on the silicon material and a planer structure. By using these technologies that are suitable for miniaturization, a 5 millimeter scale generator was achieved. Moreover, the two different bearing structures; fluid-dynamic bearing system and miniature ball bearing system; were designed, and these structures are discussed and compared. The rotational speed of the MEMS air turbine generator with fluid-dynamic bearing system was 18,000 rpm, and then the output power was 1.42 μVA. The rotor with miniature ball bearing system showed stable rotational motion. This result suggested that the mechanical bearing system has potential of achieving higher output power.

PACRIM Symposium 12: Design, Development, and Applications of Ceramic-Matrix Composites

CMC II

Room: Kohala 3

Session Chair: Ji Yeon Park, Korea Atomic Energy Research Institute

1:15 PM

(PACRIM-S12-011-2017) Ceramic matrix composites with improved high-temperature stability (Invited)

H. Klemm*[1]; C. Steinborn[1]; W. Kunz[1]; K. Schönfeld[1]

1. FhG IKTS Dresden, Germany

Ceramic matrix composites (CMC) offer a high potential for applications at elevated temperatures, e.g. as structural parts in advanced gas turbines. During recent years, significant progress in material development of oxide and non-oxide CMC has been achieved, however, there are still considerable deficits especially in the long-term behavior of the materials in hot gas conditions. The present study, two of the main challenges to be solved in the development of CMC for gas turbine applications will be focused. First some idea about the development of high-temperature stable ceramic fiber coatings in order to assure long-term damage tolerant behavior in hot gas conditions will be suggested. In the second point the oxidation and corrosion behavior of the CMC in hot gas environment will be focused. Based on a detailed understanding of these processes at elevated temperatures, general concepts for the development of environmental barrier coatings (EBC) will be discussed. Multilayered EBC systems with various functions, e.g. self-healing protection mechanisms, are recommended to be promising solutions to obtain systems with high corrosion resistance and long-term stability.

1:40 PM

(PACRIM-S12-012-2017) DSMC Simulation of High Mach Number Taylor-Couette Flow

S. Pradhan*[1]

1. Indian Institute of Science, Department of Chemical Engineering, India

The main focus of this work is to characterise the Taylor-Couette flow of ideal gas between two coaxial cylinders at Mach number Ma = (U_w / \sqrt{kb T_w / m}) in the range 0.01 < Ma < 10, and Knudsen number Kn = (1 / (\sqrt{2} \pi d^2 n_d (r_2 - r_1))) in the range 0.001 < Kn < 5, using two-dimensional (2D) direct simulation Monte Carlo (DSMC) simulations. In a compressible Taylor-Couette flow, we examine the result that the splitting of the Taylor vortices takes place proportional as (L/(r_2 - r_1)). The resolution suggested by our simulation is that even though the Mach number based on the wall velocity and temperature is large, the local Mach number based on the local dissipation velocity in regions of high shear decreases due to an increase in temperature. Due to this, the ratio of the mean free path and characteristics flow scale (lambda/(r_2 – r_1)) appears to taper off in the high Mach number limit. A modification of the velocity profile in the viscous rotating boundary layer near the wall, which takes into account temperature and density variations, is derived. The variation of the velocity and temperature is predicted under the assumption that the increase in temperature across the viscous rotating boundary layer is larger than the wall temperature.

1:55 PM

(PACRIM-S12-013-2017) Novel MAX-phase/SiC fiber composites: Processing, properties and near net shaping

J. Gonzalez-Julian*[1]; J. Llorente[2]; M. Bram[1]; M. Belmonte[2]; R. Vassen[1]; O. Guillon[1]

1. Forschungszentrum Juelich, Germany
2. Institute of Ceramics and Glass, CSIC, Spain

MAX phases are excellent candidates for high temperature application (> 1000 °C) due to their unique combination of properties, bridging the gap between ceramics and metals. As ceramics, they are lightweight, and show excellent oxidation and corrosion resistances, meanwhile as metals, MAX phases present good damage tolerance, and high thermal and electrical conductivities. Incorporation of fibers to improve properties, mainly the mechanical ones, has been extensively explored in advanced ceramic systems, leading to ceramic matrix composites (CMCs). However, investigations of CMCs based on MAX phases are very limited despite their large potential for high temperature applications. In this work, processing of the MAX composites containing short SiC fibers and their mechanical and tribological response are presented. Cr_2AlC phase was synthesized from its elemental constituents and mixed with different contents (5 and 10 wt.%) of SiC fibers. Afterwards, the composites are fully densified using Field Assisted Sintering Technique. Regarding the properties of the developed composites, mechanical properties were characterized by Vickers indentation and the tribological response by reciprocating ball-on-plate configuration under dry conditions. In addition, gear wheels of Ti_2AlC/SiC fibers have been successfully produced by injection molding, obtaining homogeneous components with excellent surface quality.

2:10 PM

(PACRIM-S12-014-2017) Mechanical Properties of SiC_f/SiC Composites with Carbon and Boron Nitride Interfacial Coatings Formed by Electrophoretic Deposition Method (Invited)

K. Yoshida*[1]; R. Shirata[1]; T. Ajito[1]; T. Yano[1]; M. Kotani[2]; T. Aoki[2]; T. Ogasawara[3]

1. Tokyo Institute of Technology, Japan
2. Japan Aerospace Exploration Agency (JAXA), Japan
3. Tokyo University of Agriculture and Technology, Japan

Silicon carbide fiber-reinforced silicon carbide matrix (SiC_f/SiC) composites have been recognized as key materials for aerospace industries, high-temperature gas turbines and future nuclear and fusion applications. Fiber/matrix interfaces act as an important role for toughening and strengthening SiC_f/SiC composites, and carbon or hexagonal-boron nitride interfacial coating has been applied for SiC_f/SiC composites. Generally these interfacial coatings have been formed by chemical vapor infiltration (CVI) or chemical vapor deposition (CVD). Present authors have developed novel process to form interfacial coatings on SiC fibers in SiC_f/SiC composites based on electrophoretic deposition (EPD) method. In this study, carbon and boron nitride interfacial coatings on polycrystalline and amorphous SiC fibers for SiC_f/SiC composites were formed by EPD method, and mechanical properties of uni-directional SiC_f/SiC composites were evaluated. In addition, the interfacial coatings for the SiC_f/SiC composites were characterized.

2:35 PM

(PACRIM-S12-015-2017) Core-shell and composites ferroelectrics ceramics for electrocaloric applications

M. Anoufa*[1]; J. Kiat[1]; C. Bogicevic[1]

1. CentraleSupelec, Laboratoire SPMS, France

The physical behavior of a ferroelectric can be deeply affected by its core-shell structure and grains inhomogeneous composition. The core-shell structure has an important impact on phase transitions whereas the compositions has a great influence on the local electric and magnetic field. We can showed theoretically that kind of structure can serve as the basis for improving the electrocaloric (ECE) properties of a ferroelectric in some given situation (the ECE effect is a promising candidate for a future refrigeration technology which is both clean and passive). The case of a conductor/ferroelectric composite is discussed in the light of our core-shell Landau model. We show that a conjunction of a specific core-shell and mixing ratio of conductor grains can lead to interesting result within the frame of electrocaloric materials. Although the design of a perfect conductor/ferroelectric composite is experimentally difficult, we have set up a chemical process which overcome several common barriers. Our preliminary measurement using IR technics for the ECE effect show an encouraging result which comfort the conclusion of previous calculations.

2:50 PM

(PACRIM-S12-016-2017) C_f/SiC-ZrC-ZrB_2 fabricated by reactive infiltration of $ZrSi_2$ into C_f/B_4C-C preform with adjustable pore structure

X. Chen*[1]; S. Dong[1]; Y. Kan[1]; H. Zhou[1]; D. Ni[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

C_f/UHTCs (continuous carbon fiber reinforced ultra-high temperature ceramic composites) have received wide attention because of their potential applications in hypersonic vehicles. So far, a lot of researches have been focused on fabrication technique of C_f/UHTCs and RMI (reactive melt infiltration) has been proved to be a quicker and lower cost fabrication technique compared with others. Fabrication of C_f/UHTCs by RMI usually proceeds in two steps: (i) preparation of porous preform and (ii) infiltration of alloy melt into the porous preform. Currently, the porous preform prepared by SI (slurry infiltration) and CVI (chemical vapor infiltration) has obvious disadvantages of inhomogeneous pore size and pore closure, which impede the melt infiltration and inevitably compromise the advantages of RMI in C_f/UHTCs fabrication. Herein, we proposed to prepare porous preform with tailored pore structure via sol-gel method. Based on the modified porous preform, C_f/UHTCs with enhanced properties were obtained by infiltrating $ZrSi_2$ melt into the preform. It was found that dynamics of $ZrSi_2$ melt infiltration and in-situ formation of UHTCs phase were closely dependent on the pore structure of the preform. Hydrodynamic reason for the improvement of infiltration process and diffusion behavior of the $ZrSi_2$ melt into fiber were studied systematically.

3:05 PM

(PACRIM-S12-017-2017) Microstructural and mechanical characterization of damage tolerant SiC/SiCN ceramic matrix composites manufactured via PIP process

B. Mainzer*[1]; R. Jemmali[1]; M. Frieß[1]; D. Koch[1]

1. DLR - German Aerospace Center, Institute of Structures and Design, Germany

Silicon carbide fiber reinforced SiC composites offer performance advantages such as higher temperature capability and significant lower density over the currently used metallic superalloys. In this work silicon carbide fiber reinforced nitrogenous SiC composites (SiC/SiCN) were manufactured by polymer infiltration and pyrolysis. As precursor a polyvinylsilazane with low viscosity was infiltrated via resin transfer molding into Tyranno SA3 fiber preforms, cured and pyrolyzed. Due to process induced shrinkage several reinfiltration and pyrolysis steps had to be performed until an acceptable porosity below 5% was achieved. The matrix precursor was investigated in terms of thermal behavior via differential scanning calorimetry and rheology measurement to find the ideal temperatures for the polymer infiltration step. Pure matrix specimens were cured and pyrolyzed. The densification during pyrolysis was investigated in terms of thermogravimetric analysis, He gas pycnometry and X-ray diffraction. Finally the microstructure of the composite and the quality of the infiltration process was characterized by SEM and μCT. To determine the mechanical properties of the SiC/SiCN composites, samples were tested by means of 3-point bending.

3:35 PM

(PACRIM-S12-018-2017) Novel Manufacturing Techniques for Oxide Fiber Composites (Invited)

W. Krenkel*[1]; G. Puchas[1]; S. Knohl[1]

1. University of Bayreuth, Germany

Oxide fiber composites (OFCs) are more and more applied in the combustion environment or in metallurgical processes due to their excellent thermo-mechanical behaviour and their high corrosion resistance. Since the properties of oxide fiber composites depend largely on the reinforcing fiber and matrix materials, a wide range of structural materials can be achieved through the appropriate selection of said materials. Novel manufacture processes for OFCs, such as two different prepreg routes, including a freeze casting step, and two consolidation steps, respectively, and a vacuum-assisted infiltration process, suitable for the fabrication of woven fabrics as well as complex three-dimensional braids, will be explained. Three different oxide fiber composite materials, namely Nextel^{TM} 610/Al_2O_3-ZrO_2 composites, Nextel^{TM} 610/YAG-ZrO_2 composites and Nextel^{TM} 720/Mullite-ZrO_2 composites were developed. These materials are compared regarding their mechanical properties, high temperature resistance and microstructure and possible fields of applications for these different materials are discussed.

4:00 PM

(PACRIM-S12-019-2017) Impact of Preform Composition and Geometry on Reactive Alloy Melt Infiltration

R. B. Reitz*[1]; F. W. Zok[1]; C. G. Levi[1]

1. University of California, Santa Barbara, Materials, USA

Reactive alloy melt infiltration can be used to produce fully dense SiC/SiC composites, but the preforms that are used for this process contain features on a variety of length scales and contain significant quantities of silicon carbide as well as carbon. This often leads to incomplete infiltration or incomplete reaction, leaving residual porosity or free silicon and limiting the operating temperature of the composite. The current work seeks to improve the processing of these composites by examining the impact of preform geometry and composition on the infiltration rates and reactions that are observed. Infiltration of pure silicon and silicon-yttrium alloys into powder beds or unidirectional fibers composed of SiC, C, or a mixture of the two will be discussed. The impact of the preform on the infiltration rate, final infiltration lengths, and phases produced will be emphasized.

4:15 PM

(PACRIM-S12-022-2017) High energy-storage density and Low loss in the niobate-based glass-ceramic composite materials for energy-storage applications

H. Wang*[1]; J. Liu[1]; J. Zhai[1]; B. Shen[1]

1. Functional Materials Research Laboratory, China

The glass-ceramic composite materials with high energy-storage density, high discharged efficiency and loss dielectric loss were prepared through the melt-quenching combined with the controlled crystallization technique in (BaO,SrO)-Na_2O-Nb_2O_5-SiO_2 (BSNNS) glass-ceramic material. By varying the compositions and crystallization temperature, phase evolution, microstructure, dielectric properties, and energy-storage performances were investigated in detail. In addition, the dielectric loss (~0.003) was decreased in the optimized BSNNS glass-ceramic system doped by MnO_2. Theoretical energy-storage density reaches up to the value of ~17 J/cm^3 at low crystallization temperature of 750°C. In addition, discharge energy density and discharge efficiency of glass-ceramic capacitor were achieved through a pulse charge-discharge circuit.

4:30 PM

(PACRIM-S12-023-2017) Mode II delamination onset in carbon fibre reinforced SiC: End-notched flexure testing and cohesive zone modelling

S. Hofmann*[1]; D. Koch[1]

1. DLR - German Aerospace Center, Ceramic Composites and Structures, Germany

Delaminations are often-cited defects in ceramic matrix composite (CMC) structures which can endanger the structural integrity. Interlaminar cracks may be initiated due to differing shrinkage of fibre and matrix during processing or due to out-of-plane stresses during service. The goal of the present work was to determine the critical energy release rate for delaminations under mode II loading, G_{IIc}, within carbon fibre reinforced silicon carbide, C/C-SiC. The adaption of end-notched flexure test standards from fibre reinforced polymers is described. Different evaluation methods are applied on the load-deflection data for fabric (0/90°) reinforced C/C-SiC. The resulting critical energy release rates are compared. The applicability of the determined energy release rate is validated by cohesive zone modelling using the experimental critical energy release rate, a maximum stress criterion and a linear softening rule within the commercial finite element code ANSYS. A good agreement of numerical and experimental crack onset load points was obtained for various initial crack lengths under interlaminar shear loading.

4:45 PM

(PACRIM-S12-024-2017) High Temperature Mechanical Properties of BN Particle Dispersion SiC Composites

T. Hinoki*[1]; S. Yanagawa[1]; K. Shimoda[2]

1. Kyoto University, Japan
2. National Institute for Materials Science (NIMS), Japan

Silicon carbide composites basically require weak fiber/matrix interphase like carbon or boron nitride (BN). The interphase material and its thickness are keys to determine mechanical properties. However precise control is the critical issue in terms of large scale production and material cost. The interphase is the weakest link for the environmental effects. The SiC composites were developed by applying BN particle dispersion in SiC matrix without the interphase. The objective is to understand the high temperature mechanical properties of the SiC composites. Silicon carbide composites were fabricated by liquid phase sintering method. Silicon carbide with BN matrix was formed by mixture of SiC and BN powder in which BN volume fraction was controlled within the range of 20~70%. Mechanical properties were characterized by tensile test before and after exposure in air up to 1750C. Fatigue tests were also carried out in air up to 1200C. Microstructures and fracture surfaces were characterized by FE-SEM. The BN particle dispersion SiC composites have uniform microstructure through thickness. No significant degradation of tensile strength wasn't observed following exposure up to 1500C in air. Oxidation of the composites were limited to near surface in particular for the fiber bundle region up to 1500C.

PACRIM Symposium 14: Novel Spray Coatings

Advanced Spray Coatings

Room: King's 3
Session Chairs: Dongming Zhu, NASA Glenn Research;
Byung-Koog Jang, National Institute for Materials Science (NIMS)

1:15 PM

(PACRIM-S14-011-2017) Solution Plasma Spray: Addressing some of the challenges (Invited)

E. H. Jordan*[1]

1. University of Connecticut, Mechanical Engineering, USA

Solution precursor plasma spray creates coatings from chemical precursors by injecting them directly into a plasma torch. The process allows very rapid exploration of compositional ratios can produce generally finer microstructures than powder spray and can produce unique microstructures that are beneficial for specific applications. These special features include cracks normal to the substrate surface and layered porosity that lowers thermal conductivity both advantages for thermal barrier coatings. However, the deposition rate is lower due in part to the energy required to evaporate the solvent and there are challenges of getting consistent droplet formation and limitations associated with too high or too low viscosity. Methods to mitigate these challenges will be presented that include using precursor additives and recent progress brought about by the use of a cascaded arc gun.

1:45 PM

(PACRIM-S14-012-2017) Advanced High Temperature Coatings by Liquid Feedstock Plasma Spraying

N. Markocsan*[1]

1. University West, Sweden

Extensive research and development efforts have been devoted over the past decades to develop new coating microstructures that give better functional performances under high temperature exposure. Liquid feedstock plasma spraying (LFPS) is an emerging coating process that enables the deposition of ultrafine droplets (typically from nano- to sub-micron size) that permits the production of coatings with unique microstructures, one or two orders of magnitude finer than those achieved typically in other thermal spray processes. For thermal barrier coating (TBC) applications the feature of interest is the generation of coatings that form vertical cracks or even truly columnar structures that can give higher strain tolerance than the state-of-art dry powder atmospheric plasma spray (APS) process. In this paper the results of a study focussed on the development high performance TBCs using LFPS is presented. The results are showing the different types of the microstructures that can be designed but also the correlation between the coating microstructure and thermal conductivity as well as between microstructure and functional performances/lifetime are presented. The good functional properties of the new TBCs suggest the LFPS process as a serious candidate for the new coatings to be used in the next generation gas turbines.

2:00 PM

(PACRIM-S14-013-2017) Solution Precursor Plasma Spray of Superhydrophobic Ceramic Coatings: Investigation of Wetting Behavior

P. Xu[1]; L. Pershin[1]; T. Coyle*[2]; J. Mostaghimi[1]

1. University of Toronto, Mechanical and Industrial Engineering, Canada
2. University of Toronto, Materials Science and Engineering, Canada

A novel and fast process to fabricate superhydrophobic ceramic coatings using solution precursor plasma spray (SPPS) was investigated in this work. Ytterbium nitrate pentahydrate dissolved in water, ethanol or a mixture of both was used as solution precursors. Ytterbium oxide coatings were formed by injecting the solution radially into the plasma generated by a commercial F4-VB torch (Oerlikon Metco). The coating hydrophobicity was characterized by measuring the water contact angle and sliding angle, and by dynamic water impact tests. The effects of various spray parameters including torch power, plasma gases, standoff distances and solvent types on the coating hydrophobicity were investigated. The wetting behavior and top surface microstructure of the coatings were investigated and correlated. The microstructure and wetting behavior of the coatings were also compared with coatings deposited by a Mettech Axial III 600 torch (Northwest Mettech Corp.) which uses axial solution injection.

2:15 PM

(PACRIM-S14-014-2017) Microstructure and Thermal Properties Characterization of YSZ Coatings with Different Porosity Deposited by Suspension Plasma Spray Process

P. Xu[1]; L. Pershin[1]; T. Coyle[2]; J. Mostaghimi*[1]

1. University of Toronto, Mechanical and Industrial Engineering, Canada
2. University of Toronto, Materials Science and Engineering, Canada

Suspension plasma spray (SPS), as a relatively new plasma spray technique, plays an important role in manufacturing finely structured coatings. In this work, the process of suspension plasma spray of yttrium stabilized zirconia (7wt% YSZ) coatings was investigated experimentally. Agglomerated nanosized 7wt% YSZ powder (Nanox^{TM} S4007, Inframat Advanced Materials) was ball-milled and made into suspension with water or ethanol as solvent. The suspension plasma spray process was operated with a commercial F4-VB torch (Oerlikon Metco) operating with Ar/H_2 plasma gas. By tailoring the plasma gas compositions, standoff distances and suspension types, coatings with porosities ranging from 5% to 20% were deposited. The correlation between the processing parameters and coating properties including microstructure and thermal diffusivity was investigated. The coatings microstructure was characterized, and the thermal diffusivity of coatings under different porosities was tested by laser flash analysis (DLF 1200, TA Instrument) at different temperatures. To compare with conventional plasma spray coatings, YSZ coatings with similar porosities were deposited using hollow spherical powder (Metco 204B-NS, Oerlikon Metco). The microstructure and thermal diffusivity were investigated and compared with coatings formed by SPS process.

2:30 PM

(PACRIM-S14-015-2017) Formation of porous ceramic coatings by plasma spraying with suspension and fine feedstock

M. Suzuki*[1]; M. Shahien[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Advanced Coating Process Research Center, Japan

Its importance significantly increases more and more to prepare the high quality porous ceramic coatings. Especially, the SPSed porous coatings are believed to be a promising candidate for next generation of TBCs for gas turbine and jet engines. Usage of finer feedstock, such as 1-5 micron in mean diameter, had been one of the possibility to obtain high quality ceramic coatings. However there are difficulties in sending such a fine feed stock and inject into the plasma jet. In this study, plasma spraying with finer feedstock with using modified powder feeder and axial feed plasma spray system. Microstructure of the obtained coatings will be compared with the SPSed coatings.

2:45 PM

(PACRIM-S14-016-2017) Thermal Spray as an Additive/Layered Manufacturing Technology for Energy Related Applications

S. Sampath*[1]

1. Stony Brook University, Center for Thermal Spray Research, USA

Thermal spraying is a melt spray deposition process, in which particles in the diameter range of 1-100 microns are heated, melted, propelled and impacted onto a prepared substrate. A rapid sequence of events occurs: melting, spreading and rapid solidification, all taking place in microsecond timescales, enabling materials synthesis from extreme conditions. Coating is resultant from successive assemblage of microscale impacted droplets producing mesoscale thick films. Resultant deposits are defected, anisotropic, layered structures with concomitant implications on properties. The layered assembly also imparts gradients in through thickness residual stresses. These effects are in large part deemed “unintentional” and incorporated in many applications with limited manipulation. With advancements in understanding of process dynamics and the ability to control microstructures, a fresh opportunity is available to engineer and properties and functionalities through optimization of layered assembly. In this presentation, embodiments of such concepts will be shown using the interplay among coating architecture design, materials and manufacturing. Specific examples include novel multifunctional thermal barrier coatings, multifunctional coatings in fuel cells and thermoelectric devices. Illustrative examples of their applicability in industrial systems will also be highlighted.

3:00 PM

(PACRIM-S14-017-2017) Functionally Graded Thermal Barrier Coatings Fabricated by Cold Spray Technique

K. Ogawa*[1]; K. Lee[1]; K. Sato[2]

1. Tohoku University, Fracture and Reliability Research Institute, Japan
2. Fujimi Incorporated, Thermal Spray Materials Dept, Japan

In recent years, application of Thermal Barrier Coatings (TBC) to turbine blade surfaces is absolutely indispensable. The TBC technique restricts temperature rise by applying thermally insulating ceramic coatings, a few hundred μm thick, to heat resistant alloy substrates. The TBC systems usually consists of a ceramic TBC top coat, an intermediate metallic-Bond Coat (BC) and a superalloy substrate. However, during service, Thermally Grown Oxide (TGO) layer initiates and grows at the interfaces between the TBC and the BC. The TGO can lead to delamination of the TBC. If such delamination occurs, substrates are exposed to high temperature environments and the lifetime of the turbine blades is shortened. Therefore, it is required to improve the delamination resistance of the TBC. Therefore, functionally graded TBCs (FG-TBCs) have been developed. In this study, the cold spray technique was applied to the fabrication of FG-TBCs. However, the cold spray has a severe problem with regard to deposition of ceramic materials. To solve this problem, cermet powder was applied to the fabrication of FG-TBC. Here, a cermet powder is used to produce a FG-TBC with a constant rate in each layer. CoNiCrAlY/YSZ cermet powders with different compositions were prepared to deposit on a substrate.

3:15 PM

(PACRIM-S14-018-2017) Photoactive Surfaces by Cold Spraying of Semiconductors

M. Villa Vidaller*[1]; A. Rzeszutek-Pistidda[2]; M. Schieda[2]; F. Gaertner[1]; T. Klassen[1]

1. Helmut-Schmidt-University. University of the Federal Armed Forces, Institute of Materials Technology, Germany
2. Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research, Institut for Materials Research, Germany

Photoactive semiconductors are of great interest for water and air purification as well as for hydrogen production by direct splitting of water under solar irradiation. Cold spraying is ideal to produce the required highly active coatings of these materials for respective solar reactors. Powder particles are accelerated in a gas stream to velocities of more than 800 m/s and bond to the substrate upon impact in solid state. Due to relatively moderate temperatures, phase transitions are usually not observed. Moreover, additional binder agents are not required. Consequently, photoactivities comparable to the initial feedstock powder are achieved. In the present work, the optimum conditions for producing active coatings by cold spraying will be discussed. Initially, titanium grade I porous coatings were obtained by cold gas spraying. Metallographic characterization was performed by quantitative image analysis using optical microscopy porosity data and SEM analysis for evaluating the coating/substrate interface integrity. Photocatalytically active TiO_2 semiconductor layers on the porous titanium coatings were also produced by cold gas spray followed by thermal oxidation for different durations and temperatures. The photoactivity of the different coatings is discussed under viewpoints of phase contents and needed thickness as well as optimum thermal treatment for the use in water splitting.

Environmental Barrier Coatings

Room: King’s 3
Session Chairs: Eric Jordan, University of Connecticut;
Kazuhiro Ogawa, Tohoku University

3:45 PM

(PACRIM-S14-019-2017) Robust Multifunctional High Temperature Coatings for Gas Turbine Components using Affordable Processing Approach (Invited)

B. Gogia*[1]; D. Hass[1]

1. Directed Vapor Technologies Intl, USA

Silicon based ceramic components are of interest in gas turbine engines to reduce fuel consumption through reduced weight and increased operating temperatures, which yields improved turbine efficiency. Thermal/Environmental Barrier Coatings (T/EBCs) are coating systems that are applied to the surface of these ceramics to protect against moisture-assisted oxidation-induced ceramic recession. However, several key coating challenges remain including higher temperature capability and prime reliance (especially in the presence of impact/erosion/corrosion conditions). As a result, advanced multifunctional T/EBC systems which are anticipated to be more complex than current systems are sought which both retain or improve the environmental protection afforded at elevated temperatures and also significantly improve the impact and erosion resistance. This would require the cost effective processing approach in which the required coating composition, microstructure and architecture is achieved. Here, a novel affordable Directed Vapor

Deposition (DVD) approach that results in the highly efficient deposition of advanced coating structures and compositions is used to deposit multifunctional T/EBC barrier coatings. Results indicate that the novel coatings created using the DVD technique can be effectively employed to improve component performance.

4:15 PM

(PACRIM-S14-020-2017) Advanced Environmental Barrier Coating Development for SiC-SiC Ceramic Matrix Composite Components

D. Zhu*[1]; B. J. Harder[1]; J. B. Hurst[1]

1. NASA Glenn Research, Materials and Structures Division, USA

This presentation reviews the NASA advanced environmental barrier coating (EBC) system development for SiC/SiC Ceramic Matrix Composite (CMC) combustors particularly under the NASA Environmentally Responsible Aviation, Fundamental Aeronautics and Transformative Aeronautics Concepts Programs. The emphases have been placed on the current design challenges of the 2700-3000°F capable environmental barrier coatings for low NO_X emission combustors for next generation turbine engines by using advanced plasma spray based processes, and the coating processing and integration with SiC/SiC CMCs and component systems. The developments also have included candidate coating composition system designs, degradation mechanisms, performance evaluation and down-selects; the processing optimizations using TriplexPro Air Plasma Spray Low Pressure Plasma Spray (LPPS), Plasma Spray – Physical Vapor Deposition and demonstration of EBC-CMC systems. This presentation also highlights the EBC-CMC system temperature capability and durability improvements under the NASA development programs, as demonstrated in the simulated engine high heat flux, combustion environments, in conjunction with high heat flux, mechanical creep and fatigue loading testing conditions.

4:30 PM

(PACRIM-S14-021-2017) Characteristics by High Temperature Exposure of RE-doped Silicate Environmental Barrier Coatings (Invited)

B. Jang*[1]; S. Ueno[2]; K. Lee[3]; S. Kim[4]; Y. Oh[4]; H. Kim[4]

1. National Institute for Materials Science (NIMS), Research Center for Structural Materials, Japan
2. Nihon University, College of Engineering, Japan
3. Kookmin University, School of Mechanical Systems Engineering, Republic of Korea
4. Korea Institute of Ceramic Engineering and Technology, Engineering Ceramic Center, Republic of Korea

Y_2SiO_5 Environmental barrier coatings (EBC) have been deposited by flame spray technique as protection layer of SiC substrate from oxidation and steam corrosion in high temperature. The isothermal heat treatments of Y_2SiO_5 EBC were performed at 1180 °C and 1480 °C with holding times of 1, 10, 50, and 100 h. The thermal behaviors such as phase transformation, microstructure and TGO formation phenomena have been examined by XRD, SEM, and EDS analysis. The different TGO growth behaviors have been found at different heat treatment. The result shows that the change of microstructure and composition of Y_2SiO_5 is not too critical, but high temperature and long exposed times are more easily to lead the phase transformation to Y_2SiO_5 crystalline phases and β-Y_2O_3 phase. The evaluation of hardness and Young's modulus was performed on the cross-section of Y_2SiO_5 coatings by nano indentation method at room temperature. The isothermal heat treatment improves the hardness and Young's modulus of Y_2SiO_5 coatings. In addition, high-temperature corrosion behavior of volcanic ash and artificial calcium-magnesium-aluminosilicate (CMAS) on sintered Yb_2SiO_5 is investigated.

5:00 PM

(PACRIM-S14-022-2017) Microstructure control of Yb silicate layers prepared by EB-PVD

T. Yokoi*[1]; N. Yamaguchi[1]; D. Yokoe[1]; T. Kato[1]; T. Matsudaira[1]; S. Kitaoka[1]; M. Takata[1]

1. Japan Fine Ceramics Center, Japan

Environmental barrier coatings (EBCs) can play an important role in enabling SiC fiber-reinforced SiC matrix (SiC/SiC) composites applied for advanced hot-section components in airplane engines. An EBC must exhibit excellent environmental shielding, thermo-mechanical durability and volatilization resistance. Yb silicates are promising substances for the EBCs. Volatilization resistance of Yb_2SiO_5 is superior to $Yb_2Si_2O_7$. Thermal expansion coefficient of $Yb_2Si_2O_7$ is closer to SiC/SiC composites than Yb_2SiO_5. Furthermore, mullite has higher oxygen shielding performance than $Yb_2Si_2O_7$. Thus, we design EBC including composition-gradient Yb silicate layer on mullite oxygen shielding layer. Surface of Yb_2SiO_5 layer has columnar structure with longitudinal gap to improve thermal shock resistance. The mullite layer bonds to SiC/SiC substrate through a Si-based bond layer. In this study, we investigated microstructure control of Yb silicate layers prepared by electron beam PVD during heating the coating surface. Monophasic $Yb_2Si_2O_7$ and Yb_2SiO_5 layers and the composition-gradient Yb silicate layer had dense and oriented structures. Microstructure of the layer were controllable from the dense structure to the columnar structure depending on coating condition. The gas shielding property and structural stability of the dense layers were quantitatively evaluated by oxygen permeation technique at high temperatures.

5:15 PM

(PACRIM-S14-024-2017) Next-Generation Graded High Temperature Ceramic Matrix Composites (CMC) Based Propulsion Components (Invited)

A. Ghoshal*[1]; M. Murugan[1]; M. J. Walock[1]; A. Nieto[1]; C. Shiao[1]; B. D. Barnett[1]; M. S. Pepi[1]; J. Swab[1]; R. Dowding[1]

1. US Army Research Laboratory, USA

Aviation propulsion system structures are subjected to challenging conditions such as extremely high velocities, ultra-high/low temperatures, and excessive dust/sand/smoke/volcanic ash condition. The goal of this collaborative research program between ARL and AMRDEC is to establish a generalized fundamental physics-based approach and probabilistic-based lifing method to extrapolate thermal loading performance and material characterization results from high performance ultra-high temperature ceramic materials such as ceramic matrix composites (CMC) based flat specimens and engine component representative specimens. High temperature structural integrity and durability and probabilistic based lifing assessment will be evaluated both analytically and experimentally under various loadings. We have identified the following four different research thrust areas and capability needs which will be expanded further in the paper: 1. Processing and Fabrication: Melt Process Infiltration, Chemical Vapor Infiltration 2. Probabilistic CMC Life Models and Experimental Validation 3. CMC Sensing and NDE and Repair 4. Environmental Barrier Coating for CMCs

5:45 PM

(PACRIM-S14-023-2017) High Temperature Degradation of Advanced Thermal and Environmental Barrier Coatings (TEBCs) by CaO-MgO-Al_2O_3-SiO_2 (CMAS)

G. Costa*[1]; D. Zhu[1]

1. NASA Glenn Research Center, USA

There is increasing interest in the degradation studies of thermal and environmental barrier coatings (TEBCs) of gas turbines by molten CaO-MgO-Al_2O_3-SiO_2 (CMAS). CMAS minerals are usually referred as silica-containing sand dust and volcano ash materials that are carried by the intake air into gas turbines, e.g. in aircraft engines, and their low-melting deposits react at high temperatures (>1000°C) with the coating materials. This causes degradation and accelerated coating failure of the static and rotating components of the turbine engines. We discuss some preliminary results of the reactions between CMAS and Rare-Earth (RE – Y, Yb, Dy, Gd, Nd and Sm) oxide stabilized ZrO_2 or HfO_2 systems, and the stability of the resulting oxides and silicates. Plasma sprayed hollow tube samples (OD Æ = 4.7 mm, wall thickness 0.76 mm and 26 mm height) were half filled with CMAS powder, wrapped and sealed with platinum foil, and heat- treated at 1310 °C for 5h. Samples were characterized by differential scanning calorimetry, X-ray diffraction and cross section electron microscopy analysis.

PACRIM Symposium 17: Advanced Functional Ceramics and Critical Materials Perspective

Advanced Functional Ceramics and Critical Materials Perspective V

Room: Kohala 2

Session Chairs: Nobuhito Imanaka, Osaka University; Satoshi Wada, University of Yamanashi; Shinji Tamura, Osaka University

1:30 PM

(PACRIM-S17-038-2017) Recent Developments in Relaxor-PT Piezoelectric Ceramics and Crystals (Invited)

F. Li[1]; S. Zhang[1]; D. Lin[1]; S. Taylor[2]; J. Luo[2]; L. Chen[1]; T. Shrout*[1]

1. The Pennsylvania State University, USA
2. (3) TRS Technologies, USA

The discovery of ultrahigh piezoelectricity in relaxor ferroelectric solid solution single crystals, e.g. PMN-PT, has led to their implementation in high performance medical ultrasound transducers and underwater sonar. A key signature of relaxor-ferroelectrics is the existence of polar nano regions (PNRs), a nano-scale inhomogeneity that coexists with normal ferroelectric domains. The contribution of these local structures has been theoretically modeled to be the origin of the ultra-high piezo activity. Based on the paradigm, recent developments have experimentally confirmed that modest changes in the polarizability of PNRS can be regarded as “seeds” to further enhance the piezoelectric activity of relaxor ferroelectrics. Both modified polycrystalline and single crystals have been shown to exhibit ultrahigh piezoelectric d 33 coefficients. Furthermore, dielectric permittivities greater than 10,000 and relatively good temperature stability have been achieved. The impact of these property improvements on applications, including ultrasound transducers and sensors, will be presented.

1:50 PM

(PACRIM-S17-039-2017) Structural, Dielectric and Magnetic Properties of $Ba_3SrLn_2Fe_2Nb_8O_{30}$ (Ln=La, Nd, Sm) Filled Tungsten Bronze Ceramics

W. Chen*[1]; W. Yang[2]; X. Liu[1]; X. Chen[1]

1. Zhejiang University, China
2. Ningbo Branch of China Academy of Ordnance Science, China

Structural, dielectric and magnetic properties have been investigated for $Ba_3SrLn_2Fe_2Nb_8O_{30}$ (Ln=La, Nd, Sm) ceramics. The single phase tetragonal filled tungsten bronze structure in space group P4/mbm is obtained for $Ba_3SrLa_2Fe_2Nb_8O_{30}$, while such tungsten bronze major phase is determined together with minor amount of secondary phases in $Ba_3SrNd_2Fe_2Nb_8O_{30}$ and $Ba_3SrSm_2Fe_2Nb_8O_{30}$. The saturated magnetic hysteresis loops with enhanced M_r are obtained in the present ceramics at room temperature comparing to the $Ba_4Ln_2Fe_2Nb_8O_{30}$ (Ln=La, Nd, Sm) ceramics and they can be ascribed to the tungsten bronze structure. Meanwhile, the typical relaxor behaviors are determined: a broad dielectric peak with strong frequency dispersion and the peak temperature following well with the Vogel-Fulcher relationship.

2:05 PM

(PACRIM-S17-040-2017) High-k dielectric thin films using A-site modified perovskite nanosheets

H. Yim*[1]; S. Yoo[1]; Y. Sung[2]; J. Choi[1]

1. Korea Institute of Science and Technology, Center for Electronic Materials, Republic of Korea
2. Seoul National University, Republic of Korea

The technology of two-dimensional (2D) nanosheets have been attracted a lot of interest due to its special properties such as great magnetic, electrical, and optical properties. Especially, Dion-Jacobson perovskites such as $Sr_2Nb_3O_{10}$ have receiving the most as a dielectric thin film material because it shows high-k performance undisturbed for thickness unlike the commercialized perovskite materials. However, the dielectric permittivity is still below than the thick film value, so development of new composite nanosheets to enhance dielectric performance is necessary. In this work, we investigated Bi-substituted $Sr_2Nb_3O_{10}$ nanosheets in order to study the effect of A-site modification on dielectric performances. 2D nanosheets have been prepared by solution-based cation exchanging process, and dielectric films have been deposited on Nb-doped $SrTiO_3$ substrate through Langmuir-Blodgett method. The structural and electrical properties of nanosheets thin film were investigated by XRD, TEM, and impedance analyzer with its precursor material. The A-site modified new composition shows great dielectric performances (dielectric permittivity of 550 and dielectric loss below 5% at 18 nm thickness), and we expect it will fulfill the requirement of next-generation electronics.

2:20 PM

(PACRIM-S17-041-2017) Low Temperature Synthesis of Perovskite-based Nano-complex Ceramics by Solvothermal Solidification Method for Dielectric and Piezoelectric Enhancement (Invited)

S. Wada*[1]

1. University of Yamanashi, Material Science and Technology, Japan

For next-generation material science, interface engineering is very key issue, and it can be expected that new phenomena and enhanced properties are originated from interface with structure gradient region. Recently, a new technique was proposed to prepare nano-structured ceramics with heteroepitaxial interfaces between barium titanate ($BaTiO_3$, BT) and potassium niobate ($KNbO_3$, KN) prepared at low temperatures below 300 C, and their dielectric and piezoelectric properties were enhanced because of their heteroepitaxial interfaces. To explain the above results, we proposed the following hypothesis, i.e., KN had larger cell volume by 0.5 % than that of BT, and BT unit cell was expanded by epitaxial junction with KN. The origin of high dielectric property of BT is considered of the large converse displacement between the Ti^{4+} ion and the O^{2-} ion octahedron. This is because in the BT unit cell, there is very space in the surrounding Ti^{4+} ion. Thus, anisotropic expansion of BT unit cell can lead to enhancement dielectric properties. On the other hand, bismuth ferrite ($BiFeO_3$, BF) had smaller unit cell volume by 1 % than that of BT. Therefore, we expected that the BT unit cell can be compressed and their dielectric properties for the BT-BF nano-structured ceramics were quiet smaller than those for the BT-KN nano-structured ceramics.

2:40 PM

(PACRIM-S17-042-2017) Reliability Studies on Dielectric Materials of Multi-Layered Ceramic Capacitors (Invited)

A. Ando*[1]

1. Murata Mfg. Co., Japan

A large amount of functional ceramic components will be used in the future electronic application fields. Multi-layered ceramic capacitor (MLCC) is one of the most widely used electronic components, and its high volume-capacitance- density has been required because of high functional integration of electronic devices. Dielectric ceramic layer thickness has been significantly decreased under 1μm. An applied electric field to the dielectric layers of MLCC has been high, then reliability and stability against the high electric fields are important for the dielectric materials of the MLCC. Furthermore, the future MLCCs will be used at various conditions including extremely harsh conditions, for example, at high temperatures, under high electric field, under high mechanical stresses, and so on. Reliability studies of dielectric materials are key issue toward the future electronics. Degradation mechanism of dielectric materials, material designs for high reliability for these dielectric ceramic materials will be discussed.

3:00 PM

(PACRIM-S17-043-2017) Microstructure and dielectric characteristics of $BiMeO_3$-$BaTiO_3$ (Me:$Zn_{1/2}Ti_{1/2}$,Al) ceramics for capacitor applications (Invited)

H. Hao*[1]; M. Liu[1]; T. Wang[1]; Y. Lu[1]; S. Zhang[1]; Z. Yao[1]; M. Cao[1]; H. Liu[1]

1. Wuhan University of Technology, China

The typical "core-shell" structure in $BaTiO_3$ ceramics can easily obtain double dielectric anomalies, which greatly improve the dielectric temperature stability for multilayer ceramic capacitors (MLCC). Bismuth-based perovskite material $BiMeO_3$-$BaTiO_3$ (Me:$Zn_{1/2}Ti_{1/2}$,Al) exhibits high Curie temperature and good dielectric temperature stability and is expected to broaden the working temperature range of MLCC. In this work, dielectric properties of $BaTiO_3$-$Bi(Zn_{1/2}Ti_{1/2})O_3$ and $BaTiO_3$-$BiAlO_3$ were investigated and dielectric temperature stability was improved by Nb_2O_5-doping and multilayer core-shell structure design. The 0.8BT-0.2BZT ceramics doped with 1.5 wt.% Nb_2O_5 was found to possess a moderate dielectric constant (ε=1170) and low dielectric loss (tanδ=1%) at room temperature, showing a flat dielectric behavior over the temperature range of -55°C to 200°C. Based on this composition, the optimized dielectric properties X9R-MLCC with Ag0.7-Pd0.3 electrode was produced at 1060°C. $BiMeO_3$-$BaTiO_3$ (Me:$Zn_{1/2}Ti_{1/2}$,Al) or Nb oxide was chosen to be shell-I (inner layer) or shell-II (outer layer) composition. The structure and dielectric properties of samples with different core to shell ratio (n_c/n_s) and compositions with different ratio were investigated.

3:45 PM

(PACRIM-S17-044-2017) Synthesis and applications of low-dimensional NBT-based micro/nano-materials

D. Zhang*[1]; X. Zhou[1]

1. Central South University, State Key Laboratory of Powder Metallurgy, China

In this study, lead-free sodium bismuth titanate ($Na_{0.5}Bi_{0.5}TiO_3$, NBT) spherical agglomerates, nanowires and microcubes were synthesized using hydrothermal method by changing the reaction parameters. The in-situ transformation process and dissolution-recrystallization mechanism were successfully used to explain the formation of different NBT morphology. Domain structures and piezoelectric characteristics were systematically studied for NBT by piezoresponse force microscopy (PFM). Besides, two-dimensional single crystalline $0.93Na_{0.5}Bi_{0.5}TiO_3$-$0.07BaTiO_3$ (NBT-7BT) platelets with a morphotropic phase boundary (MPB) were synthesized by the topochemical technique, using bismuth layer-structured $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NBIT) platelets as the precursor. The NBT-7BT platelets were used as templates to prepare grain oriented lead-free NBT-7BT ceramics. The NBT-7BT ceramic with 89% degree of grain orientation had an excellent actuating performance with up to 0.7% free strain at 7 kV/mm at room temperature, corresponding to a field-induced S_{max}/E_{max} of as high as 1000 pm/V. The synthesized NBT and NBT-7BT platelets were also used as fillers in poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) matrix to prepare dielectric composites for energy storage application.

4:00 PM

(PACRIM-S17-045-2017) Dielectric properties and resource criticality aspects of hexagonal manganites

S. Krohns*[1]; D. Meier[2]; A. Ruff[1]

1. University of Augsburg, Experimental Physics V, Germany
2. Norwegian University of Science and Technology, Materials Science and Engineering, Norway

Hexagonal manganites exhibit a broad variety of highly interesting features as, e.g., domain vortex structure, geometric improper ferroelectricity and antiferromagnetic ordering. The exact mechanism for ferroelectricity is still under debate as well as the impact of the vortex structure to macroscopic quantities (e.g., the dielectric constant). A technique to determine the multiferroic, ferroelectric and domain wall polarisation phenomena is the measurement of the dielectric response to ac and dc electric fields as well as non-linear measurements, like hysteresis loop or PUND. Here, we thoroughly analyse the dielectric response of $ErMnO_3$ single crystals in a broad temperature and frequency range. Two relaxation processes occur at temperatures below 300 K. One points to an extrinsic so-called Maxwell-Wagner relaxation and the second relaxation seems to be of intrinsic origin. This detailed dielectric analysis allowed a thorough ferroelectric characterisation. Fundamental temperature and frequency dependent materials properties, as coercive fields and polarisation were investigated. These are essential quantities for e.g. using this material in a mulitferroic capacitor. Furthermore we provide, even at this early state of materials research, a long-term based comprehensive study of the restrictions and benefits associated with the usage of the raw materials for hexagonal manganites.

4:15 PM

(PACRIM-S17-046-2017) Freeze-Casting of Lead-Free Dielectric Composites

E. Gorzkowski*[1]; E. Patterson[2]; G. L. Brennecka[3]; M. A. Beuerlein[3]

1. Naval Research Lab, USA
2. ASEE, USA
3. Colorado School of Mines, USA

In previous research freeze-casting was used to construct ceramic-polymer composites in which the two phases are arranged in an electrically parallel configuration. By doing so, the composites exhibit dielectric constant (K) up to two orders of magnitude higher than that of composites with ceramic particles randomly dispersed in a polymer matrix. This technique has been successful with both an aqueous and camphene based ceramic slurry that is frozen uni-directionally to form templates such that ceramic aggregates are aligned in the temperature gradient direction. Freeze-casting is a versatile processing technique that has been demonstrated to work with many ceramic systems. In this paper we will discuss the continued study of freeze-cast processing of composites based around non-saturating $Bi(Zn_{0.5}Ti_{0.5})O_3$ – $BaTiO_3$ ceramics for use in high power capacitor applications. The processing parameters (mold material, particle size, etc.), composite dielectric properties, and composite microstructure will also be presented.

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

Phosphor

Room: Kohala 1
Session Chair: Mariya Zhuravleva, University of Tennessee

1:15 PM

(PACRIM-S20-034-2017) Rapid Screening of Novel Phosphor Materials Using Melt Quenching Method (Invited)

K. Toda*[1]

1. Niigata University, Japan

In this study, we synthesized novel polycrystal, singlecrystal and glass phosphors by a melt quench synthesis technique using arc-imaging furnace. The melt synthesis technique using arc-imaging furnace is suitable for synthesizing phosphors with high luminescence efficiency. The melt reactions are extremely rapid and homogeneous because of liquid mixing and rapid diffusion in the liquid phase, in contrast with the conventional solid-state reactions. Melting using arc-imaging furnace requires no container at various atmospheres up to high temperatures even higher than 2200 K. Furthermore, this method contains rapid cooling process, which indicates that this method is not only suitable for synthesizing powder phosphors but also suitable for synthesizing singlecrystal and glass phosphors.

1:45 PM

(PACRIM-S20-036-2017) Single crystal phosphors for high-power white lighting (Invited)

K. Shimamura*[1]; V. Garcia[1]; D. Inomata[2]; K. Iizuka[2]

1. National Institute for Materials Science, Japan
2. Tamura Corporation, Japan

Conventional white lighting packages consist of blue-LEDs and the yellow Ce^{3+}:$Y_3Al_5O_{12}$ (Ce:YAG) ceramic powder phosphors (CPPs). However, in applications that require high-brightness (HB), a conventional packaging possesses several drawbacks. That is why, a new concept of high-brightness white LEDs based on yellow Ce:YAG single crystal phosphors (SCPs), which can overcome the conventional temperature- and photo-degradation problems of CPPs, is proposed. SCPs demonstrated high internal quantum efficiency (QE_{int}) (over 95%), outstanding thermal stability of QE_{int} in the temperature range 25-300ºC, and quit low temperature increase under high blue irradiation, which contrast with the performance of CPPs. Ce^{3+}:$Lu_3Al_5O_{12}$ (Ce:LuAG) SCP is also proposed as an efficient and clear green source. SCP powders obtained by crashing SCPs have shown the same performances as SCPs. These natures favor the binder free HB packaging based on LD.

2:15 PM

(PACRIM-S20-037-2017) Photoluminescence properties and application of yellow $Ca_{0.65}Si_{10}Al_2O_{0.7}N_{15.3}$:$xEu^{2+}$ phosphors for white LEDs

B. Wang*[1]; Y. Liu[1]; J. Chen[1]; Y. Xia[1]; J. Tang[1]

1. China University of Geosciences, School of Materials Science and Technology, China

A series of yellow-emitting oxynitride $Ca_{0.65}Si_{10}Al_2O_{0.7}N_{15.3}$:$xEu^{2+}$ phosphors with α-sialon structure were synthesized. The phase composition and crystal structure were identified by X-ray diffraction and the Rietveld refinement. The excitation and emission spectra, reflectance spectra and thermal stability were investigated in detail, respectively. Results show that $Ca_{0.65}Si_{10}Al_2O_{0.7}N_{15.3}$:$0.12Eu^{2+}$ phosphors can be efficiently excited by UV-vis light in the broad range of 290-450 nm and exhibit broad emission spectra peaking at 550-575 nm. The concentration quenching mechanism are discussed and determined to be the dipole-dipole interaction. When the temperature increased to 150°C, the emission intensity of $Ca_{0.65}Si_{10}Al_2O_{0.7}N_{15.3}$:$0.12Eu^{2+}$ phosphor is 75.1 % of the initial value at room temperature. White LED was fabricated with N-UV LED chip combined with blue $Ca_3Si_2O_4N_2$:Ce^{3+} and yellow $Ca_{0.65}Si_{10}Al_2O_{0.7}N_{15.3}$:$Eu^{2+}$ phosphors. The color rendering index and correlated color temperature of the white LED are 78.16 and 6779.21 K, respectively. All the results demonstrate that the as-prepared $Ca_{0.65}Si_{10}Al_2O_{0.7}N_{15.3}$:$xEu^{2+}$ may serve as a potential yellow phosphor for N-UV w-LEDs.

2:30 PM

(PACRIM-S20-038-2017) Synthesis and Characterization of Fluorochromic Phosphor Materials

S. Fujihara*[1]; R. Hara[1]; Y. Tsuchiya[1]; M. Hagiwara[1]

1. Keio University, Japan

Fluorochromism is a phenomenon where fluorescence or luminescence is changed in response to external physical or chemical environment. We have attempted to induce fluorochromism in inorganic phosphor materials having excellent chemical, thermal, and mechanical durability compared to organic materials. In the present study, four kinds of phosphors, namely $CePO_4$:Tb^{3+}, CeO_2:Sm^{3+}, $CaWO_4$:Eu^{3+}, and Y_2WO_6:Eu^{3+}, were synthesized as nanoparticles and thin films by liquid processes and their fluorochromic properties were examined under redox conditions. Basically, redox interactions were promoted at the surface of phosphor particles. In oxidation, a few part of lower-valence ions in the host material were oxidized to higher-valence ions, which induced light absorption by an inter-valence charge transfer. This is the case with $CePO_4$:Tb^{3+}, resulting in quenching of Tb^{3+} emissions. Reduction of the oxidized $CePO_4$:Tb^{3+} could recover its luminescence. In the case of CeO_2:Sm^{3+}, $CaWO_4$:Eu^{3+}, and Y_2WO_6:Eu^{3+}, reduction and oxidation led to luminescence quenching and its recovery, respectively. As a result, redox-mediated fluorochromism was achieved in these phosphor materials, which would be expected as a new kind of fluorochromic sensors and probes.

2:45 PM

(PACRIM-S20-039-2017) Mechanisms of Li^+ ions in the Emission Enhancement of $KMg_4(PO_4)_3$:Eu^{2+} for White Light-emitting diodes

J. Chen*[1]; Y. Liu[1]; B. Wang[1]; J. Tang[1]

1. China University of Geoscience Beijing, School of Material Science and Technology, China

Codoping with Li^+ is a prevalent strategy to improve the optical efficiency of luminescent materials, while the mechanisms of enhancement are still ambiguous. Herein, we delineate the major ways by which Li^+ enhanced the emission of orthophosphate phosphor $KMg_4(PO_4)_3$:Eu^{2+} and quantify the relative contributions of each mechanism. Results from X-ray diffraction, scanning electron microscopy, steady-state and time-resolved fluorescence spectroscopies show that the 3.8-fold increase in emission intensity caused by optimized Li^+ doping was attributed to flux effect (~30.84%), crystal-field splitting (~6.34%) and a reduction in concentration quenching (~62.82%), respectively. The as-synthesized materials also show excellent thermal stability and an increased internal quantum efficiency of 84.02% compared with 53.13% of non-doped phosphors. The WLEDs employing $KMg_4(PO_4)_3$:Eu^{2+}, Li^+ as a blue-emitting component exhibit superior electroluminescence properties. The above results demonstrate that introducing Li^+ ions can obviously enhance the luminescence efficiency of $KMg_4(PO_4)_3$:Eu^{2+} phosphor.

3:00 PM

(PACRIM-S20-040-2017) Enhanced persistent luminescence properties of Ce^{3+} activated garnet (Invited)

Y. Katayama*[1]

1. University of Tokyo, Graduate School of Arts and Sciences, Japan

Persistent luminescence (PersL) is a luminescent phenomenon observed at ambient temperature, in most cases at room temperature (RT), and lasts for seconds, minutes to even hours after ceasing excitation sources. This phenomenon can often be qualitatively explained by an electron trapping-detrapping process in insulators and semiconductors. The key point to develop persistent phosphor with bright emission and long duration is tuning the “trap depth” between the bottom of CB and the electron trap to form a proper energy gap favorable for the detrapping process working at RT. We report bright green PersL of Ce^{3+}, Bi^{3+} codoped $Y_3Al_{5-x}Ga_xO_{12}$ (YAGG:Ce^{3+}-Bi^{3+}, x from 0 to 4) due to 5d→4f transition of Ce^{3+} after blue excitation, in which Bi^{3+} related defects work as efficient electron traps. The trap depths, which can be tunable by changing Ga^{3+} content, x from 0.31 to 1.07 eV, were estimated by initial rise method based on thermoluminescence glow curve results. Vacuum referred binding energy diagrams of YAGG:Ce^{3+}-Bi^{3+} phosphors including energy levels of CB and electron trapped trivalent Bi states, $Bi^{3+}+e^-$ or Bi^{2+} were constructed to explain the mechanism of persistent luminescence.

PACRIM Symposium 23: Materials for Solar Thermal Energy Conversion and Storage

CSP Absorbers and Reactors / Thermal Storage Materials

Room: Queen’s 4
Session Chairs: Martin Roeb, DLR - German Aerospace Center; Anthony McDaniel, Sandia National Laboratories

1:15 PM

(PACRIM-S23-001-2017) New solar-selective CSP receiver coatings studied by environmental in situ methods (Invited)

M. Krause*[1]; R. Wenisch[1]; I. Heras[2]; F. Lungwitz[1]; D. Janke[1]; E. Guillén[2]; A. Erbe[1]; R. Escobar Galindo[2]; S. Gemming[1]

1. Helmholtz-Zentrum Dresden - Rossendorf, Inst. for Ion Beam Physics and Materials Research, Germany
2. Abengoa Research, Spain

The development of solar-selective CSP receiver coatings with high-temperature and environmental stability requires new concepts of design and in operando monitoring. Solar receiver tubes are a key component of solar thermal power plants. The increase of their operation temperature from today’s maximum of 550°C to about 800°C could increase the CSP efficiency by approximately 15 to 20% and improve the competiveness of this technology compared to other ones of carbon-free electricity generation. Potential alternatives to fast degrading state-of-the-art pigment paint receiver tube coatings are based on refractive metal carbides, nitrides, and oxides because of their high thermal stability and oxidation resistance. New types of solar-selective coatings were studied in situ at temperatures of up to 830°C by Rutherford backscattering spectrometry, Raman spectroscopy, and spectroscopic ellipsometry within a cluster tool. They include carbon- and oxynitride-absorber based multilayers[1] as well as a solar-selective transmitter based on a transparent conductive oxide. Financial support by the EU, grant No. 645725, project FRIENDS[2], and the HGF via the W3 program (S.G.) is gratefully acknowledged.

1:45 PM

(PACRIM-S23-002-2017) Ceramic structured reactors for solar H_2 production

S. Lorentzou*[1]; A. Zygogianni[1]; C. Pagkoura[1]; G. Karagiannakis[1]; A. G. Konstandopoulos[1]

1. CERTH, Aerosol & Particle Technology Laboratory, APTL, Greece

The two-step redox-based solar thermochemical H_2O splitting cycle is considered to be among the most promising approaches for the production of H_2 from entirely renewable sources such as solar energy and water, and has been the object of investigation from several research groups around the world. Most research efforts focus on cyclic reduction-oxidation of metal oxides, where the high temperatures needed for the reactions are provided from concentrated solar radiation on reactors/receivers located at solar tower or solar dish platforms. The current work focuses on structured reactors that consist of ceramic monolithic bodies. The preparation of structured redox reactor components can be conducted either via conventional slurry coating of the active redox material on appropriate porous substrates, or via construction of the components entirely from the active redox material. In the current work, different redox porous monolithic structures (honeycombs or foams, coated or consisting entirely of the redox materials) were investigated with respect to H_2O-spitting activity and durability (multiple cycles) on small laboratory segments and reached the actual full-size reactor scale. Honeycomb monoliths were tested for over 1000h of cyclic operation. Future investigations will focus on improvement of foam and monolith structures aiming to enhance the accessibility of the active redox mass and increase the H_2 yield and durability.

2:00 PM

(PACRIM-S23-003-2017) Spectral absorptivity of alumina beads for solar particle receivers

M. Schmucker*[1]; C. Happich[2]; B. Gobereit[2]

1. German Aerospace Center, Institute of Materials Research, Germany
2. German Aerospace Center, Institute of Solar Research, Germany

Commercial low-cost proppants made of sintered bauxite can be used as absorber and heat transfer media in a solid particle receiver employed for CSP applications. High absorptivity in the solar wavelength spectrum, sufficient temperature stability and good abrasion resistance are the required properties for this application. Investigated sintered bauxite proppants consist of alpha-alumina, mullite, a glassy phase and $FeAlTiO_5$. Relative high spectral absorptivity is provided by transition metal ions which either may form oxide phases such as $FeAlTiO_5$ or enter the mullite structure or the glassy network, respectively. To improve spectral absorptivity particle coating was taken into account but resulting abrasion resistance is poor. As alternative, commercial black pigments were applied on the proppants’ surfaces and heat-treated subsequently at 1200 °C to induce diffusion of the transition metal ions into the glassy phase. The internal coloring results in significant increase of solar absorptivity. Another approach to improve solar absorbance is tailoring bauxite raw materials by addition of coloring pigments. Spectroscopic data show that pigment black 26 is most efficient. Alternatively, raw materials having high amounts of transition metals by nature could be an efficient and low-cost approach to produce highly absorbing particles. Sintered pellets made from such raw materials show a solar absorptivity of >90%.

2:15 PM

(PACRIM-S23-004-2017) Cobalt Oxide Thermochemical Heat Storage for Concentrated Solar Power Applications (Invited)

N. Vahedi[1]; Q. Ranjha[1]; A. Oztekin*[1]

1. Lehigh University, Mechanical Engineering and Mechanics, USA

Thermochemical energy storage (TCES) has more potential to be used with concentrated solar power plants (CSP) than sensible and latent heat storage systems due to higher stability and energy density. Among high temperature TCES materials, the most suitable candidates are the multivalent metal oxides. In this study Cobalt Oxide is used as storage material. Reduction and oxidation reactions of Cobalt Oxide are investigated for heat storage/retrieval. A cylindrical fixed bed filled with fine particles of Cobalt Oxide (<30mm) is considered as reaction bed and air flows through the porous reaction bed as both reactant and heat transfer fluid (HTF). Equations governing the reaction kinetics, mass and energy transport through the bed are solved for charging/discharging process. Transient simulations are carried out using finite elements based COMSOL modules. Oxidation and reduction reactions are carried out at 785^0C and 985^0C, respectively. Temperature distribution and conversion rate throughout the bed are presented as a function of time. Effects of particle size, porosity, bed dimensions and air mass flow rate on the conversion rate, output temperature and pressure losses are considered for optimize and design the module. It has been observed from the calculated results that particle size and porosity are dominant parameter affecting both rate of reaction and pressure drop.

2:45 PM

(PACRIM-S23-005-2017) Investigations of Graphite Foam-$MgCl_2$ Based Latent Heat Thermal Energy Storage (LHTES) Prototypes for Concentrated Solar Power (CSP) Plants

D. Singh[2]; W. Yu[2]; T. Kim[2]; D. France[3]; W. Zhao*[1]

1. University of North Texas, USA
2. Argonne National Lab, USA
3. University of Illinois at Chicago, USA

Graphite foam-$MgCl_2$ has been proposed as high-temperature LHTES medium for CSP applications because of its high thermal energy storage density and excellent heat transfer characteristics. $MgCl_2$ is the phase change material (PCM) for latent heat energy storage; graphite foam acts as a thermal conductivity enhancement additive in the system. Experimental investigations were conducted for the lab-scale graphite foam-$MgCl_2$ LHTES prototypes to verify the thermal performances of the graphite foam-$MgCl_2$ for thermal energy storage. The experiment measurements were compared with numerical simulation results from COMSOL to verify the simulation model and the thermal properties of graphite foam-$MgCl_2$. Both charging and discharging experiments were carried out and repeated for the prototypes. The corresponding experimental temperature profiles were compared to the predicted results from simulations to investigate the melting and solidification in the PCM as well as the repeatability of the graphite foam-$MgCl_2$ based LHTES system after multiple thermal cycles. Through the lab-scale prototype experiments, the feasibility of the proposed LHTES system has been demonstrated. The results obtained in this study provide important information for designing and implementing full-scale graphite foam-PCM based LHTES systems for applications in CSP plants.

3:00 PM

(PACRIM-S23-006-2017) Mn-based combined oxides and porous structures for hybrid sensible/thermochemical solar energy storage in air-operated solar thermal power plants

C. C. Agrafiotis[1]; T. Block[2]; S. Tescari[1]; M. Roeb*[1]; C. Sattler[1]

1. DLR - German Aerospace Center, Institute of Solar Research, Germany
2. DLR - German Aerospace Center, Institute of Materials Research, Germany

The concept of regenerative sensible heat storage in porous solids employed in air-operated solar thermal power plants can be hybridized with thermochemical storage by coating/manufacturing entirely the heat exchange modules with oxides of multivalent metals undergoing reduction/oxidation reactions with significant heat effects. In this perspective a specific Mn_2O_3-Fe_2O_3 composition and $CaMn_{1-x}B_xO_{3-\delta}$ perovskites doped in the B site with Ti, Al or Mg were investigated. The work involved the feasibility of shaping the powders to porous foams which, together with pellets, were comparatively tested to clarify the effect of structure porosity on redox performance. The Mn_2O_3-Fe_2O_3 composition underwent cyclic, reproducible reduction/oxidation with significant reaction enthalpies within a wide range of heating/cooling rates, even in the form of foams that maintained their structural integrity. The attribute of perovskites for continuous, quasi-linear oxygen uptake/release can be beneficial to hybridization of thermochemical with sensible storage within a wider temperature range. Addition of Ti was found to improve the perovskites' long-term redox stability. However the induced heat effects of the perovskites' redox reactions were substantially lower and need to be improved for commercial-scale applications.

3:15 PM

(PACRIM-S23-007-2017) Structured active materials for thermocehmical energy storage

G. Karagiannakis*[1]; S. Lorentzou[1]; K. Sakellariou[1]; N. Tsongidis[1]; C. Pagkoura[1]; A. G. Konstandopoulos[1]

1. Centre for Research & Technology Hellas, Aerosol & Particle Technology Laboratory, Greece

Thermochemical Energy Storage (TCS) is an emerging approach for the realization of high energy density storage systems for CSP plants. TCS relies on the exploitation of heat effects of reversible chemical reactions. The endothermic step is used to store excess heat produced by the solar field during sunny hours while the exothermic one discharges this heat when sun is not available, thereby substantially prolonging power production. Among numerous reaction schemes proposed, most efforts so far have been devoted to gas-solid reactions. Prominent examples are certain redox couples as well as oxide/hydrate and oxide/carbonate systems. Although each case entails its own unique characteristics, they all share a common challenge; namely cyclic phase changes. The latter, particularly upon long-term operation, can adversely affect the structural integrity of solid active materials with potentially detrimental effects on reactors operation. The present work relates to definition and evaluation of strategies to substantially mitigate the above mentioned challenge for 3 reaction couples: Co3O4/CoO, CaO/Ca(OH)2 and CaO/CaCO3. The concept relies on the identification of suitable ceramic additives to ensure sufficient cycle-to-cycle structural stability and reactivity. Such an approach is in-principle valid for different reaction designs, spanning from porous monolithic reactors to moving and fluidized beds.

Materials for Solar Fuel Production

Room: Queen's 4
Session Chair: Weihuan Zhao, University of North Texas

3:45 PM

(PACRIM-S23-008-2017) Redox Materials for Solar Thermal Energy Conversion

M. Roeb*[1]; M. Schmucker[1]; C. Sattler[1]

1. DLR - German Aerospace Center, Germany

Coupling concentrated sunlight to suitable sequences of thermochemical reactions enables the production of fuels by water and CO_2 splitting and the thermochemical separation of air. One of the major barriers of those processes is the identification of suitable redox materials exhibiting satisfactory durability, reactivity and efficiencies. Such processes utilize metal oxides like ceria or perovskites as reactive intermediates. An analytical thermodynamic model is developed to relate material properties to process performance. Perovskites like $SrFe_{0.95}Cu_{0.05}$ $O_{3-\delta}$ and $Ca_{0.8}Sr_{0.2}MnO_{3-\delta}$ show large gravimetric oxygen storage capacities in air. The experimentally measured re-oxidation reaction of those materials is one order of magnitude faster than with state-of-the-art materials. The use of particulate redox materials enables to decouple the reduction from the oxidation reaction and the absorption of solar radiation from the reaction and a counter current heat exchanger design. A numerical model was developed to analyze the heat losses of a particle conveyor using an insulated container in a cycled operation. The model calculates that temperature losses reach values of about 2-4K per lifting. A model of the heat exchanger calculates the process performance considering temperature dependent material data. The system reaches a heat recovery rate over 70% in case of six stages, connected in a quasi-counter-current principle.

4:00 PM

(PACRIM-S23-009-2017) Redox kinetics of pure and Zr^{+4} doped CeO_2 used for thermochemical hydrogen production

N. Knoblauch*[1]; L. Hoffmann[1]; C. Esser[1]; F. Seeliger[1]; H. Simon[1]; M. Schmucker[1]

1. DLR - German Aerospace Center, Germany

Kinetics of pure and Zr^{+4} doped CeO_2, synthesized via Pechini method, was investigated in view of their applicability as redox material for thermochemical hydrogen production. In pure CeO_2 several reduced sub-oxide phases were formed after reduction, as evidenced by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). In Zr-doped CeO_2 Zr-rich phases were formed at the pellet surface after treatment at high temperature under low partial pressure of oxygen (pO_2) which is attributed to selective Ce evaporation. Reduction kinetics between 1543K and 1753K under various pO_2 was monitored by Thermogravimetric analyses (TG) using pure and Zr^{+4} doped CeO_2 pellets sintered at different temperatures. TG data show that Zr doping of CeO_2 is beneficial in view of reduction but may be thermodynamically detrimental for re-oxidation by water vapor. Evidence suggests that the sintering temperature of Zr-doped CeO_2 pellets affects the water-splitting efficiency.

4:15 PM

(PACRIM-S23-010-2017) A novel solar thermochemical water splitting material $BaCe_{0.25}Mn_{0.75}O_3$ for hydrogen production

D. Barcellos[2]; M. Sanders[2]; J. Tong[3]; A. McDaniel*[1]; R. O'Hayre[2]

1. Sandia National Laboratories, USA
2. Colorado School of Mines, Metallurgical and Materials Engineering Department, USA
3. Clemson University, Department of Materials Science and Engineering, USA

Solar thermochemical hydrogen production (STC) is a method predicated on simple metal oxide thermochemistry that utilizes the entire solar spectrum as high-temperature process heat to produce hydrogen by water splitting (WS). Of particular interest are two-step thermochemical process that use non-volatile metal oxides as the redox-active material. In step one, the oxide is defected by driving oxygen from the lattice at high temperature. In step two, and upon exposure to steam at a lower temperature, oxygen is stripped from the water molecule and transferred back into the oxide. This completes the cycle and results in the net production of hydrogen. A principle advantage of STC over other WS- techniques like photo-electrolysis (e.g. integrated as in PEC or disintegrated as in PV-electrolysis) is that STC does not require precious metal catalysts or costly morphological alterations of complex inorganic materials. We will describe a novel material, the perovskite $BaCe_{0.25}Mn_{0.75}O_3$ (BCM), that is able to produce 3 times more hydrogen than ceria, the current state-of-the-art water splitter, when cycled at lower temperature (reduction temperature ~1350ºC). This material also shows enhanced oxidation kinetics when compared to another popular perovskite ($Sr_xLa_{1-x}Mn_yAl_{1-y}O_{3-\delta}$, SLMA), as BCM ultimately outperforms SLMA under realistic reactor conditions when both steam and hydrogen are present.

4:30 PM

(PACRIM-S23-011-2017) Solar fuel production: Ceramic materials development, evaluation and simulation

D. Dimitrakis[1]; M. Syrigou[1]; S. Lorentzou*[1]; A. Zygogianni[1]; C. Pagkoura[1]; G. Karagiannakis[1]; M. Kostoglou[2]; A. G. Konstandopoulos[1]

1. CERTH, Aerosol & Particle Technology Laboratory, APTL, Greece
2. Aristotle University of Thessaloniki, Department of Chemistry, Greece

Solar thermochemical processes are promising routes for the production of renewable fuels (solar-fuels), based on the use of concentrated solar radiation as energy source for high-temperature reactions for the conversion of various fossil and non-fossil raw materials (e.g. natural gas, CO_2 and H_2O). This work focuses on the development of ceramic materials and structures for the active solar thermochemical splitting of H_2O and CO_2 towards solar syngas. The synthesis of redox materials was complemented with DFT calculations for the selection of candidates with a prominent redox potential. Different material families (ferrites, cerium oxides, perovskites, etc.) were synthesized via combustion routes and evaluated with respect to their redox performance at the scale of the powder for H_2O and CO_2 splitting. In general, the activity of materials is aligned with the DFT results. At a next step selected materials ($NiFe_2O_4$, cerium oxides) were investigated for their structuring into ceramic monoliths involving extrusion, casting and 3D-printing techniques, and were evaluated with respect to their redox activity. Finally, a refined kinetic model describing the multicyclic operation and product yield optimization of solar redox thermochemical splitting was developed building upon previous kinetic models for fixed bed reactors. Simulations were performed both at the powder and the monolithic scale.

4:45 PM

(PACRIM-S23-012-2017) Catalytic SO_3 Decomposition Activity and Stability of Supported Molten Vanadate Catalysts for Solar Thermochemical Water Splitting Cycles

M. Machida*[1]; T. Matsukawa[1]; S. Hinokuma[1]

1. Kumamoto University, Japan

SiO_2-supported molten alkaline metal oxides (A–V–O/SiO_2) were studied as SO_3 decomposition catalysts for solar thermochemical water-splitting. Their catalytic activities at moderate temperatures (≤600 °C) that were superior to those of Cu–V–O/SiO_2 catalysts were dependent on A, exhibiting the following sequence: Cs>Rb>K>Na and increased with the A/V ratio. This result is in accordance with the basicity, which favors the adsorption of SO_3 to form sulfate. Another important effect of A is to form molten liquid phases, which dissolve the sulfate and facilitate its decomposition to SO_2/O_2. However, the molten phase with high A/V ratios led to the collapse of the porous SiO_2 structure by a corrosion effect. Consequently, the highest catalytic activity was achieved at the composition around A/V=1.0 for A=K and Cs. The long-term stability test of K–V–O/SiO_2 at 550 °C demonstrated no indication of noticeable deactivation during the first 100 h, whereas 20% deactivation occurred during the following 400 h. The deactivation mechanism involves the vaporization loss of active components from the molten phase, which is accelerated in the presence of SO_3.

PACRIM Symposium 26: Advances in Materials and Technology for Perovskite and Next Generation Solar Cells

Synthesis and Functionalization of Nanomaterials for Photovoltaic Applications

Room: King's 1
Session Chairs: Yoon-Bong Hahn, Chonbuk National University; Qingwen Li, Suzhou institute of Nanotech and Nanobionics

1:15 PM

(PACRIM-S26-001-2017) Dye-sensitized Tandem Solar Cells: Design and Applications (Invited)

J. Park*[1]; K. Choi[2]; H. Kim[3]

1. Yonsei University, Republic of Korea
2. UNIST, Republic of Korea
3. Korea University, Republic of Korea

Tandem architectures using organic/inorganic hybrid semiconductors are a promising strategy to overcome the Shockley–Queisser limit of single-junction (SJ) solar cells. In this seminar, I will present a highly-efficient dye-sensitized solar cell (DSSC)/silicon (Si) monolithic tandem cell and DSSC/DSSC tandem cell by utilizing PEDOT:FTS as an interfacial catalytic layer, which has higher transparency and lower charge-transfer resistance compared to conventional Pt. In addition, the amount of dye adsorbed on the surface of TiO_2nanoparticles is fine-tuned for precise current matching between the two sub-cells. Based on these rational approaches, the DSSC/Si tandem cell exhibited a much higher power-conversion efficiency (PCE) of 17.2% compared to the stand-alone SJ devices of DSSCs (–11.4%) or Si (–12.3%) cells. The PCE of the best tandem cell is 18.1%. In addition, we will also introduce DSSC/DSSC tandem cells, which exhibits the efficiency more than 13% PCE. The tandem solar cells are externally connected to a Pt electro-catalyst for use as water splitting cells. We expect that a tandem architecture based on organic–inorganic hybrid materials can provide a promising way to realize low-cost and high-efficiency photovoltaic devices for solar cells and hydrogen generation.

1:45 PM

(PACRIM-S26-002-2017) Advanced Materials and Devices for the Flexible Photovoltaics: Dye-Sensitized and Perovskite Solar Cells (Invited)

M. Ko*

2. Hanyang University, Department of Chemical Engineering, Republic of Korea

There have been significant progresses in the dye-sensitized (DSSCs) and perovskite solar cells (PSCs). Further cost reduction in high-speed manufacturing can be accomplished by continuous roll-to-roll printing processes using a flexible plastic substrate. Lightweight and flexible plastic solar cells can be installed even on non-flat surface, which makes them a possible ubiquitous power source for mobile electronics. The conventional TiO_2 photoelectrodes of DSSCs and PSCs are prepared via a high-temperature sintering at 500 °C after deposition of the TiO_2 paste on fluorine-doped tin oxide (FTO) glass. However, the plastic substrates cannot withstand a sintering process at a temperature above 150 °C. This sintering process is essential since tight TiO_2 interparticle connections are required for better performance, resulting in the reduction of internal resistance and fast electron transport. Most of low temperature sintering methods contain quite complicated multi-step processes, not proper for the rapid production of DSSCs and PSCs using the R2R process. We have developed several facile methods for the fabrication of efficient flexible solar cells on plastic substrates. In this talk, several starategies to address these issues will be introduced.

2:15 PM

(PACRIM-S26-003-2017) Air-processable and scalable formation of high quality organic films on an aqueous substrate

J. Lee*[1]

1. Korea Advanced Institute of Science and Technology, Graduate School of EEWS, Republic of Korea

In this talk, we show an ultrafast and scalable technique to ensure the deposition of high quality organic films on a water substrate by using spontaneous spreading phenomenon. Ultrafast removal of solvent during the process causes the films to have uniform and high quality nanomorphology because oxygen diffuses into the polymer films rapidly through the remaining solvent between the polymer chains. Furthermore, the polymer films were successfully transferred onto various substrates. Finally, we demonstrated high performance of PSCs prepared using the proposed process, comparable to that of PSCs prepared by spin coating. We expect that this approach can be extended by roll-to-roll production to achieve high-quality films.

2:30 PM

(PACRIM-S26-004-2017) Inorganic Carbon Nanotube Hybrids for Photovoltaic Applications (Invited)

Q. Li*[1]

1. Suzhou Institute of Nanotech and Nanobionics, Division of Nanomaterials, China

Nanocarbons, in particular carbon nanotubes and graphene, are gaining increasing interest in the development of novel and high-performance optoelectronic materials and devices. The rich surface functionality of nanocarbons has made them ideal scaffolds for anchoring foreign semiconductor nanoparticles or conjugated polymers to form hybrid structures. The recent progress in achieving some scalable macro-assemblies of nanocarbons like transparent network, aligned film and fibers etc. also helps pave up more routes for the fabrication of multifunctional nanocarbon-based hybrids and photovoltaic devices. As a result, three related issues will be covered in my talk which include: 1)Fabrication of aligned CNT-Si heterogeneous junctions for high-efficiency solar cells; 2) Controllable fabrication of transparent CNT@TiO2 hybrid structures for photoanodes; 3) Efficient growth of perovskite on a flexible CNT fiber and its application wearable fibrous solar cell.

3:00 PM

(PACRIM-S26-005-2017) Air-Stable High Efficiency Hybrid Solar Cells with Metal Oxide and Graphene Based Nanocomposites (Invited)

Y. Hahn*[1]

1. Chonbuk National University, School of Chemical Engineering, Republic of Korea

One of critical issues for practical applications of hybrid solar cells is how to enhance the photocurrent and air stability of the perovskite materials. To solve this issue, we developed simple methods for synthesizing $CH_3NH_3PbI_3$-NiO nanoparticles ($MAPbI_3$-NiO NPs) composite for perovskite solar cells (PSCs) and Ag nanoparticles-anchored reduced graphene oxide (Ag-rGO) composite for bulk-heterojunction solar cells (BHJ-SCs). By introducing the former into the active layer of hole-conductor-free PSCs with FTO/c-TiO_2/mp-TiO_2/$MAPbI_3$-NiO/Au architecture, dramatic enhancement of photocurrent density (J_{sc}) was attained, i.e. 26.41 mA/cm^2 which is 97% of theoretical maximum (i.e., 27.2 mA/cm^2). Compared to the power conversion efficiency (PCE) of $MAPbI_3$ only HCF-PSC (i.e., 5.43%), the $MAPbI_3$-NiO NPs composite-based HCF-PSC showed a high PCE of 12.14 %. The latter (i.e., Ag-rGO composite) was introduced into the active layer of P3HT:PCBM based BHJ-SCs. Compared to the P3HT:PCBM only device, the Ag-rGO implemented devices showed dramatic enhancements in photocurrent (33 % increase) and PCE (42% increase). More interestingly, the composite-based HCF-PSCs and BHJ-SCs without encapsulation showed remarkable air stability with retaining ~90 % of its original PCE and ~94% of photocurrent for 60 days under ambient environment.

Advances in Materials and Technologies for Perovskite-based Solar Cells I

Room: King's 1
Session Chairs: Fang-Chung Chen, National Chiao Tung University; Jin Young Kim, Seoul National University

3:45 PM

(PACRIM-S26-006-2017) Strategies for enhancing stability of highly efficient p-i-n type planar perovskite solar cells (Invited)

J. Kim*[1]

1. Seoul National University, Department of Materials Science and Engineering, Republic of Korea

The p-i-n type perovskite solar cells especially with a planar structure are promising next generation solar cells owing to their simple and low-temperature processes compatible with flexible substrates, negligible hysteresis effect, and potential tandem configuration with other highly efficient inorganic solar cells. However, the p-i-n type planar devices have issues of lower conversion efficiency compared with the n-i-p type counterparts and poor stability resulting from the use of organic hole-extraction layers. During recent years, we have reported several strategies for enhancing the device performance of the p-i-n type planar perovskite solar cells, especially focusing on the fill factor. As a result, a high fill factor of 0.8 and a high conversion efficiency of 20% could be achieved. In this presentation, a series of approaches that we have made for achieving high fill factor and efficiency will be presented. In addition, recent progresses in our research group regarding the enhanced stability of the p-i-n type planar perovskite solar cells including the stability against humidity, temperature, and the electric field will be introduced.

4:15 PM

(PACRIM-S26-007-2017) High-efficient organic and perovskite photovoltaic devices for low-power indoor applications (Invited)

F. Chen*[1]

1. National Chiao Tung University, Department of Photonics, Taiwan

Organic and perovksite photovoltaic devices have attracted considerable attention in recent years because of their potential use as low-cost renewable energy sources that are light in weight and have mechanical flexibility. The power conversion efficiencies (PCEs) of organic photovoltaic devices (OPVs) devices have reached as high as 11%; the PCE of perovksite solar cells (PSCs) even have achieved exceeding 20%. Herein, we will present our recent progress on the development of high-efficient organic and perovskite photovoltaic devices. We have constructed various metal nanostructures, such as nanoparticles and their nanocomposites and integrated with OPVs to trigger localized surface plasmon resonance for enhancing the device efficiencies. The effects of cathodic interfacial layers on the performance of PSCs will be also discussed. In particular, we have found that OPVs and PSCs exhibited extremely high performance under the indoor illumination conditions, thereby making them suitable for low-power indoor applications. A PCE higher than 20% is achievable under illumination of low-power light sources. The details of the device characterization will be described.

4:45 PM

(PACRIM-S26-008-2017) Band-gap engineering in $KNbO_3$-$BiMeO_3$ (Me=Mn, Fe and Co)

C. Pascual-González*[1]; G. Schileo[2]; A. Feteira[1]

1. Sheffield Hallam University, Material Engineering Research Institute, United Kingdom
2. Dyesol UK Ltd, United Kingdom

Band-gap engineering of ferroelectrics such as $KNbO_3$ allows us to explore several photoresponsive phenomena such as photovoltage, photostriction and photocatalysis. In order to exploit those phenomena in technological applications one should be able to tune the band-gap into the visible range. In this study, we investigated the impact of $BiMeO_3$ (with Me=Mn,Fe and Co) doping on the structure, dielectric and optical properties of $KNbO_3$. XRD data combined with Raman Spectroscopy was employed to monitor both the average and local crystal structure evolution with increasing $BiMeO_3$ content. Band-gaps varying from 3.2 eV down to 2.2 eV were estimated from reflectivity data collected using a spectrometer with an integrating sphere. In-situ Raman spectroscopy analysis corroborated the polar nature of these materials over a wide temperature range. The ability to control the band-gap while maintaining the spontaneous polarisation makes $KNbO_3$-$BiMeO_3$ solid solutions interesting for photoinduced processes in a wide temperature range.

PACRIM Symposium 30: Glasses and Ceramics for Nuclear and Hazardous Waste Treatment

Waste Vitrification Technologies: Development and Implementation

Room: Kona 1
Session Chairs: Kevin Fox, Savannah River National Laboratory; Yifeng Wang, Sandia National Laboratories

1:15 PM

(PACRIM-S30-001-2017) Basic Research for French Industrial Vitrification Process (Invited)

S. Schuller*[3]; G. Barba Rossa[3]; P. Brun[3]; M. Delaunay[3]; R. Didierlaurent[1]; J. Hollebecque[3]; V. Labe[3]; S. Lemonnier[3]; A. Ledoux[3]; L. Meslin[1]; C. Michel[3]; E. Sauvage[3]; E. Régnier[2]; E. Rousset[1]

1. AREVA NC LCV, France
2. CEA, DEN, DTCD, SECM, LDMC, France
3. CEA, DEN, DTCD, SCDV, LDPV, France

Highly focused research programs are currently underway in the Joint CEA-AREVA Laboratory to develop and optimize vitrification processes for the production of waste containment glasses. The main issues are to accommodate new types of waste and higher waste loading, while enhancing the glass quality and increasing the production capacity and robustness of plants. This requires extensive knowledge on vitrification processes, technologies and physical-chemistry of vitreous materials. Basic research supported by a modelling approach, is conducted on calciner, off-gas treatment and crucible melter technologies from laboratory-scale and mock-up, to full-scale non-radioactive facilities. This presentation deals with the contribution of French research regarding the industrial applications. First we discuss how the knowledge of the properties of calcine and optimization of adjustment parameters leads to a proper calcine. Moreover, we show how knowledge of the reaction mechanisms and thermodynamic parameters (demixtion, crystallization temperatures) can help optimizing the vitrification conditions. Then, we present the successful correlation of the 3D numerical simulation of fluid flow, heat transfer and electromagnetic of melting glass with experimental data. Finally, this presentation highlights that the basic research conducted today will enable us to meet the stimulating challenges facing in the coming years.

1:45 PM

(PACRIM-S30-002-2017) Recent Progress of Nuclear Waste Vitrification in China (Invited)

K. Xu*[1]; L. Liu[2]; M. Chen[3]; F. Wang[4]; L. Wu[4]; Y. Qiao[5]; Q. Liao[4]; P. Lin[3]; X. Zhao[1]

1. Wuhan University of Technology, State Key Laboratory of Silicate Materials for Architectures, China
2. China Institute of Atomic Energy, China
3. China Nuclear Power Technology Research Institute, China
4. Southwest University of Science and Technology, China
5. Shanghai Institute of Applied Physics, Chinese Academy of Science, China

Due to increasing concerns about air pollution, climate change and fossil fuel shortage, nuclear power is the fastest-growing electricity source in China (29% growth in 2015). China nuclear power plants (NPPs) are expected to provide at least 58 GW of capacity by 2020, then up to 150 GW by 2030, and much more by 2050. With such rapid growth of nuclear power, the spent fuel generated from those NPPs will reach more than 80,000 tons by 2050. China's policy is to have a closed nuclear fuel cycle, thus, huge amount of high-level radioactive waste (HLW) will be soon generated from the reprocessing of the spent fuel. Meanwhile, certain amount of HLW has been produced in support of the nation's defense programs, and has been in interim storage facilities for several decades. Those liquid wastes need to be vitrified as early as possible for long-term management. This talk will thus review the recent progress of nuclear waste vitrification in China. The main efforts will cover (i) development of the new vitrification technology, including cold-crucible induction melter and plasma torch melter, (ii) investigation of waste glass formulation and performance, and (iii) development of the wasteform for the waste from Thorium-based fuel.

2:15 PM

(PACRIM-S30-003-2017) Advanced Glass Property: Composition Models and their Impacts on Hanford Waste Glass Estimates

J. Vienna*[1]; G. Piepel[1]; D. Kim[1]

1. PNNL, USA

Recent glass formulation and melter testing data have suggested that significant increases in waste loading in high-level waste (HLW) and low-activity waste (LAW) glasses are possible over current system planning estimates. The glass property data from a variety of different studies were combined, evaluated, and used to fit glass property-composition models and formulation constraints applicable to high waste loaded glasses formulated from the full range of Hanford tank waste batches. A fundamental tenet underlying the research reported in this study was to be less conservative, but still realistic, compared to previously reported sets of glass property-composition models and constraints. The less conservative approach should allow for estimating glass masses that may be realized if the current efforts in enhanced glass formulations are completed over the coming years, and are as successful as results from the previous approximately four years of effort indicate they will be. These models and constraints were applied to a set of estimated Hanford tank waste batches to be delivered to the LAW and HLW vitrification facilities over the life of the River Protection Project (RPP) mission. The resulting amount of glass estimated to be produced is described along with anticipated impacts of uncertainties.

2:30 PM

(PACRIM-S30-004-2017) Accumulation of spinel crystals during vitrification of high-level waste glasses

J. Matyas*[1]; M. Edwards[2]; G. Sevigny[3]; J. Venarsky[4]; A. A. Kruger[5]

1. PNNL, Radiological Materials & Detection, USA
2. PNNL, Actinide Science, USA
3. PNNL, Nuclear Chemistry and Engineering, USA
4. PNNL, Process Engineering, USA
5. DOE-ORP, USA

The Tank Waste Treatment and Immobilization Plant at the Hanford Site in Washington State will use Joule-heated ceramic melters to vitrify radioactive waste in borosilicate glass. To fully utilize this technology a crystal-tolerant glass approach is being developed with a goal to maximize the loading of high-level waste in borosilicate glass without accumulating spinel crystals $[Fe,Ni,Mn,Zn][Fe,Cr]_2O_4$ in the glass discharge riser during melter idling. The research scale melter was employed to validate the crystal accumulation rates obtained at lab-scale, to investigate a possibility of at least partial removal of the accumulated layer during pouring after periods of idle time, and to test conductivity probe method for real-time monitoring of crystal accumulation. The presentation will discuss the findings; compare the results to the lab-scale data and to the predictions of empirical model of crystal accumulation.

2:45 PM

(PACRIM-S30-005-2017) Practical Aspects of Crystallization in High Level Nuclear Waste Glasses

K. M. Fox*[1]; D. McClane[1]; J. Amoroso[1]; M. Fowley[1]; D. Miller[1]; A. A. Kruger[2]

1. Savannah River National Laboratory, USA
2. US Department of Energy - Office of River Protection, USA

The US Department of Energy safely immobilizes defense high level nuclear waste in borosilicate glass using Joule heated, ceramic lined melters. The degree of waste loading in the glass can be limited by the formation of crystals within the glass. Some crystalline phases, such as spinel, do not impact the performance of the waste form but may hamper melter operation. This presentation will provide an overview of efforts underway to better understand the potential impacts of controlled spinel crystallization to maximize waste loadings in glass while protecting melter operation, including strategies for removing excess accumulations of spinel crystals. A full-scale, room temperature system has been developed for observation of particle settling and resuspension. Tailored formulations of glass forming chemicals have been developed to dissolve accumulated spinel crystals. Nepheline crystals, which tend to form in glasses with high concentrations of aluminum and sodium, do detract from durability of the waste glass. Results of thermal analyses to better understand the kinetics of nepheline formation in complex waste glasses during cooling will also be presented.

3:00 PM

(PACRIM-S30-006-2017) High Alumina Borosilicate Glass Development for High-Level Waste, Part II: Viscosity and Electrical Conductivity

Y. Chou*[1]; M. J. Schweiger[1]; J. Vienna[1]; B. McCarthy[1]; J. L. Mayer[1]; J. B. Lang[1]; V. Gervasio[1]; L. P. Darnell[1]; R. L. Russell[1]; G. Piepel[1]; S. K. Cooley[1]; A. A. Kruger[2]

1. Pacific Northwest National Lab, USA
2. US DOE, USA

Pacific Northwest National Laboratory has led the efforts to develop glass composition-property models for HLW at Hanford Site, WA. In the first phase a matrix was statistically designed to efficiently augment existing high-alumina HLW glasses with 46 additional compositions containing Al_2O_3 up to 30 wt%. In the second part of this series of work properties of viscosity and electrical conductivity were reported and compared to the requirements of waste treatment plant under construction at Hanford Site. The measured properties were also tested with existing models for both viscosity and electrical conductivity. Overall the current models failed to predict both properties with high accuracy, and no discernable trend could be identified with Al_2O_3 mass fractions. For electrical conductivity modelling, attempts were made to establish composition-property relationship by considering only the main charge carriers (i.e., alkalis) and Al_2O_3. In the end, a simplified model for electrical conductivity was proposed based only on Al_2O_3, alkalis, and binary interactions between alkalis and compared to models containing more full set of glass components. The simplified model will be tested with current set of data as well as published data and applicability be addressed

3:15 PM

(PACRIM-S30-007-2017) Solubility of Cs_2O and ZrO_2 into iron-phosphate glass system, Cr_2O_3-CoO-Al_2O_3-Fe_2O_3-P_2O_5

T. Yano*[1]; H. Kofuji[2]

1. Tokyo Institute of Technology, Department of Materials Science and Engineering, Japan
2. Japan Atomic Energy Agency (JAEA), Fast Reactor Fuel Cycle Technology Development Department, Advanced Fast Reactor Cycle System R&D Center, Japan

Solubility of Cs_2O and ZrO_2 compounds into iron-phosphate glass system has been investigated. Encapsulation of high-level radioactive wastes into glass is one of the most important issues for the immobilization and stabilization of nuclear wastes from nuclear power plant, especially Cs and Zr are the typical long-lived fission product (LLFP) elements. The glass matrix for the encapsulation of these LLFP has to have high chemical durability and thermal stability. In this study, Cr_2O_3-CoO-Al_2O_3-Fe_2O_3-P_2O_5 system is chosen as the matrix glass because it possesses high chemical durability and high solubility of radioactive wastes. 4 mass% ZrO_2 and 0-40 mass% Cs_2O are added into the molten glass and quenched to obtain the sample glasses. These are subjected to the characterization of TMA, DTA, XRD, and XRF analyses. Solubility of ZrO_2 into this glass system is found to be strongly dependent on the concentration of Cs_2O. There is an optimum Cs_2O concentration range to stabilize the dissolution of ZrO_2 into glass. Chemical durability test, MCC-1, (7 and 90 days) has also conducted to evaluate the effect of the introduction of Cs_2O and ZrO_2 on the corrosion behavior.

3:45 PM

(PACRIM-S30-008-2017) Development of a new glass formulation for the immobilisation of HLW containing molybdenum and large amounts of sodium

R. J. Hand*[1]; C. Brigden[1]; L. Hollands[1]; M. T. Harrison[2]; C. Stephen[2]; T. Taylor[2]; M. Cowley[4]; K. Spencer[4]; C. J. Steele[4]; J. Longmore[3]; R. Patel[3]

1. University of Sheffield, Materials Science & Engineeering, United Kingdom
2. NNL, United Kingdom
3. Cera Dynamics Ltd, United Kingdom
4. Sellafield Ltd, United Kingdom

A study to develop a new high level waste (HLW) glass formulation for waste from the highly active liquor storage (HAL) tanks at Sellafield is described. The waste is expected to contain significant quantities of molybdenum (& other elements) however the amount of sodium carbonate to be used in the likely tank washout strategy requires a waste form which can accommodate a large amount of sodium. Titanium is not currently used in existing HLW formulations in European nuclear waste glasses, however, literature suggests that titanosilicate glasses can accommodate large amounts of sodium, even up to 50 mol%. A range of sodium titanosilicate glasses have been made in the current project examining the effects of adding various components including aluminium, calcium and boron to sodium titanosilicatethese glasses. In particular boron has been found to significantly reduce phase separation of the sodium molybdate phase. A comprehensive study is being carried out including glass characterisation, durability studies and base glass-waste combination experiments and results will be presented.

4:00 PM

(PACRIM-S30-009-2017) Compositional dependence of molybdenum solubility vs. retention in aluminoborosilicate glasses

A. Brehault[1]; H. Kamat[1]; L. M. Thirion[2]; J. C. Mauro[2]; D. S. Patil[3]; R. Youngman[2]; J. McCloy[3]; A. Goel*[1]

1. Rutgers University, USA
2. Corning Incorporated, USA
3. Washington State University, USA

An innovative glass-ceramic waste form is being developed to immobilize non-fissionable waste streams of alkali/alkaline-earths, lanthanides, and transition metals generated by the projected TRUEX^{plus} process. The major hurdle in the development of this glass-ceramic is the high MoO_3 (~14 mass%) and alkali (Rb_2O, Cs_2O ~12 mass%) content of the waste stream. The presence of these species can lead to liquid-liquid phase separation and the uncontrolled crystallization of alkali/alkaline-earth molybdates. The present study aims at understanding the fundamental science controlling the solubility/retention of molybdenum in nuclear waste glasses. The compositional dependence of MoO_3 solubility in simplified nuclear waste glass compositions in the system Na_2O-CaO-B_2O_3-Al_2O_3-Nd_2O_3-SiO_2 has been studied. The solubility vs. retention limit of molybdenum in these glasses has been determined by inductively coupled plasma – optical emission spectroscopy. The molecular structure of glasses has been studied by various spectroscopic techniques, while phase separation and crystalline phase evolution in glasses and glass-ceramics has been followed by electron microscopy, and X-ray diffraction, respectively. The obtained results pertaining to solubility/retention of molybdenum in glasses along with the discussion about structural mechanisms controlling the same will form the gist of the presentation.

4:15 PM

(PACRIM-S30-010-2017) Effect of Rare Earths on the solubility and crystallization of Mo in borosilicate glasses for nuclear waste immobilization

D. S. Patil*[1]; M. Konale[1]; A. Brehault[2]; J. Marcial[1]; E. Nienhuis[1]; A. Goel[2]; J. McCloy[1]

1. Washington State University, Mechanical and Materials Engineering, USA
2. The State University of New Jersey, Department of Materials Science and Engineering, USA

The incorporation of molybdenum is a major challenge in the vitrification of nuclear waste, due to its low solubility and tendency to phase separate and crystallize Mo-rich phases. This segregation of Mo has deleterious effects on the integrity of the wasteform, particularly when the molybdate oxyanions associate with alkali, resulting in water soluble phases. Low Mo solubility also limits the overall HLW waste loading in borosilicate glass. To increase waste loading without phase separation and crystallization and the chemical durability of immobilized glass, it is necessary to improve solubility of Mo. There has been much research on the chemistry of Mo and its correlation with alkali and alkaline earth metals, but the effects of rare earths (REs) are comparatively less well studied, though it is known in general that REs improve MoO_3 solubility. We know of no studies of the effects of RE of differing ion sizes on the incorporation of Mo in glass. For this reason, we studied the effect of RE's (La, Ce, Nd, Sm, Er, & Yb) of varying concentrations on the solubility of Mo. We use absorption, luminescence, diffraction, and Raman spectroscopy techniques to show the role of RE in an alumino-borosilicate glass. We have also performed heat treatments of the glass and show the incorporation of the differing rare earths in crystal phases.

4:30 PM

(PACRIM-S30-011-2017) Rheological Study of the Cold Cap

B. McCarthy*[1]; D. Dixon[1]; M. Wheeler[1]; D. Cutforth[1]; M. J. Schweiger[1]; P. Hrma[1]; R. Pokorny[2]; M. Hujova[2]

1. Pacific Northwest National Lab, USA
2. University of Chemistry and Technology Prague, Czech Republic

Immobilization of nuclear waste through vitrification proceeds by mixing waste with glass forming additives and charging the mixture into a joule heated melter. The aqueous feed slurry creates a cold cap floating on the melt surface. The feed-to-melt conversion advances in three stages that occupy three regions (horizontal layers) within the cold cap: boiling slurry, reacting solids, and foam layer. While the rheology of the latter has been studied, less is known about the rheology of the other two regions. The boiling slurry region was reproduced by gradually reducing the water content from 50 to 35 wt%, which resulted in the yield stress increase from 20 to 260 Pa. To study the reacting solids region, feed slurry was charged into a ~200°C metal mold. Water rapidly boiled away leaving a block of solidified feed from which were cut ~8 x 8 x 30 mm bars. The bars were subjected to static forces from 10 to 500 kPa at a heating rate of 5 K min^{-1}. Yield temperatures from 540°C to 690°C are reported at 10% deformation from initial height, while the feed density increased from 1.3g cm^{-3} to 1.7g cm^{-3}. However, the degree of densification decreased with yield temperature. To understand spreading of the cold cap on the melt surface in the melter, these initial observations will continue by investigating the interaction of the reacting feed solids with slurry flowing over the dried cold cap surface.

4:45 PM

(PACRIM-S30-012-2017) Comparison between a Melter-Produced and Laboratory-Fabricated Cold Cap

D. Dixon*[1]; B. McCarthy[1]; M. Wheeler[1]; D. Cutforth[1]; M. J. Schweiger[1]; P. Hrma[1]; R. Pokorny[2]; M. Hujova[2]

1. Pacific Northwest National Lab, USA
2. University of Chemistry and Technology Prague, Department of Chemical Engineering, Czech Republic

Nuclear waste can be immobilized by combining with glass forming additives and vitrifying into glass. The cold cap is the layer of reacting liquid waste plus glass forming additives, called feed, that floats on top of the glass melt pool during waste-to-glass conversion in an electric melter. The cold cap is comprised of three distinct regions: boiling feed slurry, reacting feed solids, and the foam layer, where gases are trapped in the transient glass matrix. The physical and thermal properties of these regions are desired for calculating a mathematical model of cold-cap behavior. Cold caps generated from a laboratory-scale melter tend to be too small to obtain desired information, so a method for preparing larger cold-cap like samples was developed. To simulate the cold-cap surface, feed slurry was charged into a hot (~200°C) metal mold where water rapidly boiled away leaving a block of dry feed. The block was heat treated to temperatures 400 to 700°C that correspond to the reacting region of the cold cap. Examination by optical and electron microscopy, x-ray computed tomography, differential scanning calorimetry, thermal gravimetric analysis, and density measurements produced similarly comparable results on both the feed block and a cold-cap sample. The feed block density varied between 1.35 and 1.10 g cm^{-3} depending on the heat treatment, while the average cold-cap density was 1.25±0.11 g cm^{-3}.

5:00 PM

(PACRIM-S30-013-2017) Evaluation of Melt Rate for High Level Waste Feeds using Integated Cold Cap-Melter Model

D. P. Guillen*[1]; A. W. Abboud[1]; R. Pokorny[2]

1. Idaho National Laboratory, Materials Science and Engineering, USA
2. UCT Prague, Laboratory of Inorganic Materials, Czech Republic

A three-dimensional computational fluid dynamics (CFD) model has been developed to study the heat transfer and fluid dynamics in the Hanford Waste Treatment Plant (WTP) melters. The CFD model simultaneously solves for heat and mass transfer within the plenum, cold cap and molten glass regions within a Joule-heated melter. The feed-to-glass conversion is accomplished by integration of a mathematical model of the cold cap developed for the assessment of the melting rate, which combines the mass and enthalpy balance of the cold cap together with the conversion kinetics of the feed. The glass conversion rates in the cold cap layer depend upon efficient heat transfer from the melt pool to the cold cap. The thermal convection currents within the melt pool due to Joule heating supplied by the electrodes are substantially altered by forced air bubbling. The addition of bubblers increases glass circulation within the melt pool and agitates the melt surface to break up insulating foam layers in the cold cap. Heat from the molten glass is continually supplied to the cold cap/glass interface, where it is used to drive the cold cap reactions. In this study, the effects of five different melter feeds at the same processing conditions are examined. The feeds were selected based on experimental campaigns performed with melt rates in the range of 550-1900 kg m^{-2} day^{-1}.

5:15 PM

(PACRIM-S30-014-2017) Thermal properties of simulated Hanford waste glasses

C. Rodriguez*[1]; J. Chun[1]; N. L. Canfield[1]; E. C. Rönnebro[1]; J. Vienna[1]; A. A. Kruger[2]

1. Pacific Northwest National Lab, Material Science, USA
2. DOE Office of River Protection, USA

The Hanford Tank Waste Treatment and Immobilization Plant (WTP) will vitrify the mixed hazardous wastes generated from 45 years of plutonium production at the Hanford site in Washington State. The molten glasses will be poured into stainless steel containers or canisters and subsequently cooled for storage and disposal. For appropriate facility design and operations to handle such highly energy-consuming processes, knowledge of the material properties are required. Thermal properties (heat capacity, thermal diffusivity, and thermal conductivity) of representative high-level and low-activity waste glasses were studied as functions of temperature in the range of 200 to 800°C (relevant to the cooling process). Simultaneous differential scanning calorimetry–thermal gravimetry (DSC-TGA), Xe-flash diffusivity, pycnometry, and dilatometry were implemented. The study showed that simultaneous DSC-TGA would be a reliable method for obtaining the heat capacity of various glasses in the temperature range of interest. Accurate thermal properties from this study were shown to provide a more realistic guideline for capacity and time constraints of the heat removal process when compared to the original conservative design-basis engineering estimates. The estimates, though useful for design in the absence of measured physical properties, can now be supplanted and the measured thermal properties can be used in design verification activities.

PACRIM Symposium 32: Nanostructured Bioceramics and Ceramics for Biomedical Applications

Nanostructured Bioceramics I

Room: Monarchy
Session Chairs: Antonio Benayas, Institut National de la Recherche Scientifique; Fiorenzo Vetrone, Institut National de la Recherche Scientifique

1:15 PM

(PACRIM-S32-001-2017) Molecular Biomimetics: Genetically-Engineered-Peptide Guided Technology and Medicine (Invited)

M. Sarikaya*[1]

1. University of Washington, Mater Sci and Eng., Chem Eng and Oral Health Sci., USA

Predictably interfacing biomolecules with solids is the key for drug delivery, enzyme immobilization, functionalization of implants, and signal transduction in biosensors. Highly specific interactions controlled by proteins guide formation of intricate supramolecular architectures in nature. Mimicking proteins, genetically engineered peptides for inorganic solids, GEPI, have become essential molecular tools. The distinguishing characteristics of dental tissues, e.g., enamel, cementum and dentin, are the formation of hydroxyapatite crystallites, regulated by tissue-specific ECM proteins. Using a combination of genetic engineering, informatics, and computational tools we identify functional domains in amelogenin, called amelogenin-derived peptides (ADPs) that guide cell-free re-mineralization of tooth in a variety of formulations in vitro and in vivo towards novel dental health care. GEPIs are also shown to form self-organized nanoarchitectures on single layer atomic materials towards genetic design of electro-optical bionanodevices. By probing the fundamental phenomena of adsorption, diffusion, and assembly of GEPIs by rational mutation, we create coherent bio/nano soft interfaces with strategic implications in nanotechnology and nanomedicine, e.g., graphene FET-based cancer biosensors. Funded by NSF-MGI, C4C-CGF, WA-LSDF, Amazon-Catalyst Programs.

1:45 PM

(PACRIM-S32-002-2017) Nanosized fluoride hosts plus lanthanide-ions doping: A cocktail with more than potential applications on imaging and nanothermometry (Invited)

A. Benayas*[1]; A. Skripka[1]; W. da Silva[2]; K. Santacruz[3]; F. Vetrone[1]

1. Institut National de la Recherche Scientifique, Energie Matériaux Télécommunications, Canada
2. UFAL, Brazil
3. UNISON, Mexico

Nowadays, better light-emitting probes are being demanded to fulfill the needs from various technology fields and, among them, the specific requirements of nanomedicine regarding multifunctional, non-invasive and biocompatible platforms. "All-optically managed" luminescent nanoparticles (NPs) now constitute a growing research field. Among the different NPs, the lanthanide (Ln^{3+})-doped systems allow us to take advantage from their ability to produce "narrow" emission lines, spectrally located both within visible (VIS) and near-infrared (NIR) ranges upon optical excitation. Thus, VIS and NIR signatures emitted from certain combinations of dopant ions have been implemented into fluoride-host NPs. Therefore, the controlled NIR-emission allows imaging, NPs tracking and non-invasive sensing, together with VIS emissions acting as activators for on-target light-triggered process Our efforts show the pivotal turn that luminescent nanothermometry is now making towards NIR range. New preliminary and just-published results are here presented and discussed within the current context of NIR-nanothermometers, regarding (a) dispersibility and colloidal stability of the NPs in aqueous solution; (b) thermal sensitivity; (c) excitation and emission wavelengths matching the so-called "biological windows" of tissue transparency.

2:15 PM

(PACRIM-S32-003-2017) Nanoscale structure and properties of Biomaterials (Invited)

F. Rosei*[1]

1. INRS, Canada

Modifying the nanostructure/chemistry of materials allows to optimize their properties. Our strategy rests on creating nanopatterns that act as surface cues, affecting cell behavior. Chemical oxidation creates unique topographies, becoming a general strategy to improve biocompatibility. Our treatment selectively inhibits fibroblast growth while promoting osteogenic cell activity in vitro. Enhancement of mechano-biocompatibility may occur by coating with spider silk. Improvement of antibacterial properties using laser and plasma strategies will also be discussed.

2:45 PM

(PACRIM-S32-004-2017) Tunable Self-Organized Bio-Interfaces: Where Solid Materials Meet Biology (Invited)

C. Tamerler*[1]

1. University of Kansas, Mechanical Engineering Department and Institute of Bioengineering Research, USA

Bio-interfaces have undoubtedly become a topic that is dynamic across the disciplines from engineering to life sciences. Solid materials systems have boundaries; how these "in-between regions" merge into one another becomes a critical challenge, which is at the forefront in emerging new technologies relevant to all aspects of life, from medical to energy related areas. Biological materials provide the inspiration for design strategies with their precise biomolecular recognition guiding the interfacial interactions. Recognizing this, our group has been exploring the smaller protein domains, i.e. peptides as the key fundamental building blocks to mimic the molecular recognition at the bio-interfaces to create functional bio-hybrid systems. Building upon the multi-modularity, we have been exploring to develop biofunctionalization of surfaces with bioactive as well as bio-repulsive attributes and bioenabled mineralization to generate gradient interfaces My talk will cover the specific examples on generating smart bio-hybrid materials for biosensing and tissue engineering applications.

3:15 PM

(PACRIM-S32-005-2017) Bioinspired Materials for Human cellular bone

J. Xiong*[1]

1. Harbin Institute of Technology, China

Three dimensional lattice bioinspired Materials are implants for protecting outside damages or pressure on the brain. These implants are minimally invasive normally used in conjunction with screws made of ceramic in patients with problems caused craniotomy or many others diseases. Conventional two dimensional tissues are not suitable for this kind of solution due to weak mechanical properties including stiffness, strength and energy absorption. The solution of our design is also very flexible: we can adjust the dimensions to a patient's specific anatomical profile. Our research results have proven that the structural behaviors of three dimensional lattice truss tissues are similar with that of real human bone and much better than traditional 2D Titanium replacements, except the present fabricating price. The regenerating effects of biological cells or molecules in the three dimensional lattice truss tissues need to be addressed in the future work. Our models can also be used to study the problem about bone fractures for ageing societies. Chronic toxicity and body compatibility medicine tests of our tissues after coating film need to be studied further. .

3:45 PM

(PACRIM-S32-006-2017) Modulating charge dynamics in composite systems for advanced applications (Invited)

A. Vomiero*[1]

1. Lulea University of Technology, Engineering Sciences & Mathematics, Sweden

Charge dynamics plays a critical role in several advanced applications based on composite nanosystems, including solar energy, water splitting, nanothermometry. In most of them, semiconducting nanocrystals exhibiting quantum confined effects (quantum dots, QDs) act as light absorbing materials, which are able to generate excitons as a consequence of photon absorption. Managing the photogenerated charges enables the exploitation of different physico-chemical processes, including charge separation and collection in photoelectrochemical systems for energy conversion or tuning photoluminescence properties in luminescent nanoprobes. Key element for driving the processes to targeted applications is the modulation of composition and size of the nanomaterials, which determines their final electronic band structure and functional properties. We will illustrate examples of composite systems for specific applications. (i) “Giant” core-shell QDs, in which modulation of core-to-shell interface induces a single- to double-color photoluminescence, to be applied as nanothermometers; (ii) Near-infrared QDs with increased Stokes shift due to suitable electronic structure of the core and shell, to be applied in luminescent solar concentrators; (iii) Composite TiO2 mesoporous film sensitized by “giant” QDs with high charge injection from the photoexcited QD to the TiO2 anode, for excitonic solar cells and water splitting.

4:15 PM

(PACRIM-S32-023-2017) A Biomimetic Approach to Remineralization of Dental Caries (Invited)

N. Saxena[1]; J. E. Mizels[1]; M. A. Cremer[1]; L. Gower*[1]

1. University of Florida, Materials Science & Engineering, USA

In the United States, dental caries remains the most prevalent chronic disease. Our biomimetic approach is to use a polymer-induced liquid-precursor (PILP) process to sequester ion clusters that can infiltrate into the collagen fibrils within a demineralized dentin lesion. This has been demonstrated in our prior reports using artificially created lesions, which appeared to remineralize fully, yet with only about 50% recovery of mechanical properties. In this talk, I will report on the differences that are seen when using polyaspartate versus osteopontin to induce the PILP process. While both polyelectrolytes are effective at sequestering ions to induce PILP nanodroplets that infiltrate collagen and lead to intrafibrillar nanocrystals, there are striking differences between the mineralization kinetics with these two polymer, as well as uniformity of mineral penetration throughout a given fibril, and crystallite sizes. By improving the reaction kinetics and mineral penetration, this work takes us a step closer to the long-range goal of restoring dentin lesions back to their native structure and properties, and which will enable improved bonding at the interface with dental cements.

4:45 PM

(PACRIM-S32-007-2017) Multifunctional Nanoplatforms Triggered by Near-infrared Light (Invited)

F. Vetrone*[1]

1. Université INRS, Centre Énergie, Matériaux et Télécommunications, Canada

The ability to stimulate luminescent inorganic nanoparticles with near-infrared (NIR) light has made possible their use in a plethora of biological and medical applications. In fact, the biggest impact of such materials would be in the field of disease diagnostics and therapeutics, now commonly referred to as theranostics. The use of NIR light for excitation mitigates some of the drawbacks associated with high-energy light (UV or blue) excitation, for example, little to no background autofluorescence from the specimen under investigation as well as no incurred photodamage. Moreover, one of the biggest limitations is of course, that of penetration. As such, NIR light can penetrate tissues much better than high-energy light especially when these wavelengths lie within the three so-called biological windows. Thus, significant strides have been made in the synthesis of inorganic nanomaterials whose excitation as well as emission bands lie within one of these three optically transparent biological windows. Here, we present the synthesis of various NIR excited (and emitting) inorganic core/shell nanostructures and demonstrate their potential use in nanomedicine. Furthermore, we will show how such nanoparticles can be used as building blocks towards developing multifunctional nanoplatforms for simultaneous detection and therapy of disease.

5:15 PM

(PACRIM-S32-008-2017) Cell Encapsulation and Delivery by Coaxial Electrosprayed Microspheres for Tissue Engineering

Y. Zhou*[1]; M. Wang[1]

1. The University of Hong Kong, Hong Kong

Different approaches including cell-based or scaffold-based tissue engineering are used for tissue regeneration and they can be combined for achieving optimal clinical outcomes. In cell-based tissue engineering, suitable vehicles for delivering living cells are required. In this study, coaxial electrospray was investigated for cell delivery for scaffold-based tissue engineering. Polymers such as sodium alginate (SA) were used to firstly fabricate cell-free microspheres. A polymer solution was fed into outer capillary and PBS was fed into inner capillary of a coaxial spinneret to produce core-shell structured microspheres. SA underwent post-spray crosslinking treatment. After process optimization, PBS was replaced by aqueous cell suspensions of human umbilical vein endothelial cell (HUVEC) or human aortic smooth muscle cell (HASMC) in coaxial electrospray for making cell-encapsulated microspheres at high (1×10^7/mL) or low (5×10^6/mL) cell density. Cell-encapsulated microspheres had spherical shapes but different diameters. Cell release from microspheres was achieved when SA shell broke down in 10 minutes after being treated with 0.055M Na-citrate solution. High cell loading efficiency was obtained. Cells exhibited high viability both after cell encapsulation and after cell release. Desirable cell encapsulation and delivery can be achieved via these microspheres for tissue engineering.

PACRIM Young Investigators Forum: Design and Application of Next-Generation Multifunctional Materials-Addressing the New Millennium’s Societal Challenges

Frontiers in Nanotechnology

Room: Kohala 4
Session Chairs: Valerie Wiesner, NASA Glenn Research Center;
Michael Walock, US Army Research Laboratory;
Yang Bai, University of Science and Technology Beijing

1:15 PM

(PACRIM-YIF-009-2017) Preparation of high-pure V_2C MXene and electrochemistry properties as Li-ion batteries (Invited)

A. Zhou*[1]; F. Liu[1]

1. Henan Polytechnic University, School of Materials Science and Engineering, China

High pure V2C MXene, quasi-two-dimensional carbide with graphene-like structure, was successfully synthesized by etching V2AlC with hydrochloric acid and sodium fluoride at 90°C for 72 h. From X-ray diffraction pattern, the quantity of starting materials

V2AlC in synthesized products decreased and then increased with the extension of etching time. Moreover, same trend was shown in the results of scanning electron microscopy and energy dispersive spectrum. The mechanisms to prepare high pure V2C was discussed and understood. The as-prepared V2C MXene showed excellent electrochemical properties anode of lithium ion batteries. The capacity can be 291 mAh g−1 at 1C rate, which is higher than previous reported capacity measured from less pure V2C. An interesting phenomenon was finding that the capacity was increased with charge cycles. It was suggested that V2C with high purity can be promising anode material with excellent performance.

1:40 PM

(PACRIM-YIF-010-2017) Morphology controlled synthesis of niobium oxide nanoparticles for functional applications (Invited)

T. Fuchigami*[1]; K. Kakimoto[1]

1. Nagoya Institute of Technology, Japan

Niobium oxide is widely used in electric and optical devices. In addition, niobium oxide powder is an important constituent of catalytic and ferroelectric materials such as $NaNbO_3$, $LiNbO_3$, and $(Na,K)NbO_3$. Their functions can be tuned by changing dimensional shapes, size, and crystalline structure of niobium oxide particles. In this study, we synthesized niobium oxide with unique nano-morphologies such as spiky- and rod-structure by hydrothermal treatment and investigated the relationship between properties and the unique structures. Niobium oxide nanoparticles with various shapes were synthesized by hydrothermal treatment of different raw material solutions: niobium oxalate, niobium malate, a mixture of niobium oxalate and alkali metal acetate solution. The particle size and morphology were determined by TEM. Optical absorption spectra were recorded with UV/VIS/NIR Spectrophotometer. Spiky nanoparticles composed of sphere core particles and nanorod were obtained from niobium oxalate solution, and their size can be tuned from 150 to 300 nm by changing niobium concentration in the niobium oxalate solution. Interestingly, band gap energies of the spiky nanoparticles decreased from 3.50 to 3.36 eV even though the particle sizes decreased. Thus, it is possible to obtain novel characteristics by controlling not only their size but also three-dimensional shapes.

2:05 PM

(PACRIM-YIF-011-2017) Particle orientation in colloidal processing with UV curable binder under magnetic field

S. Baba*[1]; S. Tanaka[1]

1. Nagaoka University of Technology, Japan

Crystal-orientation using the colloidal processing in a high magnetic field is effective for improving property of the polycrystalline ceramics. We have examined on the colloidal processing with UV curable binder, and reported the fabrication of a particle-oriented green sheet. The polymerization by the UV light could shorten the duration time in the magnetic field for several ten seconds. The objective of this study is to examine the influence of experimental parameters on the orientation degree of the green sheet. In principle, the orientation degree depends on the magnetic flux density, duration time in the magnetic field, and the viscosity of the slurry. Here, the viscosity could be controlled with the temperature and the solid loading in the slurry. In the experiment, the well-dispersed slurry with solid loading of 45 vol% was prepared from the UV curable acrylic binder, photoinitiator, and dispersant. The slurry was cast on a PET film and placed in magnetic fields with 6 and 10 T. After duration for various times, the UV light was irradiated to the tapes in the magnetic field. In the strong magnetic field at 10T, the orientation degree was saturated in several seconds in any viscosity, whereas it increased gradually with increasing the duration time and the viscosity of the slurry at 6T.

2:25 PM

(PACRIM-YIF-012-2017) Cationic polymer-anionic surfactant complex as multi-functional surface modifier of nanoparticles for material processing

M. Iijima*[1]; T. Tsutsumi[1]; M. Kataoka[1]; K. Hasegawa[1]; S. Morita[1]; J. Tatami[1]

1. Yokohama National University, Graduate School of Environment and Information Sciences, Japan

In this report, we introduce cationic polymer-anionic surfactant complex system as multi-functional surface modifier which can act as all-purpose dispersant, binding agent for nanoparticle alignment control, and segments to form cross-linking networks with various polymeric matrixes. PEI complexed with anionic surfactant having organic chain branched into alkyl based chain and PEG based chain near the head group possessed efficient adsorption properties on wide species of nanoparticles through various surface modification protocols, such as direct adsorption, simultaneous adsorption with milling process, and ligand exchange, and the surface modified nanoparticles were dispersible in a series of solvents regardless of their polarity. A simple mixing of bare particles in suspensions of PEI-complex stabilized nanoparticles resulted to the alignment of nanoparticles along the bare particles as stable nanocomposites in solvents, which can be a powerful tool toward nanoparticle alignment control. It was also found that PEI-complex can be used as reaction sites with monomers, which was effective to improve mechanical properties of polymer nanocomposites and spay dried granules as well as to realize complex-structured shaping from non-aqueous slurries.

2:45 PM

(PACRIM-YIF-013-2017) From Molecules to Materials: A Scientific Trip around the Globe (Invited)

E. Hemmer*[1]

1. University of Ottawa, Chemistry and Biomolecular Sciences, Canada

Mobility and networks are two aspects that are considered as essential for the development of a scientific career in our days. But what does this mean? Do we have to be mobile in order to build up our network? Or do we need a strong network in order to become mobile? This presentation will provide a snapshot on the journey of a materials scientist from Germany moving via Japan to Canada. In the luggage: multifunctional lanthanides in molecules and nanomaterials. Some experience from the time being a PhD student, from the period discovering new countries and research areas as a postdoctoral fellow, and the most recent ongoing adventure of starting an independent research group will be shared with the audience. While the search for the ultimate recipe for the straight forward achievement of a scientific career is still going on, some of the basics that may be required for a scientific trip by any young researcher or scientist will be suggested for discussion. These basics clearly include curiosity, self-motivation and an open mind, not to forget about endurance as well frustration tolerance, while taking pleasure in what we do must always be kept in sight. (Disclaimer: Unfortunately, the author won't be able to provide an all-inclusive-package for success in science. She is still looking for it herself…)

Innovative Materials Manufacturing

Room: Kohala 4
Session Chairs: Aiguo Zhou, Henan Polytechnic University;
Teruaki Fuchigami, Nagoya Institute of Technology

3:45 PM

(PACRIM-YIF-014-2017) Low-temperature nitridation of oxides via $NaNH_2$ melt (Invited)

A. Miura*[1]; M. Higuchi[1]; K. Tadanaga[1]

1. Hokkaido University, Japan

Nitrides and oxynitrdies are promising materials for optical, electronic, magnetic and catalytic properties. However, their synthesis often faces the difficulty by breaking highly stable metal-oxygen bonding, and thus the synthesis mostly requires high-temperature treatment above 300 °C in an ammonia flow. Here, we show the low-temperature nitridation of oxides using $NaNH_2$ melt for the synthesis approach of nitrides and oxynitrides. This approach has the advantages of low reaction temperature, reduced consumption of ammonia, employing nonspecialized equipment. Highly active and highly concentrated NH^{2-} reacts with oxides, and the formation of NaOH as a byproduct is a thermodynamic driving force for the nitridation. The synthesis of manganese oxynitirdes and their catalytic activity for the oxygen reduction reaction catalysts are highlighted.

4:10 PM

(PACRIM-YIF-015-2017) Micropore aligned films based on Metal Organic Frameworks heteroepitaxially-grown on metal hydroxide scaffold

K. Okada*[1]; K. Ikigaki[2]; M. Takahashi[2]; P. Falcaro[3]; C. Doonan[4]; Y. Tokudome[2]; K. Machida[1]

1. Osaka University, Graduate School of Engineering, Japan
2. Osaka Prefecture University, Japan
3. Graz University of Technology, Austria
4. The University of Adelaide, Australia

Thin films of porous materials are of great interest for various applications such as separation, storage, electronics and photonics. It has long been expected a pore alignment in a large scales exceeding cm-scale. However, the formation of thin films with alignment of pores remains a significant challenge especially for microporous crystalline materials including zeolite and metal-organic frameworks (MOF). This is because entropy dominate micropore formation proses. Here we focus on the use of surface hydroxyl groups on metal hydroxides, which can be further used as scaffolds for the growth of different materials. In the present study, microporous crystalline MOF is found to be grown on the nano metal hydroxides surface through heteroepitaxial mechanisms. Our approach is based on: (1) The regularity of hydroxyl groups on the nano metal hydroxides was well-matched with that of organic parts of MOFs, leading to an epitaxial growth of MOFs on metal hydroxides. (2) Metal hydroxide nanomaterials (e.g. nanobelts, nanowires) were deposited on substrates with crystallographic orientation and the ordered hydroxyl groups in a large scales were used as scaffolds for epitaxial growth. Optical and electrical devises with anisotropic properties could be fabricated by impregnating functional molecules into the aligned microporous channels of the oriented MOF film.

4:30 PM

(PACRIM-YIF-016-2017) Flexible control of positive and negative electrocaloric effect in ferroelectric materials for high-efficient solid state cooling (Invited)

Y. Bai*[1]

1. University of Science and Technology Beijing, China

For the great demand of specialized energy applications, electrocaloric materials offer a promising route to providing high-efficiency and environmentally-friendly solid-state refrigeration technology due to special advantages of easy miniaturization, high conversion efficiency and easy manipulation. Normally, a polar material releases heat when applying electric fields and absorbs heat when removing it. The ferroelectrics with first ordered phase transition (FOPT) always exhibit a giant ECE value dominated by phase transition. If the FOPT is diffused by ion substitutions, the ECE peak turns wider and lower, but the ECE maximum also occurs around the phase transition temperature, while an optimized value always occurs around the morphortropic phase boundary. If there are complex phase transitions, the negative ECE may occur in some special materials. For example, the negative ECE in PMN-30PT single crystals is caused by the field-induced formation of metastable M phase and its transition process between R and T phases. If the negative and positive ECEs are flexibly controlled and well combined under multiple fields, the cooling efficiency can be improved remarkably.

4:55 PM

(PACRIM-YIF-017-2017) Knowledge transfer from academia to industry: A business model from SMEs for SMEs

T. Fischer*[1]; S. Mathur[1]

1. Materials Alliance Cologne, Steinbeis GmbH & Co. KG für Technologietransfer, Germany

The knowledge transfer from universities to industry, especially small and medium sized enterprises (SME) is often limited to either third party funded projects with a consortium from both academia and industry or employment of graduate students and Ph.Ds in the company of interest. On the other hand, small scale projects, targeted analytical services or consulting was and most often still is not an option for academia, due to legal and/or financial constraints, but would be a perfect tool for identifying future partners in industry and to provide state of the art technology to SMEs, apart from large commercial scientific service agencies. With more than 1000 transfer enterprises worldwide the Steinbeis network based in Germany offers the possibility to offer knowledge transfer to industry, while providing administrative back offices and legal consulting as well as financial controlling. In this B2B environment, backed up with the university infrastructure, projects can be realized easily. This presentation will provide insight of realizing entrepreneurship based on the Steinbeis network and highlight the challenges and opportunities associated with industry projects offered as a service.

5:15 PM

(PACRIM-YIF-018-2017) On the Development of Novel MAX Reinforced Metal (MRM) Composites

F. AlAnazi*[1]; S. Gupta[1]

1. University of North Dakota, Mechanical Engineering, USA

$M_{n+1}AX_n$ (MAX) phases (over 60+ phases) are thermodynamically stable nanolaminates which has unusual and unique, properties. The MAX phases are highly damage tolerant, thermal shock resistant, readily machinable, and with Vickers hardness values of 2–8 GPa, are anomalously soft for transition metal carbides and nitrides. MAX phases display nonlinear, hysteretic, elastic behavior due to kink band formation in the basal planes. The composites of MAX phases with metals (MAXMET) are also important from both fundamental and applied perspective. Recently, we showed that lower concentrations of MAX Phases can also reinforce metal matrix and improve its tribological behavior. In this presentation, we will report the recent progress in the designing MRMs.

Thursday, May 25, 2017

GOMD Award Lectures

Varshneya Glass Science Lecture

Room: Kona 5

8:35 AM

(GOMD-PL-004-2017) Pathways of glass→crystal transformation (Invited)

H. Jain*[1]

1. Lehigh University, International Materials Institute for New Functionality in Glass, USA

The inevitable transformation of glass to crystal can occur via multiple pathways, producing different results. For example, spontaneous devitrification of glass, known for over six decades, produces polycrystalline glass-ceramics on heating, which are exploited in numerous products. By comparison, the possibility of transforming glass into its complete antithesis - a *single crystal*, was demosntrated only very recently. In this case one needs to heat (cool) the glass (melt) to its nucleation temperature to form just one nucleus and then heat it further to grow to the desired size and shape. The difficlty arises from unwanted nucleation in the glass matrix around the growing crystal. We will examine physical and chemical strategies that have successfully overcome this challenge. One such pathway has led to single crystals of compositions that decompose, transform to some undesirable phase, or melt incongruently on heating, which has not been feasible by conventional methods. Another variation has yielded a novel form of solid – the rotaing lattice single crystal. The resulting 1D and 2D single crystal architecture in glass fabricated by such pathways by CW laser heating, and in 3D by fs laser, will be examined for new functionalities and applications in optical communication, integrated optics, etc. Separate parts of this work were supported by the US DoE (DE-SC0005010) and NSF (DMR-0906763 and DMR- 1508177).

GOMD Symposium 1: Fundamentals of the Glassy State

Glass at High Temperature

Room: Kona 4

Session Chairs: Anita Zeidler, University of Bath; Liping Huang, Rensselaer Polytechnic Institute

9:45 AM

(GOMD-S1-078-2017) Accessing supercooled liquid dynamics of extremely poor glass formers by a containerless levitation viscometer (Invited)

Y. Yue*[3]; H. Liu[1]; R. Pan[3]; N. Greaves[2]; H. Tao[3]; Z. Shan[3]

1. Aalborg University, Denmark
2. University of Cambridge, United Kingdom
3. Wuhan University of Technology, China

Assessing the supercooled liquid dynamics (SCLD) of extremely poor glass formers is critical for understanding the nature of glass formation and glass transition. So far, the SCLD of such glass formers is poorly understood. This is because the SCLD of poor glass formers is not assessable using conventional techniques as their crystallization kinetics is far beyond the time window of viscosity measurements. However, some promising development has recently been achieved in assessing the SCLD of poor glass formers using a levitation viscometer. The viscometer is capable of not only determining viscosity at high temperature, but also of drastically broadening the supercooled region. This allows us to investigate the SCLD of refractory oxide. Here, we report our recent findings about the dynamical behavior of calcium aluminate. The viscosity is measured in a broad supercooled range (up to 450 K) by the levitator. The results show the fragile-to-strong transition in the supercooled region. The structural and thermodynamic origin of such transition is explored by performing calorimetry, Raman spectroscopy, NMR and XRD experiments on the melt-quenched glasses. The compositional dependences of T_g, fragility, glass forming ability and configurational heat capacity are found to be rather different from literature, and the source of such difference is discussed.

10:15 AM

(GOMD-S1-079-2017) Aluminum Local Structure and Dynamics in Refractory Melts: An In-Situ High-Temperature ^{27}Al Nuclear Magnetic Resonance Point of View (Invited)

P. Florian*[1]; V. Sarou-Kanian[1]; A. Novikov[1]; C. Le Losq[3]; D. R. Neuville[2]; D. Massiot[1]

1. CEMHTI-CNRS, France
2. IPGP-CNRS, France
3. The Australian National University, Research School of Earth Sciences, Australia

We have developed experimental settings allowing us to perform NMR experiments from room-temperature up to 2400°C using CO_2 laser as a source of heating. We early showed that changes of the coordination state of aluminum are a key mechanism controlling the macroscopic properties of aluminum-rich refractory melts such as aluminates. Recent investigations of sodium aluminosilicates across the glass transition temperature (up to 1300°C) showed indeed a clear increase of the $Al^{[5]}$ concentration with increasing temperature. When considering melt fragility and heat capacity, our data demonstrate that $Al^{[5]}$ is a transient unit at high temperature in highly polymerized melts which increases the glass' stability due to its ability to carry threefold coordinated oxygen atoms in its first coordination shell. Rare-earth aluminosilicate melts (1700°C-2200°C) also show an important presence of "minor" $Al^{[5]}$ species yet not linked to the macroscopic shear viscosity as opposed to Ca-based compositions for which relaxation times for viscosity, electrical conductivity and ^{27}Al NMR relaxation processes in the melt are the same. This (dis)similarity points to a (de)coupling between the rate of Al-O bond exchange and the structural relaxation involved in viscous flow and we are currently investigating this behaviour in Sr-, Ba- or Zn-based aluminosilicate melts.

10:45 AM

(GOMD-S1-080-2017) Raman linewidths of the 800-1200 cm^{-1} region of crystals, glasses and melts with implications for curve fitting of Raman spectra

W. Nesbitt[1]; G. Bancroft[2]; G. Henderson*[3]; C. O'Shaughnessy[3]

1. University of Western Ontario, Earth Sciences, Canada
2. University of Western Ontario, Chemistry, Canada
3. University of Toronto, Earth Sciences, Canada

Raman spectra of the symmetric stretching (800-1200cm^{-1}) region of alkali and alkaline-earth silicate glasses are often interpreted in terms of Q^n species vibrations (where n=the number of bridging oxygens attached to a tetrahedron and varies from n=0-4). Curve fitting of this high frequency envelope is used to obtain the relative proportions of the different Q^n species in the glass. However, a number of problems result from this approach: 1) Fitted curves are often unconstrained and have varying widths (full width half maxima, FWHM) and 2) the number of fit peaks often exceeds the number of Q species present resulting in extra peaks in the spectral envelope that cannot be logically explained. Here we address four major questions: 1) Are all the peaks in the high frequency envelope due to TO_4 (T= Si, P, S) symmetric stretches; 2) are the peaks at well defined energies; 3) are the line shapes and FWHM at well defined energies and; 4) What are the additional peaks due to? We show that the envelope is due to symmetric stretching of the TO_4 polyhedron, the lineshapes and line widths with increasing temperature (T) are remarkably consistent for silicate, phosphate and sulphate glasses (at least for Q^n, n=0-3) and, furthermore, that the additional peaks are most likely due to bridging oxygens with 1 or more alkali or alkaline-earth atoms attached to them.

11:00 AM

(GOMD-S1-081-2017) Understanding Sodium Borate Glasses and Melts from Their Elastic Response to Temperature

S. Jaccani*[1]; L. Huang[1]

1. Rensselaer Polytechnic Institute, Materials Science and Engineering, USA

In-situ Brillouin light scattering (BLS) experiments were carried out to measure the high temperature elastic moduli of sodium borate glasses and melts from room temperature to temperatures beyond the glass transition temperature (T_g) over a large composition range. Besides composition, we also varied the cooling rate to study the effect of thermal history on the room temperature properties and on the elastic response to high temperature. On heating air-cooled glasses of lower Na_2O content, elastic moduli increase anomalously with increasing temperature just below their T_g, whereas this behavior is absent in corresponding annealed glasses. This anomalous increase of elastic moduli with temperature was not observed in glasses of higher Na_2O content. These differences were explained by different structural relaxation mechanisms in the glass transition range in sodium borate glasses of different compositions based on Raman spectroscopy.

11:15 AM

(GOMD-S1-082-2017) Effects of Iron and Water on Effective Thermal Conductivity of Glass Melts

H. Tokunaga*[1]; K. Hayashi[1]

1. Asahi Glass Co., Ltd., New Product R&D Center, Japan

Thermal conductivity is a main factor to determine temperature distribution of glass melt at each phase of the manufacturing process. Recently, there has been considerable interest in the commercial production of high transmission glasses for TFT substrate and light guide panel and thermal conductivity data for such glasses is demanded to produce them with high yield. Although thermal conductivity is consists of the three elements of heat transfer (lattice vibration, radiation and convection), the radiation heat transfer is the dominant for glass melts because it increases with cube of temperature. In this study, effective thermal conductivity was measured by steady-state method and radiation heat transfer was measured by high-temperature transmittance. Since the effective thermal conductivity of the clear glass melts were much higher than conventional glass melts, it will cause small temperature distribution and decrease convection flow. To conditioning thermal conductivity, we investigated the effects of water which has no influence to UV-VIS transmittance. The effect of other elements will be discussed in the presentation.

11:30 AM

(GOMD-S1-083-2017) High Temperature Infrared Transmitting Chalcogenide Glasses for Remote Sensing

J. Roth*[1]; S. W. Martin[1]

1. Iowa State University, MSE, USA

Interest in chalcogenide glasses has grown for decades. Unlike oxides, their large anions and weaker bonding sacrifices high melting and glass transition temperatures (T_g) for increased infrared (IR) transparency. While most research has been focused on increasing the IR transparency of these materials little has been done to maximize both IR transparency and T_g, but a new set of chalcogenide glasses built around ionic bonding schemes have shown promise in optimizing both of these properties. One application demanding such properties is remote sensing in new advanced small modular nuclear reactors (AdvSMNR) to detect trace amounts of gaseous compounds inside of the reactor environment. This work focuses on maximizing T_g and IR transparency of sulfide based glasses as they give the optimal compromise between the highly transparent tellurides and selenides and high T_g oxides. Ternary $BaS+La_2S_3+GeS_2$ glasses were prepared by sealing and melting stoichiometric amounts of sulfide compounds together in silica ampoules at ~1100°C. These glasses show great promise as they achieve T_gs in excess of 500°C and have an IR transmission cutoff of $1000cm^{-1}$. This allows for the detection of IR active species in the molecular fingerprint region of the IR spectrum at elevated temperatures. Irradiation of the glasses is currently underway to determine the effect nuclear radiation has on both GeS_2 and ternary glasses.

11:45 AM

(GOMD-S1-084-2017) Mobility and local environment of Zr diffusion in glass furnace

M. Ficheux*[1]; L. Cormier[2]; E. Burov[1]; K. Plevacova[3]

1. Saint-Gobain, SVI, France
2. IMPMC, France
3. EV - Saint Gobain Recherche, France

To guarantee high tempertaure resistance (1500°C) and low polution in glass, Zr containing refactories are used in glass furnaces. Due to matter exchange between the amorphous glass and the crystallized refractories, several phenomena can occur, such as crystallization in the glass or corrosion of refractories. The present work is focused on the study of zirconium mobility between the two materials in furnace conditions. Particularly, we adress the Zr mobility issue in glass through multicomponent diffusion approach, considering local Zr environment modifications along diffusion profile. The objectif is to find out a model that describes the Zr diffusion in the glass and its behavior in the glass structure. Therefore, we performed diffusion experiments on couples of glasses around a central composition xx%Na2O –XX%CaO-Al2O3-SiO2 +/-5%Zr which is representative of industrial glass polluted by zirconium. The local structure modifications along the diffusion profile were investigated by XAS and Raman spectroscopy. This model will be then extended to describe the interaction between the amorphous glassy phase and the crystallized grains inside the refractory.

GOMD Symposium 3: Optical and Electronic Materials and Devices: Fundamentals and Applications

Sciences and Applications of Optical Ceramics and Glass-ceramics

Room: Waikoloa 3
Session Chair: Woohong (Rick) Kim, Naval Research Laboratory

9:30 AM

(GOMD-S3-065-2017) Eu-doped SiAlON and borophospate glass composites for white LED

H. Segawa*[1]; N. Hirosaki[1]

1. National Institute for Materials Science (NIMS), Japan

Europium-doped Ca-α-SiAlON (SiAlON) is known to emit yellow light by irradiation of blue light and produce a white light-emitting diode (LED) when the SiAlON was embedded in resins as powder. However, the heat generated by the high-power blue LED caused the deterioration of the resin, shortening the lifetime of the device. Glasses are more suitable than the resin as a host material to disperse the phosphor powder. In this study, composites with borophosphate glass and SiAlON phosphor were prepared by melting, and the photoluminescence spectra were measured to determine the feasibility of using the composites in white LEDs. Zinc borophosphate glasses, $xZnO-yB_2O_3-(100-x-y)P_2O_5$ (mol%), were melted. The mixtures of the obtained glass and SiAlON were re-melted, resulting in glass-phosphor composites. The composites were polished and photoluminescence spectra were measured. Glass forming region of the mother glasses was decided. In particularly, the mother glasses could not be obtained when the P_2O_5 concentration was 20 mol%. In the case of x=60, the composites with y=30 glasses showed higher quantum efficiency than the others, and the quantum efficiency increased with increase of SiAlON concentration from 1 to 3 mass% and reached to the same vale of the SiAlON powder. The chromaticity of the composites was controlled by the SiAlON concentration and sample thickness, resulting in the near white color.

9:45 AM

(GOMD-S3-066-2017) Structural Determination of the Stillwellite $LaBGeO_5$ Transparent Ferroelectric Nanocomposite

A. L. Paterson*[1]; A. Hannon[2]; U. Werner-Zwanziger[1]; J. Zwanziger[1]

1. Dalhousie University, Chemistry, Canada
2. Rutherford Appleton Laboratory, ISIS Facility, United Kingdom

We present a combined neutron diffraction and solid state nuclear magnetic resonance study of the $LaBGeO_5$ system. The synthetic stillwellite $LaBGeO_5$ is a valuable example of the transparent ferroelectric nanocomposite (TFN) class of materials. TFN materials have promising capabilities in optical computing and photonics. The $LaBGeO_5$ crystal structure has been previously determined, but the glass structure is presently unknown. Early models suggested that the local structure of the glass was identical to that of the crystal. ^{11}B MAS NMR revealed a significant difference in the B-O coordination number between the crystalline and glassy phases. Using a combination of pulsed neutron diffraction and solid state NMR we probe the local structure of the $LaBGeO_5$ glass, as well as the silicate analogue $LaBSiO_5$. Our results suggest that the $LaBGeO_5$ glass has higher Ge-O and lower La-O coordination numbers than those seen in the $LaBGeO_5$ crystal.

10:00 AM

(GOMD-S3-067-2017) Nanoparticles in glass: When gold meets surface

Y. Wei*[1]; J. Zhao[1]; H. Ebendorff-Heidepriem[1]

1. ARC Centre of Excellence for Nanoscale BioPhotonics, Institute for Photonics and Advanced Sensing, The University of Adelaide, Australia

We developed a new but facile method to homogeneously precipitate Au NPs in tellurite glasses, where the tunable size of Au NPs in bulk glass promises applications ranging from colored glasses, nonlinear devices to transparent displays. The method is based on a two-step process: melting tellurite glass in a gold crucible at elevated temperature T_1 (>750 °C) in air to form precursor glass, and remelting the precursor glass powders in a gold crucible at varying low temperature T_2 (< 580 °C) and melting time t (< 30min) to controllably produce different size Au NPs. At T_1, Au^+ ions are dissolved into the precursor glass from the crucible under the hot glass melt erosion. Subsequently, the precursor glass is ground, which is critical to create abundant surfaces to lower the reduction potential of $Au^+ \rightarrow Au^0$. Thus, the surfaces in the remelting process stimulate the reduction of $Au^+ \rightarrow Au^0$ which followed diffusing, nucleating and growing into NPs. Due to the strong localized surface plasmon resonance (LSPR) of Au NPs, the resulting hybrid glasses have shown obvious dichroism (blue in transmission and red in reflection). The red-shift of LSPR peak is observed with increasing remelting temperature and/or time due to the growth of Au NPs. In the presence of Au NPs, we demonstrate that upconversion luminescence of Er^{3+} in glass is enhanced where the amplification factor depends on NPs density and pumping power.

10:15 AM

(GOMD-S3-068-2017) Additive Manufacturing of Ceramic Optical Components (Invited)

J. Choi*[1]; A. W. Cook[1]; C. DiAntonio[1]; B. Jared[1]; E. Winrow[1]

1. Sandia National Laboratories, USA

Fabrication of optical components typically requires high precision processes to generate desired surface figure and finish. Primarily due to the stringent requirements on surface figure, the fabrication of optical components has not benefited much from the recent growth of additive manufacturing (AM). There is, however, an opportunity to take advantage of AM in optical systems, especially with aggressively light-weighted reflective optical systems. Additively manufactured ceramic components, with higher modulus of elasticity and lower coefficient of thermal expansion properties compared to metals, present a unique design trade space for optical systems. We will use the ceramic AM technology to fabricate ceramic mirrors and polish the optical surfaces to improve surface figure and finish and test against optical requirements. Processes to produce an optical finish on AM ceramic components will be discussed. In addition, test methods for characterizing the optical performance of printed parts will be discussed along with the results. Additionally, methods to feed optical characterization results back to the formulation, compounding, and feedstock design for AM to produce components with higher optical quality will be presented.

10:30 AM

(GOMD-S3-069-2017) Laser Induced Glass-Ceramics for GRIN applications

L. Sisken*[1]; M. Melvin[1]; I. Mingareev[1]; M. Richardson[1]; C. R. Baleine[2]; K. Richardson[1]

1. University of Central Florida, CREOL, USA
2. Lockheed Martin, Missiles and Fire Control, USA

GRIN glass-ceramic elements with tailorable spatial index profiles hold the potential to improve the toolbox of candidate materials available to optical designers. Specifically, gradient refractive index (GRIN) optical components can potentially decrease the number of optical components needed to carry out the desired optical function in increasingly compact optical systems. A multi-component infrared glass has been developed that can be 'cerammed' (locally converted from glass to ceramic) utilizing spatially-selective direct write laser irradiation and blanket furnace heat treatments. This material processing methodology enables the fabrication of GRIN elements realized through controlled patterning (a nucleation step) and subsequent conversion (growth) only within laser exposed regions. The influence of irradiation conditions, including wavelength and energy dose, on the resulting material modification is discussed, along with a summary of other associated post-conversion physical property changes in the resulting glass ceramic component.

10:45 AM

(GOMD-S3-071-2017) Color Conversion Property Modification of Cd-S-Se Quantum Dot Embedded Glasses via Compositional Change for White LED

K. Han*[1]; W. Im[2]; J. Heo[3]; W. Chung[1]

1. Kongju National University, Advanced Materials Engineering, Republic of Korea
2. Chonnam National University, School of Materials Sci. and Eng., Republic of Korea
3. Pohang University of Science and Technology(POSTECH), Dept. of Materials Sci. and Eng., Republic of Korea

Quantum dots (QDs) have been extensively studied for white LED applications due to their high conversion efficiency and good tunability of their emission bands simply varying their size. However, conventional QDs fabricated by colloidal methods inevitably possess organic passivation layers which significantly reduces long-term stability of QDs due to their weak thermal and chemical stability. Recently, we synthesized a Cd-S-Se QD embedded glass (QDEG) based on silicate system and successfully fabricated white LED demonstrating its long-term stability. However, the quantum yield of the QDEG was less than 20% and requires further enhancement. In this study, we modified glass composition to improve color conversion efficiency of the QDEG. Glasses varying CdO, ZnS and ZnSe content were prepared and their emission intensity as well as color conversion properties were monitored. Rare earth ions were also added to modify Cd-S-Se QD. QD formation was examined by Raman and TEM analysis. White LED has been achieved with the modified QDEGs and enhancement of QY was inspected with integrating sphere.

11:00 AM

(GOMD-S3-072-2017) Preparation and densification of $CaLa_2S_4$ ceramics by Hot Pressing (Invited)

G. R. Durand*[1]; O. Merdrignac-Conanec[1]; X. Zhang[1]; N. Hakmeh[1]

1. UMR CNRS 6226 “Institut des Sciences Chimiques de Rennes”, Equipe Verres et Céramiques, France

This work focuses on the preparation of compounds of the $CaLa_2S_4$ – La_2S_3 (CLS) system for IR optical applications. CLS compounds are alternative materials to the most commonly used zinc sulfide ZnS, mainly based on their superior mechanical properties, better erosion resistance and larger transmission range from visible to LWIR (0.5μm to 14μm). A higher transparency in the infrared significantly improves the performance of the infrared optical systems and allows the use of uncooled detectors (operate beyond 12μm), resulting in a significant reduction in system cost. Ceramics powders were synthesized by a new patented combustion method and post-heat treated under H_2S. The CLS powders were subsequently hot pressed to full densification. Combustion synthesis method is a time-saving route leading to highly sinterable submicron powders of different compositions of the solid solution. Extreme care is required to avoid oxygen which induces absorption bands in the IR range. Optical properties, microstructure and hardness of ceramics made from various compositions were measured. Best results for both sinterability and optical transmission were obtained for compositions with lower Ca contents.

11:15 AM

(GOMD-S3-073-2017) Densification and Grain Growth of Calcium Lanthanum Sulfide Infrared Optical Ceramics via Field Assisted Sintering (Invited)

Y. Li*[1]; Y. Wu[1]

1. Alfred University, Kazuo Inamori School of Engineering, USA

Calcium lanthanum sulfide ($CaLa_2S_4$, CLS) has been developed and researched as material for infrared window ceramics because of its high transmittance over a broad range of wavelengths in the infrared range, as well as its favorable mechanical strength and high rain erosion resistance. In this work, CLS infrared optical ceramics were consolidated via the Field Assisted Sintering Technique (FAST). Sintering mechanisms were determined and discussed through densification behavior and grain growth kinetics analyses of the CLS ceramics. The FAST-processed CLS ceramics were further compared with the hot-pressed CLS ceramics in terms of phase composition and microstructural features, in order to study and compare the characteristics associated with different pressure-assisted sintering techniques.

11:30 AM

(GOMD-S3-074-2017) Preparation of silica glass incorporating metastable β-Zn_2SiO_4:Mn nano-phosphor

T. Akai*[1]; M. Murakami[1]; T. Uchida[1]; M. Yamashita[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Inorganic Functional Rearch Institute, Japan

Dispersion of nano-crystal phosphor in nano porous silica has been studied to avoid the aggregation of nano-crystal phosphor. Because of the restriction of space, size of the phosphor can be controlled, and sometimes metastable phase is stabilized. We have found that metastable β-Zn_2SiO_4:Mn nanocrystals can be stabilized in amorphous silica. Zn and Mn ions were incorporated in mesoporous silica by immersing aqueous solution of Mn^{2+} and Zn^{2+}, and the mesoporous silica was sintered at 1000-1100°C in reducing atmosphere. β-Zn_2SiO_4:Mn were formed along with -Zn_2SiO_4:Mn in sintered mesoporous silica when diameter of pore is as small as 2.4nm. The composite exhibits green and yellow photoluminescence originated from α-Zn_2SiO_4:Mn and β-Zn_2SiO_4:Mn, respectively. The α-phase was able to be removed by leaching the composite by aq. 1N $HNO_{3,}$ and silica incorporating pure β-Zn_2SiO_4:Mn was obtained. In this paper, preparation and optical properties of b-Zn_2SiO_4:Mn stabilized in silica will be presented.

Glasses in Detector Applications

Room: Kona 3

Session Chairs: Mario Affatigato, Coe College; S. Sundaram, Alfred University

9:45 AM

(GOMD-S3-075-2017) Rare Earth Activated Glasses: Exploratory Investigation Toward New Scintillators (Invited)

L. G. Jacobsohn*[1]; U. Akgun[2]

1. Clemson University, Materials Science and Engineering, USA
2. Coe College, Physics, USA

Scintillators are optical sensors for the detection and measurement of ionizing radiation. They convert high energy X-ray and gamma-ray photons into thousands or more ultraviolet/visible photons, which are then detected and quantified. Glass scintillators find application in the detection of thermal neutrons, for the detection of alpha, beta, and gamma-ray in severe environmental conditions, and more recently for X-ray imaging. In this work, glasses with a variety of compositions and rare earth (RE) activators were prepared by the melt quenching method in air. Glass compositions were selected based on the final application, with glasses for thermal neutron detection made rich in boron while lacking high atomic number elements, glasses for gamma-ray detection lacking elements with high thermal neutron absorption cross section, and with high density for X-ray detection. Raman scattering spectroscopy was used to characterize the structural arrangement, while optical characterization focused on determining the ultraviolet transmission threshold. Particular emphasis was placed on the luminescence response under X-ray and ultraviolet excitation. These results were discussed in terms of luminescent defects of the host matrix and of the different environments of the RE luminescence centers. This material is based upon work supported by the National Science Foundation under Grants No. 1207080 and 1407404.

10:15 AM

(GOMD-S3-076-2017) Luminescent glasses for hadron calorimeter (Invited)

C. Siligardi*[1]; C. Mugoni[1]; S. Barbi[1]; C. Gatto[2]; M. Affatigato[3]

1. University of Modena and Reggio Emilia, Department of Engineering "Enzo Ferrari", Italy
2. Fermi National Accelerator Laboratory, USA
3. Coe College, USA

Heavy glasses are promising alternatives to crystals and polymers for applications in energy physics such as scintillating material in the hadron calorimeter. This work is focused on the development of transparent heavy metal oxide glasses (bismuth borate and lead borate glasses) as host materials for scintillating rare earth oxides (Dy_2O_3, Er_2O_3, Nd_2O_3, CeO_2). High density and high transparency over ultraviolet and visible regions, low refractive index, high emission intensity and high lifetime decay have to be obtained. The glasses, synthesized by a melt quenching method, were characterized by means of density, Raman and UV-Vis spectroscopy. The scintillating properties under UV and X-ray excitation were studied with a UV-Vis Spectrophotometer and a high energy electrons and ions beam at the Fermilab Test Beam Facility. All the properties measured showed a non-linear trend with increasing rare-earths ions concentration in the glass matrix. High densities (5-6.5 g/cm^3) were reached for all the studied systems. Erbium ions doped glasses showed the highest emission intensity and lifetime decay. All the studied glass demonstrated peculiar characteristics that, if properly tuned, can match the requirements needed for particle energy measurement. Finally, organic activators, normally used to prepare scintillating plastics, were doped in glasses and the scintillating properties were measured and compare with the HMO glasses.

10:45 AM

(GOMD-S3-077-2017) Electrical Conductivity of Doped Tellurium Vanadate Glass Systems

M. Hedlund*[1]; I. Illari[2]; L. McDonald[1]; S. Feller[1]; M. Affatigato[1]

1. Coe College, Physics, USA
2. Barnard College of Columbia University, Physics and Astronomy, USA

This research originated from prior work with an emphasis on detector development. This previous work focused on samples that were highly glassy with no visual defects, as they were being tested as candidates for glass detectors. In this work, ternary systems were explored to determine the factors affecting conductivity at room temperature, and tellurium vanadate glasses that were doped with copper and silver oxides are highlighted. The samples' DC conductivity, structure, and V4+ ion concentrations were investigated. Our results led to a better understanding of the effects of modifiers in the binary tellurium vanadate glassy network, the associated changes in electrical conductivity, changes in the glass' structure, and changes in V4+ to V5+ ratios. Experimental research also included determining electrical conductivity of samples at varying temperatures by using a conductivity furnace set-up. Evidence of phase separation was examined with DSC measurements. Change in structure of the samples, as well as potential evidence of crystallization, was found using X-ray diffractometry and Raman spectroscopy. This work was performed with support from grant NSF PHY-REU-1358968 and Coe College.

11:00 AM

(GOMD-S3-078-2017) Photomultiplier Tube (PMT) Glass Optimization and Property Evaluation for Neutrino Detection Application – MD Simulation and Experimental Study

R. Dongol*[1]; A. Tandia[2]; S. K. Sundaram[1]

1. Alfred University, Materials Science and Engineering, USA
2. Corning Incorporated, USA

Photomultiplier tubes (PMTs) are vital components for Water-Cherenkov neutrino detection application. The commercial PMTs are of seven oxide soda-alumino-borosilicate composition. Structural and Young's modulus optimization was performed on a specific glass compositional space using molecular dynamics (MD) simulation. Experimental validation work on a set of selected glasses were performed. These glasses were characterized for their thermal and mechanical properties. We will present these results and identify the optimized composition with the best performance for this application.

11:15 AM

(GOMD-S3-079-2017) Study on the large area MCP-PMT glass radioactivity reduction

J. Zhao[1]; X. Zhang*[1]

1. Insitute of High Energy Physics, Chinese Academy of Sciences, China

The Jiangmen Underground Neutrino Observatory (JUNO) is a multiple-purpose neutrino experiment with a 20 kiloton liquid scintillator (LS) detector. Low background is essentially important for the low energy physics, such as reactor antineutrinos and solar neutrinos. The singles rate induced by the material radioactivity should be controlled to be about 10 Hz within the detector fiducial volume ($R < 17.2$ m) with the visible energy greater than 0.7 MeV, which leads to about one accidental coincidence per day. From the full detector Monte Carlo simulation, besides the LS, PMT glass has the largest contribution to this background. Various technologies have been developed in the Chinese industry to control the environment and to improve the production process, and the radioactivity of the glass bulb now can reach 1.3 Bq/kg for U238, 0.4 Bq/kg for Th232 and 0.5 Bq/kg for K40. Details about the environment and process control will be introduced in this talk.

GOMD Symposium 4: Glass Technology and Crosscutting Topics

Glass Surfaces and Treatments I

Room: Kona 2
Session Chairs: Robert Schaut, Corning Incorporated;
Nicholas Smith, Corning Incorporated

9:45 AM

(GOMD-S4-034-2017) Water on Glass Surfaces: Dissolution, SCC vs Strengthening, Proton Transport (Invited)

S. H. Garofalini*[1]

1. Rutgers Univ, USA

Although well studied, recent experiments and computations have provided new insight about the water/glass interface. Here we present reactive molecular dynamics simulations to determine the atomistic behavior with respect to the structure of water at the interface and its effect on expansion and glass strengthening and the role of OH's vs H2O's on this expansion, stress corrosion cracking, reaction sites and dissolution, and proton transport. Results are consistent with experimental data, where available, but provide the specific atomistic mechanisms. Simulations and analysis of the differences between bulk and surface structures and compositions of multicomponent alumino-borosilicate glasses and the effect of exposure to moisture will also be presented.

10:15 AM

(GOMD-S4-035-2017) Potentiality of zinc salts treatment for ancient glass objects showing atmospheric alteration in museums

F. Alloteau[1]; O. Majerus[1]; I. Biron[2]; P. Lehuédé[2]; D. Caurant*[1]

1. Chimie Paristech CNRS, IRCP, France
2. C2RMF, France

Until now the best protective method implemented in museums for chemically unstable ancient glasses is the environment monitoring

(temperature, humidity, pollutants). Nevertheless, by acting directly on the glass surface, much more efficient methods could be proposed. Inspired by industrial process to protect manufactured glass windows during their storage and transport, we focus on the potentiality of zinc salts deposits. In this view, the mechanisms underlying the atmospheric alteration and the protective action of Zn(II) are studied by the mean of ageing tests in climatic chamber (temperature and humidity control) on relevant glass replica (silicate rich in alkalis). Ageing temperature, glass composition and zinc treatment effects on the chemical, morphological, structural and microstructural evolution of the glass surface are evaluated. Our results highlight the positive effect of small amount of Zn(II) to slow down the hydration kinetics of silicate glasses with various Na/K ratio. A buffering effect is postulated: Zn(II) on glass surface precipitate with OH^- ions originating from the first stages of the hydration process that would slow down the silicate network hydrolysis. A passivation effect reducing the water diffusion into the glass network is also supposed and research is carried out on the speciation of Zn(II) detected outside the hydroxide crystals.

10:30 AM

(GOMD-S4-036-2017) Surface Structure and Reactivity of CAS Glasses

L. Wang*[1]; A. Cormack[1]; G. Agnello[2]; N. J. Smith[2]; R. Manley[2]

1. Alfred University, Ceramic Engineering, USA
2. Corning Incorporated, USA

Calcium aluminosilicate (CAS) compositions form the basis for many glasses of contemporary technological applications, so understanding their surface structures and reactivity is of some importance. In this presentation we will discuss the modeling of a series of CAS glasses along the CaO-Al2O3 join, with varying silica content. Bulk and surface structures were obtained using “standard” classical potentials and the GROMACS MD code. The reactivity of the surface structures, that is, the interaction of the surfsces with a layer of water, was subsequently investigated using a reactive forcefield potential, Reaxff, and the LAMMPS computer code. The results will be discussed with particular reference to the surface structural features which favor chemisorption, i.e. the dissociative interaction, of water molecules.

10:45 AM

(GOMD-S4-037-2017) Two ways of solving glass chemical durability challenges in manufacturing: Yield improvement for NCVM process

Y. Jin*[1]; A. Li[1]

1. Corning Incorporated, USA

In manufacturing, glasses are often treated with various chemical processes prior to use. These treatments not only modify the glass surface but also may introduce (or reveal) surface defects and reduce product yield depending on the treatment conditions and the chemical durability of the treated glass. Two strategies can be employed to deal with the chemical durability challenges in manufacturing. One way is to improve the chemical durability of glass by tuning glass composition. Another way is to optimize the chemical treatment conditions and avoid exposing glasses in harsh chemical environment. This presentation will cover the following topics: (1) the chemical durability challenges in the NCVM (Non Conductive Vacuum Metallization film) process, and (2) the approaches to solve NCVM process problem in manufacturing.

11:00 AM

(GOMD-S4-038-2017) Water speciation and reactions at/in soda lime silica and calcium aluminosilicate glass surfaces

S. H. Kim*[2]; C. G. Pantano[4]; N. Sheth[4]; J. Luo[1]; J. Barnerjee[3]

1. University of Massachusetts, Chemical Engineering, USA
2. Pennsylvania State University, Chemical Engineering, USA
3. Pennsylvania State University, Materials Research Institute, USA
4. Pennsylvania State University, Materials Science and Engineering, USA

Water adsorption and reaction on glass surfaces play important roles in chemical and mechanical durability of glasses. Compared to metals or crystalline oxide materials, the surface chemistry of multicomponent glasses in humid ambient is much less understood. This is in part because the adsorbed water can often be dissociated or diffused into the glass; in addition, glass itself can have some hydrous species (hydroxyl and molecular water) in the subsurface or bulk. Since glass is in non-equilibrium state, the water adsorption and reaction behaviors vary in a complex manner with glass composition, thermal history, surface treatment, and environment condition. We employed vibrational sum frequency generation spectroscopy, and other spectroscopy techniques that provide complementary information, to investigate surface composition and structures of pristine and acid-treated soda lime silica (float, bottle) and alkalifree aluminosilicate (E-glass) surfaces.

11:15 AM

(GOMD-S4-039-2017) Monitoring Early Corrosion Kinetics with In-situ pH and Conductivity Probes

R. Schaut*[1]; S. Tietje[1]

1. Corning Incorporated, S&T, Glass Research, USA

The corrosion of glass surfaces by neutral water involves several steps and changes in reaction mechanism over time. First, reactive modifier cations (i.e. Na, K, or Ca) undergo ion-exchange with charged water species. The release of these cations causes an increase in the solution pH from neutral to basic. The increased solution pH causes hydrolysis of the silicon-oxygen bonds and increases the release of network species to solution. As this shift in mechanism occurs (from ion-exchange to hydrolysis), the corrosion process shifts from incongruent (leaching) to more congruent (dissolution). Here, we apply simultaneous, in-situ measurements of pH and conductivity as real-time monitors of corrosion kinetics to distinguish the timescales of these individual steps. We compare these responses to periodic measurements of solution chemistry by ICP-MS and surface chemistry by XPS or D-SIMS. Results will be discussed for a few silicate glasses – both alkali-containing and alkali-free.

11:30 AM

(GOMD-S4-040-2017) Temperature-Resolved ToF-SIMS of Display Glass Surfaces

C. V. Cushman*[1]; B. M. Lunt[3]; C. T. Dahlquist[1]; N. J. Smith[2]; M. R. Linford[1]

1. Brigham Young University, Chemistry and Biochemistry, USA
2. Corning Incoroporated, Science and Technology Division, USA
3. Brigham Young Univeristy, Information Technology, USA

Multicomponent glasses are preferred substrates for manufacturing flat panel displays, and their surface properties can influence the display manufacturing process. Among the relevant surface attributes, the hydroxylation state of the surface is thought to be important in mediating properties like adhesion and charging. Few studies address the surface hydroxyl concentration of planar substrates, and fewer still attempt to quantify them on multi-component glass surfaces. This is a challenging analytical task because (i) planar substrates have low surface area and relatively low hydroxyl density, (ii) glass surface composition typically varies from its bulk composition, and (iii) multicomponent glasses can have hydroxyl groups of different identity, and analyses are complicated by the presence of mobile modifier ions. Here, we use temperature-resolved time-of-flight secondary ion mass spectrometry

(ToF-SIMS) to evaluate the surface-hydroxyl concentration on glass substrates representative of display glass materials. These samples were exposed to various surface treatments, including aqueous solutions, believed to significantly alter surface chemistry. We have previously characterized how similar treatments alter the inorganic surface composition of such glasses. Accordingly, in this study, we aim to link complex interactions between surface composition and hydroxylation.

11:45 AM

(GOMD-S4-041-2017) Multi-Instrument Depth Profiles of Display Glasses

C. V. Cushman[1]; B. Sturgell[1]; G. I. Major[1]; B. M. Lunt[2]; C. T. Dahlquist[1]; P. Bruener[3]; J. Zakel[3]; T. Grehl[3]; N. J. Smith[4]; M. R. Linford*[1]

1. Brigham Young University, Chemistry and Biochemistry, USA
2. Brigham Young University, Information Technology, USA
3. IONTOF GmbH, Germany
4. Corning Incorporated, Science and Technology Division, USA

It is important to understand how surface composition affects the physical properties of display glass in order to improve device yield and display glass compositions. Surface composition can have a profound influence on glass properties such as thin film adhesion, rate of contamination, and static charge build-up. Display glass surfaces can be altered by exposure to production line chemistries including acids, bases, detergents, etches, and plasmas. Therefore, attempts to understand display glass surfaces must account for the effects of these treatments. Here, we present multi-instrument depth profile information of Corning® Eagle XG®, a widely used display glass, using a suite of surface sensitive techniques including low-energy ion scattering (LEIS), angle-resolved X-ray photoelectron spectroscopy (AR-XPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Together, these techniques provide information about all major glass constituents at multiple information depths. A series of Eagle XG samples exposed to various surface treatments were analyzed. The treatments included hydrochloric acid, hydrofluoric acid, a model base, industrial detergents, and atmospheric-pressure plasma treatment, all of which are compared to the composition of fracture surfaces. This study is foundational for understanding the link between surface composition and glass behavior.

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium IV

Room: Kona 5

Session Chairs: Akihiko Sakamoto, OLED Material Solutions Co.; Jong Heo, Pohang University of Science and Technology(POSTECH)

9:45 AM

(GOMD-S6-012-2017) Control of crystallization in glass for photonic device (Invited)

J. Qiu*[1]

1. College of Optical Science and Engineering, Zhejiang University, China

Glass-ceramics possess the advantages of both glass and ceramic (or crystal), making them promising candidates for photonic devices. There have been extensive investigations on the control of nucleation and crystallization in glass in past decades. In this talk, we will introduce our recent results on control of crystallization in glass. For practical applications in the field of information technology, usually it is necessary to fabricate glass ceramic fibers or waveguides with low optical attenuation. However, many glasses are prone to crystallize during fiber drawing at softening temperature, and often excessive crystallization may occur, resulting in large Raleigh scattering and even Mie scattering. To realize enhanced optical function and low optical attenuation, controllable nucleation and crystallization are necessary in order to minimize light scattering. We proposed and demonstrated a melt-in-tube fiber drawing technique combined with successive heat treatment for the fabrication of glass ceramic fibers with low optical attenuation. In addition, Fs laser with high repetition rate is used as a localized heating source for direct writing of glass ceramic waveguides with low optical attenuation. We have demonstrated various optical devices, e.g., broadband optical amplification based on the developed fibers and waveguides.

10:15 AM

(GOMD-S6-013-2017) Single crystal growth by laser-induced solid-solid conversion: Concepts and Applications (Invited)

K. Veenhuizen[1]; C. Au-Yeung[1]; S. McAnany[2]; D. Nolan[3]; B. Aitken[3]; H. Jain[2]; V. Dierolf*[1]

1. Lehigh University, Physics, USA
2. Lehigh University, Material Science, USA
3. Corning Incorporated, USA

Transforming glass into a single crystal by spatially selective heating with a laser offers a unique capability to precisely control the conversion of a glass into a single crystal. In particular, we have shown that it is possible to perform this conversion without ever melting the glass. In such a solid-solid conversion, the growth conditions are highly constrained, which produce unusual crystallization characteristics such as preferred orientation of seed crystals and a continuous rotation of the crystal lattice orientation that can be precisely controlled by the polarization of the laser light and its intensity profile. These concepts will be introduced for crystallization on the surface of a chalcogenide glass using a cw-laser as well as for 3D-crystallization inside a lithium niobosilicate glass. This novel capability enables several potential applications. We will discuss the potential for quasi phase matching in non-linear applications, index-graded crystals for improved waveguiding, and chiral crystals for non-reciprocal optical devices.

10:45 AM

(GOMD-S6-014-2017) On-chip fabrication of glass microsphere laser by localized laser heating (Invited)

T. Kishi*[1]; T. Kumagai[1]; N. Matsushita[1]; T. Yano[1]

1. Tokyo Institute of Technology, Japan

We have developed a localized laser heating (LLH) technique for fabricating glass microsphere lasers based on whispering gallery modes (WGMs). A Nd3+-doped K2O-WO3-TeO2 glass particle on a transparent substrate was irradiated by a continuous-wave laser with the wavelength of 806 nm and the power of 100–300 mW. The glass particle was heated and melted by absorption of the laser light, and then its shape changed into sphere with high sphericity (>0.99) and extreme smooth surface, which are very suitable for the WGM resonator. The microspheres with the diameter of 5–200 μm exhibit more than few-mW-order threshold for laser oscillation at around 1.06 μm wavelength. An air bubble can be introduced into the microsphere by controlling the power of the heating laser and position of the spot during the LLH process. The bubble acts as an unique entrance for free-space coupling with pumping light at the broad-band wavelength because of many excitation modes due to non-degenerate WGMs induced by the bubble. The air bubble containing microsphere showed lower threshold lasing of less than 1 mW.

11:15 AM

(GOMD-S6-015-2017) Femtosecond Laser Writing of Electro-optic Crystalline Structures in Glass (Invited)

C. M. Liebig*[1]; J. Goldstein[1]; S. A. McDaniel[2]; K. Douglas[1]; G. Cook[2]

1. Air Force Research Laboratories, Materials and Manufacturing, USA
2. Air Force Research Laboratories, Sensors Directorate, USA

Electro-optic (EO) crystals are of wide interest to the optical community due to a lack of inversion symmetry which enables second-order nonlinear optical processes such as sum/difference frequency generation (SFG/DFG) and Pockel's effect. Recently, a crystal growth technique used high repetition rate (>200 kHz) femtosecond lasers to precipitate aligned, non-centrosymmetric, single EO crystals within glasses supersaturated with the appropriate constituents. Furthermore, the polar axis of the precipitated EO crystals was aligned along the inscription direction which enabled control of the crystallization and the nonlinear optical properties. The demonstration of femtosecond precipitation of EO crystals in glass is an example of a low-cost alternative to bulk crystal growth methods which require expensive equipment and long growth times. In this study, lithium niobate, a widely used EO crystal, was precipitated in $33LiO_2$-$33Nb_2O_5$-$34SiO_2$ (mol%) (LNS) glass, forming aligned crystalline structures within an amorphous matrix. The characteristics of the crystalline $LiNbO_3$ were measured to optimize the writing conditions for obtaining aligned crystalline structures. This procedure was used to grow crystalline structures for photonic applications.

11:45 AM

(GOMD-S6-016-2017) A compositional strategy for laser-induced fabrication of single crystal architecture in glass

S. McAnany*[1]; K. Veenhuizen[2]; B. Aitken[3]; D. Nolan[3]; V. Dierolf[2]; H. Jain[1]

1. Lehigh University, Materials Science & Engineering, USA
2. Lehigh University, Physics, USA
3. Corning Incorporated, USA

Using femtosecond (fs) laser irradiation, it is possible to selectively crystallize glass to create 3D crystal architecture in glass, which offers a promising method for creating photonic integrated circuits for optical communications. In order to grow desired crystal architecture without scattering from defects such as grain boundaries, nucleation of extraneous crystals must be controlled. Recently, formation of single crystal $LaBGeO_5$ waveguides has been demonstrated inside the glass of the same composition by scanning the laser fast enough that other nucleated grains cannot maintain growth. In practice, however, this method limits the orientation and geometries of the structures that can be formed. A different strategy to avoid unwanted nucleation is to employ the composition of the glass different from the stoichiometry of the crystal phase. With appropriately selected composition it should be feasible that the glass composition ahead of the growth front would suppress the nucleation rate as the crystal grows. To validate this strategy we have investigated fs laser-induced growth of $LaBGeO_5$ single crystal in xLa_2O_3-B_2O_3-$2GeO_2$ with x = 0.8 - 1.2, and Al_2O_3-doped La_2O_3-B_2O_3-$2GeO_2$ glass systems. Using DSC, SEM, and electron backscattered diffraction, we investigated the effect of glass composition on single crystal growth under laser irradiation, and demonstrated proof of concept.

PACRIM Symposium 01: Characterization and Modeling of Ceramic Interfaces: Structure, bonding, and Grain Growth

Interface Thermodynamics

Room: Kohala 3
Session Chairs: Klaus van Benthem, University of California, Davis; Wolfgang Rheinheimer, Karlsruhe Institute of Technology

8:30 AM

(PACRIM-S1-001-2017) Spontaneously-Formed 2-D Interfacial Phases: From Tailoring Materials for Energy Applications to Forecasting Activated Sintering (Invited)

J. Luo*[1]

1. UCSD, USA

On one hand, a variety of surface phases can form spontaneously as the thermodynamic equilibrium states. Nanometer-thick surface phases, which are thermodynamically two-dimensional (2-D), can be utilized as a class of nanocoatings with self-regulating thicknesses that are made by thermodynamics. In this talk, a series of our recent studies to utilize such spontaneously-formed 2-D surface phases to tailor battery cathode and anode materials, photocatalysts, nanowire-based fast oxygen-ion conductors, and pseudocapacitors will be reviewed. On the other hand, analogous 2-D interfacial phases formed at grain boundaries (GBs), which are also known as "complexions," often control sintering, grain growth, and a variety of GB-controlled properties (e.g., ionic conductivities). Here, a major scientific effort is to extend the bulk CALPHAD methods to GBs to compute GB "phase" (complexion) diagrams as an extension to bulk phase diagrams. Such GB diagrams can be a generally-useful materials science tool, e.g., to forecast activated sintering behaviors. In this area, our past efforts have been focused on simpler metals (as a start point); recently, we have made great efforts to extend the successful studies from simpler metallic alloys to more complex ceramic systems, such as TiO_2-CuO as one most recent example.

9:00 AM

(PACRIM-S1-002-2017) Predicting phase behavior of interfaces with evolutionary algorithms (Invited)

Q. Zhu[2]; R. E. Rudd[1]; T. Frolov*[1]

1. Lawrence Livermore National Laboratory, USA
2. University of Nevada Las Vegas, Department of Physics and Astronomy, USA

Recent years have seen a rapid growth of evidence suggesting that materials interfaces are capable of first-order structural transformations in which the interface properties undergo discontinuous changes. Experiments have linked these transitions to abnormal grain growth in ceramics, activated sintering and liquid metal embrittlement and raised a number of fundamental questions concerning the atomic structures and kinetic properties of these interface phases. Using improved simulation methodology recent modeling efforts in relatively simple metallic systems discovered new multiple structural states of grain boundaries and demonstrated first order transitions between them. Same studies also showed that grain boundary structures can be very complex and current modeling capabilities are too limited to predict structures of grain boundaries in complex materials. We developed a new computational tool based on USPEX code that uses evolutionary algorithms to predict complex interface structures in multicomponent systems. Applications of this tool to several materials systems are discussed. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

9:30 AM

(PACRIM-S1-003-2017) Characterization of interface, segregation and phase separation structures by analytical TEM

S. Cheng*[1]

1. Lawrence Berkeley National Laboratory, Molecular Foundry, USA

Analytical TEM combines high resolution image, electron diffraction patterns with X-ray energy dispersive spectroscopy and electron energy loss spectroscopy together in a single instrument. Structural and chemical information of specimens with high spacial resolution can be obtained from the same instrument. However, the high energy electron beam, used as the probe, sometime causes radiation damages on the specimens. This talk will give several examples of applications of analytical TEM in characterizing interface, segregation and phase separation structures. The emphasis of the talk is to discuss the artifacts appeared in studying radiation sensitive specimens and how to overcome the problems.

9:45 AM

(PACRIM-S1-004-2017) Atomistic simulations of energetically stable grain boundary structures and its diffusional property in MgO

T. Yokoi*[1]; A. Nakamura[1]; K. Matsunaga[1]

1. Nagoya University, Materials Science & Engineering, Japan

Grain boundary (GB) is a critical factor in the material properties of polycrystalline oxides. To understand the GB- property relationship, firstly it is necessary to determine precisely atomic arrangement and understand electronic structure at GB in detail. In this study, we employed simulated annealing (SA) techniques with atomistic simulations to determine energetically stable atomic arrangement at various tilt GBs in MgO. In addition, molecular dynamics simulations were performed to evaluate the diffusional properties of the individual stable GBs. Consequently it was found that stable GB structures obtained by the SA techniques agreed with previous studies and furthermore the misorientation-dependence of GB structures are successfully predicted. In addition, our results indicated that some of the GBs exhibit various different types of stable atomic arrangements even for one GB and thus it is expected that the real atomic arrangement of the GBs are represented by superposition and/or combination of its stable atomic arrangements. Furthermore, both cation and anion diffusion along GB were also discussed based on the obtained stable structures.

10:15 AM

(PACRIM-S1-005-2017) Zero Grain Boundary Excess Energies in Oxides (Invited)

R. Castro*[1]

1. University of California, Davis, Material Science & Engineering, USA

Grain growth inhibition is typically faced as a kinetic problem since the grain boundary energy is an undefiable driving force such that grain boundary movement must be mitigated by the usage of drag forces. In contrast, here we demonstrate the possibility of decreasing the grain boundary energy with the usage of dopants prone to segregation and show that the excess energy can eventually zero, representing a negligible driving force for growth. The existence of this highly metastable condition thus allows for the design of stable nanocrystalline materials. To demonstrate the zero excess energy condition, rare earth doping was used in nanocrystalline cubic zirconia dense systems. The dopants were observed to segregate to the grain boundaries, and the respective excess energy was shown to decrease with increasing dopant content, as directly assessed by microcalorimetry. For gadolinium doped zirconia, the energy decreased down to 0.05 J/m^2, leading to grain growth “stopping” at that condition. Kinetic analysis of the problem demonstrated that the dopant segregation had minimal effects on the mobility of the grain voundary. Although the zero-excess energy condition was demonstrated to exist, we also report that it is a condition depedent on the temperature of processing, since the segregation of dopants to interface is affected by this parameter.

10:45 AM

(PACRIM-S1-006-2017) Atomic-resolution STEM-EDS characterization of grain boundary chemistry in yttria-stabilized zirconia

B. Feng*[1]; N. Lugg[1]; A. Kumamoto[1]; Y. Ikuhara[1]; N. Shibata[1]

1. The University of Tokyo, Japan

Yttria-stabilized ZrO$_2$ (YSZ) has been widely used as electrolyte materials in oxide fuel cells. However, such performance is usually limited by the ionic conductivity at grain boundaries (GBs), which is two orders of magnitude lower than the bulk region. Therefore, many studies have been performed to investigate GBs in YSZ, focusing on their atomic structures and chemistries. Although Y segregation in the GBs has been experimentally verified, it is still challenging to experimentally quantify the local oxygen vacancy distribution across GBs. As a result, the physical picture of interface chemistry is still under controversy. Here the local oxygen distributions at four different YSZ GBs fabricated by bicrystal method were directly determined using scanning transmission electron microscopy (STEM) energy-dispersive x-ray spectroscopy (EDS). Our STEM-EDS system (JEM-ARM200CF) is equipped with double silicon drift detectors, which enables ultrahigh sensitivity X-ray detection, and thus suitable for light element analysis. Combining with electron dynamical scattering theory, we unambiguously show that the oxygen concentrations increase at the GB cores. These results indicate local point defect distribution across the GBs is mainly governed by the long-range electric interactions. The detailed mechanisms will be discussed in the presentation.

11:00 AM

(PACRIM-S1-007-2017) Atomic structure of (001) low-angle tilt grain boundary with a slight twist component in strontium titanate

Y. Furushima*[1]; Y. Arakawa[1]; A. Nakamura[1]; E. Tochigi[3]; K. Matsunaga[1]

1. Nagoya University, Japan
3. University of Tokyo, Japan

Dislocations are one-dimensional lattice defects in crystalline materials, and their unique atomic configurations can affect functional properties of materials. Thus, detailed investigation of dislocation structures is required. We focused on dislocations in strontium titanate (SrTiO$_3$). SrTiO$_3$ bicrystals including a (001) low-angle grain boundary with 4° tilt component and a slight twist component were fabricated, and dislocations formed at the boundary were observed by TEM and STEM. It was revealed that the grain boundary consists of two types of dislocations which are periodically arranged. One is a [001] edge dislocation that compensates the tilt angle of the boundary. The other is a [012] dislocation with both edge and screw components. The [012] dislocation had a specific core structure with the dissociation into three partial dislocations, which is considered to be formed to compensate the twist angle of the boundary. At stacking faults formed with the dissociation, two (001) Ti-O layers were located to be neighbors across the stacking fault plane due to missing of a (001) Sr-O layer. It was found that a slight twist component of the boundary induces such specific dislocation structure with nonstoichiometry.

11:15 AM

(PACRIM-S1-008-2017) Effect of Applied Electric Field on Grain Boundary Core Structures in Strontium Titanate Bicrystals

L. A. Hughes*[1]; K. van Benthem[1]

1. University of California, Davis, Materials Science and Engineering, USA

Grain boundary core structures influence the mechanical and electrical properties of materials. Quantification of the relationship between material processing parameters, like applied electric

field, and boundary core structures allows for direct manipulation of a material's physical properties. Application of electric fields is known to alter surface oxygen vacancy concentrations in ceramic oxides. However, there is limited information regarding electric field effects on grain boundary formation. Bicrystal formation is one method to systematically elucidate this relationship. In this study, two (100) strontium titanate ($SrTiO_3$) single crystals were oriented with a nominal twist angle of 40° along the <100> axis and diffusion bonded in an air environment. These bicrystals were formed with and without an applied electric field of 1000 to 2000 V/m during bonding. Transmission electron microscopy techniques combined with spatially resolved electron energy-loss spectroscopy and electric measurements show distinct changes in the structure, chemistry, and electric properties of the $SrTiO_3$ bicrystal formed with an electric field compared to without an electric field. These results indicate an electric field applied throughout bicrystal formation reduces the grain boundary thickness, the oxygen vacancy concentration across the boundary, and the dielectric relaxation phenomenon.

11:30 AM

(PACRIM-S1-009-2017) Surfaces and Interfaces in Oxides Under Oxidizing and Reducing Conditions: The Effect of Nickel (Invited)

A. Morrissey[2]; I. Reimanis*[1]; J. R. O'Brien[3]

1. Colorado School of Mines, USA
2. CoorsTek, Incorporated, USA
3. Off Grid Research, USA

Transition metal oxide dopants such as nickel oxide are known to influence the sintering, microstructure development, and properties of ceramics. Nickel oxide in particular is interesting and technologically very useful especially for catalysts and fuel cells which experience reduction/oxidation (redox) conditions. This presentation will describe the very different roles of nickel in redox conditions in two different ceramic systems, yttria stabilized zirconia and barium yttrium zirconate. The magnetic state of nickel is tracked with SQUID magnetometry to help establish its role during processing in air and during exposure to reducing conditions under which metallic nickel is formed.

PACRIM Symposium 04: Polymer-Derived Ceramics (PDCs) and Composites

Chemistry and Synthesis of PDCs

Room: King's 3
Session Chair: Paolo Colombo, University of Padova

8:30 AM

(PACRIM-S4-001-2017) Application of Novel Silsesquioxane and Silsesquiazane Derivatives; Polymeric Precursors for Ternary SiOC and SiON Ceramics (Invited)

Y. Iwase*[1]; Y. Horie[1]; Y. Iwamoto[2]

1. Toagosei Co Ltd., General Center of Research and Development, Japan
2. Nagoya Institute of Technology, Japan

In this paper, recent R & D in Toagosei Co., Ltd. of organic-inorganic hybrid polymers and their application will be presented. Our sol-gel derived silsesquioxanes, "SQs" have been originally developed as a coating or a sealing agent in the organic-inorganic hybrid state. Then, further study on the SQs has been performed to synthesize thermally stable amorphous SiOC ceramics. They were pyrolyzed at 1073 K under N_2 flow. By varying the organic substituents, the C/Si molar ratio of the amorphous SiOC was controlled in the range of 0.52 to 1.97. Among our SQs, a novel "VH-SQ" having vinyl and Si-H groups was successfully converted to amorphous SiOC with a composition close to the stoichiometric $SiC_xO_{2(1-x)}$ (x = 0.52) which keeps X-ray amorphous up to 1873 K under Ar. As our extended work, silsesquiazane derivatives, $ROSi(NH)_{1.5}$ have been also developed. They exhibited a distinctive pyrolytic behavior with evolution of most of carbon element as gaseous alkene below 1073 K, leading to the formation of ternary amorphous SiON with a unique thermal stability up to 1673 K in N_2. In addition, the local structure of these amorphous ceramics were further studied by several spectroscopic analyses, and the results will be discussed from a viewpoint to develop novel polymeric precursors for amorphous SiOC and SiON ceramics with enhanced thermal stability.

9:00 AM

(PACRIM-S4-002-2017) Silicon-Based Non-Oxide Ceramics and Nanocomposites through Chemistry of Modified Organosilicon Polymers

S. Bernard*[1]

1. CNRS, France

Non-oxide ceramics are significantly less investigated than oxide ones most probably because their strong and predominantly covalent atomic bonds impose high temperature solid-state sintering, thereby increasing their cost in comparison to oxide types. However, there are ceramic processing techniques based on precursor chemistry that may significantly reduce the synthesis temperature of these high-tech ceramics while offering the possibility to tailor their shape, structure and texture in a way not known with high-temperature sintering. A very convenient precursor route is the polymer derived ceramic (PDC) route. Polyorganosilazane-derived silicon nitrides and carbonitrides are candidates for high-temperature application, and have also potential for environmental and green technologies. Adding (transition) metals and metalloids to these ceramics advantageously modifies some of their intrinsic properties. In the present paper, the chemistry behind the synthesis and the pyrolytic behavior of polyorganosilazanes modified with these elements as well as their processability and high temperature behavior are presented to gain new knowledge toward a more rational approach to the preparation of SiBCN, SiAlCN ceramics as well as of MN/Si_3N_4 (M=Ti, Zr, Hf) nanocomposites.

9:15 AM

(PACRIM-S4-003-2017) Molecular Design of Preceramic Polymers (Invited)

T. Zhao*[1]

1. Institute of Chemistry, Chinese Acdemy of Science, China

Soluble organic-inorganic hybrid polymers with metal elements (Zr, Al, Ti, Ta, Hf) in the molecular structure were developed by polymeric synthesis. The polymer properties of the precursors enable significant breakthroughs in ceramic processing technologies, such as the development of ceramic fibers, coatings and composite ceramics. It is quite easy to get an ultrathin catalytic ceramic coating less than 20 nm. Furthermore, precursors could be used as additives in forming process of ceramics. After suitable modifications of the molecular structure, ZrO_2 and Al_2O_3 precursors were able to use as dispersant to get high powder content slurry with better dispersibility than normal organic or polymeric dispersants. Other advantage of the precursor dispersants and binder is that it could be transformed into ceramic phase, giving some contribution to the densification of the whole ceramic bulk. The liquid MC, MC-SiC (M=Zr, Hf, Ta), $ZrC-ZrB_2-SiC$ and $Hf_xTa_{1-x}C$ pre-ceramic resins were further synthesized by introduced carbon source into the resin system. Pure non-oxide ceramics could be obtained at 1400-1600 °C. These liquid pre-ceramic resins are suitable for preparing CMCs. At high temperature under air atmosphere, these non-oxide ceramics could constantly form fine and dense oxide ceramic surface layers to give good protection of bulk materials. Their CMCs exemplars exhibit excellent high-temperature anti-oxidation and thermal shock resistance.

9:45 AM

(PACRIM-S4-004-2017) Chemical formation of AlN from Al-carbodiimide polymer

Y. Iwamoto*[1]; Y. Daiko[1]; S. Honda[1]; E. Ionescu[2]; G. Mera[2]; R. Riedel[2]

1. Nagoya Institute of Technology, Japan
2. TU Darmstudt, Germany

Polymeric precursors for AlN ceramics were synthesized by reacting $AlCl_3$ with bis(trimethylsilyl)carbodiimide. FT-IR spectrum of the synthesized precursor exhibited characteristic absorption bands assigned to the N=C=N group at 2150-2250, and 851 cm^{-1}, while the solid state ^{27}Al MAS NMR spectrum of the precursor exhibited single peak at 103 ppm assigned as $Al(N=C=N)_4$ unit. The subsequent pyrolysis and heat treatment in Ar were initially investigated by the XRD measurements. The AlN crystallization was found to start above 1073 K, and fully crystallized AlN was obtained at 2073 K. In addition to the ex-situ FT-IR and NMR spectroscopic analyses, the effects of pyrolysis and heat treatment condition on the chemical formation of the polymeric carbodiimide-derived AlN was monitored in-situ by the simultaneous TG-MS analysis. These results will be shown and discussed from a viewpoint to develop a novel synthesis method for AlN-based ceramics through the polymer-derived ceramics (PDCs) route.

Processing of PDCs

Room: King's 3
Session Chair: Peter Kroll, UT Arlington

10:15 AM

(PACRIM-S4-005-2017) New source of large and pure h-BN nanosheets (Invited)

Y. Li[2]; S. Yuan[2]; V. Garnier[2]; A. Brioude[1]; P. Steyer[2]; C. Journet[1]; B. Toury*[1]

1. University of Lyon, Laboratoire des Multimatériaux et Interfaces, France
2. Laboratoire Matériaux Ingénierie et Science, University of Lyon, France

Since graphene's properties are strongly linked to the substrate on which it is deposited, it is clear that the promising future development of practical graphene devices will necessarily go through the development of insulating substrates on which graphene can be deposited without changing its intrinsic properties. One of the most suitable substrates appears to be the hexagonal variety of boron nitride (h-BN, also called "white graphite"), which is isostructural and isoelectronic of graphene, with a lattice matching that of graphene. As a consequence, the development of a novel source for highly crystallized h-BN crystals, suitable for a further exfoliation, is a prime scientific issue. This presentation proposes a promising approach to synthesize pure and well-crystallized h-BN flakes, which can be easily exfoliated into Boron Nitride NanoSheets (BNNSs). This new accessible production process represents a relevant alternative source of supply in response to the increasing need of high quality BNNSs. The synthesis strategy to prepare pure h-BN is based on a unique combination of the Polymer Derived Ceramics (PDCs) route with the Spark Plasma Sintering (SPS) process. Through a multi-scale chemical and structural investigation, it is clearly shown that obtained flakes are large (fig.1), defect-free and well-crystallized, which are key-characteristics for a subsequent exfoliation into relevant BNNSs.

10:45 AM

(PACRIM-S4-006-2017) Additive Manufacturing of ceramics from polysiloxanes

P. Colombo*[1]; J. E. Schmidt[1]; G. Franchin[1]; H. Elsayed[1]

1. University of Padova, Industrial Engineering, Italy

Ceramic structures for various applications were fabricated by additive manufacturing using stereolithography (DLP) and Direct Ink Writing (DIW). For stereolithography, different commercially available polysiloxanes were selected, physically combined and photocrosslinked using visible light. By changing the rations between the components in the liquid mixture, we were able to modify characteristics of the material (after pyrolysis) such as the carbon content of the resulting SiOC ceramic, the shrinkage and the ceramic yield. DIW was used for the fabrication of bioceramics (after the addition of suitable powder fillers) and ceramic-matrix-composites (after the addition of suitable powder fillers and chopped carbon fibers). This work demonstrates that it is possible to use different AM technologies together with preceramic polymers, to fabricate advanced ceramics components with complex and well controlled geometries.

11:00 AM

(PACRIM-S4-007-2017) Preceramic Polymer-Derived SiBCN Fibers with tunable properties by Electrospinning and the polymer-derived ceramics route

Q. Chen*[1]; Z. Yang[1]; D. Jia[1]; Y. Zhou[1]

1. Harbin Institute of Technology, China

Silicon boron carbon nitride (SiBCN) fibers were successfully fabricated by electrospinning a mixture of polyvinylpyrrolidone (PVP) and polyborosilazane followed by curing in ammonia and subsequent pyrolysis at 1000 °C in Argon. An amorphous ceramic was obtained. The pyrolysed fibers showed a fiber thickness ranging. The influence of the processing procedure (solvent selection, concentrations and additives) on the morphology of the produced fibers was investigated. For the dichloromethane/ N,N-Dimethylformamide system, the rheological properties of the precursor could be tuned by adjusting the polymer/solvent ratio. Solutions with 40 wt% polymer and 10 wt%PVP were reproducibly spun into preceramic fibers.

11:15 AM

(PACRIM-S4-008-2017) Facile synthesis, microstructure and photophysical properties of core-shell nanostructured (SiCN)/BN nanocomposites

Q. Zhang*[1]; D. Jia[1]; Z. Yang[1]; X. Duan[1]; Y. Zhou[1]

1. Harbin Institute of Technology, China

Increasing structural complexity at nano length scale can permit superior control over photophysical properties in precursor derived semiconductors. We demonstrate here the synthesis of silicon carbonitride (SiCN)/boron nitride (BN) nanocomposites via a polymer precursor route wherein cobalt polyamine complexes used as catalyst provide novel composite structures and photophysical properties. The High Resolution Transmission Electron Microscopy (HRTEM) analysis show that the SiCN–BN core–shell nanocomposite with diameter of 50-400 nm and BN shells of 5-25 nm. BN nanosheets (BNNSs) are also observed with average particle size of 5-15 nm. The photophysical properties of these nanocomposites were characterized using the UV-Vis and photoluminescence (PL) analyses. The as-produced composites radiative behavior include emission lifetime 2.5 ns (±20 ps) longer that observed in BN doped SiCN than that seen for SiC nanoparticles. Our results suggest that the SiCN/BN nanocomposites act as semiconductor displaying superior width photoluminescence at wavelengths spanning the visible to near-infrared (NIR) spectral range (400-700 nm) compared with pure SiC nanoparticals, owing to the heterojunction of the interface between the SiC(N) core and the BN nanosheets shells.

11:30 AM

(PACRIM-S4-009-2017) High surface area lotus type porous SiOC ceramics

D. Zeydanli*[2]; C. Vakifahmetoglu[1]

1. Istanbul Kemerburgaz University, Department of Mechanical Engineering, Turkey
2. Istanbul Technical University, Department of Chemistry, Turkey

Porous ceramics with aligned porosity are developed by a simple and an inexpensive technique. The processing route based on blends of three types of preceramic polymer and a catalyst, followed by

curing and pyrolysis. SiOC bodies with interconnected channels are formed via the directional heating procedure from the bottom of the molds. SEM, tomography, BET, water immersion porosimetry and permeation to gas flow were used to specify the structural and physical properties of the porous materials. Axially oriented channels (average diameter in between 0.59 – 1.25 mm) with the specific surface area values ranging in between 4.8 – 121.9 m^2/g were obtained together with the open porosity values from ~70 to 85 vol% and permeability up to $3.83x10^{-9}$ m^2. These SiOC ceramics can be used as catalytic supports and adsorption components in environmental control applications.

11:45 AM

(PACRIM-S4-010-2017) Polymer-derived SiC nanofibers via electrospinning: fabrication and properties

B. Wang*[1]; K. Jian[1]; C. Shao[1]

1. National University of Defense and Technology, China

SiC fibers are widely used in aerospace, military, nucleus fusion and electronics industries. Herein, SiC and carbon-rich SiC nanofibers (SiC NFs and C-SiC NFs) were successfully fabricated via electrospinning combined with polymer-derived ceramics route. The SiC NFs with average diameter of 200 nm were synthesized by the carbothermal reaction between electrospun carbon nanofibers and silicon powders. In the absence of a noble metal co-catalyst, the hydrogen evolution efficiency of SiC NFs is significantly improved under both simulated solar light (180.2 μmol g^{-1} h^{-1}) and visible light irradiation (31.0 μmol g^{-1} h^{-1}) in high-pH solution. The C-SiC NFs with diameter range from 505 to 875 nm were resulted from the electrospinning of polycarbosilane (PCS)/polystyrene solution followed by oxidizing and annealing at 1100 ºC. The obtained C-SiC NFs also display outstanding thermal stability and chemical resistance. These two kinds of SiC nanofibers were promising materials for stable, high efficiency, and co-catalyst-free photocatalysts, catalyst supports and high-temperature filters in harsh environment.

PACRIM Symposium 05: Advanced Powder-Processing and Manufacturing Technologies

Nanoparticle and Powder Design and Synthesis

Room: King's 2

Session Chairs: Junichi Tatami, Yokohama National University; Qian Liu, Shanghai Institute of Ceramics, Chinese Academy of Sciences

10:15 AM

(PACRIM-S5-001-2017) Rapid Preparation and Optimization of Inorganic Luminescent Materials by Combinatorial Method (Invited)

Q. Liu*[1]; Q. Wei[1]; Z. Zhou[1]; G. Liu[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, The State Key Lab. of High Performance Ceramics and Superfine Microstructure, China

Rapid Preparation and Optimization of Inorganic Luminescent Materials by Combinatorial Method Combinatorial approach adapts parallel design, synthesis, and high-throughput characterization of material chips, not only to build up the relationship between composition-processing-microstructure-property of materials, but also to increase the rate and efficiency of materials exploration and development process, embodying the core idea of materials genome initiative (MGI). At present stage, the parallel synthesis of powder chips usually uses an automatic liquid injector to dispense the desired components in a block array of cells to obtain more powder samples. Meanwhile, the high-throughput characterization platforms possess high spatial and temporal resolution, rapid scanning, and multi-channel parallel detection functions. In the present report, it shows some rapid and effective optimization results of different inorganic luminescent materials with high emission intensity and short decay time, including rare earth-doped YAG-based scintillator ($Y_3Al_5O_{12}$), GPS-based scintillator ($Gd_2Si_2O_7$), and BSO-based phosphors ($Bi_4Si_3O_{12}$), combined with energy gap simulation and combinatorial synthesis of material ships using liquid injector strategy. The optimized results suggest great potential candidates for medical nuclear imaging scintillator and warm white-emitting LED phosphors.

10:45 AM

(PACRIM-S5-002-2017) Emulsion templating of poly (acrylic acid) by ammonium hydroxide/sodium hydroxide aqueous mixture for high-dispersed hollow silica nanoparticles

C. Takai*[1]; M. Ando[1]; M. Noritake[1]; H. Razavi Khosroshahi[1]; M. Fuji[1]

1. Nagoya Institute of Technology, Advanced Ceramics Research Center, Japan

A water-in-oil (W/O) emulsion, in which the water phase including poly (acrylic acid) (PAA), ammonium hydroxide (NH_3 aq.), and sodium hydroxide aqueous solutions (NaOH aq.) dispersed in ethanol (EtOH), was proposed for producing hollow silica nanoparticles. The PAA molecules with the NH_3-NaOH mixture are insoluble in EtOH and can be a template. When tetraethoxysilane (TEOS) is added as a silica source, a silica shell is formed on the PAA-NH_3-NaOH template to form a core-shell particle and the addition of water removes the template to form hollow silica nanoparticles. The optimum volume ratio of 25 % NH_3:1.0 M NaOH was 2:1 to obtain high-dispersed hollow silica nanoparticles. A thermogravimetric analysis indicated that the condenseation force of the PAA molecules in the PAA-NH_3-NaOH template is similar to that in the PAA-NH_3 template. The small angle x-ray scattering (SAXS) analysis also showed that the electron densities in the PAA-NH_3-NaOH and PAA-NH_3 templates are similar. In the proposed PAA-NH_3-NaOH system, NH_3 aq. mainly contributes to form PAA condensation by an ionic interaction and NaOH aq. preferentially work as a sol-gel catalyst for the fast silica coating on the template surface. Acknowledgement: A part of this study was supported by JSPS Research Fellow.

11:00 AM

(PACRIM-S5-003-2017) Fabrication of Amorphous SiBN powders by Mechanical Alloying and its Crystallization Process

X. Liao*[1]; Z. Yang[1]; D. Jia[1]; Y. Zhou[1]

1. Harbin Institute of Technology, China

Because of the excellent mechanical properties and high thermostability, SiBN ceramic has aroused ever increasing attentions. We propose here a simple and inexpensive method to prepared amorphous SiBN powders with different Si/B atomic ratio by mechanical alloying using amorphous nano-Si_3N_4 and h-BN as raw materials. The phase composition, Morphology and microstructure of amorphous SiBN powders have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM). The results showed that after high energy ball milling for 20 h we can fabricate totally amorphous SiBN powders with Si and N evenly distributed. After the high temperature treatment from 1200 to 1700 ºC under the N_2 atmosphere for 30 min, amorphous SiBN powders start crystallization at 1600 ºC, and form α-Si_3N_4, β-Si_3N_4 and BN.

11:15 AM

(PACRIM-S5-004-2017) Monitoring Compaction and Densification of Ceramic Powders

R. A. Gerhardt*[1]

1. Georgia Institute of Technology, Materials Science and Engineering, USA

Achieving the desired properties of ceramics hinges on our ability to create good bonds between the constituent nanoparticles. This not only affects the mechanical properties of the materials but also the electrical properties. In this talk, we will review how the presence of porosity can affect the measured electrical properties of both insulating and conducting ceramics and how electrical measurements can be used to monitor the porosity of ceramic materials regardless of their end use application. Once a good green compact is obtained, then we need to be able to induce solid state sintering to achieve the degree of densification desired. Many different methods have been used over the years to obtain the desired degree of densification: pressureless sintering, hot pressing, hot isostatic pressing, field assisted sintering and cold sintering. Regardless of method used, one may also use electrical testing to monitor the bonding between the individual particles and the different stages of sintering either in-situ or ex-situ. Examples of in-situ compaction experiments and ex-situ sintering experiments of a series of insulating and conducting ceramic powders will be presented which will provide the roadmap for monitoring of the green density and the properties of the grain boundaries or junctions between the initial precursor materials.

11:30 AM

(PACRIM-S5-005-2017) Simulation of irregular shaped particles breakage using ADEM

S. Ishihara*[1]; J. Kano[1]

1. Tohoku University, IMRAM, Japan

Grinding is one of the most effective operations to produce fine particles. Grinding has been used in many fields, for example, foods, medicines, mining and so on. However, in general, the efficiency of grinding is quite low because the mechanism of grinding have not elucidated. Therefore, it is necessary to clarify the grinding mechanism and also to control the grinding process. In this work, it has been attempted to analyse the grinding phenomena using computer simulation. A new simulation model "ADEM (Advanced Distinct Element Method)" has been developed and it can represent both non-spherical particles motion and particle breakage behaviour. In ADEM, cluster particle is represented by agglomerate of primary particles, and primary particles are connected each other by joint-spring. A cluster particle breakage behaviour was analysed by ADEM. Simulation of impact test of a cluster particle has been done at different velocities from 0.1 to 0.5 m/s. The size of fragments becomes smaller with increasing in the impact velocity. The maximum strain and structure of primary particle are found to be two important parameters to represent the shapes of fragments after breakage. It can be seen good agreement with experimental results when adjusting these parameters. These results suggest that ADEM would be a useful tool to analyse the particle breakage behaviour and grinding process.

11:45 AM

(PACRIM-S5-006-2017) Pulverization of Y_2O_3 nanoparticles by using nanocomposite particles prepared by mechanical treatment

J. Tatami*[1]; K. Jeong[1]; M. Iijima[1]; T. Takahashi[2]

1. Yokohama National University, Japan
2. Kanagawa Academy of Science and Technology, Japan

Nanoparticles are being extensively investigated in industries and academia due to their widespread applications in various areas of science and manufacturing. Unfortunately, nanoparticles easily aggregate. This problem of nanoparticle aggregation creates challenges for various applications. In this study, we focus on using nanocomposite particles prepared via mechanical treatment to pulverize the aggregated Y_2O_3 nanoparticles. $CaCl_2$ and aggregated Y_2O_3 nanoparticles were mechanically treated using a process in which high shear and compressive stress are applied to them in order to generate nanocomposite particles. In order to rinse out $CaCl_2$, the nanocomposite particles were then added to distilled water to dissolve the $CaCl_2$ cores, and they centrifuged before supernatant solution was decanted. The recovered Y_2O_3 nanoparticles had a significantly smaller particle size and larger specific surface area than the aggregates. Thus, we confirmed that the aggregated Y_2O_3 nanoparticles were effectively pulverized in a short time by using nanocomposites prepared by mechanical treatment. Further, the relative density of the sintered body prepared from the pulverized Y_2O_3 nanoparticles was higher than that of the as-received and ball-milled Y_2O_3 nanoparticles.

PACRIM Symposium 10: Multifunctional Nanomaterials and Their Heterostructures for Energy and Sensing Devices

Multifunctional Integration for Chemical and Biosensors I

Room: Queen's 5

Session Chairs: Thomas Fischer, University of Cologne; Yong Yang, Shanghai Institute of Ceramics, Chinese Academy of Sciences

8:30 AM

(PACRIM-S10-022-2017) Functional Silicon Nanostructures and Their Use for Biological Applications (Invited)

Y. He*[1]

1. Soochow University, Institute of Functional Nano & Soft Materials (FUNSOM), and Collaborative Innovation Center of Suzhou Nano Science and Technology (NANO–CIC), China

Taking advantages of non- or lowly-toxic property of silicon, exploration of silicon nanostructures for biological and biomedical applications is of particular interest and has been extensively studied in recent years. Based on recent research efforts in our group, we herien summarize representative and promising achievement to highlight the remarkable development of silicon nanotechnology for biological and biomedical applications in recent years, with the hope to promote the awareness of the realm of silicon nano-biotechnology [1-7]. In particular, silicon structures with unique electronic/optical/mechanical properties have been widely employed for constructing a number of biosensing devices with excellent sensitivity and specificity, high reproducibility, and multiplexing capabilities. On the other hand, silicon-based bioprobes featuring strong fluorescence, robust photostability, and excellent biocompatibility have been extensively explored for long-term and real-time bioimaging in vitro and in vivo. More recently, silicon-based nanoagents have been exploited as novel therapeutic agents for treatment of cancer with encouraging outcomes. In vitro and in vivo experiment demonstrates the silicon-based drug nanocarriers are highly efficacious for cancer diagnosis and treatment.

9:00 AM

(PACRIM-S10-023-2017) High sensitivity, low energy consumption H2 and NO2 sensors with Pt/oxide/Pt sensor configuration (Invited)

B. Saruhan-Brings*[1]; A. A. Haidry[2]

1. DLR - German Aerospace Center, Institute of Materials Research, Germany
2. Nanjing University of Aeronautics and Astronautics (NUAA), College of Materials Science and Technology (CMST), China

A top-bottom electrode (TBE) sensor configuration is described for low temperature H_2 and NO_2 sensing. The sensors based on TBE

configuration and doped TiO_2 show improved sensing properties to wide range of concentration in contrast to the sensors fabricated with classical interdigitated electrodes (IDEs). The substitution of trivalent Cr^{3+} (0.755 Å) within Ti^{4+} (0.745 Å) lattice modified the electronic structure of TiO_2 and showed p-type semiconductor sensor response towards. The sensors with TBE-TiO_2:Cr layers showed highest NO_2-sensor response at 200 °C with negligible drift and noise. As for H_2-sensing, high sensitivity RT-detection of a few hundred ppm was possible without the use of any heater. These sensors consume extremely low energy during operation and are capable of being constructed as self-powered sensors. By means of impedance spectroscopic studies, sensing mechanism is predicted and the processing related influences on the sensing are correlated by means of microstructural (GDEOS, SEM/EDX and XRD) analysis. The impedance equivalent circuit modelling identified the contributions of the Pt-electrodes, sensing layer and interface between them. These tests revealed that the gas reaction beneath Pt-TE is dominating and the interfaces between the Pt-electrodes and the semiconductor sensing layers have individually significant contribution in the sensing mechanism.

9:30 AM

(PACRIM-S10-024-2017) Nanostuctured Oxide Ceramics for Sensors and Photocatalysts

P. Gouma*[1]

1. SUNY Stony Brook, MSE, USA

Our research group has pioneered the concept of selective chemosensors by using specific polymorphs of metal oxides that provide for gas selectivity along with superior sensitivity. Thus, a range of sensing probes have been developed for breath-based diagnostics (asthma breathalyzer, diabeted breathalyzer, etc). At the same time, ceramic oxide nanotechnology has also been developed for high efficiency photocatalytic remediation of the water using solar energy and for water splitting and hydrigen production. This presentation highlights the crystallo-chemical approach to the sensing and catalytic processes that has led to breakthrough materials and applications, such as the Nanogrids™.

9:45 AM

(PACRIM-S10-025-2017) Selective Gas Sensors using Co_3O_4-SnO_2 Hollow Hetero-nanostructures Prepared by Galvanic Replacement

H. Jeong*[1]; J. Kim[1]; S. Jeong[1]; C. Kwak[1]; J. Lee[1]

1. Korea University, Materials Science and Engineering, Republic of Korea

Selective detection of methyl benzenes (toluene and xylene) is important for monitoring harmful indoor pollutants. In general, the gas responses of oxide semiconductor chemiresistors to methyl benzenes are lower than other ubiquitous indoor pollutants such as formaldehydes and ethanol and the distinction between chemically similar benzene and methyl benzenes remains challenging. Galvanic replacement is a facile chemical route to prepare uniform hetero-nanostructures by replacing the host materials with other materials. In this study, Co_3O_4 hollow spheres are prepared by ultrasonic spray pyrolysis, which are converted into three different compositions of Co_3O_4-SnO_2 core-shell hollow spheres by galvanic replacement. The sensors using Co_3O_4-SnO_2 core-shell hollow spheres showed high responses to sub-ppm-level of methyl benzenes with low cross-responses to other interference gases such as benzene, ethanol, formaldehyde, acetone, and carbon monoxide. Moreover, gas selectivity to xylene could be also achieved by controlling the sensor temperature. The mechanism underlying the selective and sensitive detection of methyl benzenes was investigated in relation to synergistic catalytic effect of nano-composites, the reforming of analyte gas into more active species using micro gas reactors, and electronic interaction between Co_3O_4 and SnO_2.

Multifunctional Integration for Chemical and Biosensors II

Room: Queen's 5
Session Chairs: Bilge Saruhan-Brings, DLR - German Aerospace Center; Yao He, Soochow University

10:15 AM

(PACRIM-S10-026-2017) Niobium Pentoxide: One Promising Surface-Enhanced Raman Scattering Active Semiconductor Substrate (Invited)

Y. Yang*[1]; Y. Shan[1]; Z. Huang[1]; D. Jiang[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Surface-enhanced Raman scattering (SERS) technique, as a powerful tool to identify the molecular species, has been severely restricted to the noble metals. The SERS substrates based on semiconductors would overcome the shortcomings of metal substrates and promote development of SERS technique in surface science, spectroscopy, and biomedicine studies. However, the detection sensitivity and enhancement effects of semiconductor substrates are suffering from their weak activities. In this work, a semiconductor based on Nb_2O_5 is reported as a new candidate for highly sensitive SERS detection of dye molecules. The largest enhancement factor (EF) value greater than 10^7 was observed with the laser excitation at 633 and 780 nm for methylene blue (MeB) detection. As far as literature review shows, this is in the rank of the highest sensitivity among semiconductor materials; even comparable to the metal nanostructure substrates with "hot spots". The impressive SERS activities are believed originated from the photo-induced charge transfer (PICT) process, as well as attributed to electromagnetic mechanism (EM) enhancement.

10:45 AM

(PACRIM-S10-027-2017) Highly selective and sensitive detection of trimethylamine using Au-loaded Cr_2O_3 yolk-shell spheres

T. Kim*[1]; J. Yoon[1]; Y. Kang[1]; J. Lee[1]

1. Korea University, Materials Science and Engineering, Republic of Korea

An ultrasensitive and selective trimethylamine (TMA) sensor was fabricated by the uniform loading of Au nanoparticles (~ 5 nm) on Cr_2O_3 yolk-shell spheres prepared by ultrasonic spray pyrolysis. The response of the pure Cr_2O_3 yolk-shell spheres with thin shells was higher than that of the Cr_2O_3 hollow spheres with thick shells, which can be attributed to the excellent gas accessibility of the yolk-shell structure with a high specific surface area and abundant pores. In addition, the Cr_2O_3 yolk-shell spheres loaded with agglomerated Au nanoparticles (size: 10-100 nm) and fine Au nanoparticles (size: ~5 nm) showed quite different gas sensing characteristics, despite having been loaded with similar amounts of Au. A superior response to TMA was found in Cr_2O_3 yolk-shell spheres uniformly loaded with fine Au nanoparticles, and this enhanced response was attributed to the gas-accessible morphology of the yolk-shell spheres, and the catalytic and electronic promotion of the gas sensing reaction by both Cr_2O_3 and well-dispersed Au nanoparticles.

11:00 AM

(PACRIM-S10-028-2017) Pt-doped SnO_2 hollow nanospheres prepared by Kirkendall effect for sensitive and selective detection of ethanol

B. Kim*[1]; J. Cho[1]; J. Yoon[1]; C. Na[1]; C. Lee[1]; J. Ahn[1]; Y. Kang[1]; J. Lee[1]

1. Korea University, Materials Science and Engineering, Republic of Korea

Kirkendall diffusion is a simple process to synthesize hollow spheres with thin shells. The solid evacuation by nano-scale Kirkendall effect occurs during the oxidation of metal particles when the inward diffusion of oxygen ion is more sluggish than the outward diffusion of cation. In this study, the pure and Pt doped SnC_2O_4-PVP composite microspheres were prepared by spray drying, which were converted into solid carbon spheres with embedded pure Sn and Pt doped Sn nanocrystals by carbonization of the PVP and crystallization of the Sn precursors through heat treatment in H_2/Ar. Subsequent heat treatment of the Sn-C(carbon) composite spheres at 500 °C in air for 5 h leads to the formation of pure and Pt doped SnO_2 hollow nanospheres by Kirkendall effect. Pure SnO_2 hollow nanospheres showed high response (resistance ratio) to 5 ppm ethanol of 101.0 at 325 °C. The response to 5 ppm ethanol was significantly increased to 1399.9 by doping Pt to SnO_2 nanospheres. In addition, Pt doped SnO_2 hollow nanospheres showed high selectivity to ethanol with low cross-responses to other interference gases at 325-450 °C. High sensitivity and selectivity are attributed to the effective electron depletion in hollow morphology with thin shell and catalytic promotion of gas sensing by Pt doping.

11:15 AM

(PACRIM-S10-029-2017) Synthesis of TiO_2-SnO_2 nanocomposites for application in the gas sensors

A. M. Marzec*[1]; Z. Pedzich[1]

1. AGH - University of Science and Technology, Department of Ceramics and Refractory Materials, Poland

The work presents the synthesis of TiO_2-SnO_2 nanostructures in alkaline conditions. X-ray diffraction measurements performed for nanocomposites TiO_2-SnO_2 reveal that nanomaterials are well crystallized and two polymorphic forms, namely anatase TiO_2 and cassiterite SnO_2 are presented. Nanocomposites are characterized by the specific surface area S_w~100 m^2/g. The sizes of crystallites estimated with use of XRD (d_{XRD} ~ 10 nm) are similar to those calculated basing on specific surface area measurements. Investigated materials, due to their microstructural, optical and electrical properties could be beneficially applied in the development of gas sensors.

11:30 AM

(PACRIM-S10-030-2017) Development of metal-organic framework-coated SAW sensors for sensitive detection of methane

J. Devkota*[1]; P. Ohodnicki[1]; D. W. Greve[2]

1. National Energy Technology Laboratory, USA
2. Carnegie Mellon University, Electrical and Computer Engineering, USA

Developing next generation of methane detectors is essential for monitoring low concentration leakages in oil and gas sites, natural gas pipelines, and industries as existing techniques are either expensive, or limited in sensitivity and response time. The colorless, odorless, and relatively inert behavior of methane has been a challenge in developing novel sensors for monitoring small leaks. Surface acoustic wave (SAW) sensors are potential candidates for ultra-sensitive detection but traditional coating materials such as polymers have limited sorption capacity for low concentration of methane. Recently, metal organic framework (FOM) materials have gained attention as a novel class of sensing materials to combine with the SAW platform for their high absorption capacity of many gases and chemicals. Here, we perform finite element modeling (FEM) of a YZ-cut $LiNbO_3$ SAW resonator using two MOFs (ZIF-8 and Cu-BTC) as the sensing layers for CH_4 detection. We compare the results with a published FEM report on CH_4 detection using a polyisobutylene (PIB)/YZ-cut $LiNbO_3$ SAW resonator. Our preliminary study shows that the sensor based on Cu-BTC can detect CH_4 gas with much higher sensitivity (~13.5Hz/100ppm) compared to the ones based on ZIF-8 (~4.7Hz/100ppm) or PIB (~5.1Hz/ppm). The experimental work is in progress for verification of this result predicted from FEM analysis.

11:45 AM

(PACRIM-S10-031-2017) Electrospun metal oxide fiber meshes for improved sensing of toxic analytes in the gas phase (Invited)

T. Fischer*[1]; Y. Gönüllü[1]; D. Graf[1]; S. Mathur[1]

1. University of Cologne, Institute of Inorganic Chemistry, Germany

Gas sensors need to combine a high Sensitivity and analyte Selectivity with acceptable readout Speed and long term Stability by not sacrificing the fabrication Scalability and System Integration capability, when it comes to commercialization (so called 6S criteria). Resistive metal oxide gas sensors with nanowire based sensing materials offer high surface areas and defined signaling pathways for improved device performance thus fulfilling most of the aforementioned criteria, but most often lack the potential of large scale integration, due to complex fabrication techniques. In contrast electrospun metal oxide fibers and fiber meshes can be fabricated in comparable large amounts at ambient conditions, thus providing ideal materials for either the active sensing layer or necessary preconcentrators and filters, respectively. A direct integration onto multifunctional gas sensing platforms is also possible in modified electropinning setups, thus providing inteconnected sensing meshes with high surface areas. The presentation will highlight the fabrication of electrospun metal oxide fibers and fiber meshes integrated in gas sensing platforms to evaluate the influence of composition, structure and system design on the sensing capability of toxic gases.

PACRIM Symposium 13: Advanced Structural Ceramics for Extreme Environments

Materials Design, New Compositions, and Composites

Room: Kohala 4

Session Chair: William Fahrenholtz, Missouri University of Science & Technology

8:30 AM

(PACRIM-S13-001-2017) Designing Ceramic Composites for use at High Temperatures (Invited)

R. N. Singh*[1]

1. Oklahoma State University, School of Materials Science and Engineering, USA

Fiber-reinforced ceramic matrix composites (CMCs), by incorporating fibers in ceramic matrices, not only exploit their attractive high-temperature strength but also enhance their toughness thereby rendering these attractive for many applications. Some of these applications require an understanding of the crack propagation and fracture behaviors in ceramic matrix composites (CMCs) for assessing their performance and life predictions. The results of the crack growth thus obtained are used to analyze fracture resistance behavior, and theoretical analyses are done to develop models to predict the crack growth and fracture resistance behaviors. Bridging stress functions are also obtained from the analytical models over a range of temperatures, which are then used in designing CMC with superior elevated temperature mechanical properties. These results on two types of SiC_f-reinforced CMCs will be presented and discussed. In addition, the prospects of using CMCs in current and future systems will be presented.

9:00 AM

(PACRIM-S13-002-2017) Developing UHTCMCs: Effect of matrix additives on the resistance to oxidation

D. Sciti*[1]; A. Vinci[1]; L. Zoli[1]

1. ISTEC-CNR, Italy

High-speed aviation brings many challenges, one being the materials used need to be able to withstand extreme temperatures and harsh environments. To face these demanding requirements we are developing innovative materials, the so called UHTCMCs, where a UHTC matrix is incorporated into a C fiber preform. The scope of this work is to answer fundamental questions such as: -Is the C fiber preform able to impart damage tolerance to the UHTC matrix? -Is the UHTC matrix able to protect the fibers from excessive oxidation during high temperature exposition? To this purpose, UHTCMCs including oxidation protecting phases such as SiC or other carbides are considered. Oxidation tests are conducted in air at different temperatures to investigate the materials' response. In parallel, microstructural characterization with particular attention to the fiber/matrix interface and fracture properties of the composites are investigated.

9:15 AM

(PACRIM-S13-003-2017) Toughened and damage tolerant SiC ceramics by adding graphene-based fillers

M. Belmonte*[1]; P. Miranzo[1]; M. I. Osendi[1]

1. Institute of Ceramics and Glass, CSIC, Spain

Silicon carbide (SiC) is one of the most demanded engineering ceramics due to its excellent corrosion/wear resistances, high thermal conductivity and good mechanical performance at high temperature. However, the Achilles' heel of SiC ceramics is their relatively low toughness, which together with their high hardness, limit its machining performance to manufacture microcomponents. To overcome these problems and considering that graphene-based structures have recently attracted a great interest as efficient reinforcing fillers, we have developed SiC/graphene composites. The fracture toughness and strength performances as a function of the filler content (0-20 vol.%) and type of graphene source (graphene nanoplatelets -GNPs- and reduced graphene oxide -rGO-) were investigated. The contact damage resistances were also analysed by performing Hertzian contact tests. rGO arise as the best graphene filler considering the outstanding toughness (162%) and strength increments (61%) attained by adding just 5 vol.%. The preferential alignment of the fillers, their dimensions, and the graphene-SiC mechanical interlock are key factors to promote crack shielding mechanisms. Furthermore, SiC became more damage tolerant when adding graphene fillers, as graphene promoted the formation of a quasi-plastic damage zone beneath the contact, redistributing the stress field and limiting the growing of subsurface cone cracks.

9:30 AM

(PACRIM-S13-004-2017) Silicon Nitride and Silicon Carbide ceramics for Avionics and Space Instruments (Invited)

K. Berroth*[1]

1. FCT Ingenieurkeramik GmbH, Germany

Silicon nitride and silicon carbide ceramics are gaining interest in avionics and space, because of lightweight stiff and strong materials with low and very low CTE and high thermal conductivity are requested to push frontiers to higher resolution in optical telescopes. Due to the excellent combination of properties gas pressure sintered, hot pressed or hot isostatic pressed silicon nitride and sintered silicon carbide ceramics are candidate materials to fulfill design engineers requirements. Silicon nitride and silicon carbide ceramics are now available in even large and complex shaped components with a CTE of down to <1.4 x 10-6/K, thermal conductivity of up to 85 W/mK at 20°C, 4-point bending strength of up to 1,100 MPa. Also highly dense, strong and fine grained sintered silicon carbide, with a thermal conductivity up to 150 W/mK, can be offered either as electrical insulator or conductor. Components are available on a commercial base with diameters up to 500 mm and length up to 1,300 mm.

9:45 AM

(PACRIM-S13-005-2017) First-principles investigation on segregation of solute atom (Y, Nb, Ta, Mo, W) in ZrB_2 grain boundaries and their effects on grain boundary strengths

F. Dai*[1]; Y. Zhou[1]

1. Aerospace Research Institute of Materials and Processing Technology, Science and Technology of Advanced Functional Composite Laboratory, China

ZrB_2 based ultra-high temperature ceramics (UHTCs) exhibit a unique combination of excellent properties that makes them promising candidates for applications in extreme environments. Evaluating the correlation between microscopic defects and macroscopic performance of these materials is crucial for the design of UHTCs. The present work deals with a first-principles investigation on segregations of solute atoms (Y, Nb, Ta, Mo and W) in ZrB_2 grain boundaries and their influences on grain boundary strengths. Opposite segregation tendency between Y and Nb, Ta, Mo or W is obtained, where Y prefers sites with long M-B bonds, while Nb, Ta, Mo or W prefers sites with short M-B bonds. The short equilibrium M-B (M = Nb, Ta, Mo or W) bonds induce local contractions around grain boundaries, which in turn strengthens grain boundaries remarkably, thereby enhances the mechanical properties of ZrB_2 at evaluated temperatures. In contrast, segregation of Y poisons grain boundaries due to local expansions induced by long Y-B bonds, which will deteriorate the performance of ZrB_2 based UHTCs. The results provide useful guidelines for the design of ZrB_2 based UHTCs, since grain boundaries play a key role in determining high temperature mechanical properties.

Novel Processing and Characterization Methods

Room: Kohala 4

Session Chair: Diletta Sciti, ISTEC-CNR

10:15 AM

(PACRIM-S13-006-2017) Non-Cooled as well as Actively-Cooled Ceramic Matrix Composites in harsh propulsion environment (Invited)

S. Schmidt-Wimmer*[1]

1. Airbus Safran Launchers, Production Technology - Materials & Processes, Germany

Ceramic matrix composites (CMCs) reinforced with continuous carbon fibers show a wide flexibility of type, microstructure, as well as thermal and mechanical properties. Thus, CMCs represent a leading group of materials for a wide range of high performance applications in aeronautics, space exploration and energy/nuclear industries. Within aeronautics and space exploration systems, these materials are utilized especially for applications in hot and highly loaded sections and harsh environments such as nozzle extensions for space propulsion, orbital thrusters, Thermal Protection Systems (TPS) for re-entry vehicles, or components for ram- and scramjet engines. Materials for such applications have to withstand high aerodynamic, thermo-mechanical and thermo-chemical loads during operation. Besides cost reduction, performance improvements are key indicators for the development and application of advanced materials or adapted cooling designs in propulsion systems. Higher combustion efficiency and performance lead to higher combustion temperatures and consequentlymaterial working temperatures (>1900 °C). Main advantages of CMCs are low density, high resistance to thermo-shocks and high temperatures, stability to chemical attack, creep resistance and low thermal expansion. Emphasis in this paper is placed upon the manufacturing techniques to testing methods and space-relevant applications.

10:45 AM

(PACRIM-S13-007-2017) Processing and Elevated Temperature Mechanical Properties of ZrB_2/ZrB_2-C Laminates

C. Wittmaier[1]; W. Fahrenholtz*[1]; G. Hilmas[1]

1. Missouri University of Science & Technology, Dept. of Materials Science and Engineering, USA

Elevated temperature flexure strength and fracture toughness of ZrB_2 and ZrB_2-C ceramics and ZrB_2/ZrB_2-C laminates were investigated. Nominally pure ZrB_2 and a mixture of graphite plus ZrB_2 were homogenously blended in separate thermoplastic polymer systems. The ceramic laden polymers were pressed into sheets using a uniaxial press heated to 150°C to produce layers of consistent thickness, which were stacked in an alternating pattern and laminated. The pressed composites were pyrolyzed to remove the polymer, and then densified by hot pressing at 2150°C and 32MPa for 1 hour in an argon atmosphere. Microstructures were examined to evaluate relative density and grain size. In addition, the flexure strength and work of fracture of the composite material were measured at room temperature as well as at select elevated temperatures ranging from 1400 to 2000°C. The microstructure and mechanical properties for the laminates were compared to conventional ZrB_2 ceramics.

11:00 AM

(PACRIM-S13-008-2017) Interplay between nanolaminated structure and electron-phonon coupling inTi-based MAX phases

S. Dubois*[1]; A. Nassour[1]; V. Mauchamp[1]

1. PPRIME Institute, France

A linear-response method to the density functional theory is used to derive lattice dynamics, transport spectral function and electron-phonon coupling (EPC) constant of Ti_2AlC and Ti_3SiC_2, two members of the very large class of nanolaminated conducting ceramics named MAX phase. By coupling ab initio calculations with the semi-classical Boltzmann transport theory for electron-phonon scattering, the experimentally observed anisotropic electrical transport properties are rationalized. This work demonstrates that the anisotropic transport properties of two of the most studied MAX phases to date, originate from a competition between the EPC and the Fermi-surface velocity. More precisely, the number of M_6X octahedra layers in between the A planes (1 in M_2AX and 2 in M_3AX_2) modifies the main origin of the anisotropic transport properties. These results, the generalization of which is still to be investigated, rationalize the strong interplay between the nanolaminated structure and the origin of the transport properties anisotropy in Ti_2AlC and Ti_3SiC_2.

11:15 AM

(PACRIM-S13-009-2017) Improvement of Densification Uniformity in C/SiC Composites by Chemical Vapor Infiltration

K. Choi*[1]; J. Seo[1]; K. Kim[1]

1. Korea Institute of Ceramic Engineering and Technology (KICET), Icheon branch, Republic of Korea

The chemical vapor infiltration (CVI) is one of the most attractive methods to produce CMC that is applicable for high temperature components like shrouds and turbine blades. A porous preform is placed in surrounding of a thermally activated reactive gas mixture (CH3SiCl3 + H2), and then it decompose and yield solid deposit that fills the pores inside the preform. After the CVI process, residual pores still exist partially in the preform. Distribution of the remained pores varies with the infiltration depth of precursor gas that is related to the gas flow and the temperature distribution of the preform. The mass transfer mechanism by which the precursor gases flow throughout the preform is governed by chemical diffusion due to the concentration gradients existed. In order to prevent poor infiltration, temperature and pressure should be maintained to be low enough to suppress the deposition rate. Lower the pressure, longer the mean free path for the source gas to infiltrate into the preform. The uniform infiltration through the preform was demonstrated with lower process pressure and temperature, which resulted in the increased mean free path and the decreased reaction rate.

11:30 AM

(PACRIM-S13-010-2017) Melt and Matrix modifications to the Reactive Melt Infiltration Process used for the manufacturing of UHTCMCs

M. Kuetemeyer*[1]

1. DLR - German Aerospace Center, KVS, Germany

For the development of UHTCMCs via Reactive Melt Infiltration (RMI), experiments have been conducted determining the contact angle and chemical behaviours of $AgZr_2$, Zr_2Cu and Cu alloys when in contact with carbide (NbC, TaC), nitride (HfN, ZrN) and boride (TiB_2) substrates. Drop-shape images of the melt shadows have been video recorded within a tube furnace, in order to determine contact angle against temperature and time. The resultant phase formations are investigated and analyzed using SEM, EDX and XRD. The purpose of these experiments is to further understand the RMI process and determine new possible fiber coatings. The infiltration height of molten metals within capillary systems is highly dependent on these contact angles, as such; it is important that the chosen fiber coating positively influences wetting behaviour. In order to maintain mechanical performance, another measure of success is the formation of a weak interfacial bond between the coating and melt. The most promising candidates will be further investigated by manufacturing UHTCMC samples.

11:45 AM

(PACRIM-S13-011-2017) Mechanical Behavior of Nuclear Grade SiC-SiC Tubing at Normal Operating and Accident Temperatures

G. Jacobsen*[1]; K. Shapovalov[1]; E. Song[1]; C. Deck[1]

1. General Atomics, Nuclear Technologies and Materials, USA

Understanding the high temperature mechanical behavior of Silicon Carbide (SiC) and SiC matrix, SiC fiber reinforced composite (SiC-SiC) is critical for their use in Gen IV reactor concepts, such as General Atomics' (GA) Energy Multiplier Module (EM^2), as well as for accident tolerant fuel in Light Water Reactor (LWR) applications. Two test techniques, C-ring and a variation on the Elastomeric Insert test, were used to measure the mechanical strength of SiC-SiC at temperatures up to 1600 ºC. For the elastomeric insert test glass inserts, heated past their softening point, were used as the expanding plug material. Testing was performed both in helium gas and air. The importance of the fiber/matrix interphase layer in context of high temperature stress/strain behavior was investigated. Retention of room temperature strength up to very high temperatures were observed. Based off the stress versus extension response, and fiber pullout, composite behavior was retained at high temperatures both in air and helium. *This work is supported by General Atomics internal funding.

PACRIM Symposium 14: Novel Spray Coatings

Energy and Environmental Applications of Aerosol Deposition

Room: Waikoloa 2
Session Chairs: Scooter Johnson, Naval Research Laboratory; Kazuaki Naoe, Hitachi, Ltd.

8:30 AM

(PACRIM-S14-025-2017) Recent progress in research and development on fabricating all solid-state lithium ion battery by aerosol deposition method (Invited)

K. Kataoka*[1]; J. Akimoto[1]; J. Akedo[1]

1. AIST, Japan

All solid-state lithium-ion battery is a promising candidate as one of the next generation energy storage devices because of its high safety, reliability and long-term cycleability. Aerosol deposition (AD) method which is room-temperature impact consideration process, has advantages in quality and variety of lithium battery electrode materials compared with other conventional thin film deposition methods. The electrode materials deposited on solid electrolytes by AD method shows excellent properties in battery capacity and electrode density. Recently, we successfully developed the garnet-type oxide solid electrolyte materials having superior lithium ion conducting properties. In addition, we have fabricated all solid-state lithium ion battery using the garnet-type oxide electrolyte. In this paper, we will report the electrochemical properties on electrolyte and battery, compared with those in the literature.

9:00 AM

(PACRIM-S14-026-2017) The role of the Aerosol Deposition process on the film properties of $Li_7La_3Zr_2O_{12}$ thick-films

D. Hanft*[1]; R. Moos[1]

1. University of Bayreuth, Functional Materials, Germany

The Aerosol Deposition Method (ADM) is a unique process to prepare dense ceramic films at room temperature and may be applied for thick-films where the depositing material can be hardly processed to dense films. A quite advanced but promising application for AD is in the field of ion conducting solid electrolytes for new battery systems. Solid electrolytes are believed to be the key for batteries with high specific capacities and are of strong scientific interest at the moment. The advantage of the oxide garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) is its high ionic conductivity in conjunction with its chemical stability. For a suitable mechanical stability, the obtained electrolyte films should be thick enough. For that reason, the film conductivity should be as high as possible. In any case, for this application the film has to be free of defects in order to prevent short-circuiting. ADM might have the potential to manufacture dense ceramic films that meet these needs. In this contribution, we show electrical properties of Li^+-ion conducting LLZO films fabricated by ADM. Using different methods for analysis, e.g. high temperature X-Ray diffraction as well as electrochemical impedance spectroscopy we correlate morphological and electrical properties of films and compare it to bulk material properties of cubic LLZO to resolve the effect of the processing technology on the film performance.

9:15 AM

(PACRIM-S14-027-2017) Aerosol Deposition of PLZT Films for Power Inverters in Electric Drive Vehicles

B. Balachandran*[1]; B. Ma[1]; T. H. Lee[1]; S. E. Dorris[1]

1. Argonne National Laboratory, Energy Systems Division, USA

Future availability of high-temperature power inverters will advance the market share for highly fuel-efficient, environmentally friendly electric drive vehicles (EDVs). An integral part of vehicle power inverters is the DC buss capacitor, which has a significant influence on inverter lifetime, reliability, cost, and temperature of operation. Advanced power inverters require capacitors that operate under high voltage conditions at under-hood conditions. Lead lanthanum zirconate titanate (PLZT) capacitors have the greatest potential for volume reduction. A high-rate aerosol deposition (AD) process is being developed at Argonne to produce PLZT films with desirable properties. The AD process can produce dense films at room temperature; thus making the process amenable for depositing PLZT films on a variety of substrates such as polymer, glass, and metal foils. Recently we demonstrated that a ≈8-μm-thick PLZT film on aluminum-metallized polyimide substrate can be deposited in less than 10 minutes by the AD process. Films deposited by the AD process exhibited dielectric constant of ≈80 at 300 V bias, dielectric loss <2%, mean breakdown voltage of ≈1000 V, and temperature-dependent properties suitable for advanced power inverters. Our results show that the AD process has great potential in reducing the manufacturing cost of high-temperature capacitors.

9:30 AM

(PACRIM-S14-028-2017) Preparation and Properties of Al_2O_3 Ceramic Insulating Layer for High Power Devices by Aerosol Deposition Method

R. Aoyagi*[1]; H. Tsuda[1]; J. Akedo[1]

1. National Institute of Advanced Industrial Science and Technology, Japan

Thermal management is one of serious problems in high power devices such as high power switching semiconductor devices and high brightness LED illuminations system. The integrated circuit boards of these devices are required to have both high insulating properties and high thermal conductivity. High thermal conductivity ceramic substrate such as AlN and metal substrate covered with insulating resin have been studied as circuit boards for high power devices. But these substrates have some problems. For example, ceramic substrates are poor in workability, and in the case of AlN, there is a problem of cost. For metal substrates, the thermal conductivity of the resin insulator is low. In this study, we focused on Al_2O_3 film deposited by aerosol deposition method (ADM) as insulating layer for metal substrate. Dense Al_2O_3 thick films (>1μm) was successfully deposited on metal substrates by ADM. The structural, electrical, thermal, and mechanical properties of the samples were investigated. The samples were composed of nano-sized particles which is much smaller than the micron sized starting particles. It was found that the samples had high breakdown voltage more than 1 kV at thickness of 10 μm and breakdown field depended on Vickers hardness of the films.

9:45 AM

(PACRIM-S14-029-2017) Plasma erosion behavior of Yttrium Oxide film formed by aerosol deposition method

H. Ashizawa*[1]; M. Kiyohara[1]

1. TOTO ltd, Japan

Aerosol deposition (AD) method is a technology for ceramics coating with impact consolidation at room temperature. The ceramic films formed by AD method have high density structure that has no pore, nanocrystalline structure that crystalline size is under 20 nm, and high adhesion with substrate material by anchoring effect. TOTO have developed AD Y2O3 films used for plasma resistance coating. In recent years the plasma etching device used for semiconductor manufacturing has been required to reduce particles in the etching process. AD Y2O3 film has been used for the chamber components of plasma etching device and helped to reduce the particles in it. In this study, I investigated the plasma erosion behavior of AD Y2O3 film compared with the thermal splay Y2O3 coating and sintered Y2O3bulk samples. The thermal splay Y2O3 film was observed plasma erosion via pores that was not observed in the AD Y2O3 film. And the sintered Y2O3 bulk was observed grain boundary erosion that was not observed in AD Y2O3 film. The difference of erosion behavior between AD Y2O3 film and the other samples such as the thermal splay Y2O3 coating and sintered Y2O3 bulk suggests that the particle size generated from AD Y2O3 film in the plasma process is much smaller than the other samples.

Novel Coating Deposition

Room: Waikoloa 2
Session Chair: Rintaro Aoyagi, National Institute of Advanced Industrial Science and Technology

10:15 AM

(PACRIM-S14-030-2017) Polymer-Assisted Deposition Epitaxial Li(Ni,Co,Mn)O_2 Thin Films

D. Huang[1]; Q. Zhou[1]; H. Luo*[1]

1. New Mexico State University, USA

Rechargeable lithium-ion batteries are widely used in mobile devices, hybrid, plug-in hybrid, and electric vehicles. The performance of batteries strongly depends on the structure, morphology, and properties of electrode materials. A great effort has been made to synthesize a variety of electrode materials and to understand the role of the electronic structure of redox active materials to improve the energy density, rate capability, and cycling stability. It is generally considered that cathode determines the specific capacity and the energy density of batteries. Li(Ni,Co,Mn)O_2, a layered material, has gained considerable attention as the cathode due to its high specific capacity and thermal stability. To understand the nature of the electrochemical reaction, it is expected that single crystal-like electrode materials may offer better understanding of its effects on crystallographic orientation on the electrochemical properties. To this end, epitaxial Li(Ni,Co,Mn)O_2 thin films of different orientations with (001), (110), and (111) planes have been successfully grown on $SrTiO_3$ substrates from a solution method, called polymer-assisted deposition. The films have been characterized by x-ray diffraction, atomic force microscope, and cross-section high resolution transmission electron microscope.

10:30 AM

(PACRIM-S14-031-2017) Scalable solution assembly of 2D nanosheets for high-performance flexible electronics

M. Osada*[1]

1. National Institute for Materials Science, WPI-MANA, Japan

Two-dimensional (2D) atomic crystals, such as 2D oxides, have attracted much attention in electronics due to their unique properties. The ultrathin thickness and high flexibility of 2D nanosheets render them appealing building blocks for constructing new electronics. However, current strategies are largely limited to the inability of high-quality large-area films. Here, we report a convenient and scalable solution approach for the hierarchical assembly of 2D oxide nanosheets on polymer substrates to obtain flexible oxide thin films. A variety of oxide nanosheets were synthesized by delaminating appropriate layered precursors into their single nanosheets via soft-chemical process. We fabricated 4-inch size monolayer nanosheet films by a PC-controlled Langmuir-Blodgett deposition. The monolayer film of 2D nanosheets can be assembled into multilayer or superlattice films through the selection of nanosheets, and precise control over their arrangement at a molecular scale. Flexible thin films from 2D nanosheets assemblies exhibit excellent electronic properties and flexibility. For example, the conducting films of ZnO/polyimide can be folded and even bent to a crease without cracking. Our approach could help facilitate the rapid fabrication of flexible electronic devices, heralding what promises to be a new approach toward next-generation electronics and ceramic nanocoating.

10:45 AM

(PACRIM-S14-032-2017) Formation of three-dimensional structures with high density composed of carbon short fibers

M. Mori*[1]; S. Mori[1]; N. Ikeda[2]; J. Kano[2]; Y. Nishina[2]; J. Akedo[3]

1. Ryukoku University, Japan
2. Okayama University, Japan
3. National Institute of Advanced Industrial Science and Technology (AIST), Japan

The aerosol deposition (AD) method has been attracted as a preparation method of ceramics thick films with a high deposition rate at lower temperature. Ceramics thick films are able to form on various substrates including glass, metal and plastic by using the AD method. On the other hand, we have been challenging to research about a new development of AD method. And we developed a new process to form carbon fibers with a high density and at a high speed. This process is based on AD method so that we call this process "fiber aerosol deposition method (FAD)". In FAD method, prepared carbon short fibers are supplied by carrier gas to a substrate. The supplied carbon short fiber pierces a non-woven fabric as the substrate. Three-dimensional structures composed of carbon short fibers are formed by entanglement of short fibers. In AD method, the film is formed by crashing and deformation of the powder on the substrate. However, in FAD method, three-dimensional structure is formed only by entanglement of fibers without crashing and deformation of short fibers. The forming mechanism clearly differs in FAD method and AD method. In the presentation, we will introduce the outline of FAD, and some results in this research. This research was supported by a grant for domestic research (Kokunai-kenkyu) of Ryukoku University (2015-2016).

PACRIM Symposium 15: Advanced Wear-Resistant Materials: Tribology and Reliability

Wear Resistant Materials: Tribology and Reliability

Room: Queen's 4
Session Chair: Kouichi Yasuda, Tokyo Institute of Technology

8:30 AM

(PACRIM-S15-001-2017) Influence of data set size on linearity in 2-parameter Weibull plot

K. Yasuda*[1]

1. Tokyo Institute of Technology, Japan

For a couple of decades, 2-parameter Weibull plot has been used to discuss the reliability of dense fine ceramics. This is based on that Weibull plot should be perfectly linear when the strength data points are plotted. However, we can find some data scattering in actual Weibull plot. So, we should check how linearity is admissible to apply 2-parameter Weibull distribution to strength data of dense fine ceramics. In this presentation, numerical simulation by inverse function method is discussed when data set size is changed from 5 to 100, and square of correlation factor of the data set is estimated to express the linearity of the plots. The average of the square of correlation factor is around 0.95 for data set size more than 30 although it depends on the shape parameter of 2-parameter Weibull distribution.

8:45 AM

(PACRIM-S15-002-2017) Strength improvement and purification of $Yb_2Si_2O_7$/SiC nanocomposites by surface crack healing (Invited)

T. Nakayama*[1]; T. Son[1]; L. He[2]; H. Suematsu[1]; K. Niihara[1]; T. Suzuki[1]

1. Nagaoka Univ of Tech, Japan
2. Idaho National Laboratory, USA

Although $Yb_2Si_2O_7$/SiC composite has been considered a promising material for high temperature applications, there has been no research on fabrication of this composite. One of the main reasons is the difficulty in synthesizing pure $Yb_2Si_2O_7$. In this research, the authors proposed a facile method to prepare $Yb_2Si_2O_7$/SiC composites by two-step processing. $Yb_2Si_2O_7$/Yb_2SiO_5/SiC composites were first fabricated by a solid state reaction/hot-pressing method. The composites were then heat-treated at 1250 °C in air for 2 h to activate the oxidation of SiC, which effectively transformed the Yb_2SiO_5 into $Yb_2Si_2O_7$ and healed the surface indentation cracks. The flexural strength of the treated composites has been not only recovered to the original value, but also exceptionally enhanced. In addition, Yb_2SiO_5 almost disappeared from the composite surface. The mechanism for crack-healing behavior and silicate transformation for this material were intensively studied. These findings can be very meaningful for developing gas turbine engine, as well as for other high temperature applications.

9:15 AM

(PACRIM-S15-003-2017) Wear and cutting resistance of Al alloy/ceramic interpenetrating composites

J. Liu*[1]; J. Binner[2]; L. Gao[1]

1. Shanghai Jiao Tong University, China
2. University of Birmingham, United Kingdom

Metal-ceramic interpenetrating composites (IPCs) can be successfully manufactured by the pressureless infiltration of ceramic foams with molten metals. The resulting IPCs, in which both phases are three dimensionally continuous, have many potential applications, including wear and cutting resistance amongst other uses. In this project, the wear mechanism of the Al alloy/ceramic IPCs was investigated and the effects of the foam density and cell size on the wear properties were determined. It was found that the alumina or spinel reinforcement-based IPCs performed better than those based on mullite. It was also found that all the foam-based IPCs were up to twice as wear resistant as MMCs made by infiltrating a bed of ceramic powder. This cutting resistance of the IPCs was investigated, with a view to understanding the underpinning mechanisms. As expected, the cutting resistance was found to be dependent on the hardness of the IPCs, however evidence was also found of the role that is played by the continuous metallic phase. Plastic deformation can consume energy and bridge cracks; strain hardening under the twin actions of compression and shearing can enhance the hardness and strength of the metal at the cut tips and adhesive wear is believed to be the main origin of rapid tool failure.

9:30 AM

(PACRIM-S15-004-2017) The Wear Response of High Performance Cermets

K. P. Plucknett*[1]

1. Dalhousie University, Mechanical Engineering, Canada

Ceramic-metal composites, or cermets, combine the desirable properties of both components, and are often used in demanding tribological and corrosion environments. The most commonly used cermet, in both bulk and coating form, is tungsten carbide, typically with a cobalt binder (i.e. WC-Co). However, WC-Co suffers from a variety of limitations, notably high mass, poor corrosion resistance, and severe property degradation at elevated temperatures. In the present work, the wear response of two cermet systems, utilising ductile nickel aluminides or stainless steels as the binder material are reviewed. The two binders are paired with either titanium carbide (TiC) or carbonitride (Ti(C,N)) ceramic phases. These materials have been assessed in terms of their fundamental mechanical behavior and wear response (e.g. sliding wear, scratch testing, etc.). It is demonstrated that these new cermet systems can offer comparable wear resistance to WC-Co, at roughly half the mass. The relative performance characteristics of these new materials will be reviewed in comparison with a range of current commercial cermet systems.

9:45 AM

(PACRIM-S15-005-2017) Ultrathin MoS_2 coated TiO_2 nanosheet with high photocatalytic H_2 evolution efficency and durability

H. Han*[1]; K. Kim[1]; J. Ryu[2]; S. Mhin[1]; W. Han[3]

1. Korea Institute of Industrial Technology, Republic of Korea
2. Korea National University of Transportation, Republic of Korea
3. Seoul Womens University, Department of Chemistry, Republic of Korea

Solar water splitting using noble-metal-free catalysts has attracted great attention for developing renewable energy resources. Here, we report a new composite material for renewable hydrogen production using solar energy. This composite is consisted of metallic molybdenum di-sulfide (MoS_2) grown on high polar surfaces (i.e., high surface energy) of titanium oxide (TiO_2) nanocubes. Each compound was synthesized via hydrothermal process with controlled solution chemistry to obtain fascinating nanostructures, and then MoS_2 was deposited onto TiO_2 nanocubes faceted with high polar surfaces. Compositional and structural analysis was performed on the prepared composites via appropriate analytical techniques, and photocatalytic activity was also tested. Lastly, density functional theory (DFT) calculation was perfomed to investigate electronic strucutre of the composite corresponding to the enhanced photocatalitic anctivity and durability.

10:15 AM

(PACRIM-S15-008-2017) Influence of SiC content on high temperature erosion wear behavior of ZrB_2 ceramics

Y. Gupta[1]; S. Sharma[1]; A. W. Selokar[1]; B. Kumar*[1]; T. Venkateswaran[2]

1. IIT Roorkee, India
2. VSSC, India

ZrB_2-SiC composites 10 vol%, 20 vol% and 30 vol% SiC contents were prepared by spark plasma sintering at 1400C for 6 min followed by 1600°C for 2 min, at 55 MPa. The behaviour of sintered composites when eroded by SiC particles at 800°C was investigated. High density with good bonding between ZrB_2 and SiC grains is achieved for ZrB_2-30 vol% SiC composite with the selected SPS conditions. Hardness, fracture toughness and elastic modulus increased with SiC content. Transgranular fracture of ZrB_2 grains, crack bridging and grain pull out of SiC particles are observed for all ZrB_2-SiC composites. Erosion resistance against SiC particles at 800°C increased with the addition of SiC vol %. The erosion rate of the composites at 800°C reduced by 21% with 30% SiC addition as compared to 10 % SiC addition. The oxide layer, rich in B_2O_3 and SiO_2 prevents composites from erosion by reduced fracture of ZrB_2 grains or pull out of SiC particles.

10:30 AM

(PACRIM-S15-009-2017) Understanding Friction in MoS2 (Invited)

M. Chandross*[1]; T. Babuska[1]; J. Curry[2]; M. Dugger[1]; B. Krick[2]; N. Argibay[1]

1. Sandia National Laboratories, USA
2. Lehigh University, USA

While great strides have been made in understanding the remarkable lubricity of molybdenum disulfide (MoS2), much remains to be learned about the atomistic mechanisms of friction. We present results of investigations into the origins of the non-Amontonian behavior of MoS2 and show that the return to Amontonian behavior is associated with an elasto-plastic transition of the contact, and that the stress-dependent friction varies with substrate composition and microstructure. Time-dependent friction evolution was also found be strongly a function of substrate material and stress, implying a connection between stress and microstructure evolution in both film and substrate. We report on investigations into the temperature-dependent friction and wear behavior of pure MoS2. In the range -150 to 250°C, we find dramatic deviations from previous literature, including transitions between thermal and athermal behavior. Deviations from Arrhenius behavior are presented, and the implications are discussed in the context of thermally-activated friction. We then develop a predictive friction model for MoS2 that includes temperature, stress, substrate effects, defect density and commensurability. Sandia National Laboratories is a multimission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Deparment of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:00 AM

(PACRIM-S15-010-2017) Design and syntheses of hard coatings for industrial applications (Invited)

K. Kim*[1]

1. Pusan National University, School of Materials Science and Engineering, Republic of Korea

Hard-phase films have been extensively applied in various parts with superior mechanical properties like high hardness, wear resistance, low friction, etc. for the applications in machining, die-casting processes. Recently, the electrochemical ones of hard layer are also spotlighted for waste-water treatments. In this presentation, two material-systems are discussed with respect to the design and syntheses for their application purposes. (1) Nanocomposite films Various new materials for the multi-function are designed. For example, various ternary, quaternary, and quinary nano-structured films in the (Ti, Cr, Mo, Al, Si)-(B, C, N) system are compared in sense of not only hardness but also other properties of corrosion, oxidation, friction etc. for the structural applications. (2) DLC and BDD films for the wasteMultilayered amorphous carbon films Diamond- like carbon (DLC) and boron-doped diamond (BDD) films have superior chemical stability and electrochemical properties. For the applications of waste-water treatment, the hard layers should have ideal interlayer structure and those multi-layered structure must show the excellent properties such as mechanical stability and electrochemical properties.

PACRIM Symposium 18: Microwave Dielectric Materials and Their Applications

Microwave Dielectric Materials and Their Applications I

Room: Kohala 2

Session Chairs: Xiang Ming Chen, Zhejiang University;
Danilo Suvorov, Jozef Stefan Institute

8:30 AM

(PACRIM-S18-001-2017) Growth of $Ag(Nb_{0.5}ta_{0.5})O_3$ thin films by pulsed laser deposition for microwave dielectric applications (Invited)

D. Suvorov*[1]; M. Spreitzer[1]; L. Li[2]

1. Jozef Stefan Institute, Advanced Materials, Slovenia
2. Zhejiang University, Laboratory of Dielectric Materials, Department of Materials Science and Engineering, China

The $Ag(Nb_xTa_{1-x})O_3$ system exhibits a unique combination of microwave dielectric properties with high dielectric constant of 400, relatively high Qf value of 600 GHz and temperature stable resonant frequency with τ_f below 100 ppm/°C. Thus it has been often investigated for applications in various passive dielectric components like band-pass filters and resonators. In the present work we investigated $Ag(Nb_{0.5}Ta_{0.5})O_3$ thin film grown on (0001) Al_2O_3 single-crystalline substrates by pulsed laser deposition with the fluence of 1.5 J/cm^2 and oxygen pressure of 0.1 mbar. When the target-to-substrate distance was 55 mm polycrystalline $Ag(Nb_{0.5}Ta_{0.5})O_3$ primary phase was obtained for the deposition temperatures of 550-625°C and frequency of 5 Hz. However, for all the films secondary phases were also detected and are mainly related to decomposition products. When the target-to-substrate distance increased to 60 mm, pure $Ag(Nb_{0.5}Ta_{0.5})O_3$ phase was indicated from XRD patterns. The thickness of as-prepared film was 150 nm, which nevertheless had to be increased for microwave-dielectric-properties measurements. Prolongation of deposition time resulted in decomposition of the matrix phase, while increase frequency of 10 Hz enabled us to prepare pure-phase polycrystalline $Ag(Nb_{0.5}Ta_{0.5})O_3$ thin film with the thickness of 300 nm.

9:00 AM

(PACRIM-S18-002-2017) Microwave Ceramics: Beyond 5G (Invited)

I. M. Reaney*[1]

1. University of Sheffield, Materials Science and Engineering, United Kingdom

The development of new and improved MW materials for telecommunications is an increasingly critical aspect in the improvement of systems to meet the data transmission requirements of mobile networks beyond those projected for 5G. This talk will review state of the art in classic passive substrate materials for resonators and antennas, focussing on key structure property relationships that have guided materials development. In addition, a number of novel concepts and materials will be proposed which in the long term should result in greater data transmission rates and enable mobile technology to move beyond 5G.

9:30 AM

(PACRIM-S18-003-2017) Structural evolution, grain growth mechanism and microwave dielectric properties of $Li_2Ti_{1-x}(Mg_{1/3}Nb_{2/3})xO_3$ (Invited)

J. Bian*[1]

1. Shanghai University, Departemnt of Inorganic Materials, China

Structural evolution and grain growth mechanism of $Li_2Ti_{1-x}(Mg_{1/3}Nb_{2/3})xO_3$ (0<x<0.6) have been studied by x-ray powder diffraction (XRD), scanning electron microscopy (SEM) and Raman spectrometry in this paper. The microwave dielectric properties of the ceramics were studied with a network analyzer at the frequency of about 8-11 GHz. The results show that continuous solid solution could be formed within the experiment compositional range. The structure changed from long range ordered monoclinic into short range ordered cubic phase as the increase in x. The doping of $(Mg_{1/3}Nb_{2/3})$ decreased the dielectric permittivity. The Q value is considerably improved by doping of $Mg_{1/3}Nb_{2/3}$. The temperature coefficient of resonant frequency changed from positive into negative value and near zero t_f value could be obtained at x=0.24 composition. The grain growth mechanism of the x=0.24 composition with different calcination temperature was also investigated in this paper. Key Words: Lithium containing compound, Grain growth, Microwave dielectric properties

10:15 AM

(PACRIM-S18-004-2017) Microwave and radio-frequency dielectric properties of oxynitride perovskite thin films (Invited)

C. Le Paven*[1]; F. Marlec[1]; R. Benzerga[1]; L. Le Gendre[1]; A. Ferri[3]; D. Fasquelle[4]; V. Laur[5]; F. Tessier[2]; F. Cheviré[2]; X. Castel[1]; A. Sharaiha[1]

1. University of Rennes 1, Institute of Electronics and Telecommunications of Rennes (IETR), France
2. University of Rennes 1, Institute of Chemistry of Rennes, France
3. University of Artois, France
4. University of Cote d'Opale, France
5. University of Brest, France

For many years, perovskite materials have been studied regarding the wide variety of their properties achieved by substitutions on A and B cations-sites in the basic ABO_3 structure. Moreover, by replacing nitrogen for oxygen, oxynitride perovskite compounds were also synthesized. They present original properties compared to their parent oxides, such as an absorption in the visible region resulting in colored materials with potential applications in the fields of visible light-driven photocatalysis and pigments. Since recently, attention has been focused on their dielectric properties; high permittivity values ranging from some tens to several thousands have been reported on ceramics and thin films. The dielectric and ferroelectric behavior of perovskite oxynitrides is currently the subject of many studies; a relaxor-type ferroelectric behavior has been proposed, which would originate from an O/N order in the perovskite structure. The purpose of the present contribution is to present an overview of the dielectric and ferroelectric properties of oxynitride perovskite compounds. It will be illustrated by our own results on oxynitride perovskite films such as $LaTiO_2N$, $SrTaO_2N$ and $(Sr_{1-x}La_x)(Ta_{1-x}Ti_x)O_2N$ solid solution. This will include dielectric and ferroelectric measurements in macro and nano scales, in low and high frequencies and versus temperature.

10:45 AM

(PACRIM-S18-005-2017) Weak Ferroelectricity and τ_f Controlling Mechanism of $Ba_2Zn_{(1+x)}Si_2O_{(7+x)}$ ($-1 \leq x \leq 1$) Low-Permittivity Microwave Dielectric Ceramics (Invited)

W. Lu*[1]; Z. Zou[1]; Z. Chen[1]; W. Lei[1]

1. Huazhong University of Science and Technology, School of Optical and Electronic Information, China

$Ba_2Zn_{(1+x)}Si_2O_{(7+x)}$ ($-1 \leq x \leq 1$) ceramics were prepared using the conventional solid-state method at 1200 °C for 3 h in air. Along with $Ba_2Zn_{(1+x)}Si_2O_{(7+x)}$ ($x = 0$) with a monoclinic structure (C 2/c), the end-member compositions exhibiting single-phase β-$BaSiO_3$ with an orthorhombic structure ($P2_12_12_1$) for x = -1 and $BaZnSiO_4$ with a hexagonal structure ($P6_3$) for x = 1, possessed a coexistence of weak ferroelectricity and low-permittivity microwave dielectric properties. The strip-type domain structure and intrinsic saturated remnant polarization (~0.006 $\mu C/cm^2$ for x = -1, ~0.005 $\mu C/cm^2$ for x = 0, and ~0.009 $\mu C/cm^2$ for x = 1) were observed. Two ε_r anomaly peaks occured at lower temperature (145 °C for x = -1 and 124 °C for x = 1) and higher temperature (500 °C for x = -1 and 479 °C for x = 1). However, only a peak at higher temperature at approximately 510 °C appeared for x=0. The $BaZnSiO_4$ phase (τ_f = -181 ppm/°C) exhibited a higher-magnitude negative τ_f value than the $BaSiO_3$ phase (τ_f = -35.4 ppm/°C) due to the stronger ε_r anomaly peak at lower temperature of the former. The Zn^{2+} deficiency in $Ba_2ZnSi_2O_7$ composition (τ_f = -51.5 ppm/°C) could inhibit the presence of $BaZnSiO_4$ phase and improve the τ_f value, whereas excessive Zn^{2+} cations prompted the formation of the $BaZnSiO_4$ phase to deteriorate significantly the τ_f value.

11:10 AM

(PACRIM-S18-006-2017) Dielectric Properties of Nano Size Magnesium Aluminum Silicates and Titanates Prepared by Soft Chemistry

C. Ozturk*[1]; E. Kondakci[1]; E. Lokcu[2]; A. Ozdemir[1]; N. Solak[1]

1. Istanbul Technical University, Metallurgical and Material Engineering, Turkey
2. Eskisehir Osmangazi University, Turkey

Nano-size Magnesium Aluminium Silicate and Titanate dielectrics have been prepared by a modified Pechini-type soft chemistry technique. For the comparison, conventional solid state ceramic sample preparation techniques were used. For particle size measurement of the calcined powder nano, sub-micron size particles SEM, XRD and ZetaSizer were used. Obtained powders were isostatically pressed (200-800 MPa) and heat treated at various temperatures. Dielectric properties were characterized by using impedance spectroscopy. As the temperature and pressure were increased an increment in relative density was observed resulting higher dielectric quality factors (low tangent loss) compared to conventional sample preparation techniques. Dielectric constant was affected not only by sample composition but also by grain size, relative density and oxygen stoichiometry. In order to control oxygen stoichiometry sintering atmosphere was changed and samples were quenched. Dielectric quality factors were improved by heat treatment under pure oxygen and air quenching. It was also determined that, by using the modified Pechini method, spinodal decomposition hindered which improves dielectric properties.

11:35 AM

(PACRIM-S18-007-2017) Ferroelectric New System of $Ba_4R_2Zr_4Nb_6O_{30}$ (R=La, Nd, Sm) with Filled Tungsten Bronze Structure

W. Feng*[1]; X. Zhu[1]; X. Liu[1]; X. Chen[1]

1. Zhejiang University, Materials Science and Engineering, China

It has been a very important issue to search Pb-free ferroelectric new materials because of the increasing environmental concerns, and the tungsten bronze family might provide the great potential for this challenge due to the various possibility of structural tailoring. In the present work, $Ba_4R_2Zr_4Nb_6O_{30}$ (R=La, Nd, Sm) ceramics with filled tungsten bronze structure have been prepared by conventional solid-state reaction, and their dielectric and ferroelectric characteristics are investigated together with the phase transitions and domain structures. $Ba_4Nd_2Zr_4Nb_6O_{30}$ and $Ba_4Sm_2Zr_4Nb_6O_{30}$ are determined as the normal ferroelectric dominated by the commensurate structural modulation, while $Ba_4La_2Zr_4Nb_6O_{30}$ indicates the typical relaxor ferroelectric behavior, originating from the incommensurate modulation. With decreasing temperature, a first order ferroelectric transition is observed followed by a low temperature dielectric relaxation in $Ba_4Nd_2Zr_4Nb_6O_{30}$ and $Ba_4Sm_2Zr_4Nb_6O_{30}$, while one diffuse dielectric peak with strong frequency dispersion is observed for $Ba_4La_2Zr_4Nb_6O_{30}$. Only micro polar regions are detected in $Ba_4La_2Zr_4Nb_6O_{30}$, and both micro polar region and macro-domains are observed in $Ba_4Nd_2Zr_4Nb_6O_{30}$ and $Ba_4Sm_2Zr_4Nb_6O_{30}$. The present new systems are expected as the promising new candidates as Pb-free ferroelectric materials.

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

Scintillator I

Room: Kohala 1
Session Chair: Lynn Boatner, Oak Ridge National Lab

8:30 AM

(PACRIM-S20-041-2017) Large Format Li Co-doped NaI:Tl (NaIL$^{\text{TM}}$) Scintillation Detector for Gamma-Ray and Neutron Dual Detection (Invited)

K. Yang*[1]; P. Menge[1]; V. Ouspenski[2]

1. Saint-Gobain Crystals, USA
2. Saint-Gobain Recherche, France

Li co-doped NaI:Tl (NaIL$^{\text{TM}}$) is a potentially game-changing scintillation material for gamma-ray and neutron dual detection. Li co-doping introduces efficient thermal neutron detection to one of the most well-established gamma-ray scintillators while retaining the favorable scintillation properties of standard NaI:Tl. NaIL exhibits excellent neutron-gamma pulse shape discrimination (PSD) capability with PSD figure of merit between 2 and 4. Simulations show that NaIL detectors with only 1 - 3% of enriched ^{6}Li doping can outperform many existing neutron detection solutions such as standard He-3 tubes or CLYC scintillator in terms of neutron detection efficiencies. NaIL will be the first spectral gamma-neutron dual mode detector available in large formats. Saint-Gobain Crystals is actively working on industrialization of this material. Performance of large format (> 500 cm^3) NaIL prototype detectors will be reported.

9:00 AM

(PACRIM-S20-042-2017) Recent Advanced Scintillation Crystals for Gamma-ray and Neutron Detection (Invited)

R. Hawrami*[1]; E. Ariesanti[1]; L. Soundara-Pandian[1]; J. Glodo[1]; K. S. Shah[1]

1. Radiation Monitoring Devices, Scintillation Detection, USA

Materials for efficient gamma-ray and/or neutron detection are currently in high demand for radiation detection and imaging. In cases where simultaneous gamma-ray and neutron detection is required, frequently a combination of two detectors, each registering neutrons or gamma-rays separately, is used. During the last 10 years, a number of scintillators from the elpasolite crystal family that provide simultaneous detection of both types of radiation were investigated. Many of these were investigated at RMD and two of them have been fully developed as commercial products: Ce-doped CLYC and CLLBC. Currently high quality crystals with sizes up to 3"×3" are available. We will give a short overview of this work. Recently, RMD's focused on improving the qualities and properties of alkali halides, alkaline earth halides, and thallium alkaline halides. Moreover continuous development efforts of new compositions has also resulted in two promising materials: Ce-doped Tl-based elpasolite Tl_2LiYCl_6 and Tl_2LaBr_5, which will be discussed in this presentation. Ce-doped TLYC emits at around 435 nm, it has energy resolution better than 4% at 662 keV, light yield close to 30k ph/MeV, and decay times of 57 ns, 405 ns, and 1170 ns for gamma-rays. Since, it contains Li, it detect neutrons. Similarly to CLYC, TLYC also has capability to differentiate neutrons from gammas based on the pulse shapes with Figure-of-Merit of 2.

9:30 AM

(PACRIM-S20-043-2017) Transparent Ceramic Scintillators (Invited)

N. Cherepy*[1]; Z. M. Seeley[1]; S. A. Payne[1]; P. Beck[2]; E. Swanberg[2]; H. Steven[2]; D. Schneberk[2]; G. Stone[2]; B. Wihl[2]; S. Fisher[2]; P. Thelin[2]; T. Stefanik[3]; J. Kindem[4]

1. Lawrence Livermore National Lab, Chemistry and Materials Science, USA
2. Lawrence Livermore National Lab, USA
3. Nanocerox, USA
4. Cokiya, USA

Transparent ceramics formed from garnet and sesquioxide structures are under development for gamma spectroscopy detectors, x-ray imaging screens, solid state lighting, and laser gain media. For lens-coupled radiographic imaging, thin transparent scintillators without optical scatter are required. For gamma spectroscopy, intra-band gap trap state distribution is critical to achieve light yield proportionality, to modify the pulse duration and afterglow. For radiography, the transparent ceramic bixbyite scintillator, (Gd,Lu,Eu)2O3, or "GLO," offers excellent x-ray stopping, due to its Zeff = 68 and density of 9.1 g/cm3. High transparency is achieved by minimizing the formation of secondary phases by adding Gd to the Lu2O3 structure. For gamma spectroscopy, we have demonstrated 5 in3 Ce-doped Gd garnet transparent ceramics, by employing intersubstitutional ions to promote phase stabilization. When pixelated, we obtain R(662 keV) = 3.0%, for GYGAG(Ce) with silicon photodiode readout. This work was performed under the auspices of the U.S. DOE by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344, and has been supported by the US Department of Homeland Security, Domestic Nuclear Detection Office, under competitively awarded IAA HSHQDC-12-X-00149 and by the US DOE NNSA, Enhanced Surveillance Program and the Office of Nonproliferation Research and Development (NA-22) under Contract No. DE-AC03-76SF00098.

10:15 AM

(PACRIM-S20-044-2017) Cesium Hafnium Halide Ceramic Scintillators (Invited)

A. Burger*[1]; B. Goodwin[1]; E. Rowe[1]; M. Groza[1]; A. Husaker[1]; V. Buliga[1]; I. Jones[2]; Z. M. Seeley[2]; P. Beck[2]; N. Cherepy[2]; S. A. Payne[2]

1. Fisk University, USA
2. Lawrence Livermore National Lab, USA

Luminescent lanthanide-containing oxide transparent ceramics have been the subject of numerous scientific studies for applications in lasers, scintillators, and phosphors. Optical ceramics offer the possibility of increasing size while improving the mechanical properties over single crystals. In this study, we introduce a new class of optical ceramics based on halide materials for scintillator applications with potential to surpass the performance of other ceramic scintillators while lowering production costs. Halides such as $LaBr_3$ (hexagonal structure) and SrI_2 (orthorhombic structure) doped with rare earth ions (Ce^{3+} and Eu^{2+}) are well known to produce ultra-bright single crystal scintillators exhibiting light yields of 60,000 to 115,000 ph/MeV, respectively [Cherepy 2009]. Unfortunately, both of these materials are hygroscopic and exhibit birefringence that leads to optical scatter in polycrystalline form. These disadvantages are potentially eliminated through the use of undoped Cs_2HfX_6 (X= Cl, Br), belonging to the cubic K_2PtCl_6 structure which is non-hygroscopic, has a high Z_{eff} number of 58, and light yields of up to 54,000 ph/MeV and low nonproportionality have been measured for single crystals [Burger 2015]. In this study we will present fabrication methods for highly transparent samples of ceramic Cs_2HfCl_6 and $Cs_2HfCl_4Br_2$ and describe their scintillation properties.

10:45 AM

(PACRIM-S20-045-2017) Development of Novel Crystal Growth method for Halide Scintillator Single Crystals (Invited)

Y. Yokota*[1]

1. Tohoku University, New Industry Creation Hatchery Center (NICHe), Japan

Chloride, Bromide and Iodide (Halide) materials have been investigated as a next-generation scintillator for various radiation detectors due to the high light yield and energy resolution originated from the small band-gap. However, most of halide materials have strong hygroscopicity and it is difficult to grow high-quality single crystals by conventional growth methods. Generally, the Vertical Bridgman (VB) method using a quartz ampoule has been used for growths of halide single crystals. On the other hand, we have developed various oxide and fluoride scintillator single crystals using the micro-pulling-down (m-PD) method. Growth rate of the m-PD method is faster than the conventional growth methods. Therefore, we developed the Halide-m-PD (H-m-PD) method with a removable chamber for material researches of halide single crystals. Single crystals of halide materials such as $CeCl_3$, Ce:$LaBr_3$, Eu:SrI_2 and $CeBr_3$ could be grown by the H-m-PD method. In addition, we developed the Halide-VB (H-VB) method with the removable chamber to grow bulk single crystals of halide materials. The H-VB method is based on the H-m-PD furnace and the high-frequency induction heating. 1~2 inch Eu:SrI_2 bulk single crystals with high scintillation properties could be grown by the H-VB method.

11:15 AM

(PACRIM-S20-046-2017) Transient absorption spectroscopy of scintillaotrs (Invited)

M. Koshimizu*[1]; S. Yamashita[2]; Y. Muroya[3]; H. Yamamoto[3]; T. Yanagida[4]; Y. Fujimoto[1]; K. Asai[1]

1. Tohoku University, Department of Applied Chemistry, Japan
2. University of Tokyo, Department of Nuclear Engineering, Japan
3. Osaka University, The Institute of Industrial and Scientific Research, Japan
4. Nara Institute of Science and Technology, Japan

Scintillators are generally comprised of insulator hosts and doped impurities as luminescence centers. In order to design scintillation materials with desired properties, it is necessary to reveal the energy transfer processes from the host to luminescence centers. Thus far, little study has been performed on the energy transfer processes, and many researchers have been using various energy transfer models which are tentative and do not have experimental basis. In this study, we analyzed experimentally the energy transfer processes by measuring transient absorption after irradiations of pulsed electron beams. The investigated samples include commercial scintillators, Ce-doped Gd_2SiO_5 (GSO). In the transient absorption spectra of Ce:GSO just after the irradiation of the pulsed electron beam, a broad band is observed at 700 nm. This broad band is also observed for the undoped GSO. An additional band is observed at 450 nm for GSO doped with Ce at 1.5 mol%. These bands can be attributed to excited states absorption in the host. In the temporal profiles of transient absorption at different wavelengths in the picosecond time scale, a fast decay component in several hundreds of picoseconds is observed. Because a rise of the same time scale is not observed in the scintillation temporal profile, the decay in the transient absorption is attributed to non-radiative decay of excited states.

PACRIM Symposium 22: Direct Thermal to Electrical Energy Conversion Materials and Applications

Theories and New Concepts

Room: Queen’s 6
Session Chairs: Michitaka Ohtaki, Kyushu University; Jong-Soo Rhyee, Kyung Hee University

8:30 AM

(PACRIM-S22-001-2017) Dynamics of entropy, charge and energy in thermoelectric materials and devices (Invited)

A. Feldhoff*[1]

1. Leibniz University Hannover, Institute of Physical Chemistry and Electrochemistry, Germany

When entropy is considered as basic substance-like quantity in equal rank to electric charge and energy, an easily interpretable transport equation can be derived, which gives the benefit of a clear view on the energy conversion processes taking place in thermoelectric materials and devices. A thermoelectric material tensor is obtained, which is only composed of the Seebeck coefficient, the isothermal electrical conductivity, and the electrically open-circuited entropy conductivity. The thermoelectric material tensor allows describe the magnitude of flux densities of entropy and electric charge, if the thermoelectric material is placed in gradients of the respective thermodynamic potentials (i.e. the absolute temperature and the electrochemical potential). The operational principle of devices, which result from the proper connection of different materials, can be easily understood. The particular case of a thermoelectric generator is discussed in the light of optimizing it for high efficiency energy conversion and/or electric power output. Demands on the thermoelectric materials are formulated and discussed on examples of in-house developed ceramic-based devices. Theoretical guidance is given to the material scientist as well as the device maker.

9:00 AM

(PACRIM-S22-002-2017) Computational Design of Nanostructured Thermoelectrics (Invited)

C. Wolverton*[1]

1. Northwestern University, Materials Science and Eng., USA

Creating nanostructures within alloyed bulk thermoelectric materials can greatly decrease the lattice thermal conductivity of the material and thereby increase the thermoelectric efficiency of these materials. However, the rational design of thermoelectric alloys with even larger figures of merit will require a quantitative knowledge of the electronic and thermal properties and phase stability of nanostructured semiconductor materials. Here, we show how first-principles based calculations can reveal the intricate but tractable relationships between properties for optimization of thermoelectric performance. The integrated optimization includes a multipronged strategy: 1) significant reduction of the lattice thermal conductivity with multi-scale hierarchical architecturing, 2) large enhancement of Seebeck coefficients with intra-matrix electronic band convergence engineering, and 3) control of the carrier mobility with band alignment between host and second phases. These techniques can simultaneously enhance the power factor and reduce the lattice thermal conductivity, thereby leading to high efficiency thermoelectric materials.

9:30 AM

(PACRIM-S22-003-2017) Chiral Materials and Thermoelectrics (Invited)

Q. Li*[1]

1. Brookhaven National Laboratory, USA

The recent discovery of chiral materials, such as graphene, topological insulators, and Dirac/Weyl semimetals, started an ongoing revolution in key areas of Physics and Materials Science. The new materials hold promise of transmitting and processing information and energy in new ways. The powerful notion of chirality, originally discovered in high-energy physics, underpins a wide palette of new and useful behaviors in chiral materials. Many of the chiral materials originate from the thermoelectric compounds, such as Bi_2Se_3, PbTe, PbSe, SnSe, SnTe, and $ZrTe_5$ having small band gaps. Some of their electronic structures display band inversion. This band inversion was calculated in 1960s. Recently, the importance of the topology of band inversion gets much attention in the study of topological phases of matter, that can lead to new quantum phenomena, for example the chiral magnetic effect in condensed matters. I will present our studies on the transport properties of chiral materials, with a view on thermoelectric applications.

Tellurides and Silicides

Room: Queen's 6
Session Chairs: Armin Feldhoff, Leibniz University Hannover;
Qiang Li, Brookhaven National Laboratory

10:15 AM

(PACRIM-S22-004-2017) Nano precipitation and interface effect in thermoelectric bulk composites (Invited)

J. Rhyee*[1]

1. Kyung Hee University, Dept. of Applied Physics, Republic of Korea

Thermoelectric bulk composites are known as an effective way to reduce lattice thermal conductivity by grain boundary phonon scattering. On the other hand, the grain boundary between distinct different phases deteriorates the electrical transport as well. However, in some cases, we observed the enhancement of electrical conductivities in composites rather than those of individual compounds. In addition, the extrinsic mixing of n-type Ag_2Te in p-type $Bi_{0.5}Sb_{1.5}Te_3$, Sb_2Te_3, and PbTe matrix gives rise to the enhancement of thermoelectric performance or significant reduction of lattice thermal conductivity. We argue that the abnormally small lattice thermal conductivity in some extrinsic phase mixing[5,6] may imply that the theoretical calculation of Lorenz number in bulk composite has been over estimated. Finally, we present the significant enhancement of thermoelectric performance in PbTe/PbSe/PbS bulk composites (ZT = 2.3 at 800 K). The exceptionally high ZT come from the phonon scattering by PbS nano precipitation as well as the enhancement of power factor due to band convergence by PbSe doping. Here we discuss the abnormal electronic and thermal transport properties in various thermoelectric bulk composites with $Bi_{0.5}Sb_{1.5}Te_3$, Sb_2Te_3, and PbTe matrix.

10:35 AM

(PACRIM-S22-005-2017) Free-electron Creation at 60º Twin Boundary in Bi_2Te_3 (Invited)

S. Baek*[1]; J. Kim[1]

1. Korea Institute of Science and Technology, Center for Electronic Materials, Republic of Korea

Interfaces, such as grain boundaries in a solid material, are excellent regions to explore novel properties that emerge as the result of local symmetry-breaking.. For instance, in the interface of a layered-chalcogenide material, potential reconfiguration of the atoms at the boundaries can lead to significant modification of the electronic properties due to their complex atomic bonding structure. Here, we report the experimental observation of the electron source at 60º twin boundaries in $Bi_2Te_{3,}$ a representative of layered-chalcogenide materials. First-principles calculation reveals that modification of interatomic distance at the 60º twin boundary to accommodate structural misfits can alter the electronic structure of $Bi_2Te_{3.}$ The change in the electronic structure generates occupied states within the original bandgap in a favorable condition to create carriers and enlarges the density-of-state near the conduction band minimum. The present work provides insight about various transport behaviors of thermoelectric and topological insulators.

10:55 AM

(PACRIM-S22-006-2017) Expanding the versatility of thermoelectric materials by the introduction of molecular-solders (Invited)

J. Son*[1]; S. Jo[1]; F. Kim[1]

1. Ulsan National Institute of Science and Technology, School of Materials Science and Engineering, Republic of Korea

Here, we propose a new strategy for the enhancement of thermoelectric properties of materials as well as the processability by the introduction of nano- and molecular-solders. These solders easily fill up the voids and interfaces between TE particles and form crystalline phases to interconnect TE particles upon heat treatment with no external pressure, which led to huge densification and substantial growth of TE grains. The chemical design of solders allowed for the selective enhancement or reduction of the majority carrier concentration near the grain boundaries, and thus resulted in doped or de-doped inter-faces in granular BiSbTe material. Furthermore, the energy filtering effect could be realized by the formation of potential well at interfaces. Finally, the low temperature sintering properties enabled us to design shapes and dimensions of TE materials and devices with high performance via a facile and cost-effective TE painting process using a brush directly on to any-shaped surfaces or 3D printing process. This new process demonstrates the versatility of thermoelectric materials in terms of materials inherent properties as well as processability for the power generation on various-shaped heat sources.

11:15 AM

(PACRIM-S22-007-2017) Thermoelectric properties of lightly-substituted melt grown higher manganese silicides (Invited)

Y. Miyazaki*[1]; H. Hamada[1]; H. Nagai[1]; M. Sato[1]; K. Hayashi[1]; K. Yubuta[2]

1. Tohoku University, Department of Applied Physics, Japan
2. IMR Tohoku University, Japan

We have prepared solid solutions of $(Mn_{1-x}M_x)Si_\gamma$ with M = Cr, V, Fe and Co, wherein the $[Mn_{1-x}M_x]$ and [Si] subsystems have an irrational c-axis ratio $\gamma = c_{Mn}/c_{Si} \sim 1.7$. Due to the irrational nature, the valence electron counts, VEC value, of the parent compound is slightly less than 14, responsible to realise good p-type performance. The VEC value of the V-solid solution is nominally represented as $7(1-x) + 5x + 4\gamma$. From Vegard's rule, the solubility limit of each M was determined to be x = 0.05 to 0.40. As the atomic radius of V, $r_V = 1.321$ Å, is appreciably larger than that of Mn, $r_{Mn} = 1.240$ Å, the γ term effectively reduces VEC and the x = 0.02 samples exhibit much higher electrical conductivity while maintaining large positive Seebeck coefficient. As a result, the thermoelectric power factor of TE = 2.4 mW/K^2m at 900 K has been achieved. This work is based on results obtained from a project commissioned by New Energy and Industrial Technology Development Organization (NEDO), Japan.

11:45 AM

(PACRIM-S22-008-2017) Crystal structure and thermoelectric properties of partially substituted melt-grown higher manganese silicides

H. Nagai*[1]; H. Hamada[1]; K. Hayashi[1]; Y. Miyazaki[1]

1. Tohoku University, Japan

Higher manganese silicide, $MnSi_\gamma$, has attracted great interest as a potential candidate for thermoelectric (TE) materials owing to the natural abundance of their constituents, low toxicity, and the reasonable chemical stability at a high temperature. We have reported melt-grown V-substituted $MnSi_\gamma$ samples exhibited higher electrical conductivity compared with that of V-free $MnSi_\gamma$ due to an increase in carrier concentration and the dissipation of layered precipitates. However, ZT of V-substituted $MnSi_\gamma$ was limited to ~0.6 owing to the high thermal conductivity of ~3 W/mK. In this study, further substitution for Mn site in melt-grown V-substituted $MnSi_\gamma$ was performed to reduce the high thermal conductivity. The substituted samples were prepared by arc melting method. The obtained alloys were pulverized and remelted in an evacuated quartz tube at 1473 K for 8 hours, and gradually cooled down to room temperature for 124 hours. As a result, the thermal conductivity at room temperature greatly decreased, for example, from 3.1 W/mK for $(Mn_{0.98}V_{0.02})Si_{1.74}$ to 1.8 W/mK for $(Mn_{0.90}V_{0.02}Ru_{0.08})Si_{1.74}$. The results presented here are based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

PACRIM Symposium 26: Advances in Materials and Technology for Perovskite and Next Generation Solar Cells

Advances in Materials and Technologies for Perovskite-based Solar Cells II

Room: King's 1

Session Chairs: Qiquan Qiao, South Dakota State University

8:30 AM

(PACRIM-S26-009-2017) Ternary solvent for the $CH_3NH_3PbI_3$ perovskite film with uniform domain size (Invited)

K. Kim*[1]

1. Ewha Womans University, Republic of Korea

A ternary solvent system consisting of dimethyl sulfoxide (DMSO), γ-butyrolactone (GBL) and N-Methyl-2-pyrrolidone (NMP) to improve the uniformity of $CH_3NH_3PbI_3$ ($MAPbI_3$) perovskite domains have been developed. Compared to $MAPbI_3$ perovskite film prepared by the binary solvent consisting of DMSO and GBL, the surface roughness and uniformity of the $MAPbI_3$ film is greatly improved by using the ternary solvent system. The thermogravimetric analysis reveals that the NMP-PbI_2-MAI intermediate, DMSO-PbI_2-MAI intermediate and $MAPbI_3$ crystals are coexisted in the as cast $MAPbI_3$ films. Furthermore, it is found that the thermal stability of intermediate phases and the solvent evaporation rate are critical for the nucleation of the perovskite crystals during the thermal annealing treatment. The thermally stable intermediates prepared with the ternary solvent converted to $MAPbI_3$ film with a highly uniform and smooth surface. The film forms intimate contact with charge transporting layer when the layer is applied as a photoactive layer in the solar cell. As a result, the power conversion efficiency of ternary solvent processed solar cells is enhanced by 38.2% compared to that of binary solvent processed one. Furthermore, the stability of the ternary processed perovskite solar cells are greatly improved, as well.

9:00 AM

(PACRIM-S26-010-2017) Nanoscale study of Perovskite solar cells for efficient charge transport (Invited)

Q. Qiao*[1]

1. South Dakota State University, USA

We report effects of temperature, humidity and water on the grain boundary potential and charge transport within the grains of pervoskite films prepared by sequential deposited technique. Grain boundary potential of perovskite film exhibited variation in electronic properties with change in humidity level, temperature and adding water concentration in methyl ammonium iodide solution for the preparation of perovskite film. X-ray diffraction (XRD) indicates the formation of PbI_2 phase in perovskite film with increasing temperature, humidity and adding larger quantity of water in methyl ammonium iodide solution. It is found that optimum amount of lead iodide helps for the passivation of perovskite film. Spatial mapping of surface potential in the perovskite film exhibits higher positive potential at grain boundaries compared to the surface of the grains. Back recombination barrier between TiO_2- perovskite increases to 378 meV for perovskite film annealed at 100 C for 15 min. Grain boundary potential barrier were found to increase from ~35 meV to 80 meV for perovskite film exposed to 75% RH level compared to perovskite film kept inside glove box. Optimum amount of water which increases the solar cell performance by increasing the crystallinity of perovskite film was found to be 5% by volume of IPA.

9:30 AM

(PACRIM-S26-011-2017) Exploitation of materials and process for facilitating commercialization of perovskite solar cells (Invited)

H. Jung*[1]

1. Sungkyunkwan University, School of Advanced Materials Science and Engineering, Republic of Korea

All solid-state solar cells based on organometal trihalide perovskite absorbers have already achieved distinguished power conversion efficiency (PCE) to over 22% and further improvements are expected up to 25%. These novel organometal halide perovskite absorbers which possess exceptionally strong and broad light absorption enable to approach the performances of the best thin film technologies. To commercialize these great solar cells, there are many bottlenecks such as long term stability, large scale fabrication process, and environmental issues. In this presentation, we introduce our recent efforts to facilitate commercialization of perovskite solar cells. For examples, we introduce a recycling technology of perovskite solar cells, which will facilitate the commercialization as well as solve the environmental issues of perovskite solar cells. Moreover, Br-concentration gradient perovskite materials were realized by using HBr treatment of perovskite materials. The enhancement in hole extraction was verified from measurement of photoluminescence spectroscopy. Also, we are going to discuss about stability issue of perovskite materials regarding charge generation and extraction.

10:15 AM

(PACRIM-S26-012-2017) Inorganic Charge Transport Layers Grown by Atomic Layer Deposition for Water-Resistant Perovskite Solar Cells and Perovskite-Perovskite Tandem devices (Invited)

H. Shin*[1]; S. Seo[1]; C. Bae[1]; S. Jeong[1]

1. SungKyunKwan University, Department of Energy Science, Republic of Korea

Halide perovskite solar cells have recently attracted huge attention because of their dramatic rise in power conversion efficiency within few years. However, high PCEs have not been guaranteed for the long-term period of the environmental stability. Here, we report highly efficient water-resistant perovskite solar cells that adapts uniform and dense inorganic charge transport layer (NiO and TiO_2 and ZnO) grown by atomic layer deposition (ALD) at relatively lower temperature. Ultra-thin NiO films with the thickness of few times of Debye length (1 ~ 2 nm for NiO) show enough conductivities achieved by overlapping space charge regions, which finally exhibited a highest PCE of 17.40 %. Furthermore, highly dense inorganic electron transport layer (ETL) has been deposited onto perovskite by ALD at low temperature (100 ºC). The unencapsulated devices shows excellent water-resistant properties compared to devices without ETL grown by ALD. We also demonstrated a two-terminal perovskite-perovskite tandem device with matched bandgaps. Inorganic ETL grown by ALD successfully enabled an additional infrared absorbing perovskite layer to be coated onto the pre-deposited wider bandgap perovskite film. Finally, newly developed tandem were fabricated and their photovoltaic performance and environmental stabilities were characterized.

10:45 AM

(PACRIM-S26-013-2017) Surface Modification and Structure Design of Perovskite Solar Cells (Invited)

M. Li*[1]

1. North China Electric Power Univeristy, School of Renewable Energy, China

Surface modification is a practical approach to reduce carrier recombination at the surface and subsurface of the perovskite films caused by the trap states and the intrinsic nature of polycrystalline organometallic perovskites. Herein, an F4TCNQ interfacial layer is introduced, which possess dual function, i.e., surface passivation and interfacial doping of the perovskite. The structure of the perovskite solar cells is another critical factor influencing the device performance of perovskite solar cells. We present a novel structure for highly-efficient and stable PSCs, i.e., the embedded structure, which utilizes TiO_2 nanoparticles embedded perovskite film as the absorption layer. The presence of TiO_2 nanoparticles in perovskite film could improve the electron extraction, and promote the formation of a compact perovskite layer with large grains. The performance of the PSCs is significantly improved with the efficiency increasing from 16.6% for planar structure to 19.2% for the embedded structure.

PACRIM Symposium 30: Glasses and Ceramics for Nuclear and Hazardous Waste Treatment

Waste Glass Structure

Room: Kona 1
Session Chairs: Joseph Ryan, Pacific Northwest National Lab; Russell Hand, University of Sheffield

8:30 AM

(PACRIM-S30-015-2017) Determination of Solubility Constants of Saponite at Elevated Temperatures in High Ionic Strength Solutions: Applications to Nuclear Waste Isolation

Y. Xiong*[1]

1. Sandia National Laboratories, USA

Saponite [general formula, $(Ca_{0.5}, Na)_{0.3}(Mg, Fe^{II})_3(Si, Al)_4O_{10}(OH)_2$•$4H_2O$; Mg-end member, $Mg_4Al_2Si_2O_{10}(OH)_2$•$4H_2O$] is an important phase that is formed when glass is corroded in $MgCl_2$ solutions. Consequently, saponite governs the chemical compositions, including hydrogen ion concentrations, of the resulting solutions. However, its thermodynamic properties are not well-defined. The lack of accurate knowledge of its thermodynamic properties makes it difficult to make reliable and accurate predictions for the evolution of chemical compositions of the solutions interacting with glass. Hence, the accurate knowledge of its thermodynamic properties is the prerequisite for modeling the glass corrosion in $MgCl_2$-dominated solutions in salt formations. In this presentation, we report our investigations of the solubility constants of Mg-end member saponite in the temperature range from 30ºC to 90ºC at an increment of 15ºC. This research is funded by the Salt R&D programs administered by the Office of Nuclear Energy of the U.S. Department of Energy. Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND2016-11500A

8:45 AM

(PACRIM-S30-016-2017) Thermodynamic Assessment of Nepheline Formation in Nuclear Waste Glass

S. A. Utlak*[1]; T. M. Besmann[1]; C. Henager[2]; S. Hu[2]; Y. Li[2]

1. University of South Carolina, Nuclear Engineering, USA
2. Pacific Northwest National Lab, Nuclear Sciences Division, EED, USA

Vitrified high-level radioactive waste that contains high concentrations of Na_2O and Al_2O_3, such as the waste stored at the Hanford site, can cause nepheline to precipitate in the glass upon cooling in the canisters. Nepheline removes oxides such as Al_2O_3 and SiO_2 from the host glass, which can reduce its chemical durability. Uncertainty in the extent of precipitated nepheline necessitates operating at an enhanced waste loading margin, which increases operational costs by extending the vitrification mission as well as increasing waste storage requirements. A critical evaluation of the Na_2O-Al_2O_3-SiO_2 system that forms nepheline was conducted utilizing the compound energy formalism and ionic liquid models to represent the solid solution and liquid phases, respectively. These were optimized with experimental data and used to extrapolate phase boundaries into regions of temperature and composition where measurements are unavailable. The intent is to import the determined Gibbs energies into a phase field model to more accurately predict nepheline phase formation and morphology evolution in waste glasses. We gratefully acknowledge the financial support of the U.S. Department of Energy's Waste Treatment and Immobilization Plant Federal Project Office under the direction of Dr. Albert A. Kruger.

9:00 AM

(PACRIM-S30-017-2017) Role of iron in the crystallization of nepheline-based aluminosilicates

M. Ahmadzadeh*[1]; A. Goel[2]; J. McCloy[1]

1. Washington State University, Mechanical and Materials Engineering, USA
2. Rutgers University, USA

Aluminosilicates are not only among the dominant constituents of the Earth's crust but also of widespread application in the glass and ceramic industries. Vitrified high level nuclear wastes (HLW) are susceptible to nepheline ($NaAlSiO_4$) crystallization which reduces the chemical durability of the final waste form. Crystallization of such glasses is a function of the composition of starting glass-forming melt. Iron plays an important role in nepheline crystallization due to its significant concentration within the Hanford HLWs. We study the $NaAlSiO_4$–$NaFeSiO_4$ join to investigate the effects of iron on the crystallization and structural behavior of nepheline-based aluminosilicates. Fe promotes the crystallization of nepheline over its high temperature polymorph (carnegieite) when substituted for Al in low additions. However, nepheline crystallization is suppressed at higher Fe additions as high concentration of iron leads to formation of hematite (Fe_2O_3) crystals. The details of non-isothermal crystallization were further studied using differential scanning calorimetery (DSC) analysis. The glass transition temperature and crystallization temperature decrease with Fe-Al substitution. Electron microprobe analysis shows that Fe incorporates significantly into the nepheline structure and substitutes for Al up to Fe/Fe+Al=0.37. Fe redox state of the glasses is also discussed by utilizing UV-Vis experiments.

9:15 AM

(PACRIM-S30-018-2017) Effect of rare earths on the thermal stability and structure of silicate glasses

D. Caurant*[1]; O. Majerus[1]; T. Charpentier[2]; P. Loiseau[1]

1. Chimie Paristech CNRS, IRCP, France
2. CEA Saclay, NIMBE, France

Rare earths (RE) are widely used in optical glasses, they are also present at high concentration in nuclear waste glasses. Indeed, RE represent one of the most abundant family of fission products in the waste recovered after spent fuel reprocessing. They are also frequently used as actinide surrogates for laboratory tests. In this paper, we present results concerning the effect of introducing increasing RE oxide content on the thermal stability of simplified silicate glasses ($SiO_2.B_2O_3.Al_2O_3.Na_2O.CaO$, $SiO_2.B_2O_3$, $SiO_2.Al_2O_3.CaO$) derived from more complex compositions developed for nuclear waste immobilization either as glassy or glass-ceramic waste forms. Uncontrolled glass crystallization during melt cooling is considered as a drawback but controlled crystallization of durable phases able to incorporate radioactive elements such as actinides can be desired (glass-ceramics). We show that, depending on composition, RE may strongly affect glass thermal stability (i.e. glass crystallization tendency) either by promoting the crystallization of RE-rich phases such as apatite ($Ca_2RE_8(SiO_4)_6O_2$) and metaborate (REB_3O_6) or by limiting or even suppressing the crystallization of phases such as molybdates ($CaMoO_4$) or zirconolite ($CaZrTi_2O_7$). Structural results using a multi-spectroscopic approach (Raman, NMR, EXAFS, optical absorption) will be presented to explain the effect of RE on glass thermal stability.

9:30 AM

(PACRIM-S30-019-2017) The effect of Li addition on the crystallization behavior of Na aluminosilicate and borosilicate glasses: Comparisons of the local structure

J. Marcial*[2]; N. Washton[3]; A. Goel[5]; D. Watson[4]; S. W. Martin[4]; J. McCloy[1]

1. Washington State University, School of Mechanical and Materials Engineering, USA
2. Washington State University, Materials Science and Engineering Program, USA
3. Pacific Northwest National Lab, USA
4. Iowa State University, Materials Science and Engineering, USA
5. Rutgers University, Materials Science and Engineering, USA

This study seeks to understand the role of lithium in the crystallization behavior of sodium aluminosilicate and borosilicate glasses through modelling of the local structure of the glasses. For vitrification, lithium substitution for sodium can be performed to improve the thermal conductivity of the melt as means to improve the rate of feed-to-glass conversion. Small additions of lithium in nuclear waste glasses, however, have been found to have a significant effect on the phase makeup of the melt on cooling. We seek to hinder crystallization to effectively immobilize the hazardous compounds of nuclear waste. Our previous studies compared the crystallization behavior of feldspathoid-like sodium lithium alumino-borosilicate glasses. It was found that lithium-bearing glasses require over twice the addition of boron to frustrate crystallization. Mixed-alkali aluminosilicate feldspathoid glasses were found to always crystalize. Local structure measurements were performed, including ^{7}Li, ^{11}B, ^{23}Na, ^{27}Al, and ^{29}Si MAS NMR, Raman spectroscopy, and X-ray scattering. Large similarities were found in the network structure of Li and Na aluminosilicate and borosilicate glasses with minor differences in the avoidance of charge-compensated network formers. This behavior is believed to play a significant role in the crystallization behavior.

9:45 AM

(PACRIM-S30-020-2017) Impact of iron on crystallization behavior and magnetic properties of sodium aluminoborosilicate glasses

A. A. Deshkar*[1]; M. Ahmadzadeh[2]; A. Scrimshire[4]; E. Han[1]; P. A. Bingham[4]; D. P. Guillen[3]; J. McCloy[2]; A. Goel[1]

1. Rutgers University, Materials Science & Engineering, USA
2. Washington State University, School of Mechanical & Materials Engineering, USA
3. Idaho National Laboratory, Materials Science & Engineering, USA
4. Sheffield Hallam University, Materials & Engineering Research Institute, United Kingdom

It is imperative to study the fundamentals underpinning the effect of iron redox (Fe^{2+}/Fe^{3+}) on nucleation and crystallization in silicate glasses since iron oxides are critical components of sodium- and alumina-rich high-level radioactive waste liquids stored in steel tanks at the Hanford site in Washington. The current strategy to immobilize the sodium and alumina rich high level waste (HLW) is to convert it into borosilicate glass. However, increasing the waste loading in the glasses results in crystallization of nepheline ($NaAlSiO_4$) like aluminosilicate phases which are undesirable for the durability and long-term stability of the final waste form. This study reports the influence of iron content and redox on the crystallization behavior and magnetic properties of aluminoborosilicate-based model nuclear waste glasses. The impact of atmosphere (oxidizing, inert, or reducing) on iron redox and crystalline phase evolution in these glasses has been studied by differential scanning calorimetry, X-ray diffraction, extended X-ray absorption fine structure, Mössbauer spectroscopy and electron microscopy. The magnetic properties of glasses and resultant glass-ceramics have been studied with vibrating sample magnetometry. This is an ongoing area of research and an overview of results will be presented.

Geopolymer, Glass-Ceramic, and Composite Waste Forms I

Room: Kona 1
Session Chairs: Russell Hand, University of Sheffield; Joseph Ryan, Pacific Northwest National Lab

10:15 AM

(PACRIM-S30-021-2017) Glass-ceramic wasteforms for UK plutonium disposition produced by Hot Isostatic Pressing

N. C. Hyatt*[1]; S. Thornber[1]; M. C. Stennett[1]

1. The University of Sheffield, Materials Science & Engineering, United Kingdom

Glass-ceramic materials are proposed for the immobilization of plutonium wastes and stockpile material in the UK, in which the glass phase provides wasteform flexibility to accommodate impurities and variations in the waste feed composition. The plutonium partitions into the more durable ceramic phase, zirconolite ($CaZrTi_2O_7$). Zirconolite has excellent wasteform properties including durability and radiation tolerance, and readily accepts actinides and rare earths into its crystal structure. In this work, the formation of zirconolite is shown to depend sensitively on glass fraction and composition, such that an Al rich glass promotes a higher yield of zirconolite and minimize undesired accessory crystalline phases, such as sphene ($CaTiSiO_5$) and zircon ($ZrSiO_4$). The partitioning of CeO_2, within the glass-ceramic wasteform, as a PuO_2 surrogate, was studied using various charge compensation mechanisms, under an imposed Fe/FeO and Ni/NiO buffer. Analysis by SEM/EDX, XRD, and Ce L_3 edge XANES, demonstrated reduction of Ce(IV) to Ce(III) to favour incorporation of Ce within a perovskite accessory phase and the glass matrix. Ce partitioning in the zirconolite phase was maximized when retained as Ce(IV). These results demonstrate a feasible wasteform formulation for disposition of UK plutonium wastes and stockpile material.

10:30 AM

(PACRIM-S30-022-2017) Long-term chemical durability testing of glass ceramics

C. L. Crawford*[1]

1. Savannah River National Laboratory, USA

Glass ceramics are being considered for immobilizing the nuclear waste such as fission products, lanthanides and noble metals from used fuel reprocessing. Formulations of the glass ceramics consist of Al/B/Ca/Li/Na/Si oxide glass phases that incorporate Nd/Mo/Ce/Cs/Zr and other minor waste components. The glass ceramic matrices are fabricated at 1300°C and higher with controlled cooling to form powellite, oxyapatite and Ln-borosilicate crystalline phases that incorporate the waste components that are above the solubility limit in the glass phases. This work reports the long term > 1 year chemical durability static leach testing of glass ceramics formulated from a statistically designed multi-component matrix. The ASTM C1285 Product Consistency Test was used to test glass ceramics over 1, 4, 16 and 64 week intervals. Inter comparison of the glass ceramic matrices shows that 25 out of 29 tested have 7-day normalized release at 1 g/m^2 or less and four of the matrices are in the range of 2 to 5 g/m^2. Long-term leach data will be compared to similar testing using the Environmental Assessment (EA) benchmark glass. Microstructure analysis of the glass ceramic powders via scanning electron microscopy will also be presented.

10:45 AM

(PACRIM-S30-023-2017) Thermal Treatment of Plutonium Contaminated Materials

L. Boast*[1]; M. C. Stennett[1]; N. C. Hyatt[1]

1. University of Sheffield, MSE, United Kingdom

The projected UK plutonium contaminated material (PCM) waste volume is >30000 m^3 with 70% arising at Sellafield. The current baseline treatment is supercompaction with cement encapsulation. Thermal treatment, i.e. in-container or plasma vitrification has been identified as the main alternative waste treatment method. The research aims to provide the evidence necessary to support a major investment in the thermal treatment of plutonium contaminated materials. Laboratory scale experiments using PCM waste simulants (using Ce as a Pu surrogate) and glass forming additives have been performed in order to understand the reactions and processes of waste digestion and incorporation during thermal treatment. The research also aims to gain a greater understanding of the vitrified product stability with respect to generic ILW disposal concepts, through accelerated dissolution experiments. The potential effects of such a high pH (12.5), calcium rich cement-based environment on the dissolution behaviour of simulant ILW glasses have been studied using a 112 day, modified version of the product consistency test (PCT). Slag samples used in the construction of a bridge during the 18th century have also been studied, providing 250 year old analogue samples to investigate the long term effects of weathering conditions on the structure of the vitrified PCM waste samples. Characterisation studies have been performed on the historic samples.

11:00 AM

(PACRIM-S30-024-2017) Hot isostatic pressing of ion exchange materials, from the Fukushima and Sellafield sites, to produce ceramic wasteforms

N. C. Hyatt*[1]; L. J. Gardner[1]; P. Heath[1]; M. C. Stennett[1]; S. Thornber[1]; R. J. Hand[1]; C. L. Corkhill[1]

1. The University of Sheffield, Materials Science & Engineering, United Kingdom

In this presentation we demonstrate the conversion of several commercial and natural inorganic ion exchange materials, aplied on the Fukushima and Sellafield sites, into multiphase ceramic wasteforms, achieving a waste loading of 100 wt% and density in excess of 97% theoretical. High resolution thermogravimetric analysis coupled with mass spectroscopy was utilised to characterise the evolution of water and volatiles during the in-can bake out step, prior to the HIP cycle. This allowed optimisation of the bake out parameters (temperature, time and vacuum) to enable complete removal of water and volatiles, affording ceramic bodies with minimal residual porosity by hot isostatic pressing at 1250ºC for 4h in stainless steel cans. Characterisation of the ceramic wasteforms by SEM /EDX and X-ray diffraction revealed the nuclides of concern to be incorporated within well known natural mineral and synthetic phases, with Sr partitioning into the SrTiO$_3$ pervoskite phase and Co, Fe, Mn and Cr partitioning into a spinel phase. Dynamic alteration experiments revealed matrix dissolution rates of less than 10^{-4} g m^{-2} d^{-1} under forward rate conditions at 90 ºC.

11:15 AM

(PACRIM-S30-025-2017) Hot Isostatic Pressing of Spent Ion Exchange Materials from the Fukushima and Sellafield Sites

L. J. Gardner*[1]; C. L. Corkhill[1]; R. A. McCaig[1]; N. C. Hyatt[1]

1. The University of Sheffield, Materials Science and Engineering, United Kingdom

Hot Isostatic Pressing (HIPing) has been utilised to showcase conceptual wasteforms for ion exchange materials (IX) that are generated through the clean-up of nuclear facilities at Sellafield, UK and Fukushima, Japan. IX materials require conditioning to produce a passively safe wasteform as they pose several challenges: i) the granular IX materials are easily dispersible resulting in loss of containment; ii) they have very high dose rates from their selectivity for short lived radionuclides (e.g. Sr-90, Cs-137); iii) radiogenic self-heating; iv) hydrogen production as a result of radiolysis of entrained water. The conversion of inorganic IX materials into multiphase ceramic wasteforms at 100 wt. % waste loading and theoretical density in excess of 97 % has been optimised by variation of pressure (10-100 MPa), temperature (950-1250 °C) and duration (1-4 hrs). Characterisation these wasteforms by XRD and SEM/EDX revealed the incorporation of nuclides in well-known natural and synthetic mineral phases, whilst dissolution experiments revealed matrix dissolution rates of less than 10^{-4} g m^{-2} d^{-1} under forward rate conditions at 90 °C. Overall, HIPing of IX materials yields durable ceramic wasteforms, with waste volume reduction and minimal voidage/porosity.

11:30 AM

(PACRIM-S30-026-2017) Chemical behaviour of nuclear waste glass in presence of hardened OPC paste

K. Ferrand*[2]; S. Mercado[1]; K. Lemmens[2]; S. Liu[2]; A. Elia[2]; F. Angéli[3]

1. CRITT Matériaux, France
2. SCK-CEN, Belgium
3. CEA, France

Mock-up tests were performed with SON68 glass in the presence of hardened Ordinary Portland Cement (OPC) paste in relatively realistic geometric conditions, to determine the glass dissolution rate and the various alteration processes involved and to validate and extend the mechanistic glass dissolution model obtained from simpler parametric experiments. For this purpose, cells were filled with a layer of confined glass powder; either in direct contact with a plug of hardened OPC paste, or separated from it by a stainless steel filter, and saturated with synthetic cementitious water at pH 13.5. The set-up allowed monitoring the solution concentrations and pH as a function of time and space, to follow glass dissolution and diffusion of species. At the end of the tests, the cells were dismantled to study the different interfaces by SEM-EDX. The dissolution rates were lower than with glass and OPC powders in suspension, which were maintained high due to the pozzolanic reaction, and similar to those with confined glass powder without OPC because, due to the slow transport through the cement plug, only the first layer of portlandite is accessible for glass components. The sharp boundary between the alteration layer and the pristine glass might be explained by a dissolution/precipitation model. Geochemical modelling shows that the solution is saturated with tobermorite, foshagite, katoite and phillipsite-K.

11:45 AM

(PACRIM-S30-027-2017) Interactions between Simulant Vitrified Nuclear Wastes and Idealised Cement Leachates

C. Mann*[1]; C. L. Thorpe[1]; N. C. Hyatt[1]; J. Provis[1]; C. L. Corkhill[1]; E. M. Pierce[2]; J. R. Eskelsen[2]

1. University of Sheffiled, Material Science and Engineering, United Kingdom
2. Oak Ridge National Lab, Environmental Science Division, USA

Within the United Kingdom (UK), it is proposed that nuclear waste will be disposed of in a geological repository, utilising an engineered barrier system that will be optimised to physically and chemically impede the transport of radionuclides to the biosphere. Interaction of groundwater with the cementitious components of the facility will lead to the presence of high pH conditions within a repository. The effect of such cement leachates on the durability of vitrified wasteforms is not well understood. Here we present results from a glass durability study using simulated cement leachates to elucidate the mechanisms that govern glass corrosion under these complex geochemical conditions. The normalised mass loss and normalised leaching rate as a function of cement leachate composition was determined by effluent solution analysis. Additionally, we present characterisation results collected on alteration layers by conducting glancing-angle x-ray diffraction and electron microscopy measurements on monolith samples. Collectively, these data provide new insight into the mechanisms that govern glass dissolution in the complex geochemical conditions expected for vitrified UK waste if water breaches the engineered barrier system in a geological repository.

PACRIM Symposium 32: Nanostructured Bioceramics and Ceramics for Biomedical Applications

Nanostructured Bioceramics II

Room: Monarchy
Session Chairs: Dagmar Galuskova, A. Dubcek University of Trencin; Rizhi Wang, University of Victoria

8:30 AM

(PACRIM-S32-009-2017) Lanthanide-based Nanostructures as Potential Players in the Biomedical Field (Invited)

E. Hemmer*[1]

1. University of Ottawa, Chemistry and Biomolecular Sciences, Canada

Lanthanide-based nanostructures are well known for their outstanding optical properties. When doped in appropriate host materials, narrow optical absorption and emission bands as well as long lifetimes of the excited electronic states of the Ln^{3+} are obtained. Following a stepwise excitation with near-infrared (NIR) light, Ln^{3+}-doped nanostructures show upconversion emission spanning the range from UV to visible and NIR. In addition, NIR light of longer wavelengths (> 1000 nm) can be emitted when appropriate Ln^{3+} dopants are chosen, which opens a whole gamut of applications including the field of optical bioimaging and sensing. Fluorides, such as $NaGdF_4$, are commonly considered as suitable host materials and their preparation via the thermal decomposition process has been widely studied. Alternatively, oxides, such as Gd_2O_3 or Y_2O_3, have been suggested as host materials for Ln^{3+} ions resulting in upconverting and NIR emitting nanostructures. Ln^{3+}-doped oxides of various sizes and shapes (nanoparticles, nanorods) can for instance be obtained by precipitation or solvothermal approaches. Various synthetic strategies leading to upconverting and NIR emitting Ln^{3+}-doped nanostructures will be discussed, and the application of the resultant materials in optical (NIR) bioimaging and beyond will be presented.

9:00 AM

(PACRIM-S32-010-2017) Atomistic Simulations of the Initial Stages of the Sol-Gel Synthesis of Bioactive Glasses (Invited)

A. Côté[2]; A. Tilocca[2]; A. Cormack*[1]

1. Alfred University, USA
2. University College London, United Kingdom

Understanding polycondensation in aqueous solutions is of central importance for the development of more effective biomaterials by sol-gel approaches. In this presentation, the atomic-scale evolutions of a calcium-containing precursor solution corresponding to a typical sol-gel bioactive glass and of a corresponding Ca-free solution were compared using reactive molecular dynamics simulations. The simulations highlight a significantly faster rate of condensation in the presence of calcium, resulting in the formation of large and ramified silica clusters within 5 nanoseconds, which are absent in the Ca-free system. This different behavior is interpreted in terms of a Ca-induced nanosegregation in calcium-rich and silica-rich regions, which promotes the condensation reactions within the latter. By identifying a possible mechanism behind the limited incorporation of calcium in the silica nanoclusters formed in the early stages of the sol-gel process, it is anticipated that further studies will facilitate the engineering of enhanced initial calcium incorporation and thus produce sol-gel biomaterials with improved properties.

9:30 AM

(PACRIM-S32-011-2017) Calcium Phosphate Nanostructured Polymer Film as a New Platform for Drug Delivery (Invited)

R. Wang*[1]; T. Zhao[1]; S. Chen[1]

1. University of British Columbia, Canada

A challenge in studying drug loading, the subsequent release and even biological tests of orthopaedic biomaterials has been to establish a standard calcium phosphate substrate with well-controlled structure. Reports in the past have been device-specific with variations in both geometry and structure, which makes systematic studies difficult to conduct. In this study, we developed calcium phosphate nanostructures into the well-controlled pores of the track-etched polymer and ceramic membranes and used them as a platform for drug interaction and release studies. Using the double-diffusion method for calcium phosphate mineralization, we investigated the effect of pore size (from 60 nm to 1 micron), processing temperature and time on the structure and morphologies of the calcium phosphate minerals. The processed structures are then tested for loading efficiency and releasing profiles of bisphosphonates, a group of anti-osteoporosis drug.

10:15 AM

(PACRIM-S32-012-2017) Release and Biological Performance of Theranostics from Novel Tissue Engineering Scaffolds for Cancer Patients (Invited)

L. Guo[1]; M. Wang*[1]

1. The University of Hong Kong, Department of Mechanical Engineering, Hong Kong

For cancer patients, new tissue needs to be formed at the original tumor site after surgery. Scaffold-based tissue engineering can regenerate human body tissues. Cancer recurrence threatens lives and hence early detection and treatment of recurring cancer is vital. Theranostics are anticancer nanodevices providing diagnostic and therapeutic functions and Au-based nanoparticles (NPs) form excellent theranostics. In this study, novel nanofibrous scaffolds with embedded theranostic-containing microspheres for cancer patients were made via concurrent electrospinning and coaxial electrospray. Fibrous scaffolds were PLGA(75:25), and PLGA(50:50) microspheres encapsulating theranostics (Au@CS-FA NPs: highly branched folic acid-chitosan-capped gold) were electrosprayed. Results showed theranostics were contained in the hollow core of PLGA microspheres which were randomly distributed in fibrous scaffolds. After 21-day immersion in PBS in in vitro tests, PLGA shell of microspheres in scaffolds broke down and theranostics were released. Released theranostics could provide strong SERS signals for cancer detection. In vitro biological results showed released theranostics could target cancer cells with high-level folate-receptor expression (HeLa cells, not MCF-7 cells) and be internalized by these cells. Fluorescent imaging of HeLa cells with internalized theranostics was achieved.

10:45 AM

(PACRIM-S32-013-2017) 3D Biomimetic Nanostructured Bioceramics and their Biomineralization Activities (Invited)

T. Shokuhfar*[1]

1. University of Illinois at Chicago, Department of Bioengineering, USA

Future prospects for nanostructured bioceramics in medical applications appear to be game changing. In orthopedic applications, there is a significant need and demand for the development of a bone implant that is multifunctional and exhibits mechanical and surface properties comparable with those of natural, healthy bone. Particularly, implants with nanometer-sized surfaces that can act as drug reservoirs have been developed and studied as novel surface modification that promote tissue regeneration, anti-inflammatory and antimicrobial properties to prevent infection or decrease inflammation. We have shown that titania ceramic nanotubes are considered a suitable alternative route for the development of drug-eluting implants due to the fact that these nanostructures are not an added coating but rather are rooted in the implants, will not delaminate from the surface, and can be tailored to patients need. In addition, we have observed that such nanostructures can promote the nucleation and growth of Ca and P and enhance the biomineralization of bone. However, the underlying mechanism behind such enhanced biomineralization phenomena in not well understood. In order to shed light on such exciting phenomena, in situ scanning transmission electron microcopy (STEM) analysis technique is being used.

11:15 AM

(PACRIM-S32-014-2017) Corrosion and low temperature degradation of zirconia based dental ceramics

D. Galuskova*[1]; S. Mikusinec[1]; A. Nowicka[1]; D. Galusek[1]

1. A. Dubcek University of Trencin, Slovakia

ZrO_2 ceramics stabilized by the addition of yttrium oxide (Y_2O_3) is often used for dental replacements. The binary system Y_2O_3-ZrO_2 is also permitted by standards for surgical applications. A failure of dental implants due to formation of micro-cracks can occur as a consequence of (t → m) phase transformation in zirconia ceramics. It has been also reported that such dental ceramics become more vulnerable to low temperature degradation (LTD) and temperature cycling after exposure to acidic corrosive media. In such case the (t → m) phase transformation is triggered at the ceramic surface that impairs durability and lifetime of dental implants. The effect of long term exposure of commercial yttria stabilized zirconia (3Y-TZP) dental materials to acidic medium, and corrosion induced migration of yttria as a stabilizing element on its LTD, which results in transformation of the tetragonal ZrO_2 to monoclinic, was evaluated. Acidic corrosion of 3Y-TZP dental ceramics is associated with leaching of yttrium from zirconia ceramics, resulting in partial destabilization of tetragonal zirconia and measurable increase of the content of monoclinic phase at the surface.

11:30 AM

(PACRIM-S32-015-2017) Synthesis and Properties of Calcium Phosphosilicate-Organic Nanoparticles (Invited)

J. H. Adair*[1]; M. Kester[2]; G. Matters[3]; G. Clawson[3]; Z. Wilczynski[3]; C. M. Gigliotti[3]; X. Tang[3]; W. Loc[3]; S. Linton[3]; C. McGovern[3]

1. Pennsylvania State University, Materials Science & Engineering, USA
2. University of Virginia, Pharmacology, USA
3. Pennsylvania State University, USA

New therapies based upon nanoscale bioceramic platforms are transforming the treatment of human disease including cancer. Nanoparticles with encapsulated conventional chemotherapeutics and novel therapies are being developed that are changing the 60 year old treatment paradigm for cancer from ‘knocking down all rapidly dividing cells always with patients experiencing toxic side effects’ to ‘kill the cancer, do no harm to the patient.’ The material – biosystem selection criteria that make the drug encapsulated-calcium phosphosilicate nanoparticles (CPSNPs) a near ideal cancer treatment system for various cancer types demonstrate the efficacy of this novel approach. The nanoparticle synthesis including a laundering system that permits scale up of large volumes of the nanocolloids will be presented for the first time. The biophysical chemistry for CPSNP solubility and colloidal properties that produce thermodynamically stable colloids in physiological systems are presented. This presentation will also focus upon the encapsulation and delivery of imaging agents to provide early detection, a critical component of successful treatment, of several types of cancer for in vivo animal models. Moreover, one of the NIR imaging agents produces a photo-immuno nanotherapeutic effect leading to the knockdown of both well-vascularized solid tumors and for non-solid cancer cells in a leukemia animal model.

GOMD Symposium 1: Fundamentals of the Glassy State

Topology and Rigidity

Room: Kona 3
Session Chairs: Mathieu Bauchy, University of California, Los Angeles; Morten Smedskjaer, Aalborg University

1:15 PM

(GOMD-S1-085-2017) Sharpness of Rigidity and Stress transitions in Chalcogenides (Invited)

P. Boolchand*[1]

1. University of Cincinnati, ECS, USA

The flexible to rigidity transition prediction made in the early 1980s continues to stimulate basic glass science today. For one, the first experimental evidence in 1998 showed that there are actually two phase transitions in binary Si-Se glasses and not one as was predicted by theory. And it led to the general recognition that there are three topological phases of glasses: Flexible-Intermediate-Stressed Rigid that are separated by two elastic phase transitions- rigidity- and stress respectively. Second, the sharpness of these two transitions in composition space, experiments have revealed, to be closely tied to melt-homogeneity, which can be tracked in real time by Raman profiling experiments as melts are reacted. Third, fragility index (m) results on especially homogenized melts show a broad minimum in m (< 20) across Intermediate Phases (IPs) but with a sharply defined global minimum near the center composition of that phase. MD simulations extended to evaluate broken constraints in melts at high-T, strikingly confirm that the superstrong behavior (m = 16) observed at the special composition x = 23.0 mole % of Ge in the Ge-Se binary derives from its isostatic nature at 900°C. Homogeneous chalcogenide melts will possess a lower fragility index than their heterogeneous counterparts. Homogenization kinetics of melts near IPs when reacted at high–T will be slow and occur over days and not hours.

1:45 PM

(GOMD-S1-086-2017) Revealing the role of rigidity on the fragility of glass-forming liquids from molecular simulations (Invited)

M. Micoulaut*[1]; C. Yildirim[1]; J. Raty[2]

1. UPMC, France
2. Université de Liège, Belgium

Molecular dynamics simulations of a typical network glass-forming liquids (Ge–Se) are realized, and it is found that that the relaxation behaviour of the supercooled liquid is strongly correlated to the variation of rigidity with temperature and the spatial distribution of the corresponding topological constraints, which ultimately connect to the fragility minima. There are important differences in the way liquids relax as they approach the glass transition, rapid or slow variation in dynamic quantities under moderate temperature changes, and a simple means to quantify such variations is provided by the concept of fragility. The present results permits extending the fragility concept to aspects of topology/rigidity, and to the degree of homogeneity of the atomic-scale interactions for a variety of structural glasses as discussed at the end of the presentation.

2:15 PM

(GOMD-S1-087-2017) Topological engineering of doped photonic glasses (Invited)

S. Zhou*[1]

1. South China University of Technology, School of Materials Science and Engineering, China

The development of doped photonic glass is of fundamental importance for various applications, including telecommunication, lasers, and photovoltaics. Despite the great advances in doping techniques, a long-standing barrier remains concerning how to gain better control over the properties of active dopants in disordered systems. Here, we provide a brief overview of recent progress on the engineering of the chemical environment and chemical state of dopants in glass by tuning the topological features, including sublattices and packing manner of the network. This inherent structure-based strategy leads to intriguing optical phenomena such as tunable luminescence and notable enhancements in radiative transition probability.

2:45 PM

(GOMD-S1-088-2017) Topological Controls on Fly Ash Dissolution Kinetics

T. Oey[1]; I. Pignatelli[1]; Y. Yu[1]; N. Neithalath[3]; J. W. Bullard[2]; M. Bauchy[1]; G. Sant*[1]

1. University of California, Los Angeles, USA
2. National Institute of Standards and Technology, Inorganic Materials Group, USA
3. Arizona State University, Ira A. Fulton Schools of Engineering, USA

Fly ash, a by-product from coal power plants, consists in fine modified calcium aluminosilicate particles, which are largely amorphous. Interestingly, fly ash represents an abundant supplementary cementitious material (SCM), valuable for replacing more carbon intensive ordinary portland cement (OPC) in the binder fraction in concrete. While it is desired to enhance the scale of fly ash utilization (i.e., to achieve higher OPC replacement levels), it is first important to understand fly ash reactivity. Here, by combining pioneering applications of molecular dynamics (MD) simulations, and vertical scanning interferometry (VSI), we establish that a fly ash's reactivity (i.e., its aqueous dissolution rate) is controlled by the number of atomic constraints placed on atoms in its amorphous aluminosilicate network. This reveals an Arrhenius-like dependence of dissolution rate on the atomic network topology. Such topological controls on fly ash reactivity are highlighted for a range of U.S. commercial fly ashes spanning CaO-enriched and SiO_2-enriched compositions.

3:00 PM

(GOMD-S1-089-2017) Dissolution Kinetics of Oxide Glasses: Effect of Network Topology

N. Mascaraque Alvarez*[1]; M. Bauchy[2]; M. M. Smedskjaer[1]

1. Aalborg University, Chemistry and Bioscience, Denmark
2. University of California, Civil and Environmental Engineering, USA

Oxide glasses gradually dissolve and corrode when they are exposed to aqueous solutions, limiting the scope of their applications. In a recent study focusing on silicate minerals and glasses, a direct relation was demonstrated between the dissolution rate at high pH and the number of chemical topological constraints per atom (nc) acting within the molecular network. Here, we extend this work by studying the dissolution kinetics of seven oxide glasses with different network former and intermediate cations through measurements of weight loss of bulk samples immersed in acid (pH = 2 and 4), neutral (pH = 7), and basic (pH = 10 and 14) solutions. A direct relationship between their chemical durability and the network topology has been found. Based on these results, we demonstrate that the rate-limiting step of dissolution, and its activation energy, depends on the pH of the solution. Altogether, this study shows that topological constraint theory could be used to discover new oxide glasses with tailored dissolution rates at a targeted pH. This would enable the design of novel bioactive glasses with improved performances.

3:15 PM

(GOMD-S1-090-2017) The Atomic Topology of the Surface Controls the Hydration of Silica

Y. Yu*[1]; B. Wang[1]; G. Sant[1]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA

Silicate glasses of technological and geological interest are often exposed to humid conditions, which can lead to dissolution or stress corrosion cracking. Understanding and predicting the reactivity of glasses in aqueous environments are of primary importance for bioactive glasses or nuclear waste immobilization. However, the influence of composition and surface structure on glasses' reactivity and hydrophilicity remains poorly understood. Here, based on reactive molecular dynamics simulations, we assess the effect of the structure of the surface a silica glass on its short-term reactivity with water. For the first time, we demonstrate that the reactivity of silica is controlled by the atomic topology of its surface, as described within the framework of topological constraint theory. Namely, the reactivity of the glass is found to decrease linearly with the number of topological constraints per atom of the surface. This suggests that the topological engineering of glass's surfaces offers an attractive approach to design novel glasses with tailored reactivity, or control hydrophilic-to-hydrophobic transitions.

3:45 PM

(GOMD-S1-091-2017) Structural Evolution of Tetrahedral Liquids and Glasses (Invited)

P. Lucas*[1]; G. Coleman[1]

1. Univ of Arizona, USA

The structure of tetrahedral and tetrahdra-containing liquids and glasses is investigated by spectroscopy and described in terms of topological constraints counting. The structural evolution of tetrahedral liquids as a function of temperature is investigated by high temperature Raman to characterize the complex mixture of edge and corner sharing tetrahedra. The conversion from corner-to-edge sharing tetrahedra affects the configurational entropy and consequently the dynamic properties such as viscosity. This process is suggested to be the source of a strong-to-fragile transition in tetrahedral liquids. It is also shown that the CS to ES conversion is the source of sub-Tg relaxation in the so-called “non-reversing” window as well as the source of heterogeneity in some tetrahedra-containing chalcogenide liquids.

4:15 PM

(GOMD-S1-092-2017) Molecular Optimization of Calcium-Silicate-Hydrates: The Competition Between Density and Network Topology (Invited)

M. Abdolhosseini Qomi*[1]

1. University of California, Irvine, CEE, USA

Hierarchically porous calcium-silicate-hydrate (C-S-H) is the principal binding phase in modern cement paste. The nanoscale stiffness of pore-free C-S-H solid is widely thought to be driven by crystallographic defects such as silicate tetrahedra omission and hence network topology, yet such hypothesis lacks direct experimental validation. Here, we use atomistic simulations of materials along with integrate experimental synchrotron-radiation-based high pressure X-ray diffraction and nanoindentation analysis, aiming to correlate the mechanical properties of nano-crystalline C-S-H to the systematically varying molecular structure of C-S-H caused by changing its chemistry. Contrary to the notwork-driven hypothesis, we observe that the stiffness of C-S-H increases with increasing Ca/Si in the range 0.8≤Ca/Si≤1.3, despite an increase in the omission sites in the silica chains. We confirm that the increase in stiffness correlates directly to the densification of the interlayer spacing, rather than the contraction of intralayer Si-O and Ca-O bonds. We furthe expand these findings to a wide range of Ca/Si ratio and provide a wholistic model that describes the competition between densification and network topology.

4:45 PM

(GOMD-S1-093-2017) Irradiation-Induced Damage is Driven by Weak Topological Constraints

N. Krishnan*[1]; B. Wang[1]; Y. Le Pape[2]; G. Sant[1]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA
2. Oak Ridge National Lab, USA

Minerals, under exposure to high-energy radiations, can undergo significant structural changes. Such changes result in the evolution of macroscopic properties such as the density, elastic modulus, and dissolution rate. Herein, using realistic molecular dynamics simulations of neutron irradiation, we assess the extent of irradiation-induced damage in a selection of ten minerals commonly used as aggregates in concrete. We observe that irradiation results in some variations of density, which greatly depend on the composition of the mineral. We demonstrate that the extent of damage can be rationalized within the framework of topological constraint theory, which isolates the important structural features that ultimately control the resistance to irradiation while filtering out less relevant atomic details. Based on this analysis, we show that the exposure to radiations results in the thermal breakage of the weaker topological constraints of the network, while stronger constraints remain largely unaffected. This leads to a strong correlation between the amount of weak constraints in the pristine atomic network and the final extent of damage, which suggest that this quantity can serve as a metric to predict irradiation-induced damage in minerals. This could enable the design of novel materials with a tailored resistance to irradiation.

5:00 PM

(GOMD-S1-094-2017) Topological Origin of Toughness and Brittleness in Silicate Glasses

Y. Yu[1]; B. Wang[1]; J. C. Mauro[2]; M. M. Smedskjaer[3]; M. Bauchy*[1]

1. University of California, Los Angeles, Civil and Environmental Engineering Department, USA
2. Corning Incorporated, USA
3. Aalborg University, Department of Chemistry and Bioscience, Denmark

Brittleness is the main limitation of oxide glasses, as impacts, scratching, or vibrations can result in undesirable or even dangerous fracture. As such, increasing the intrinsic ductility of glasses would allow one to design tougher yet transparent materials, which is one of the “Grand Challenges” in glass science. Here, based on molecular dynamics simulations, we show that, despite being brittle at the macroscale, some silicate glasses can feature some ductility at the nanoscale. We demonstrate that a brittle-to-ductile transition can be observed by tuning the topology of the atomic network. Namely, thanks to their internal degrees of freedom, glasses characterized by a flexible network have the ability to undergo local plastic reorganizations, whereas stressed-rigid glasses fail in a brittle way as their network is locked by the high atomic connectivity. Finally, we show that isostatic glasses, which are free of both internal degrees of freedom and eigen-stress, feature an optimal balance between nano-ductility and surface energy and, hence, show maximum fracture toughness. This topological approach could enable the computational design of tough inorganic solids, which has long been a “holy grail” within the non-metallic materials chemistry community.

5:15 PM

(GOMD-S1-095-2017) In-situ small-angle X-ray scattering study of electron density fluctuations in vitreous silica under the stress field of an indenter tip

G. N. Maurício de Macedo*[1]; S. Fuhrmann[1]; C. Krywka[2]; L. Wondraczek[1]

1. Friedrich-Schiller-University Jena, Chemistry and Geo Sciences, Germany
2. Helmholtz-Zentrum Geesthacht, Germany

An inherent characteristic of glasses is the lack of long range structural order. The dynamic freezing process of supercooled liquids generates density fluctuations in the nanometer range of view. They can be correlated to the degree of disorder and vary with freezing conditions, i.e. temperature and pressure. In this study we show how the local stress field of an indenter tip influences the electron density fluctuations in vitreous silica during a series of wedge indentations. The indentation tests were done with various loads and analyzed in-situ by means of small angle X-ray scattering (SAXS) experiments performed at the Nanofocus Endstation P03 of PETRA III at DESY in Hamburg. It is shown that the unloaded and loaded states exhibit a clear difference of the level of electron density fluctuations and X-ray transmission over the sample. Below the indenter tip stronger effects, which vary with the applied load, are detected. The results allow to access information on the changes of the glass topological homogeneity under the stress field produced by the wedge indenter.

5:30 PM

(GOMD-S1-096-2017) Dynamic Light Scattering in Mixed Na-Zn and Na-Al Metaphosphate Melts

D. Vu[1]; D. Sidebottom*[1]

1. Creighton University, Physics, USA

Dynamic light scattering has been conducted on a series of mixed metaphosphate glass melts of the form $[Zn(PO_3)_2]_y[NaPO_3]_{1-y}$ and $[Al(PO_3)_3]_y[NaPO_3]_{1-y}$ near the glass transition point. Photon correlation spectroscopy provides a representation of the liquid’s dynamic structure factor from which the relaxation time and KWW stretching exponent can be evaluated as a function of temperature and composition. Unique to the Na-Zn system is the appearance of an ultraslow relaxation in the dynamic structure factor (slower than the viscoelastic process) that can be traced to the random diffusion of Zn cation in Na-rich compositions. The fragility of each glass composition has been determined and is compared with values recently reported in the literature as well as with predictions of a coarse-grained connectivity model. We observe that the fragility of the $NaPO_3$ is systematically decreased by the introduction of either 4-coordinated Zn units or 6-coordinated Al units that both serve to increase the average bridging oxygen bond density. This decrease with increasing connectivity is consistent with model predictions and underscores important differences between alkali ions and other modifier ions in contributing to network connectivity.

Glass under Flux

Room: Kona 4
Session Chair: Benoit Ruffle, Montpellier University

1:15 PM

(GOMD-S1-097-2017) Femtosecond laser modifications of fused silica for three-dimensional printing of complex devices (Invited)

Y. Bellouard*[1]

1. Ecole Polytechnique Fédérale de Lausanne (EPFL), STI/IMT, Switzerland

Femtosecond laser exposure combined with chemical etching on fused silica has emerged over the last decade as a key technology for three-dimensional printing of complex devices. While the technology is entering an age of industrial maturity, the underlying physical mechanism is still far from being fully understood. Here, we will review the current status of our understanding about unconventional laser-matter interaction from the viewpoint of material transformation, in particular self-organization processes and densification mechanisms. Furthermore, we will discuss new approaches to achieve higher energy confinement levels in the materials based on spatial-temporal focusing methods. Lastly, we will also present novel applications of tailored stress states and its applications in micro-technologies as well as our research effort to generate high pressure phases in the material.

1:45 PM

(GOMD-S1-098-2017) Evaluation for the plasma resistance of alumino-silicate oxide glasses contained Y, B, Ca element under CF_4 / O_2 / Ar plasma mixture

J. Choi*[1]; H. Park[1]; Y. Han[1]; H. Kim[1]

1. Korea Institute of Ceramic Engineering and Technology (KICET), Engineering Ceramic Center, Republic of Korea

The foreign particle contamination from degraded apparatus of chamber by repeated plasma exposure chipped off would be able to cause defective products in semiconductor or display industry. In order to solve the problem, six kinds of alumniosilicate oxide glasses containing high resistant elements for fluorocarbon plasma were evaluated under CF_4 / O_2 / Ar gas plasma. All glasses show below the etch rate of 65 nm/min which is lower than that of sintered polycrystalline Al_2O_3 (~65 nm/min), and single crystal Al_2O_3 (~50 nm/min). Moreover, the surface roughness (R_a) of six glasses was similar with initial polished surface with near 0.05 um. No difference in microstructure before and after plasma etching was observed in six kinds of glasses whereas polycrystalline Al_2O_3 after plasma etching showed the damaged surface that is believed to be a source of particle contamination. According to XPS analysis of the etched surface, the fluoridation was proceeded from bottom of surface to 2 nm etched layers. Finally, we suggested the corrosion mechanism of glass having amorphous structure surfaces under fluorocarbon plasma in the view of sublimation temperature of fluoride compounds and atomic binding energy.

2:00 PM

(GOMD-S1-099-2017) Local glass structure modification during diffusion in Na_2O-CaO-Al_2O_3-SiO_2 (NCAS)

E. Burov*[1]; E. Gouillart[1]; C. Claireaux[2]; M. Toplis[3]

1. Saint-Gobain, Laboartoire Mixte Saint-Gobain/CNRS, France
2. Saint-Gobain Recherche, France
3. University Toulouse III, IRAP, France

No Longer Available

2:15 PM

(GOMD-S1-100-2017) Transition between chaotic and self-organized patterns during femtosecond laser writing in glass: A tool for investigating glass fracture mechanics

C. E. Athanasiou*[1]; M. Hongler[1]; Y. Bellouard[1]

1. Ecole Polytechnique Fédérale de Lausanne, Microengineering, Switzerland

Under certain laser exposure conditions, self-organized patterns form in the bulk and on the surface of transparent materials. These patterns consist of sub-wavelength nanoplanes that self-organize, parallel one to another, and are oriented perpendicular to the laser light polarization. Associated with the formation of these regular patterns is the generation of compressive stress. Recently, we reported that under certain exposure conditions these nanoplanes transition intermittently and spontaneously between disordered and self-organized. Here, we will discuss our investigations on this intermittency from the view point of fracture mechanics. In particular, we will present how the randomness of the process finds its origin in the crack formations as well as how this method could be used to rapidly determine Weibull parameters without performing numerous experiments.

2:30 PM

(GOMD-S1-101-2017) Is there any evidence of amorphous to amorphous phase transformation due to radiation in oxide glasses?

S. Peuget*[1]; A. Mir[2]; C. Jegou[1]

1. CEA, France
2. University of Huddersfield, School of Computing and Engineering, United Kingdom

In amorphous material, the understanding of how the structure reacts with respect to radiation is still debated. Many studies have been performed on oxide silicate glasses using γ rays, electrons, ions, neutrons irradiations, radioactive decays of unstable isotopes incorporated in the glassy network, and molecular dynamic simulations of the damage induced by heavy ions. These studies have described the changes occurring in the glassy network, but there is still no unified theory to explain why such changes are observed according to the irradiation conditions. Because of the metastable character of the glassy state, an open question is related to its stability with respect to the excess of energy introduced by radiation into the material, particularly we still do not know if radiation can favor a more stable state and could induce crystallization or amorphous to amorphous transformations. In the current article we propose to compare how a specific sodium borosilicate glass reacts to various irradiation conditions, involving both electron energy loss (at low and high level) and nuclear energy loss, and therefore could help to go further into this discussion on the stability of the glassy state under irradiation. Mono beam irradiations will be compared to sequential double beam irradiations to describe the glass response as function of its initial glassy state.

2:45 PM

(GOMD-S1-102-2017) Irradiation-Induced Damage in Quartz: The Critical Role of the Enthalpy Landscape

N. Krishnan*[1]; B. Wang[1]; Y. Yu[1]; Y. Le Pape[1]; G. Sant[1]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA

SiO_2 is an archetypical silicate system known for its excellent glass-forming ability. Under irradiation, quartz exhibits a disordering of the atomic network resulting in the loss of any long-range order. Understanding the nature of such irradiation-induced disordering in an atomic structure is of both fundamental and practical importance. Here, using realistic molecular dynamics simulation, we show that irradiation-induced amorphization differs from that observed upon vitrification. It is observed that the disordering follows a sequence of short- and medium-range rearrangements before reaching the final saturated state. The intermediate states sample forbidden regions of the enthalpy landscape, that is, which are not accessible through quenching or melting. Further, we demonstrate that irradiation-induced damage saturates when the system reaches the local enthalpy landscape of an allowable liquid. The saturated stage is associated with lower energy barriers, which allow the system to relax to a large number of degenerate configurational states, thereby preventing any further accumulation of defects. This highlights the critical role of the enthalpy landscape in controlling irradiation-induced disordering, and the upper limit thereof.

3:00 PM

(GOMD-S1-103-2017) Structure and point defects formation in densified silica glasses irradiated by 2.5 MeV electron

N. Ollier*[1]; K. Piven[1]; V. Martinez[2]; M. Christine[2]

1. CEA, France
2. ILM, France

Permanent densification of silica glass (up to 21 %) can be obtained by high pressure (HP). Irradiation (neutrons, electrons, fs or UV laser) can also lead to a compaction of the silica network. The aim of the present paper is to combine HP and irradiation to study their simultaneous effects on the silica glass structure and point defect formation. Silica glass samples with densities from 2.30 to 2.56 obtained from HP and high temperature in a Belt press were irradiated at different doses up to $4x10^9$ Gy with 2.5 MeV electrons. For doses higher than $9x10^8$ Gy, the glass structure whatever the initial density shows a significant increase of the 3-membered rings number and a larger Si-O-Si angle distribution. Brillouin spectroscopy measurements will be performed and the structural evolution of silica will be discussed regards to the macroscopic density. The pre densification of the silica glass impacts also strongly the point defects formation. Thank to time resolved photoluminescence, we evidenced at least 3 components in the green red region. A “green emission” band at 540 nm that was observed in neutron-irradiated silica, whose origin is still unclear is found to be intense in densified irradiated glass. Moreover, we evidenced a broadening of the 650 nm emission corresponding to the Non Bridging Oxygen Hole Center defects with a 620 nm unsual contribution, having a 5 µs lifetime.

Glass Processed under Extreme Conditions

Room: Kona 4

Session Chairs: Yuanzheng Yue, Aalborg University; Yves Bellouard, Ecole Polytechnique Fédérale de Lausanne (EPFL)

3:45 PM

(GOMD-S1-104-2017) Functional oxide glasses fabricated by aerodynamic levitation technique (Invited)

A. Masuno*[1]

1. Hirosaki University, Japan

Aerodynamic levitation technique, which enables a melt to be levitated in the air by gas flow, prevents the melt from crystallization at the boundary between the melt and a container wall. Accordingly, materials with a very low glass forming ability are often vitrified. Various binary glass systems without any network-former oxides have been developed by the levitation technique. TiO_2-based, Nb_2O_5-based, and WO_3-based glasses have attracted much attention due to colorless and transparency and the high refractive index n > 2.0 with low wavelength dispersion in visible range. The structural analyses combined with experiments and theoretical calculations revealed that the high refractive index glasses were highly ionic and densely packed consisting of oxygen ions and large cations. Furthermore, recently, it was found that Al_2O_3-based glasses had very high elastic moduli. Among them, $60Al_2O_3$-$40SiO_2$ glass showed a crack-resistant behavior. These results indicate that the aerodynamic levitation technique allows us to fabricate novel glass systems with new functionalities.

4:15 PM

(GOMD-S1-105-2017) Network cation coordination in calcium aluminoborosilicate glasses: Pressure effects on recovered structural changes and densification

S. Bista*[1]; J. Stebbins[1]

1. Stanford University, Geological Sciences, USA

In this study, boron and aluminum coordination increases with pressure in several compositions of calcium aluminoborosilicate glass with varying B/Si ratio were studied using ^{11}B and ^{27}Al MAS NMR spectroscopy. Samples recovered from pressures of 1-3 GPa in a piston cylinder apparatus with temperatures near to the glass transition temperature (Tg) show significant increases in aluminum and boron coordination with pressure. High pressure experiments were done at several temperatures to confirm the structural relaxation. In aluminoborosilicate glasses containing excess modifier oxides, such coordination increases can occur through the simple consumption of non-bridging oxygen, at least in the low pressure regime. However, in our present study, the equal mole percents of calcium oxide and alumina, and thus relatively low contents of non-bridging oxygen, could require a different mechanism to support the significant increases in boron and aluminum coordination observed from NMR spectroscopy. We also compare the structural changes in boron and aluminum with the measured densification for glasses containing various amounts of boron.

4:30 PM

(GOMD-S1-106-2017) Void structure in silica glass observed with positron annihilation lifetime spectroscopy: The effect on its optical properties

M. Ono*[1]; M. Fujinami[2]; S. Ito[1]

1. Asahi Glass Company, Research Center, Japan
2. Chiba University, Department of Applied Chemistry & Biotechnology, Japan

We examine voids in silica glasses with different fictive temperatures using positron annihilation lifetime spectroscopy. The pick-off annihilation lifetime of ortho-positronium increases with the fictive temperature, T_f, indicating that the void size increases. High T_f leads to high density and low degree of network polymerization so that increasing void size means that the density fluctuation of the silica glass increases with high T_f. Assuming that such density fluctuation causes light scattering, the previously reported T_f dependence of the Rayleigh scattering coefficient can be well explained by the change in void size. In order to further suppress the Rayleigh loss in silica glass, we applied hydrostatic pressure onto the silica glass up to 200 MPa at 2073 K. Void size was observed to decrease with increasing pressure by positron annihilation lifetime measurements. Correspondingly, the Rayleigh scattering intensities of the samples were markedly lowered. These phenomena intensified with increasing pressure and pressure holding time. The void-containing network structures of the samples were investigated through density, refractive index and Raman spectral peak intensity measurements.

4:45 PM

(GOMD-S1-107-2017) Temperature analysis of ultrashort laser processed HPFS® glass through SEM images and thermal stress analysis

A. Rezikyan[1]; M. R. Ross[1]; J. Wu*[1]; P. J. Lezzi[1]; J. Luo[1]; A. Liu[1]

1. Corning Incorporated, USA

Glass laser processing using ultrashort pulsed lasers involves multiple areas of physics including nonlinear optics, thermal dynamics, plasma generation, and shock wave generation. Due to a wide range of interactions at different time scales, from femtoseconds to microseconds, it is often difficult to measure the key process parameters, such as temperature and morphology in real time. SEM images on laser processed HPFS® enable us to observe morphology of the glass surface details and bulk cross-section of the laser processed region. We are able to estimate the process temperature to be above 2000 °C. This information could be used to estimate the thermal stress generated from the laser process in different glasses. Calculation on thermal stress shows that it is largely correlated to the thermal expansion of the glass. SEM cross section image also shows a series of voids along the laser path. Molecular dynamic simulation estimated a much higher temperature than 2000 °C to produce voids in fused silica. The discrepancy suggests that other effects such as shock wave and/or material modification play a crucial role in the void generation.

5:00 PM

(GOMD-S1-108-2017) Pressure effects on intermediate range and structural heterogeneity of glasses: From congruent compaction to local divergence (Invited)

L. Wondraczek*[1]

1. University of Jena, Germany

Pressure-induced changes in glass structure have been a subject of interest accross various fields of application, ranging from the consideration of high (> 5 GPa) isostatic pressure in geoscience to contact mechanics (1-15 GPa) and mild compaction (< 1 GPa) in, e.g., pressure-assisted material processing. Many recent studies focus on variations in short-range structural parameters (cation coordination, connectivity, etc.), but it has become clear that these are hardly sufficient to explain the observed deviations between entropy- (volume) and enthalpy- (potential energy) driven changes. Instead, distinct effects of pressure on structural heterogeneity - the presence of differently elastic domains - have been suggested as another parameter. This consideration will be continued in the present talk, comparing isostatic compaction of glasses with different degrees of bond localization and its effects on non-Debye normalization of the VDOS.

GOMD Symposium 4: Glass Technology and Crosscutting Topics

Glass Surfaces and Treatments II

Room: Kona 2
Session Chairs: Robert Schaut, Corning Incorporated;
Nicholas Smith, Corning Incorporated

1:15 PM

(GOMD-S4-043-2017) Relationship between surface µ-roughness and interface slurry particle spatial distribution during glass polishing

T. I. Suratwala*[1]

1. Lawrence Livermore National Laboratory, Optics & Materials Science & Technology, USA

Glass optics with ultra-low roughness surfaces (<2 Å level rms) are strongly desired for high end optical applications. In this study, the polishing slurry pH and the generation glass removal products are shown to influence the slurry particle spatial and height distribution at the polishing interface and the resulting µ-roughness of the glass workpiece. An electrostatic DLVO 3-body force model, using the measured zeta potentials, was used to calculate the particle-particle, particle-workpiece, and particle-pad attractive & repulsive forces as a function of pH and the incorporation of glass products at the interface. The model predicts an increase in particle-pad attraction with increase in pH and phosphate glass products consistent with the measured slurry distribution on the pads during phosphate glass polishing. Next, a slurry 'island' distribution gap (IDG) model has been formulated which utilizes the measured interface slurry distributions and a load balance to determine the interface gap, the contact area fraction, and the load on each slurry 'island'. The IDG model was then used to simulate the workpiece surface topography and µ-roughness; the results show an increase in roughness with pH similar to that observed experimentally.

1:30 PM

(GOMD-S4-044-2017) Effects of variable contact dynamics and surface quality on flat glass-metal surface attraction

G. Agnello*[1]; R. Manley[1]; T. Brown[1]; C. Cole[1]

1. Corning Incorporated, USA

One of the major challenges associated with flat panel display manufacture is the unwanted stiction between a glass substrate and metallic surface, like a vacuum chuck or susceptor. If the stiction force between the surfaces exceeds the bulk strength of the glass, breakage can occur during decoupling, leading to losses in yield. In the current study, we report experimental results that explore flat glass-metal surface attraction as functions of contact dynamics (contact load/time, vacuum force, etc.) and glass and/or metal surface characteristics (nano through macro-scale roughness, flatness, surface chemistry, chuck channel configuration specific to metal, etc.) using a newly developed measurement system. The results suggest that the condition of both glass and metal surfaces as well as the nature of the contact process greatly influence the extent to which the materials tend to remain connected, as well as the forces required to separate them.

1:45 PM

(GOMD-S4-045-2017) Kinetics and Mechanisms of Phase Separation in Barium Borosilicate Glass Thin Films deposited by Magnetron Sputtering

J. Fonné*[1]; E. Gouillart[1]; E. Burov[1]; H. Montigaud[1]; S. Grachev[1]; D. Vandembroucq[2]

1. Saint-Gobain Recherche, UMR 125 CNRS/Saint-Gobain - Surface of Glass and Interfaces, France
2. UMR 7636 CNRS/ESPCI/Paris 6 UPMC/Paris 7 Diderot, Physics and Mechanics of Heterogeneous Media Laboratory, France

Industrial glass surfaces are now often functionalized with metallic and dielectric thin films in order to add new properties. In this study we investigate Phase Separation (PS) in glass thin films in order to test whether such a phenomenon could be used as a glass surface nano-structuring way. In order to understand the kinetics and mechanisms of this phenomenon, barium borosilicate glass thin films were studied after annealing at high temperature (i.e between 650°C and 1050°C). Various techniques such as SEM, AFM, SIMS, etc... were used for the evaluation of the local composition and the microstructure characterization. Compared to PS in bulk glasses, we have observed that PS in glass thin films is also influenced by additionnal parameters such as the glass layer thickness, gas pressure and power (applied on the target) during deposition, the substrate used, etc… All these parameters have allowed us to obtain various morphologies and to control the size of the objets after PS. We have also observed that the kinetics of this phenomenon in glass thin films is very different compared to the bulk. Finally, we have recently observed that it is possible to obtain the same morphology with BaO-rich droplets in a SiO_2-rich matrix for these glass thin films, but with two different mechanisms : fragmentation of interconnected domains or nucleation and growth.

2:00 PM

(GOMD-S4-046-2017) Self-Healing Thin-Glass Coatings for High Temperature Applications

F. O. Mear*[1]; T. Carlier[1]; S. Saitzek[2]; J. Blach[2]; L. Montagne[1]

1. Lille 1 University, France
2. Artois University, France

Glass or glass-ceramics are a technological solution to achieve efficient materials able to operate at high temperatures. To overcome cracking of the glass when subjected to thermal cycles, self-healing is shown to be a promising solution. The self-healing property is defined as the capacity of a material to recover its integrity and initial properties after destructive actions of external environment or under internal stresses. Coillot et al. have shown that the self-healing processing can be obtained in two different ways: autonomous or non-autonomous. Based on the non-autonomous processing, we propose an innovative approach based on self-healing glassy thin films. They can be used for protective coating applications in the aerospace, nuclear, fuel cell fields or others. The present study is based on a heterostructure made of alternating layers of glass-ceramics and active particles, deposited by pulsed laser ablation. The properties of the deposited films are function of many parameters such as: number of pulse, laser power, atmosphere, temperature of the substrate, target-substrate distance, etc. The characterization of the multi-layers films has been carried out with different techniques: ellipsometry, ToF-SIMS, XPS, AFM, Castaing microprobe, ATR-FTIR spectroscopy. The efficiency of the self-healing effect is demonstrated by an in-situ experiment performed into an environmental scanning electron microscope.

2:15 PM

(GOMD-S4-047-2017) Strain in PMMA by water absorption; Implications for TV light guide plate shape

D. C. Allan*[1]; S. J. Koseba[1]; T. L. Werner[1]; L. K. Cornelius[1]

1. Corning Incorporated, Glass Research, USA

Polymethyl methacrylate (PMMA or plexiglas) plates are commonly used as light guide plates to provide illumination in modern liquid crystal display televisions. As the trend in television design goes toward thinner front to back dimensions, swelling and shape distortion of PMMA by natural water absorption becomes more of a concern. We present quantitative measurements and simple physical models for both swelling and warping caused by water absorption and temperature-dependent water diffusion in PMMA at different levels of ambient humidity. We compare these effects with similar swelling and warping in PMMA associated with thermal expansion and typical thermal gradients in thin televisions.

2:30 PM

(GOMD-S4-048-2017) Effect of Alkali Size on Network Dilation in Mixed Alkali-Aluminosilicate Glasses

E. A. King*[1]; C. Smith[1]; D. C. Allan[1]; J. C. Mauro[1]

1. Corning Incorporated, Glass Research, USA

Chemically strengthened glasses produced via ion exchange processes are currently of great interest due to their high strength and damage resistance. Such strengthening is the result of an atomic size mismatch between exchanged alkali ions, leading to elastic strain within the glass network and ultimately changes in the glass dimensions. Dilation of the glass network during such processes is captured by the linear network dilation coefficient (B), defined as the strain per molar concentration of exchanged alkali ions, and is critical to understanding the fundamental strengthening mechanisms during ion exchange processes. Previously we have shown how to directly access B via direct strain measurements, allowing us to track the dimensional changes associated with the elastic strain in the network. These dimensional changes are found to be linearly proportional to the fractional weight gain (a measure of the number of atoms exchanged) of the glass during the ion exchange process. Past work has shown that in K for Na ion-exchange, network dilation is independent of glass thermal history and the temperature of ion-exchange, across a range of alkali-aluminosilicate glasses if structural relaxation is taken into account. Here we investigate the effect of alkali size on network dilation in K for Na, and Na for Li ion-exchange in mixed alkali glasses.

2:45 PM

(GOMD-S4-049-2017) Effect of chemical tempering variables on structure evolution and mechanical properties of soda-lime-silicate glass

H. Hassani[1]; V. M. Sglavo*[1]

1. University of Trento, Italy

In the present work, the structure evolution of soda-lime silicate glass subjected to variable ion-exchange processes was initially studied. Glass samples were subjected to chemical strengthening in pure molten KNO_3 at different temperatures and four variable times. Ion-exchanged glass was characterized from a mechanical (residual compression and case depth, strength, surface crack formation), chemical (surface composition) and structural (by Nuclear Magnetic Resonance spectroscopy) point of view. Case depth and potassium surface concentration increase with processing time and temperature at the expense of surface compression. Crack initiation tendency decreases in samples treated at lower temperature for shorter duration; this latter result is correlated to NMR results which indicate larger distribution of Q^3 species, indicating network distortion, for longer tratment times.

3:00 PM

(GOMD-S4-050-2017) Modifying the surface of soda lime silica glass by thermal poling in different chemical environments

J. Luo*[1]; C. G. Pantano[2]; S. H. Kim[1]

1. Pennsylvania State University, Chemical Engineering, USA
2. Pennsylvania State University, Material Science & Engineering, USA

Thermal poling in different chemical environments is adopted as a novel way of modifying the composition and structure of a soda lime silica (SLS) in the surface region. When thermal poling is performed on the SLS glass with a non-blocking electrode, a sodium-depleted layer can be formed. In order to compensate the charge due to the sodium removal, chemical reactions need to take place between the chemical species in the environment and the glass as well as within the glass itself. When the thermal energy and electric potential energy are held constant, the chemical reactions are largely dependent on the reactants and their concentration. Therefore, the chemical structure of this sodium-depleted layer can be modified differently when the chemical species and their concentration vary during thermal poling. In this study, sodium-depleted surfaces are prepared in environments where different amounts of nitrogen, oxygen and water are present. It is found from various spectroscopic analyses that the thickness, chemical composition, chemical species introduced from the environment, chemical environment of the hydrous species (Si-OH & H_2O) in the glass and silicate network structure of these surfaces, all vary significantly in these conditions. This study aims to provide new insights for modifying the surface optical and mechanical properties of SLS glass.

3:15 PM

(GOMD-S4-051-2017) Electric field-assisted ion-exchange of silicate glass

V. M. Sglavo*[1]; A. Talimian[1]; E. Debattisti[1]

1. University of Trento, Italy

In the present work, electric field – assisted ion exchange was carried out to enhance sodium-potassium interdiffusion and improve the mechanical performances of soda-lime-silicate and soda-borosilicate glass. Electric fields with variable intensity were applied cyclically in both direct and inverted polarization. Compression test and Vickers indentation were used to characterize the mechanical performances of the strengthened material. Energy Dispersion X-ray Spectroscopy was carried out to determine the potassium concentration in the surface layers of the samples. It is shown that the application of the electrical field allows to enhance Na-K interdiffusion to a large extent, thus reducing the treatment time well below the hour. The cyclic process allows to reinforce both surfaces thus allowing to reach very high mechanical performances.

Challenges in Glass Manufacturing I

Room: Waikoloa 3
Session Chairs: Mathieu Hubert, CelSian Glass & Solar;
Andreas Prange, RWTH Aachen University

1:15 PM

(GOMD-S4-052-2017) Needs for new melting technologies in specialty glass industry (Invited)

M. Hahn*[1]

1. Schott AG Germany, R&D, Germany

The main drivers for technological innovation in the specialty glass industry are the variable requirements of the customers. The knowledge of customers need is essential for successful technology improvements. In addition to cost and quality the suppliers of specialty glass have to be fast and flexible at always decreased lot sizes in production. To fulfill these requirements melting technologies have to be developed in: Improved/new glass compositions to reduce costs, to improve glass quality and to enable new applications Improved/new melting technologies for optimized glass quality and flexibility Reduced energy costs in glass melting and post processing Fundamental for improvements in melting technology is a detailed process understanding from batch to post processing supported by New sensors and datamining Lab- and pilot melting systems Adjustments and process optimization based on mathematical modelling Specific needs to reach improved process understanding will be shown. But be sure - any kind of innovation find its way into industrial practice only if customer requirements are fulfilled.

1:45 PM

(GOMD-S4-053-2017) Characterization of raw and waste materials to be used for production of stone wool melt

V. Schultz-Falk*[1]; P. A. Jensen[3]; K. Agersted[2]; M. Solvang[1]

1. ROCKWOOL International A/S, Denmark
2. Technical University of Denmark, Department of Energy Conversion and Storage, Denmark
3. Technical University of Denmark, Department of Chemical and Biochemical Engineering, Denmark

A key element in the production of mineral wool is forming a melt that can be spun into fibers. As the demand for insulation materials increases so does the amount of mineral wool waste resulting from renovation and demolition of buildings. The ROCKWOOL Group has invented a new cyclone based melting technology for stone wool melt production: the Integrated Melting Furnace (IMF). The impact of introducing waste materials into the IMF process is investigated through a comparative study of the melting properties of a conventional raw material charge and mineral wool waste. The study combines Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD) and Hot Stage Microscopy (HSM). DSC reveals that the raw material charge and wool waste have fundamentally different heat responses: the charge decarbonizes and the wool crystalizes before both melting. XRD is used to investigate sample crystallinity. Comparing the specters of the charge and wool waste clearly show their fundamental difference in terms of material properties and heat response. The differences observed in DSC and XRD are also reflected in the HSM data. They show that adding 25% wool waste will make the charge behave almost as pure wool waste. The observed differences between a raw material charge and wool waste indicate that introducing wool waste into the IMF will have an influence on the overall IMF energy consumption.

2:00 PM

(GOMD-S4-054-2017) Effects of raw materials and furnace atmosphere on batch-to-melt conversion in industrial glass melting (Invited)

A. Faber[1]; M. Rongen[1]; P. Marson[1]; O. Verheijen*[1]

1. CelSian Glass & Solar, Netherlands

In this paper the effects of raw materials and furnace atmosphere on batch-to-melt conversion processes will be evaluated experimentally. An in-house developed laboratory method, including CelSian's High Temperature Observation and Monitoring System (HTMOS), coupled to an Evolved Gas Analysis (EGA) unit, has been used to characterize the melting process of various raw materials batches for soda lime silicate and alkali-free (boro)silicate glasses. The atmosphere above the raw materials batch, which is contained in a transparent quartz glass crucible, can be controlled in order to simulate more oxidizing (with more O_2) or more reducing furnace atmospheres. Besides, the way of heating the batch in an air-gas fired, an oxy-gas fired or an electrical cold top furnace atmosphere can be simulated with help of a gas mixing and control unit. Exemplary measuring results show a highly accelerating effect of grinding and pelletizing coarse raw materials on the melting kinetics of these batches. Besides, experiments demonstrate the dissolution of crystals in primary glass melts and the effects of the redox state of raw materials batches and of the furnace atmosphere on the melting and foaming behavior. It is concluded that the HTMOS-EGA system

is a powerful tool to study and predict batch-to-melt conversion processes of raw materials batches under industrial conditions.

2:30 PM

(GOMD-S4-055-2017) Neutron diffraction investigation of reactions in sodium aluminosilicate glass batch

J. Rygel*[1]; I. Peterson[1]; D. Ma[2]

1. Corning Incorporated, USA
2. Oak Ridge National Lab, USA

Neutron diffraction experiments were conducted on sodium aluminosilicate glass batch using the VULCAN beamline at Oak Ridge National Laboratory's Spallation Neutron Source. Batch reactions were interrogated during a series of continuous thermal ramps as well as during heating to 1500 °C in 100 °C steps. Batches with the same composition, but different particle sizes, were also investigated to quantify the influence of particle size on batch reactions. Successful analysis of these glass batches indicates that neutron diffraction is a promising technique for investigating batch reactions during the glass melting process.

2:45 PM

(GOMD-S4-056-2017) Waste Treatment and Immobilization Plant, Applying Fundemental Glass Science for Engineering Solutions (Invited)

A. A. Kruger*[1]

1. US Department of Energy, Office of River Protection, USA

The feed for vitrification to produce a nuclear waste glass is a mixture of waste with glass-forming and modifying additives that is charged onto the cold cap that covers 90–95% of the melt surface. The cold cap consists of a layer of reacting molten glass floating on the surface of the melt in an all-electric, continuous glass melter. As the feed moves through the cold cap, it undergoes chemical reactions and phase transitions through which it is converted to molten glass that moves from the cold cap into the melt pool. Multiple overlapping reactions occur within the cold cap. The process involves a series of reactions that generate multiple gases and subsequent mass loss and foaming significantly influence the mass and heat transfers. The rate of glass melting, is greatly influenced by mass and heat transfers, affects the vitrification process and the efficiency of the immobilization of nuclear waste. Therefore, understanding the cold-cap reactions over the temperature range of the conversion process is critical. It also helps to formulate melter feeds for higher production rate, initiation of crystal forming reactions, and chemical reactions that determine the ultimate fate of technetium in the glass melt. Insertion of mature technological chemical processes and mechanical components can have a significant impact on the duration of the treatment mission.

3:15 PM

(GOMD-S4-057-2017) Calculating Reaction Kinetics During the Batch-to-Melt Conversion

I. Peterson*[1]; J. Wright[1]; E. Stapleton[2]; A. Credle[2]; W. Johnson[3]

1. Corning Incorporated, Process Research, USA
2. Corning Incorporated, Science and Technology, USA
3. Corning Incorporated, Process Modeling, USA

A wide variety of experimental techniques are available to study the batch-to-melt conversion. In this study, the reactions in a sodium aluminosilicate glass batch are investigated at the laboratory scale using in-situ observation, x-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, evolved gas analysis and other measurements. The results of using kinetics equations from the literature to describe the data from different types of experiments will be discussed.

Challenges in Glass Manufacturing II

Room: Waikoloa 3
Session Chairs: Mathieu Hubert, CelSian Glass & Solar;
Oscar Verheijen, CelSian Glass & Solar

3:45 PM

(GOMD-S4-058-2017) Fundamentals of glass-rheology dependencies in tribologic systems relevant for glass forming (Invited)

A. Prange[1]; C. Roos*[1]

1. RWTH Aachen University, Glass and Ceramic Composites, Germany

Glass forming relies on visco-elastic behavior over a large range of viscosity. The glass experiences a huge change of viscosity over the complete forming process from about 10^3 dPas to more than $10^{7,6}$ dPas. In forming, the rheological - and hence structurally and chemically dependent - properties of the glass often need to be considered in combination of the tribological situation of the whole forming. But questions still remain fundamentally unsolved, especially related to the interface behavior of the glass when it is in contact with another material. The situation even gets more complicated when the inner glass temperature at forming is well above the transition temperature whereas the critical surface temperature of the glass is close to Tg. Friction, sticking, diffusion and other “properties” in glass-forming are strongly viscosity and hence temperature depended. The presentation will give insight into investigations in the field of glass-material contact and mechanisms of glass-material interactions will be presented. Measures of improving these interactions, also in the light of coatings and lubricants, will be discussed.

4:15 PM

(GOMD-S4-059-2017) Towards glass wool and stone wool hybridization

C. Claireaux*[1]; N. Legendre[2]; O. Pons Y Moll[3]; J. Bernard[3]

1. Saint-Gobain Recherche, Elaboration des Verres, France
2. Saint-Gobain Isover G+H Aktiengesellschaft, Germany
3. Saint-Gobain Isover, France

WITHDRAWN

4:30 PM

(GOMD-S4-060-2017) Furnace Start-Up Glass Defects: AZS Exudation or Corrosion?

K. R. Selkregg*[1]

1. Monofrax LLC, Technical, USA

Glass defects, such as knots, cords and cat scratches, are often attributed to fused-cast AZS refractory. The mechanism behind these defect formations is thought to be either run down of viscous liquid containing high concentrations of Al2O3, Na2O and low concentrations of ZrO2 from superstructure AZS or disruption of the boundary layer on the glass contact AZS. When this viscous liquid does not completely dissolve in glass melt, glass defects are formed, often containing ZrO2 inclusions. Such defects have been reported both shortly after start-up, and also during the life of the furnace campaign. The focus of this investigation was on glass defects observed during furnace start-up involving various sodalime glass types. In addition, exudation and corrosion experiments were performed to understand the differences between these two phenomena.

4:45 PM

(GOMD-S4-061-2017) Interaction between a high zirconia refractory and a float glass

M. Ficheux*[1]; L. Cormier[2]; E. Burov[1]; K. Plevacova[3]

1. Saint-Gobain, SVI, France
2. IMPMC - CNRS, France
3. EV - Saint Gobain Recherche, France

Zirconium oxide is used as a component in several ceramic and refractory materials to increase their resistance to high temperatures and limit their corrosion in glass furnaces. Understanding and controlling the interactions and stabilities of these materials with the glass bath present a major industrial asset. Exchange of matter between the amorphous glass and the crystallized refractories is inevitable during the life of a furnace. The role of and behavior of Zr is particularly important in this refractory/liquid interaction process. We have studied Zr environment evolution from the crystalline phases in the refractory(with Zr in 7 fold coordination) to its incorporation within the glassy network(with Zr in 6 fold coordination). Diffusion experiments on refractory/glass couples were performed to determine the diffusion profile, through EMPA analysis. The structural modifications along the diffusion profile were investigated by Zr K-edge X-ray absorption and Raman spectroscopies. The first results showed the presence of the small Zr saturated zone on the interface refarctory and the glass with low aluminum content. At the same time the structural investigations of this zone showed that Zr is presented under 6 fold coordination with very similar configuration to the low Zr contained glass. We didn't observe any trace of Zr 7 fold coordination or some intermade site in this zone and along diffusion profile.

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium V

Room: Kona 5
Session Chairs: Tsuyoshi Honma, Nagaoka Univeristy of Technology; Edgar Zanotto, UFSCar

1:15 PM

(GOMD-S6-017-2017) Shape control of Li_2O-Al_2O_3-SiO_2 glass powder in heat treatment for crystallization (Invited)

S. Nakane*[1]; Y. Hosoda[1]

1. Nippon Electric Glass, Japan

Li_2O-Al_2O_3-SiO_2 low-expansion glass-ceramics were developed by Stookey more than 50 years ago. The glass-ceramics have been widely used for home and cook appliances, electronic and optical devices, and production process equipment, but there have been few efforts to put it to a powder product. To explore new application, we have developed shape-control technology of the powder particles utilizing viscous flow during heat treatment for crystallization, in which it enables to make spherical-shape particles and low thermal-expansion sealing powder. The mother glass contained SiO_2, Al_2O_3, and Li_2O as its principal constituents and TiO_2 and ZrO_2 as nucleation agents. Shape change to sphere was observed by SEM in high temperature, and precipitated crystal species and crystallinity were measured by XRD. Spherical time agreed with that expected from the Nichiporenko theory before the precipitation of main crystal, and it became extremely long after the crystallization where the crystal encumbered the viscous flow even the crystal size was small, 50 nm. Regulation of crystallization by material design and heat schedule would be necessary to control the shape of the powder particles in heat treatment for crystallization.

1:45 PM

(GOMD-S6-018-2017) Relationship between crystallization of oxide glasses and the preparation condition (Invited)

H. Masai*[1]; Y. Takahashi[2]; T. Fujiwara[2]

1. Kyoto University, Institute for Chemical Research, Japan
2. Tohoku University, Department of Applied Physics, Japan

We have examined the physical properties and crystallization of oxide glasses depending on the preparation condition. The temperature at which the oxide glass melts are held in a molten state (called the "melt temperature" in the present paper) affects various optical parameters, which is mainly due to the valence state change. The changes in the absorption coefficients and the refractive indices, which increased with the increasing melt temperature, were reversible in the air melting, and temperature-dependent structures, i.e. transient state of glass melt, were formed in the glass. In the remelted BaO-TiO_2-GeO_2 glass with short remelting duration, a black coloration and the precipitation of Pt nanocrystallites were observed. The precipitated Pt nanocrystallites acted as nucleation sites to induce crystallization by heat treatment at 10°C below the glass transition temperature. Since crystallization of the glass is affected by each transient state, the evaluation of the structural analysis will be more important in the near future.

2:15 PM

(GOMD-S6-019-2017) Nontraditional molybdate and tungstate borate glasses, their crystallization behavior and immiscibility (Invited)

L. I. Aleksandrov*[1]; R. Iordanova[1]; Y. Dimitriev[2]; T. Komatsu[3]

1. Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Bulgaria
2. University of Chemical Technology and Metallurgy, Deapartment of Silicate Technology, Bulgaria
3. Nagaoka University of Technology, Japan

The structure and crystallization tendency of glasses in the MoO_3-La_2O_3-Nd_2O_3, MeO_3-La_2O_3-B_2O_3, MeO_3-Nd_2O_3-B_2O_3 and MeO_3-ZnO-B_2O_3 (Me=Mo and W) were examined. The structural model for the glass network was suggested base on IR, Raman and XPS spectra as well as the crystal data of $LaMeBO_6$, $ZnMeO_4$ and LnB_3O_6. We assumed that the network of the glasses in the present systems situated in the metaborate composition range is built up by BO_3 triangles associated with BO_4 tetrahedra. It was found that the replacement of BO_3 by MeO_3 leads to the BO_4 to BO_3 conversion which is accompanied by gradual depolymerisation of the borate network. The isolated MeO_4 groups build up the borate glass network, while MeO_6 units form the molybdate and tungstate glass network for compositions with a high MeO_3 content. Different types of microheterogeneities in the range of stable liquid phase separation were determined. The reason for the immiscibility was explained by the low tendency to generate mixed Me–O–B bonds at the expense of B–O–B and Me–O–Me bridges. The formation of Mo–O–La(Nd) linkages was found. That is why the lanthanum plays an important role in the formation of a homogeneous network.

2:45 PM

(GOMD-S6-020-2017) Impact of stress formation on crystal structure and luminescence in glass-ceramics synthesized by crystallization of glass and supercooled melt (Invited)

K. Shinozaki*[1]; T. Akai[1]; M. Affatigato[3]; T. Komatsu[2]

1. National Institute of Advanced Industrial Science and Technology (AIST), Inorganic Functional Materials Research Institute, Japan
2. Nagaoka University of Technology, Department of Materials Science and Technology, Japan
3. Coe College, Physics Department, USA

Glass-ceramics were synthesized via two paths; (1) heat-treatment on glass (a conventional glass crystallization technique), and (2) solidification of supercooled melt in a containerless process, where a levitation melting technique was used to obtain precursor glass and ceramics beads. Stoichiometric compositions of $SrAl_2O_4$:Eu^{2+},Dy^{3+} and $Y_3Al_5O_{12}$:Ce^{3+} were investigated in this study. High temperature phase of hexagonal $SrAl_2O_4$ (b‘-phase) was obtained via both paths, avoiding the stable monoclinic phase (a-phase, well-known as one of the best afterglow materials). The hexagonal phase showed brighter broad green emission, higher intensity of PLE peak in visible region (l=400-500 nm), and longer duration of afterglow compared to the monoclinic structure. PL property of $Y_3Al_5O_{12}$:Ce^{3+} sample (also synthesized by using a levitation technique) was also studied. PL peak in glass-ceramics was shifted toward longer wavelength ~10nm. It is proposed that large stresses during crystallization force the crystal into the high temperature phase and push the PL peak towards a longer wavelength.

GOMD Symposium 6: Professor Komatsu Kinen Honorary Symposium VI

Room: Kona 5
Session Chair: Mario Affatigato, Coe College

3:30 PM

(GOMD-S6-021-2017) Incorporation of some transition and noble metal ions in glasses and glass ceramics: Polarizability, basicity and non-random segregation (Invited)

L. Wondraczek*[1]

1. University of Jena, Germany

Color, photoluminescence, magnetic properties and, e.g., optical non-linearity of oxide glasses and glass ceramics are largly determined by the way in which optically active ion species are incorporated into the respective matrix material - a subject area on which Prof. Komatsu's studies have set the ground for many of today's approaches to novel optical materials. Considering examples of transition, post-transition and noble metal ions, the present talk will review some of this work to show how these fundamental findings can now be used in the further development of solid-state light sources, colored glasses, and magnetic glass fiber.

4:00 PM

(GOMD-S6-022-2017) VO_2-dispersed Glass as New Latent Heat Storage Material (Invited)

K. Muramoto[1]; Y. Takahashi*[1]; N. Terakado[1]; T. Fujiwara[1]

1. Tohoku University, Department of Applied Physics, Japan

Energy-storage technology (Heat, photon, etc.) is essential for sustainable society, and its realization is strongly supported by materials development. Our research group has engaged in study on energy-preservation and -harvest on the basis of physical/material-science aspects: Oxide glass possesses a high durability, and the amorphous structure without periodic ordering provides an excellent formability and controllability, which enable the large-scale production. These provokes us to create new material for thermal-management toward a reuse of heat energy. Vanadium dioxide, VO_2, with strongly-correlated electron shows a structural phase-transition, resulting the metal–insulator (Mott) transition and large heat of transition, which is comparable to H_2O. In addition, volume variation during solid–solid phase-transition in the VO_2 is relatively smaller than the variation in solid–liquid phase-transition. In this presentation, we report a recent study on fabrication of VO_2-dispersed glass as new latent heat storage material and its performance.

PACRIM Symposium 01: Characterization and Modeling of Ceramic Interfaces: Structure, bonding, and Grain Growth

Interface Structure and Composition

Room: Kohala 3
Session Chairs: Jian Luo, UCSD; Katsuyuki Matsunaga, Nagoya University

1:15 PM

(PACRIM-S1-010-2017) Interface and Surface Atomic Structures of Li Ion Battery Materials (Invited)

Y. Ikuhara*[1]

1. Univ.Tokyo, JFCC, Tohoku Univ., Japan

The properties of lithium ion battery are strongly dependent on the behavior of lithium ions during charge/discharge process. Since this behavior determines the stability, lifetime and reliability, direct visualization of Li site is needed to understand the mechanism of the properties. Recently we have proposed that annular bright field (ABF) scanning transmission electron microscopy (STEM) is very powerful technique to produce images showing both light and heavy element columns simultaneously. In this study, light elements in several lithium battery related materials such as $LiFePO_4$, $LiCoO_2$, $La_{2/3-x}Li_{3x}TiO_3$ (LLTO) are directly observed by ABF STEM, and the mechanism of lithiation/delithiation is discussed based on the observation results. The properties of Li ion batteries is also influenced by the atomic structures of the surfaces and embedded interfaces. In this study, the surface of $LiFePO_4$ single crystal and the interface of the epitaxially grown $LiMn_2O_4$ thin film are investigated by exploring the detailed structural and compositional variations in the vicinity of the surfaces and interfaces. A part of this work was supported by the RISING II project of NEDO, Japan.

1:45 PM

(PACRIM-S1-011-2017) Atomic Structure Investigation of Alumina Σ13 Grain Boundary Fabricated in Controlled Atmospheres

S. Ishihara*[1]; E. Tochigi[1]; N. Shibata[1]; Y. Ikuhara[1]

1. University of Tokyo, Institute of Engineering Innovation, Japan

Ceramic materials are typically fabricated by sintering method, and in some ceramic materials, sintering behaviors and resultant properties are strongly affected by the sintering atmospheres. Such phenomena are expected to be closely related to the behaviors of grain boundaries (GB) under particular sintering atmospheres. In this study, we investigated the atomic structures of a GB in α-alumina which was fabricated under controlled atmospheres, using aberration corrected scanning transmission electron microscopy (STEM). An alumina bicrystal with the Σ13 {10-14}/<1-210> GB was fabricated by diffusion bonding at 1500 °C for 10 h under a mixed gas flow of 97%Ar-3%H_2. Subsequently, the GB structures were observed by STEM(ARM-200F, 200kV, JEOL) along the <1-210> direction. The STEM observations revealed that the GB consisted of two kinds of atomic structures: one with the mirror symmetric (M) structure and the other with the glide mirror symmetric (G) structure. It has been reported that the Σ13 GB fabricated in air always showed the M structure. It is, therefore, considered that the G structure is stabilized in the reduction atmosphere. The present results demonstrate that the GB atomic structures can be affected by the atmosphere during GB formation. In the presentation, we will discuss the GB atomic structure and its formation mechanism depending on sintering atmospheres in detail.

2:00 PM

(PACRIM-S1-012-2017) Atomic-resolution STEM-EDS mapping of residual impurities in MgO Σ5 grain boundary

M. Saito*[1]; R. Ishikawa[1]; I. Ohnishi[2]; H. Sawada[2]; K. Inoue[3]; N. Shibata[1]; Y. Ikuhara[1]

1. The University of Tokyo, Japan
2. JEOL Ltd., Japan
3. Tohoku University, Japan

Real materials including ceramics and minerals are, in general, of polycrystalline nature, and the presence of crystal grain boundaries (GBs) often influences significantly their mechanical, physical, and electrical properties. Especially, GBs can provide shortcut paths for mass transport and also act as nucleation sites for precipitation, corrosion, fracture and plastic deformation. They serve as effective sinks for impurities or defects. Therefore, GBs structure characterization including impurities is essential to elucidate how impurities segregation may trigger structural transformation of GBs and consequently modify material properties. Here, magnesium oxide (MgO) Σ5(310)[001] GB with CSL orientation relationship was adopted as a model system. We used a bicrystal technique to fabricate the symmetrical tilt GB. MgO included a small amount of residual impurities. STEM observations were performed by JEOL JEM-ARM300F with Dual SDD EDS detectors (Cs-corrected STEM, 300 kV). The high-angular annular dark-field (HAADF) images and the atomic-resolution EDS mappings revealed formation of periodic structure units (SUs) at the GB and co-segregation of calcium (Ca), titanium (Ti) impurities at the specific atomic sites of the SUs. In the Σ5 MgO GB, a periodical super structure is self-organized at atomic scale through interaction between Ca, Ti impurities, vacancies, interstitials, charges, and the SUs.

2:15 PM

(PACRIM-S1-013-2017) Subsurface Space-Charge Solute Segregation to Compensate Surface Excess Charge in Oxides (Invited)

S. Chung*[1]

1. Korea Advanced Institute of Sci. & Tech. (KAIST), Graduate School of EEWS, Republic of Korea

Since the first prediction by Frenkel, many follow-up studies have been carried out to show the presence of subsurface space-charge layers having the opposite sign to that of the excess charge at the surface for overall neutrality in ionic crystals. Early theoretical works largely dealt with a free surface rather than other types of interfaces, and suggested a plausible distribution of charged defects and dopants near the surface. However, no precise experimental evidence demonstrating how the aliovalent solutes segregate in the space charge region beneath the surface has been provided over the past several decades. In this work, we elucidate the characteristics of space-charge-driven solute segregation, which is completely distinct from the segregation driven by the misfit elastic strain between the solute and solvent atoms. By utilizing both atomic-scale physical imaging and chemical probing, we precisely determine the origin of the surface excess charge and the position of segregated solutes and thereby discriminate the grain-boundary core and the top-most surface from the space-charge region at atomic resolution. The findings in this work highlight the impact of the space-charge contribution to the solute distribution near the surface in oxide crystals, and thus information from the surface and the subsurface space-charge layer is necessary to fully understand the surface region.

2:45 PM

(PACRIM-S1-014-2017) Dopant segregation at (110) low-angle tilt grain boundaries in magnesium oxide

A. Nakamura*[1]; K. Sawada[1]; E. Tochigi[2]; Y. Ikuhara[2]; T. Yokoi[1]; K. Matsunaga[1]

1. Nagoya University, Japan
2. University of Tokyo, Japan

A dislocation in a crystalline material has dangling bonds at its core and strong strain field in its vicinity. As a result, a dislocation has a potential to give rise to unusual phenomena locally or to induce unique physical properties. Thus, atomic structure of dislocations is of great significance in a crystalline material. In this study, we fabricated magnesium oxide (MgO) bicrystals with (110) low-angle tilt grain boundaries, and analyzed atomic structure of introduced dislocations at the boundary and dopant segregation behavior at the dislocations by using scanning transmission electron microscopy (STEM). It was confirmed that the dislocations with b=1/2<110> were periodically formed at the boundaries and that the 1/2[110] dislocations were present as perfect dislocations without dissociation of dislocation core. It was also found that localized and intense dopant segregation have arisen only within a few columns at the dislocations. It is suggested that this dopant segregation behavior would be dominated by the electrostatic interaction between structural charge at the dislocation core and charge with the dopant, not by strain field in the vicinity of the dislocations.

3:00 PM

(PACRIM-S1-015-2017) Single Boundary Measurements of Fracture Toughness to Understand Effects of Chemistry (Invited)

S. J. Dillon*[1]

1. University of Illinois Urbana-Champaign, USA

Many ceramics are known to embrittle with increasing grain size, relative to Hall-Petch extrapolations between fine grain material and the single crystal. In fact, as the grain size of materials like Al_2O_3 increase towards the macroscopic scale their strength tends towards zero. Grain size effects are often consider as an isolated variable, but vastly different grain sizes must often be obtained under widely varying processing temperatures and times. However, in many oxides the atomic structures of grain boundaries and their associated chemistry will be different at different temperatures. We hypothesize that this could be the dominant effect in the embrittlement of ceramics as a function of increased grain size. This hypothesis is difficult to prove using experiments based on polycrystals, because the counter argument is that flaw sensitivity is grain size dependent and thus an apparent embrittlement with increased grain size is fundamental to the particular system. To test our hypothesis, we perform nano-cantilever fracture toughness experiments on single grain boundaries fabricated from polycrystalline samples. We will present results for single grain boundary fracture measurements performed on different doped Al_2O_3 materials pre-annealed at different temperatures. The experiments are performed using in-situ TEM based nanomechanical testing.

3:45 PM

(PACRIM-S1-016-2017) Ultrahigh permittivity in core-shell ferroelectric ceramics: Theoretical approach and practical conclusions

J. Kiat*[1]; M. Anoufa[1]; C. Bogicevic[1]

1. Labo SPMS, Ecole Centrale-CNRS, France

Classically, in most usual ferroelectric materials such as $BaTiO_3$ (BT), the ferroelectric anomalies tend to become diffuse and eventually vanishes when diminishing the grain sizes in such a way that the existence of ferroelectricity at very small sizes has been questioned many times. However there is also reports of ultra-high values of permittivity when specific processes or doping are performed, for instance in the BT-family, or in the $CaCu_3Ti_4O_{12}$- family.

Interpretations in literature using internal barrier layers (IBLC) have been proposed. We have considered these effects in the framework of a core-shell model of ceramics, previously applied to energy storage and electrocaloric effect. Size-dependence of amplitude, diffusivity and temperature of the permittivity anomalies were first calculated for conventional ceramics and a progressive cancelation of permittivity was obtained. Then the ultrahigh values mentioned above could be reproduced by introducing a conductivity of the dielectric or the ferroelectric core. In particular a huge background of permittivity and a Maxwell Wagner relaxation were obtained in agreement with the experimental situation. Grain size distribution, mixing of conductive and non-conductive phases, porosity have also been considered and their effects are discussed. Finally we have evaluated the potentiality of energy storage in IBLC compounds.

4:00 PM

(PACRIM-S1-017-2017) DPC STEM characterization of ceramic interfaces (Invited)

N. Shibata*[1]

1. The University of Tokyo, Japan

Differential phase contrast (DPC) scanning transmission electron microscopy (DPC) is becoming very powerful tool to directly map local electromagnetic field distribution at very high resolution. Using DPC STEM imaging technique, we can directly obtain local field information, but using such information, we may also access to local potential structures and charge density distributions by numerical treatments based on Maxwell equations. In this study, we will show our recent application of this technique to the characterization of ceramic interfaces and local defect structures inside materials.

4:30 PM

(PACRIM-S1-018-2017) Grain Boundary Resistance on Heat Transport (Invited)

M. Yoshiya*[1]; S. Fujii[1]; K. Funai[1]; M. Tanemura[1]; T. Yokoi[1]

1. Osaka University, Department of Adaptive Machine Systems, Japan

Lattice discontinuity at grain boundaries often has negative impact on many kinds of transport properties, which is often referred to as grain boundary resistance. Ionic conductivity is one of them as some of mobile ions are trapped at grain boundaries, decreasing its mobility and net carrier concentrations. Electronic conductivity and thermal conductivity both of which determine thermoelectric energy conversion efficiency are also affected by the grain boundaries. This is why the grain boundary resistance tends to be understood in the same or similar terminology from macroscopic viewpoints. However, the way those transport properties are affected by grain boundaries are significantly different among those transport properties as microscopic mechanism behind them are different. In this talk, based on atomistic simulations, difference in the modification of those transport properties, especially heat transport, are discussed, with particular attention to quantum nature of the transport properties.

PACRIM Symposium 04: Polymer-Derived Ceramics (PDCs) and Composites

Structure and Properties of PDCs

Room: King's 3
Session Chair: Gurpreet Singh, Kansas State University

1:15 PM

(PACRIM-S4-011-2017) Characterizing the Impact of "Free" Carbon on Structure and Interfaces in Silicon Oxycarbide Ceramics (Invited)

P. Kroll*[1]

1. UT Arlington, USA

Combining structure modeling, ab-initio molecular dynamic simulations, million-atom-simulations, experimental as well as computational NMR studies we explore structure and impact of "free" carbon in SiCO ceramics. Our simulations show a particular multi-stage development of the "free" carbon system for a wide range of compositions. It starts with isolated carbon units provided by the molecular precursor. Upon annealing these units combine to larger extended but finite sheet-like segregations. Further annealing shows the formation of tubular structures, which ultimately convert into graphite segregations. The intermediate stages are impacted by the viscosity of the surrounding SiCO glass phase, which in turn is determined by composition.

1:45 PM

(PACRIM-S4-012-2017) Control the thermal conductivity of SiC by modifying the polymer precursor

Y. Wang*[1]

1. Northwestern Polytechical University, China

Compared to other methods, the fabrication of SiC from precursors allows designing the microstructure and thus the properties of the ceramic material by adjusting the microstructure of the precursor materials. In this study, we used a divinylbenzene (DVB) isomer mixture to modify the polycarbosilane (PCS) precursor via the chemical modification method. The ceramics derived from the modified precursors showed different thermal conductivities. The SiC prepared from PCS without DVB exhibited a very low thermal conductivity at low and at high temperatures. A proper doping with DVB led to clean SiC grain boundaries, resulting in the typical thermal conductivity behaviour of coarse SiC ceramics. An excess doping with DVB led to the precipitation of free carbon around the SiC grains, resulting in a still suitable thermal conductivity which was between the other two values. The results clearly demonstrate that adjusting the thermal properties by modifying the microstructure is a promising approach.

2:00 PM

(PACRIM-S4-013-2017) (Thermo)mechanical properties of SiOC glasses and glass ceramics with different composition and microstructure

C. Stabler*[1]; M. Heilmaier[2]; L. Wondraczek[3]; T. Rouxel[4]; E. Ionescu[1]; R. Riedel[1]

1. Technical University Darmstadt, Germany
2. Karlsruhe Institute of Technology, Germany
3. University of Jena, Germany
4. University of Rennes 1, France

In the present study, thermomechanical and mechanical properties of silicon oxycarbides (SiOC) with special focus on the high-temperature creep behavior were assessed. Dense monolithic SiOC glasses and glass ceramics with different chemical composition and microstructure (i.e. single-phasic and phase-separated) were prepared and chemically and structurally characterized. The effect of two different types of carbon on the high-temperature creep behavior of SiOC will be discussed: (i) the incorporation of carbon into the SiOC glass network leads to an increased creep resistance and viscosity in comparison to vitreous silica. It is shown that the viscosity of a SiOC glass ceramic without segregated carbon phase is higher than the theoretical apparent viscosity of a SiO$_2$/SiC composite. This is discussed in terms of the interface between SiC particles and the amorphous SiO$_2$ matrix. (ii) The incorporation of a segregated carbon phase leads to an additional increase in viscosity. Furthermore, the effect of the chemical composition and microstructure (single-phasic and phase-separated) of SiOC glasses and glass ceramics on their elastic properties (Young's modulus, Poisson ratio), hardness as well as their thermal conductivity will be presented and discussed. Their behavior is in accordance to the degree of connectivity of the glass network.

2:15 PM

(PACRIM-S4-014-2017) A low temperature study of magnetic properties of polymer derived SiCN ceramics, doped with Fe ions

S. K. Misra*[2]; S. I. Andronenko[1]; A. Rodionov[1]; I. Gilmutdinov[1]; R. Yusupov[1]

1. Kazan Federal University, Physics, Russian Federation
2. Concordia University, Physics, Canada

SiCN ceramics doped with 3-d transition ions is a new class of materials exhibiting superparamagnetic behavior. They are potentially useful in developing high-temperature magnetic sensor devices. Magnetic properties of polymer derived SiCN ceramics, annealed at 800° C, 1000° C, 1100° C, 1285° C, 1400° C, and activated with Fe (III) acetylacetonate, were investigated at liquid-helium temperatures. The magnetization of SiCN ceramics, activated with Fe ions, annealed at different temperatures, was measured in the range from 4 K to 400 K as a function of temperature ZFC (zero field cooling) and FC (field cooling). It was found that the blocking temperature strongly depends on annealing temperature. The magnetization and X-band EPR were measured as a function of magnetic field at temperatures from 4 K to 120 K. An unusual behavior of the hysteresis curve (butterfly-like) was found in the temperature range just above the blocking temperature. SiCN/Fe ceramics reveal superparamagnetic behavior due to various sources, mainly due to nanoparticles of Fe$_5$Si$_3$ and Fe$_3$Si, as well as due to Fe$_{70}$Si$_x$C$_{30-x}$ nanoparticles, dispersed in SiCN nanoceramics. This research was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) (SKM); SIA is grateful to Ministry of Education of Russian Federation, for partial support in the frame of project 14-70, allocated to KFU.

2:30 PM

(PACRIM-S4-015-2017) Physical properties and thermal resistance of Si-O-C(-H) ceramics obtained by polysiloxane pyrolysis

M. Narisawa*[1]; S. Takeuchi[1]; K. Sasakawa[1]; T. Kawai[1]; H. Inoue[1]

1. Osaka Prefecture University, Japan

Ceramic yields of linear polysiloxanes are generally low because of cyclic oligomer repulsion process during the heating. In order to increase the ceramic yields, a dense cross-linked structure, which prevents the bond rearrangement process, is necessary. Introduction of vinyl or phenyl groups in original molecular structure is also known to be effective for increasing the apparent ceramic yields. There is, however, the concern that during pyrolysis such side groups are converted to free carbon domains. In an inert atmosphere, once formed SiOxCy materials from polysiloxanes are considered to be decomposed beyond 1,400 °C. If the free carbon content in the Si-O-C material is high, SiC and excess carbon are formed during the carbothermnal reduction. On the other hand, our group in Osaka Prefecture University succeeded in synthesis of "white" SiOxCy materials, which contained almost no free carbon, by using hydrogen for a pyrolysis atmosphere of a kind of polymethylsiloxane. Behaviors of such "white" SiOxCy materials at high temperature beyond 1,400 °C in various atmosphere were investigated, and obtained results were analyzed in terms of thermodynamic calculation. Recent try of using hydrogen for pyrolysis of the polysiloxanes which contains a high amount of phenyl groups will be also introduced as a recent topic.

2:45 PM

(PACRIM-S4-016-2017) SiCO Anode Materials: DFT Simulations of Li Insertion

P. Kroll*[1]; S. Haseen[1]

1. UT Arlington, USA

We present combined modeling and simulation studies of Li insertion in amorphous SiCO ceramics to understand the high capacity of these novel anode materials. Atomistic models of amorphous SiCO in various forms, glasses with and without so-called "free" carbon, idealized SiO$_2$-C bilayer systems, and nano-structured SiCO models have been crafted and investigated within density functional theory. Random insertion of Li atoms tests for sites with high and favorable insertion energy. As shown previously, Li prefers bonding to O as cationic Li$^+$, while the surplus electron is promoted to unoccupied state. Availability and locality of an electron reservoir determines enthalpy of insertion and charge distribution in the system. A fortuitous balance between Li-O bonding and electron promotion exists for aromatic carbon embedded in SiCO. When inserting multiple Li into SiCO we observe a strong correlation between the amount of Li possible to insert and the number of C atoms in aromatic segregations. This trend matches matches experimental observation. Thus, our computational studies provide fundamental understanding of the high Li capacity of SiCO compounds.

3:00 PM

(PACRIM-S4-017-2017) Flexible SiZrOC ultrafine fiber mat with ehanced high-temperature stability

Y. Wang*[1]; J. Wang[1]; H. Wang[1]

1. National University of Defense and Technology, China

Despite tremendous efforts have been devoted to enhancing thermal stability of SiOC fibers, developing a simple and straightforward method to prepare SiZrOC ultrafine fibers still remains a challenge. Owing to easy processability, tailored composition and structure, polymer-derived ceramics (PDCs) route presents distinct advantages in preparing complicated silicon-based fibers. Herein, we provide a flexible zirconium modified silicon oxycarbide (SiZrOC) fiber mat via a simple electrospinning process combined with PDCs route. The spinning solution was prepared from a sol-gel system composed of zirconium n-butoxide and vinyltrimethoxysilave as raw materials, polyvinylpyrrolidone as the polymer for the fibers formation, acetic acid as a stabilizer and HNO$_3$ as a catalyst in water/alcohol solvent, separately. After reaching a suitable viscidity at ambient condition, the precursor solution was electrospun to be ultrafine fibers. Subsequent pyrolysis in nitrogen atmosphere turned the green fibers into SiZrOC ceramic fibers. Both the green fibers as well as the ceramic fibers were investigated by FTIR, XRD, SEM and TGA. The SiZrOC ultrafine fibers are relatively uniform with a diameter of 600-900 nm, without any noticeable flaws in the surface. The SiZrOC ultrafine fiber show good high temperature stability and flexibility. The residue weight at 1200 °C was 97.5 wt% for SiZrOC and 90.9 wt% for SiOC.

3:15 PM

(PACRIM-S4-018-2017) Promising attempts to get ultrathin boron nitride layers by Polymer Derived Ceramics

F. Gombault*[1]; B. Toury[1]; A. Brioude[1]; C. Journet[1]

1. Université de Lyon, Laboratoire des Multimatériaux et Interfaces, France

Polymer Derived Ceramics (PDC) route is an efficient method to synthetize ceramics with various shape such as monoliths and thins films. Starting from a monomer precursor, the polymerization process allows to adjust the chemical and physical properties to optimize the shape of the desired ceramic. Graphene attracts great interest owing to its distinctive band structure and physical properties. However it is highly sensitive to extraneous environment. Graphene grown on standard SiO_2 substrates exhibited high disorder structrues, which is detrimental to its intrinsic electric properties, indeed. Hexagonal boron nitride (h-BN), due to its isostructure to graphene, has demonstrated to be a promising substrate for graphene growth. The synthesis of thin films of h-BN is investigate using the PDC route. The boron nitride precursor used in the present study is borazine $B_3N_3H_6$, which was synthesized with an upgraded procedure of Wideman and Sneddon. After a polymerization process in a sealed tube during 5 days at 45 or 50°C leading to polyborazylene, this polymer is deposited on different substrates by dip coating. After a short stabilization process at 200°C under inert atmosphere BN ultra thin films can be obtained by a ceramisation treatment up to 1500°C under argon or nitrogen. The BN layers were fully characterized by SEM and Raman spectroscopy. Promising results will be presented.

PDCs Composites

Room: King's 3
Session Chair: Yuji Iwamoto, Nagoya Institute of Technology

3:45 PM

(PACRIM-S4-019-2017) Polysiloxane-Derived Porous SiOC Ceramics (Invited)

K. Lu*[1]; D. Erb[1]

1. Virginia Tech, USA

Much work has been done for room temperature high surface area materials, such as porous carbons, mesoporous silicates, and (metal-)organic frameworks. However, many applications require the porous materials to be thermally stable and the specific surface area to be higher than a few hundred m^2/g. In our study, bulk SiOC ceramics have been fabricated through the pyrolysis of a base polysiloxane (PSO) and subsequently etching with hydrofluoric acid to create micro/mesopores. Different organic species were added to the PSO during crosslinking to alter the Si/C and Si/O contents within the precursor. Different solvents were used during the PSO crosslinking. The effect of the organic additives, solvents, and the pyrolysis atmosphere on the SiO_2 and SiC phase formation before and after HF etching was investigated. Water vapor injection caused a drastic difference in the SiO_2 formation for the different additives, giving specific surface areas ranging from 804.24 m^2/g to 1953.94 m^2/g, while maintaining average pore sizes between 1.66 nm and 3.27 nm. Different pyrolysis behaviors of the polymers in the presence of water vapor is due to both the chemical bonding/species within the polymers and their possible reactions with water. The ability to drastically alter the specific surface area of the ceramics through pyrolysis atmosphere and additives presents a promising processing route for porous SiOC ceramics.

4:15 PM

(PACRIM-S4-020-2017) Creep/Stress Rupture Behavior and Failure Mechanisms of Full CVI and Full PIP SiC/SiC Composites at Elevated Temperatures in Air

R. Bhatt*[1]; J. D. Kiser[1]

1. Ohio Aerospace Institute, USA

SiC/SiC composites fabricated by melt infiltration are being considered as potential candidate materials for next generation turbine components. However these materials are limited to 24000F application because of the presence of residual silicon in the SiC matrix. Currently there is an increasing interest in developing and using silicon free SiC/SiC composites for structural aerospace applications above 24000F. Full PIP or full CVI or CVI/PIP hybrid SiC/SiC composites can be fabricated without excess silicon, but the upper temperature/stress capabilities of these materials are not fully known. In this study, the on-axis creep and rupture properties of the state-of-the-art full CVI and full PIP SiC/SiC composites with Sylramic-iBN fibers were measured at temperatures to 27000F in air and their failure modes examined. In this presentation creep rupture properties, failure mechanisms and upper temperature capabilities of these two systems will be discussed and compared with the literature data.

4:30 PM

(PACRIM-S4-021-2017) Processing and Characterization of Graded CMCs with Through Thickness Thermal Conductivity Control

D. King[1]; M. Y. Chen*[1]

1. Air Force Research Lab, USA

For a given fiber reinforced ceramic matrix composites (CMCs), the selection of matrix & filler materials could influence the heat dissipation speed and its direction via in-plane or through thickness. Carbon fiber based CMCs were fabricated using polymer infiltration and pyrolysis (PIP) methods with the goal of ply-by-ply compositional variation to control through thickness thermal conductivity. Graded CMCs matrices were B-staged, such that a controlled grade of the CMC matrix composition was produced with particulate additions to the pre-ceramic polymer. The resulting CMCs were graded HfB_2 to SiC, SiC to Si_3N_4, and HfB_2 to SiC to Si_3N_4. The effects of the matrix grading on thermal conductivity were examined by comparing with non-graded control specimens. Through thickness thermal conductivity was measured by laser flash for each CMC. Graded and control specimens were also tested in an oxy-acetylene torch test bed, serving as a mock scenario to assess the compatibility of such CMCs in a hypersonic flight conditions.

4:45 PM

(PACRIM-S4-022-2017) Microstructural modification and mechanical properties of Magnesium Matrix Composites processed using polymer precursor

M. K. Surappa*[1]; C. Nagaraj[2]; H. Singh[3]; R. Raj[4]

1. Indian Institute of Science, Materials Engineering, India
2. Indian Institute of Technology, India
3. Indian Institute of Technology, Mechanical Engineering, India
4. University of Colorado, USA

As-cast magnesium matrix composite was fabricated by injecting liquid polymer directly into molten magnesium and having it converting to 2.5 vol% SiCNO ceramic phase, liquid stir-casting method. These composites were subjected to single pass friction stir processing (FSP) in order to modify their microstructure and Mechanical Properties. Results indicate as-cast composite exhibit grain boundary segregation of SiCNO particles, FS processed composites exhibit improved homogeneity in the SiCNO particle distribution. In addition, FS processed composite showed particle refinement (mean particle size of about 100-300 nm) and matrix refinement (mean grain size of 2.5 mm). Micro-hardness, yield stress, ultimate compressive stress, strain hardening exponent and ductility of the as-cast composites are improved by 61.74%, 150%, 123%, 80% and 22.1% respectively after FSP.

5:00 PM

(PACRIM-S4-023-2017) Crystallization Behavior of Polymer-Derived Si-O-C during Ceramic Matrix Composite Processing

D. L. Poerschke*[1]; A. Braithwaite[1]; C. G. Levi[1]

1. University of California Santa Barbara, USA

The challenges encountered when manufacturing dense, hermetic matrices for SiC-based ceramic matrix composites (CMC) prevent wider adoption of these materials. Processing routes utilizing preceramic polymers are being developed as a cost-effective method to manufacture CMCs with improved temperature capability. The notional approach involves repeated polymer/precursor infiltration and pyrolysis (PIP) cycles to form the matrix. Heat treatment at higher temperature then converts the amorphous polymer derived ceramic (PDC) to crystalline SiC, typically with additional off-gassing of CO and/or SiO. However, the heterogeneous nature of the CMC microstructure, with variations in the PDC feature size and pathways for gaseous egress, influence the local crystallization kinetics. Additionally, reactions with the fibers and fiber coatings can reduce the composite strength. This talk will describe e complementary experiments on crushed powders, fiberless matrix monoliths, and fiber reinforced composites used to elucidate the influence of composition, geometry, and temperature on the crystallization kinetics and composite properties in order to develop improved CMC processing protocols.

5:15 PM

(PACRIM-S4-024-2017) Fabrication of three-dimensional four-directional (3D4D) braided SiC_f/SiC composites using EPD method and PIP process

X. Zhou*[1]; M. Li[1]; H. Wang[1]; J. Yu[1]; H. Hou[1]

1. National University of Defense Technology, Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, China

SiC_f/SiC composites are the most attractive materials for the structural and functional components used in future fusion reactors. This paper used the electrophoresis method together with the polymer infiltration and pyrolysis (PIP) process to fabricate a dense SiC_f/SiC composite with a 3D4D braided preform which was coated with 100nm pyrolytic carbon interphase. A well-dispersed aqueous suspension of submicron SiC particles was homogenized by a strong ultrasonic power and a pH adjusted to 10 by titration of NaOH solution. EPD was under taken in this suspension, after which the weight gain ratio of the preform reached to nearly 150%. The green deposited preform was then infiltrated with a liquid precursor named LPVCS under vacuum, followed by a hot mould pressing of 3 MPa before the first circle of pyrolysis. After shorter circles of PIP at a sintering temperature of 1200°C, the composites were produced and their microstructures, thermal and mechanical properties were investigated. The density, the flexural strength, and the thermal conductivity of the composites achieved a relatively high level ever we had in our laboratory respectively, due to the existence of the highly packed SiC particles and the outstanding performance of the 3D4D SiC preform, indicating that the composites we fabricated can be used as the potential materials for future fusion reactors.

PACRIM Symposium 05: Advanced Powder-Processing and Manufacturing Technologies

Particle Dispersion Control in Liquid or Polymer

Room: King's 2
Session Chairs: Jean-Pierre Erauw, Belgian Ceramic Research Centre; Chika Takai, Nagoya Institute of Technology

1:15 PM

(PACRIM-S5-007-2017) Rheological Behavior of h-BN Composite Based on the Difference of Aspect Ratio and Surface Condition

Y. Tominaga*[1]; Y. Hotta[1]

1. National Institute of Advanced Industrial Science and Technology, Japan

Hexagonal boron nitride (h-BN) has been widely used as fillers for polymer composite and ceramic composite with high thermal conductive properties. It is known that the performance of its composite is strongly dependent on various parameters, such as aspect ratio of h-BN particles, orientation of h-BN particles in composite, and interaction between h-BN particles and matrix. Therefore, the investigation of rheological behaviors of h-BN particles is of importance for the development of composite materials with high reliability. In this study, we will demonstrate to evaluate the rheological behaviors by using h-BN particles with different surfaces. Firstly, we exfoliated h-BN particles with high aspect ratio by using a wet-jet milling. The exfoliated h-BN particles showed that the apparent viscosity was decreased in the range of high shear rates compared with raw h-BN particles. Furthermore, we also prepared h-BN particles with rough surface by ball-milling and investigated the difference of rheological behaviors of h-BN with inert surface. As results, the rheological behaviors of composites were different greatly based on the surface conditions of h-BN particles.

1:30 PM

(PACRIM-S5-008-2017) Internal structures of dispersed and flocculated slurries with high concertation

S. Tanaka*[1]; Y. Nagasawa[1]

1. Nagaoka University of Technology, Materials Science and Technology, Japan

Particle dispersion of slurry is crucial for a powder compact and ceramics with homogeneous microstructure. Recently, we reported in-situ direct observation of the inside structure of a concentrated slurry with the confocal laser scanning fluorescent microscope (CLSFM). The objective of the study is to examine the dispersed or flocculated state in concentrated slurries. Mono-dispersed silica spheres with 2.3 μm in diameter were used. The silica slurry with 30 vol% was prepared by a glycerol solution which refractive index is the same with silica, so that the concentrated silica slurry shows transparency. Either PAA (Polyacryl ammonium acid) or PEI (Polyethylene imine) was used as additives. The dispersed state in slurries under shear flow were observed with CLSFM. Besides, dispersability of particles was characterized by the rheology measurement and the interaction force measurement. A PEI added slurry showed a Newtonian behaviour, and the particles flowed independently in slurry. On the other hands, a slurry with PAA showed shear thinning and flocculated behaviour. Many agglomerations were observed and connected in the slurry. The agglomerated particles deformed to chain-like structure gradually under shear stress. This was a reason why the slurry showed the shear thinning behaviour.

1:45 PM

(PACRIM-S5-009-2017) PEI-fatty acid complex as dispersants for multi-component non-aqueous slurries and lubricants for Si_3N_4 based spray dried granules

M. Iijima*[1]; N. Okamura[1]; S. Sueyasu[1]; J. Tatami[1]

1. Yokohama National University, Graduate School of Environment and Information Sciences, Japan

Techniques to prevent raw particle aggregation in multi-component non-aqueous slurries as well as to design spray dried granules which can be densely packed in the green compact during compaction will be important key issues to manufacture highly reliable non-oxide ceramics. Herein, we report a new concept for using polyethyleneimine (PEI)-fatty acid complex as multi-functional additives which can act as dispersants for multi-component slurries and lubricants for spray dried granules. PEI-oleic acid (PEI-OA) complex has successfully prepared by a simple mixing process and found that it can effectively stabilize multicomponent (Si_3N_4-Y_2O_3-Al_2O_3-AlN-TiO_2) toluene dense slurries. The spray dry process of PEI-OA stabilized slurry treated with (poly(maleic anhydride-alt-1-octadecene)) as reactive binder resulted to obtain Si_3N_4 based granules successfully. Compared to the Si_3N_4 based granules prepared from the multicomponent (Si_3N_4-Y_2O_3-Al_2O_3-AlN-TiO_2) ethanol slurry stabilized with PEI, the green compact density after uniaxial pressing and CIP process has improved by using granules prepared from PEI-OA stabilized slurry. The effect of PEI-OA additive content on the microstructure of prepared granules, flowing properties, and compaction properties will be presented.

2:00 PM

(PACRIM-S5-010-2017) Green and sintering compacts prepared by centrifugal compaction process using a stable slurry

Y. Hotta*[1]; K. Sato[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

We have demonstrated that wet-jet milling processes led to stable Al_2O_3 slurries. The wet-jet milled slurries have a low viscosity compared to the ball-milled slurries, and the viscosity of the wet-jet milled slurries was stable for a long time, whereas that of ball-milled slurries was increased with time. In this work, we studied the properties of compacts prepared by centrifugal compaction process using wet-jet milled Al_2O_3 slurry. Wet-jet milled slurries showed a lower sediment height compared with the ball-milled slurries at same content after centrifugal compaction, and the relative packing density estimated from the sedimentation layer was to be 68% at the solid content of 30 vol%. On the other hand, in the case of ball-milled slurry, the relative packing density was to be 55% at the same solid content. These differences between both relative packing densities are corresponded to the behavior of the viscosity, stability of slurries and the particle surface statement in slurries. Therefore, the particles prepared from wet-jet milled slurries are able to pack particles easier. The most consequence is that the stable slurry leads to green compacts with high density.

Novel Forming and Sintering Technology

Room: King's 2
Session Chair: Motoyuki Iijima, Yokohama National University

2:15 PM

(PACRIM-S5-011-2017) Achieving homogeneity in Spark Plasma Sintered fine ceramics (Invited)

J. Erauw*[1]; L. Boilet[1]; V. Dupont[1]; M. Cambier[1]; V. Lardot[1]; F. J. Cambier[1]

1. Belgian Ceramic Research Centre, Belgium

Spark Plasma Sintering has been shown very effective to achieve high densities of both conductive and non-conductive powder compacts. However, the high heating rates used do not allow reaching a steady state temperature field and often result in a non-uniform temperature spatial distribution that may impact both the transient densification behavior and the homogeneity of the final microstructure. With non-conductive powders, it has been theoretically shown that optimization of tool dimensions enables reducing the temperature gradients within the compact ; with conductive powders, one way to minimize the temperature gradients is to rely on hybrid heating, combining the direct electrical heating characteristic of SPS with an additional external heating source. In the present study, the effectiveness of both solutions was investigated. Sintering experiments have been performed on the one hand on a HPD10 system with graphite tools of varying dimensions, on the other hand on a HHPD125 system in which the additional heating source consists in a peripheral graphite resistor. The influence on the densification behaviour and transient radial temperature gradients of sintering parameters such as heating rate, holding time and in the case of hybrid heating, ratio between the heating power delivered by the peripheral heat element and that of the SPS system, has been assessed.

2:45 PM

(PACRIM-S5-012-2017) Fabrication of Highly Textured Hydroxyapatite Ceramics by Colloidal Processing in a High Magnetic Field and Sintering

Y. Sakka*[1]

1. National Institute for Materials Science (NIMS), Japan

Hydroxyapatite (HAP) is a main component in the human bodies and teeth, and a specific crystal orientation is required because of the different properties for each crystal plane. We have demonstrated a new processing of textured ceramics with a feeble magnetic susceptibility by slip casting in a high magnetic field and subsequent heating. In this study, three kinds of hydroxyapatite powders were used for the fabrication of a textured HAP. The effect of the processing parameters on the orientation were examined. Using the de-agglomerated particle by a milling procedure, it can be possible to control the particle orientation, but when using heavily agglomerated particles, it was impossible to control the particle orientation by applying a high magnetic field. Highly-textured HAP can be fabricated by slip casting using a well-dispersed suspension in a high magnetic field (above 4 T) followed by sintering above 1373 K.

3:00 PM

(PACRIM-S5-013-2017) A Facile Way to Fabricate Carbon-Ceramic Nanocomposites through Mechano-chemical Treatment Without Sintering Process

B. Peng*[1]; S. Goto[1]; C. Takai[1]; H. Razavi Khosroshahi[1]; M. Fuji[1]

1. Nagoya Institute of Technology, Japan

To exploit numerous assets of ceramic-based composite, carbon-ceramic was investigated for realizing functional and structural nanocomposite. A novel method named Non-Firing Ceramics Fabrication Process was proposed without sintering, which means treat surface of raw ceramic powder by mechanically activation and continuously dispersed powder in alkaline solvent to form precipitates to prepare ceramics solidified body eventually. In this work, carbon material was believed to be an ultimate reinforcement into ceramic composites by incorporating with the matrix. Silica nanopowder was activated by planetary ball mill using zirconia as media before mixing with carbon. To ensure well mixture, compounded powder was transfer to tumbler ball mill. Slurry with KOH dropped was kept 5h at 80°C for solidify. Parts of matrix grains are obtained because minimum amount of the active powder surface necessary for solidification is dissolved and precipitated. Importantly, carbon network among solid body provide the possibility of electroconductivity path when reach percolation threshold. Electrical resistivity of 2.30 Ω.cm and bending strength of 7.28 Mpa are obtained, which is substantial improves when compare with common insulate ceramic material. This research is partially supported by "Knowledge Hub Aichi", Priority Research Project from Aichi Prefectural Government.

3:15 PM

(PACRIM-S5-014-2017) Laser cladding of Inconel 625 - tungsten carbide composites

D. Kata*[1]; J. Huebner[1]; J. Kusinski[2]; J. Lis[1]; A. Tajdus[3]; T. Slomka[4]

1. AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Poland
2. AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Poland
3. AGH University of Science and Technology, Faculty of Mining and Geoengineering, Poland
4. AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Poland

The effect of laser cladding on structural and mechanical properties of Inconel 625 - (WC) composite is shown. Inconel 625 polycrystals were modified by fine tungsten carbide particles ($\phi \approx 0.54$ μm) in order to obtain better mechanical properties. Three powder mixtures containing different amount of tungsten carbide: 10, 20 and 30 weight % were prepared by following process parameters: laser beam diameter $\phi \approx 500$ μm, scanning velocity - 10 m/min, laser power - 320 W, distance between tracks - 0.8 mm. The SEM microstructure observations showed uniform, crack and pore free polycrystals having excellent bonding to the substrate material. Because of chemical composition of Inconel 625 superalloy, secondary carbides of WC, W_2C, NbC, (NbW)C, $W_6C_{2.54}$ and $(W,Cr,Ni)_{23}C_6$ were detected at grains boundaries. They appeared in samples containing increased amount of WC - 30 wt %. High cooling rate during cladding process was the reason of fine microstructure in prepared polycrystals. TEM observation showed two types of precipitations: angular carbides and spherical oxides containing increased amount of Cr, Si and Ti. Hardness measurements showed improvement as a function of WC addition from 396.3 ± 10.5 HV for pure Inconel 625 to 469.9 ± 24.9 HV for 30 weight % of WC. Additionally, nanohardness measurements showed that eutectic had significantly higher average hardness of 534.2 HV, than metallic Inconel 625 grains - 306.2HV.

Nano/Microstructure Control

Room: King's 2

Session Chairs: Yuji Hotta, National Institute of Advanced Industrial Science and Technology (AIST); Shingo Ishihara, Tohoku University

3:45 PM

(PACRIM-S5-015-2017) Tailored Property and Processing Particle-Filled-Glass Composite Design and Development (Invited)

K. Ewsuk[1]; L. Criscenti*[1]

1. Sandia National Laboratories, USA

Experimentally-validated modeling science and technology are being developed to design and manufacture particle-filled-glass composites (FGCs) with processing and properties engineered for materials joining. Tailored microstructure and property FGCs with processing latitude and robustness have significant potential as improved performance and reliability hermetic glass-to-metal (GtM) seals. This paper will present and discuss work being completed to develop FGCs using a combination of fundamental materials science and materials engineering, employing: 1) experimentally-validated molecular modeling to better understand and control bulk and interface glass chemistry-structure-property relations to improve seal performance and reliability; and 2) composite property and process modeling to facilitate FGC design, and to optimize FGC manufacturability and properties. Results of characterizing and modeling barium aluminosilicate (BAS) glass chemistry-structure relations will be presented. Additionally, the processing and properties of ceramic-filled BAS glass FGCs will be presented and discussed. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:15 PM

(PACRIM-S5-016-2017) Enhancement infrared absorption inspired from natrual optical structure (Invited)

W. Zhang*[1]; D. Zhang[1]

1. Shanghai Jiao Tong University, State Key Lab of Metal Matrix Composites, China

Recently, an increasing number of researchers have directed their attention to the wings of lepidopterans (butterflies and moths) because of their dazzling colors. According to one previous study, these iridescent colors are caused by periodic structures on the scales that make up the surfaces of these wings. These materials have recently become a focus of multidiscipline research because of their promising applications in the display of structural colors, advanced sensors, and solar cells. This work will provide a broad overview of the research into these wings. Specifically, the review focuses on characterization and simulation of bioinspired optical materials templated from lepidopteran wings scales.

4:45 PM

(PACRIM-S5-017-2017) Si based green body prepared through wet processing route and their microstructure effects on nitridation and post-reaction sintering properties

S. Morita*[1]; M. Iijima[1]; J. Tatami[1]

1. Yokohama National University, Graduate School of Environment and Information Sciences, Japan

Post-reaction sintering technique of green bodies processed from Si particles is one of the candidate for low cost Si_3N_4 manufacturing. The arrangement control of multi-component particles comprising Si and sintering aids in the processed green bodies plays an important role to improve the properties of Si_3N_4 ceramic such as degree of nitridation and density. Herein, we report a wet processing route to fabricate Si-based green bodies with controlled particle arrangement from non-aqueous dense slurry stabilized by polyethylenimine-oleic acid complex (PEI-OA). Adding Si raw particles into a non-aqueous toluene suspension of Y_2O_3 and MgO particles stabilized by PEI-OA resulted to form composites of Si particles decorated with Y_2O_3 and MgO particles. It was found that green bodies prepared from wet vacuum casting of PEI-OA stabilized Si-Y_2O_3-MgO slurry can be homogeneously nitrided by 2 hours of nitriding at 1375°C while green bodies prepared through dry shaping of Si-Y_2O_3-MgO composite particles collected from the multi-component slurry required longer nitriding time with relatively in-homogenous structures. The effect of microstructures of Si based green body prepared from different shaping process on their nitridation properties and structures of post-reaction sintered Si_3N_4 ceramics will also be discussed.

5:00 PM

(PACRIM-S5-018-2017) Orientation behavior of multilayered-graphene coated glass fiber in a magnetic field

T. Takahashi*[1]; J. Tatami[2]

1. Kanagawa Academy of Science and Technology, Japan
2. Yokohama National University, Japan

Anisotropy of diamagnetic susceptibility ($\Delta\chi$) of material is the origin of particle orientation in a magnetic field. A very strong magnetic field is required to orient common diamagnetic particles because of their small $\Delta\chi$. The intensification of $\Delta\chi$ should be effective in orientation by a low magnetic field. In our previous work, multilayered-graphene (MG), which is well-known as a substance having very large $\Delta\chi$, was coated on the surface of Si_3N_4 particles to make c-axis oriented Si_3N_4 ceramics by molding in a low magnetic field. Orientation behavior has not been clarified yet, though it is important to control the orientation. The purpose of this work was to clarify experimentally and theoretically the orientation behavior of the MG coated particles. The MG coated glass fibers were prepared by a mechanical treatment. They were oriented even at a low magnetic field of 0.5 tesla. The rotation of the fibers dispersed in a solvent was observed directly by an optical microscopy and it was quantitatively evaluated by image analysis. The $\Delta\chi$ of the MG coated glass fibers was estimated from the relationship between the time and the rotation angle. As a result, it was almost the same as the value estimated from the batch composition. This means that the orientation of MG coated glass fiber resulted from $\Delta\chi$ of coated MG.

PACRIM Symposium 06: Synthesis and Processing of Materials Using Electric Currents and Pressures

Electric Currents I

Room: King's 1
Session Chairs: Takashi Goto, IMR Tohoku University; Javier Garay, University of California, San Diego

1:15 PM

(PACRIM-S6-001-2017) Thermal Runaway in Flash Spark Plasma and Microwave Sintering (Invited)

E. A. Olevsky*[1]; C. Maniere[1]

1. San Diego State University, USA

An ultra-rapid process of flash hot pressing (or ultra-rapid spark plasma sintering) is developed based on the conducted theoretical analysis of the role of thermal runaway phenomena for material processing by flash sintering. The present study experimentally addresses the challenge of uncontrollable thermal conditions by the stabilization of the flash sintering process through the application of the external pressure. The effectiveness of the developed flash spark plasma sintering technique is demonstrated by the few seconds–long consolidation of SiC powder in an industrial spark plasma sintering device. Similarly to flash spark plasma sintering, the experimentally known thermal instability of microwave sintering is theoretically explained. It is shown that the sample location has a great impact on the temperature distribution and decreasing the sample size promotes temperature homogenization thereby assisting the overall sintering stabilization.

1:45 PM

(PACRIM-S6-002-2017) Flash sintering of alumina: Evidences of oxide partial reduction

M. Biesuz*[1]

1. University of Trento, Department of Industrial Engineering, Italy

Flash Sintering (FS) represents an innovative sintering technology for ceramics that allows a consistent reduction of consolidation time and temperature. Although the operative conditions for flash sintering and its applicability to several ceramics have been extensively studied, the mechanisms behind the process have not been clarified yet. In previous works a model for the thermal runaway, which provides a reasonably good description of the onset condition for FS has been proposed. Nevertheless, the reasons behind the enhanced electrical conduction and the rapid densification have not been completely explained. In the present work microstructural features and evolutions of flash sintered alumina have been studied in detail by using complementary experimental techniques. The results show anomalous grain growth phenomena and partial reduction of the oxide. This latter phenomenon could be responsible for the electronic conduction increase during the flash event and could accelerate the densification/grain coarsening phenomena as a result of a faster mass transport mechanism.

2:05 PM

(PACRIM-S6-003-2017) Direct Joule heated (Flash) Sintering of Ionic Conductive Ceramics in a Conventional Spark Plasma Sintering Furnace Using Standard Graphite Tooling

L. S. Walker*[1]

1. Thermal Technology, USA

Direct joule heating of ionic conductive ceramics, also known as 'flash' sintering, has attracted great interest of recent due to the extremely high sintering rates achieved through the rapid heating process. The basic approach involves heating a powder compact of an ionic conductive ceramic such as zirconia in a furnace to a temperature high enough for it to conduct electrical current and rapid joule heating to high temperature using a current controlled power supply to achieve rapid sintering. The apparatus for such an experiment is generally complex and control over the experiment is also generally limited to current control of the power supply. Presented here is a simplistic approach to achieve the 'flash' sintering effect in a conventional spark plasma sintering (SPS) furnace using either current control or temperature control. The method requires no pre-sintering or compaction of the powder and uses only conventional tooling typical to the SPS process without any sacrificial heaters. The setup and operation of the technique will be presented in addition to the scalability potential to larger samples.

2:25 PM

(PACRIM-S6-004-2017) Energy Coupled to Matter for Electric Field-Enhanced Sintering (Invited)

R. E. Brennan*[1]; B. McWilliams[1]; V. L. Blair[1]; J. Yu[1]; M. Kornecki[1]; F. Kellogg[1]; S. V. Raju[1]

1. US Army Research Laboratory, USA

Energy Coupled to Matter (ECM) research is focused on the study of field interactions with materials to produce outcomes that are unattainable through conventional means, expanding materials-by-design and processing/manufacturing science capabilities. Technological advancements in ECM can have a significant impact on Army efforts for developing novel materials with tailored microstructures to produce unprecedented properties, and enhancing processing and manufacturing capabilities for rapid production of unique components. For electric field-enhanced sintering, a number of methods are currently being explored, including electric field-assisted sintering, flash sintering, and single-mode microwave sintering. All of these methods use electric fields for field-enhanced heat treatment of materials, significantly reducing temperature and time requirements for enabling full densification. The ability to rapidly densify materials under less extreme processing conditions exemplifies a major advantages of ECM, as the smaller final grain size can be uniquely preserved, resulting in enhancement of physical and mechanical properties that are relevant to Army applications (i.e. strength, hardness, fracture toughness, etc.). Breakthrough results for fabricating ceramics, metals, and hybrid materials using the aforementioned techniques will be presented to demonstrate the implications of these exciting capabilities.

2:55 PM

(PACRIM-S6-005-2017) Spark plasma sintering: From Finite Element Modeling of the process up to the elaboration of complex shapes (Invited)

C. Maniere[1]; L. Durand[2]; E. Brisson[3]; H. Desplats[3]; P. Carre[3]; P. Rogeon[3]; C. Estournes*[1]

1. CIRIMAT, LCMIE, France
2. CEMES, France
3. LIMATB, France

Pulsed Electric Current Sintering (PECS) techniques have known a huge development over the last two decades. In particular, Spark Plasma Sintering (SPS) is an extremely powerful technique to sinter all classes of powders (metallic, ceramic) as well as composites. Recently, the modeling of Spark Plasma Sintering by finite element method has known drastic development. Coupling three main physics, Electric Thermal and Mechanic (ETM), it allows now to predict the evolutions of temperature, grain size and porosity during the process. The electrical and thermal parts of the ETM model are used to calibrate the contact (thermal and electrical) resistances and to calculate the temperature at any point of the SPS tool and column. Ex-situ measurements of contact resistances were also performed in different conditions to compare the results of the calibrations. Creep parameters are identified on dense and porous materials, and sintering models (Olevsky and Abouaf) are used to predict the densification of the powders to be sintered. Last, a grain growth law coupled with the densification model may also be considered. Finally this type of modeling enables the definition of the optimized SPS parameters and tool geometry in order to minimize the porosity and microstructure gradients in a complex shape part.

3:40 PM

(PACRIM-S6-006-2017) Flash sintering of TCP bioceramics

M. Frasnelli*[1]; V. M. Sglavo[1]

1. University of Trento, Industrial Engineering, Italy

In this work, sintering behavior of tricalcium phosphate (TCP) ceramics under the effect of an external electrical field (in flash sintering configuration) was analyzed to obtain dense bio-resorbable components. The aim was to understand the physical condition leading to the flash phenomenon and to study the effect of consequent reduction in sintering time and temperature on the undesired $\beta \rightarrow \alpha$-TCP phase transition occurring at high temperature. TCP powders were synthesized by conventional solid state reaction and then shaped into cylindrical green body by uniaxial cold-pressing. Their sintering behavior was studied by dilatometry under different E-field at constant rate heating. The presence of α-TCP and the microstructure were investigated by XRD and SEM techniques. It is shown that a flash phenomenon takes place at furnace temperature below 1000°C. In addition, although $\beta \rightarrow \alpha$ transition occurs at ~1150°C for pure TCP, the detection of both polymorphs within the sintered bodies indicates that higher temperature is reached in the material, which is very likely associated to Joule effect induced by the current flow along the sample.

4:00 PM

(PACRIM-S6-007-2017) Magnetic Field Processing and Sintering of Rare-Earth Doped Aluminum Oxide

V. L. Blair*[3]; N. Ku[1]; C. A. Moorehead[2]; J. Elward[1]; B. C. Rinderspacher[3]; R. E. Brennan[3]

1. ORISE, USA
2. Drexel University, USA
3. US Army Research Laboratory, Weapons and Materials Research Directorate, USA

Energy Coupled to Matter (ECM) is an emerging technology area that goes beyond the traditional limits of materials research by exploring the use of applied physics-based fields and their influence over materials structure, properties, and response. The objective of the current research effort is to characterize and exploit effects of various energetic fields (magnetic, electric, microwave, etc.) on microstructural development of materials in order to formulate a physical explanation of the fundamental mechanisms of material interactions during processing. This presentation will focus on unexpected results observed during high magnetic field processing of diamagnetic ceramic materials. Over the past three years, ARL has successfully doped rare earth cations into nanosized alumina powders and aligned the doped powders under a magnetic field in a ceramic/polymer composite. The result was the unexpected alignment of the alumina particles to the (006) plane, which can lead to future crystallographic texture. Additionally, ARL has shown that crucial phase transformation temperatures in aluminum oxide synthesis can be affected by an applied magnetic field during the calcination process, which has implications in future densification studies. Current and future work will also be described; detailing new synthesis procedures under exploration and densification of ceramics under applied fields.

4:20 PM

(PACRIM-S6-008-2017) Industrial Applications of Direct Current Based Spark Plasma/Field Assisted Sintering; Large Components and Uniformity

L. S. Walker*[1]

1. Thermal Technology, USA

Direct current sintering also known as field assisted and spark plasma sintering has achieved great success in academia and industrial based research with its ability to rapidly produce high quality material systems. Industrial acceptance, however, has been slow to evolve due to limited access to large industrial scale systems for proof of concept work and experienced operators. Here we present the production of large parts (>10cm) for industrial applications while achieving high part uniformity and part-to-part consistency. In-situ temperature measurements within the tooling are used to measure the process uniformity at multiple sites. Microstructure and material properties will be investigated to show the results of sintering larger samples using different material systems, and the process uniformity achieved.

4:40 PM

(PACRIM-S6-009-2017) A Finite Element Based Model to Validate Temperature Distribution Measurements in Electrical Insulator and Electrical Conductor Ceramics Using SPS

E. L. Corral*[1]

1. The University of Arizona, Materials Science and Engineering Department, USA

Spark plasma sintering (SPS) is capable of precisely controlling material microstructures and achieving non-equilibrium phases due to rapid heating and cooling rates through the simultaneous application of pressure and direct current. Due to these characteristics, SPS is an ideal for processing high temperature ceramics at temperatures greater than 1500°C. However, desired microstructure must be maintained throughout the geometry of the part thus, we developed a finite element analysis model to ensure processing conditions result in desired microstructures. Our model is a coupled thermal-electrical finite element analysis model to investigate the effect of tooling, contact resistance, and current density on the resultant processing conditions for an electrical conductor, zirconium diboride, and an electrical insulator, silicon nitride. The model is experimentally verified and material properties are optimized in order to calibrate the model.

PACRIM Symposium 13: Advanced Structural Ceramics for Extreme Environments

Structural Stability in Extreme Environments

Room: Kohala 4
Session Chairs: Raj Singh, Oklahoma State University; Dechang Jia, Harbin Institute of Technology

1:15 PM

(PACRIM-S13-012-2017) Cyclic fatigue durability of EBC coated 3D SiC/SiC composites under thermal gradient conditions at 2700°F in air

C. Smith*[2]; B. J. Harder[2]; D. Zhu[2]; R. Bhatt[1]; S. Kalluri[1]

1. Ohio Aerospace Institute, USA
2. NASA Glenn Research Center, USA

Ceramic matrix composites (CMCs) such as SiC/SiC are currently being designed and implemented in high temperature sections of aerospace turbine engines. Such components will be subject to through-thickness thermal gradients, which may affect the durability. In this study, SiC/SiC CMCs with a hybrid chemical vapor infiltrated (CVI) and polymer infiltration and pyrolysis (PIP) matrix were loaded in tension while one surface was heated with a laser and the opposite surface was cooled. The samples were each coated with an environmental barrier coating (EBC), which was produced by either electron beam physical deposition (EBPVD) or plasma spray physical vapor deposition (PSPVD). Results for the two coating types will be discussed.

1:30 PM

(PACRIM-S13-013-2017) The Microstructure, Mechanical Properties and Ablative Mechanism of Dense SiBN Monoliths by Mechanical Alloying and Hot Pressing

D. Jia*[1]; X. Liao[1]; Z. Yang[1]; Y. Zhou[1]

1. Harbin Institute of Technology, China

The novel SiBN ceramics with excellent mechanical properties and outstanding high-temperature property are regarded as one of the best comprehensive performance materials using for high temperature application. The fabrication of dense SiBN monoliths is a processing challenge for conventional polymer precursors pyrolysis process and chemical vapor deposition. We report here successful densification of SiBN monoliths achieved by mechanical alloying and hot pressing at 1800°C and 40MPa. The dense amorphous/nano-crystal SiBN monoliths show the controllable microstructure and mechanical properties with the range of which bending strength is 74MPa to 270MPa and elastic modulus is 35GPa to 169GPa at room temperature, respectively, by designing the Si/B atomic ratio and sintering parameters. Meanwhile, the dense SiBN monoliths own outstanding anti-ablation property of which the lowest mass ablative rates is only 0.0001g/s.

1:45 PM

(PACRIM-S13-014-2017) Ultra High Temperature Ceramics with controlled porosity

L. Larrimbe*[1]; L. Vandeperre[1]

1. Imperial College London, Department of Materials, United Kingdom

Ultra High Temperature Ceramics (UHTCs) with controlled porosity are suitable for application in transpiration cooling systems for jet engine turbine and hypersonic flights. These systems are highly efficient in terms of reducing the amount of cooling air and increasing cooling efficiency. This work addresses the manufacturing of innovative porous UHTCs by establishing a densification route which does not require pressure and allows producing the components in the correct shape without requiring extensive machining or large amounts of material loss. Samples of ZrB_2 and HfB_2 with homogenous porous structures were manufactured by partial sintering or by addition of different volume fractions of fugitive inclusions, using starch as a pore former. Morphological features of the fugitive agent were characterized by scanning electron microscopy (SEM) and laser diffraction techniques. Moreover, it was demonstrated using thermogravimetric analysis (TGA) that burning out the starch in air should not oxidise the ceramic powders. Characterization of the sintered porous UHTCs was focussed on measuring systematically the relationship between pore structure, porosity and some properties such as thermal conductivity, strength or flow. All this information enabled to select the most relevant candidate which is able to maintain excellent thermal and structural properties whilst moving to a high porosity.

2:00 PM

(PACRIM-S13-016-2017) Fiber-reinforced ceramic composites made by precursor impregnation and pyrolysis process: Effects of filler materials

S. Lee[1]; J. Kim[1]; L. Zhao*[1]

1. Korea Institute of Materials Science, Republic of Korea

Tyrano-SA3 SiC or T-300 carbon fiber woven fabrics with PyC coating were used for the fabrication of the SiC_f/SiC or C_f/Si(B)CN ceramic matrix composites (CMC) by precursor impregnation and pyrolysis (PIP) method. The CMCs suffered from strong deterioration at 1500°C. The high temperature thermal behavior as well as the corresponding phase characterization of the PCS precursor after pyrolysis was analyzed. Although a major mass loss was completed before 1400°C, a further mass loss in the temperature range of 1400°C to 1500°C was still detected. The oxygen which was contained in the PCS mainly caused the deterioration of properties at 1500°C. The dispersion and infiltration of non-oxide fillers in the 2D-woven fiber fabrics were performed in order to get over the high temperature deterioration of the matrix phase. SiC was proved to be the most appropriate filler materials in terms of mechanical properties and thermal stability. However, SiO_2 layer which was formed on the surface of SiC filler strongly deteriorated the high temperature properties of the CMC. The problem could be solved by removing the oxide layer before the beginning of PIP cycle. By the optimization of the filler and precursor-derived ceramic matrix, the high temperature strength of the CMC could be improved at and above 1500°C.

2:15 PM

(PACRIM-S13-017-2017) Thermal shock resistance and oxidation resistance of BN matrix composite ceramics

D. Cai*[1]; D. Jia[1]; Z. Yang[1]; Y. Zhou[1]

1. Harbin Institute of Technology, School of Materials Science and Engineering, China

The effect of magnesium aluminum silicate (MAS) glass on the thermal shock resistance and the oxidation behavior of h-BN matrix composites were systematically investigated at temperature differences from 600 °C up to 1400°C. The residual strength rate of the composites rose with increasing addition of MAS showing a maximum value at the 60 wt. % MAS. Compared with the original strength, the residual strength of the specimen after thermal shock increases 77 % ($\Delta T = 1000$ °C). The strengthening effect of MAS and the surface microstructural evolution of composites are responsible for the improved thermal shock resistance. Surface oxidation of the composites during the thermal shock process plays a positive role in enhancing the residual strength with self-healing cracks and the appearance of the compressive stress. The oxide layer also acts as a thermal-barrier to decelerate the actual thermal stress. Furthermore, this dense layer also improved the oxidation resistance of h-BN matrix composites by prevent diffusion of oxygen. These results indicate that short-term surface oxidation during thermal shock process is favorable to the enhancement of the thermal shock resistance of BN-MAS composite ceramics.

2:30 PM

(PACRIM-S13-018-2017) A novel approach to the development of MeB_2 UHTCs: Improving oxidation resistance while maintaining structural performance

E. Zapata-Solvas*[1]; D. Gomez-Garcia[2]; A. Dominguez-Rodriguez[2]; W. E. Lee[1]

1. Imperial College London, Centre for Nuclear Engineering. Dpt. of Materials, United Kingdom
2. University of Seville, Condensed Matter Physics, Spain

Ultra-high temperature ceramics (UHTCs) are promising candidates for hypersonic applications as a consequence of their high melting points, in excess of 3000 °C for ZrB_2 and HfB_2 UHTCs. The UHTCs community has traditionally focused on development of more oxidation-resistant UHTC composites as a consequence of poor oxidation resistance of monolithic UHTCs, which has led to the choice of SiC-reinforced MeB_2 (where Me is Zr or Hf) as the baseline material for extreme environments. However, SiC-reinforced MeB_2 are structurally unstable and show poor creep resistance above 1800 °C which highlights the need for more fundamental understanding of the structural properties of monolithic MeB_2. Studies of high temperature creep have shown a remarkable behavior, in which, HfB_2 plastically deforms like an hcp-metal with a higher creep resistance

than SiC-reinforced HfB_2, which suggest that structural performance is lost by SiC addition. Therefore a new approach based on maintaining exceptional structural stability of HfB_2 while improving its oxidation resistance is of particular interest for future MeB_2 UHTCs components. In this work, the high temperature mechanical properties and oxidation behavior of HfB_2/2 wt.% La_2O_3 will be described.

2:45 PM

(PACRIM-S13-019-2017) Theoretical Investigations on the High Temperature Mechanical and Thermodymanic Properties of TMB_2 (TM = Ti, Zr, Hf)

H. Xiang*[1]; Y. Zhou[1]; Z. Feng[1]; Z. Li[1]

1. Aerospace Research Insitute of Materials and Processing Technology, China

As promising candidates for ultra high temperature applications, high temperature properties, which are quite rare and fragmentary, have great significance to TMB_2 (TM = Ti, Zr, Hf). In this work, thermodynamic and mechanical properties of TMB_2 from 0 K to 2000 K were investigated by a combination of first principles calculations and quasi-harmonic approximations. The ground-state properties, including lattice parameters, elastic constants, phonon dispersion and mode-Grüneisen parameters are calculated. The theoretical thermal expansion, mechanical and thermodynamic properties at elevated temperatures were evaluated theoretically and compared with experiments. By discussing Grüneisen parameters anisotropy, the mechanism for the thermal expansion anisotropy of TMB_2 is uncovered. The influence of direction-dependent sound velocities on the anisotropy of thermal conductivity is also discussed.

Joining, Machining and Properties

Room: Kohala 4
Session Chair: Sylvain Dubois, PPRIME Institute

3:30 PM

(PACRIM-S13-020-2017) Joining of ZrB_2-$MoSi_2$ composite using powder-based metallic interlayer

N. Saito*[1]; K. Nakashima[1]

1. Kyushu University, Department of Materials Science and Engineering, Japan

Ultra-high temperatures ceramics are the subject of intense worldwide research effort, and their stability in severe environments makes them candidates for aerospace, nuclear and solar energy applications. Widespread usage UHTCs requires the development of effective and reliable joining methods that facilitate the fabrication of large, complex-shaped, and potentially multimaterial components and devices. Joining of ZrB_2 composite that exhibits outstanding thermo-mechanical and thermochemical properties and good erosion and corrosion resistance, was the focus of the present study. ZrB_2–10vol%$MoSi_2$ composite was joined at 1500 °C with Ni-ZrB_2 powder-based interlayers, which can provide us more rapid interfacial reaction of interlayer because of surface area that could be involved into the intensive reaction. No void and crack were observed at the interface region, which indicates the joining of ZrB_2 composite have successfully done. The four-point bending test on the joints revealed 660±84.6 MPa at the room temperature. Additionally, the joints were oxidized at 1500 °C for 6 h under air condition, then the bending strength of oxidized joints was measured. The bending test of the oxidized joints revealed 625±38.6 MPa, which indicates the interlayer maintained the strength of the joints even after the oxidation process.

3:45 PM

(PACRIM-S13-021-2017) Ablative and wear performances of graphene/glass-ceramics coatings for aerospace applications

E. Garcia[1]; A. Gómez-Gómez[1]; A. Nistal[1]; M. I. Osendi[1]; M. Belmonte[1]; P. Miranzo*[1]

1. Institute of Ceramics and Glass, CSIC, Spain

Graphene nanoplatelets (GNPs) have proved to be effective fillers for enhancing the mechanical and tribological properties of ceramics and glasses, also with the added benefit of developing electrical and thermal functionalities. Recently, we have reported enhanced transport performance for Y_2O_3-Al_2O_3-SiO_2 (YAS) glass-ceramic coatings containing a small amount of GNPs, which are intended for thermal protection systems (TPS) in aerospace applications. This work explores the ablative and wear behaviors of YAS/GNPs coatings flame sprayed over SiC substrates. Wear rate (W_R) and friction coefficient (μ) are analysed under unlubricated ball–on-plate reciprocating tests at increasing loads, whereas protection performance under ablative test conditions is explored up to 1350 C while blowing gases. The flame spraying process induces a coating structure with a preferential surface parallel arrangement of the GNPs that imparts exceptional performance to the coatings. Superior ablation resistance is achieved for coatings having just 1.1 vol.% of GNPs, withstanding up to 30 thermal cycles (from 200 to 1350 C) without damage, as degradation is constrained to the upper-most layer. On the other hand, W_R and μ decrease by 35% and 65%, respectively, for 3.6 vol.% of GNPs, linked to the progressive exfoliation of the GNPs and their beneficial effect on preventing crack propagation within the coating.

4:00 PM

(PACRIM-S13-022-2017) Evaluation of Environmental Barrier Coatings for Silicon Carbide

R. H. Bryden*[1]; L. Mertins[1]; J. Lebrun[2]; D. Woolley[2]; O. Kwon[2]; M. Kuhn[1]

1. Saint-Gobain, Ceramics - High Performance Refractories, USA
2. Saint-Gobain, R&D, USA

Structural ceramics such as silicon carbide for use in high temperature reactors for energy and chemical processing applications suffer from high mass loss (recession) in the presence of steam-rich atmospheres. Within the framework of a Department of Energy (ARPA-E program) funded effort at Saint-Gobain, we have screened candidate ceramics for potential use as protective coatings for silicon carbide components in high temperature steam environments. To evaluate recession, the ceramics were tested in a flowing steam condition at 1500 C and mass loss was quantified. This screening study involved testing a variety of materials, though primary work focused on stabilized tantalum oxide which has a close thermal expansion coefficient to silicon carbide. Due to high recession rates observed for this material, efforts have shifted to alternative candidates. Those which exhibit stability in steam will be developed further as environmental barrier coatings for silicon carbide.

4:15 PM

(PACRIM-S13-023-2017) Oxidation Resistance of β-Sialon/TiN Composites: An Ion Beam Analysis (IBA) study

P. Calloch*[1]; W. J. Trompetter[2]; I. W. Brown[1]; K. J. MacKenzie[3]

1. Callaghan Innovation, Advanced Materials, New Zealand
2. GNS Science, New Zealand
3. MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand

The oxidation resistance of β-Sialon processed with Y_2O_3 sintering additive and β-Sialon/TiN composites containing 1-10 w% TiN was studied using Ion Beam Analysis (IBA) techniques, augmented by XRD and SEM measurements. Rutherford Back Scattering (RBS) was used to monitor the movement of Y and Ti in the oxidized samples, and the diffusion of oxygen and nitrogen was observed by Particle Induced Gamma Emission (PIGE) and Nuclear Reaction Analysis (NRA). These techniques showed that the combined presence of yttrium aluminium garnet (YAG) and TiN protects the β-Sialon phase by forming an oxygen-rich crystalline barrier layer. The movement of yttrium and titanium, the replacement of nitrogen by oxygen in the glassy yttrium-phase, and major crystalline and chemical changes in an outer oxidized layer were observed. These details of the oxidation mechanism of the β-Sialon/TiN composites could not readily have been obtained by any other techniques, and illustrate the value of IBA for oxidation studies of non-oxide ceramics.

4:30 PM

(PACRIM-S13-024-2017) Effect of machining on mechanical properties of CMCs and OCMCs

R. Goller*[1]

1. University of Applied Sciences, Mechanical Engineering, Germany

Cearmic matrix composites (CMCs) entered the commercial market in 2000 with the introduction of Ceramic Brake Disks. 2016 CMCs entered the aircraft turbines for more efficient fuel burning. Because of their inhomogenious structure CMCs do not only have anisotropic properties, they also behave different in final machining compared to their monolithic ceramic relatives. In particular no standard materials exist and hence no standard processes to machine CMCs. The development of a series production therefore bares high risks in material damage and part destruction through unknown operations. The work contributes to the phenomena occuring during mechanical machining of CMCs and OCMCs and their effect on the surface damage and mechanical strength.

4:45 PM

(PACRIM-S13-025-2017) From Ab-Initio Design to Synthesis of Coatings with Enhanced Hardness and Toughness

D. Edström[1]; D. G. Sangiovanni[1]; L. Hultman[1]; I. Petrov[2]; J. E. Greene[2]; V. Chirita*[1]

1. Linkoping University, IFM, Sweden
2. University of Illinois at Urbana-Champaign, MRL and Materials Science Department, USA

Enhanced toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure. Density Functional Theory (DFT) investigations predicted significant improvements in the toughness of several B1 structured transition-metal nitride (TMN) alloys, obtained by alloying TiN or VN with MoN and WN. The calculations reveal that the electronic mechanism responsible for toughness enhancement stems from the high valence electron concentration (VEC) of these alloys, which leads to the formation of alternating layers of high/low charge density orthogonal to the applied stress, and allows a selective response to deformations. This effect is observed for ordered and disordered ternary TMN alloys. Recently, these results have been validated experimentally. Single-crystal VMoN alloys, grown by dual-target reactive magnetron sputtering together with VN and TiN reference samples, exhibit hardness > 50% higher than that of VN, and while nanoindented VN and TiN reference samples suffer from severe cracking, the VMoN films do not crack. New DFT calculations, suggest similar toughness improvements may be obtained in pseudobinary NaCl structured transition-metal carbide (TMC) compounds by alloying TiC or VC with WC and MoC, as inferred from the electronic structure analysis and stress/strain curves obtained for the newly formed ternary TMC alloys.

5:00 PM

(PACRIM-S13-026-2017) Pressureless Sintering of TiB_2-TiC composites with improved fracture toughness

Y. Wang*[1]

1. Harbin Institute of Technology, Institute for Advanced Ceramics, China

TiB_2-TiC composites have attracted much attention due to their high electronic conductivity, strength, hardness and wear resistance. These properties make them promising candidates as cutting tools, bulletproof armors, and thermal protection components, etc. However, high melting point, strong covalent bonding and low self-diffusion coefficient inhabit their sintering and applications. High energy ball milling followed by two-step pressureless sintering is used to fabricate high-performance TiB_2-TiC composites accoding to the densification rate against temperature curve. For comparision, low temperature sintering and one step high temperature sintering methods were also used to fabricate TiB_2-TiC composites. A novel in-situ TiB_2 plate-toughened microstructure is formed in TiB_2-40wt%TiC composite during two-step pressureless sintering. The flexural strength and fracture toughness of TiB_2-40wt%TiC composite are 776 MPa and 11.20 $MPa.m^{1/2}$, respectively.

5:15 PM

(PACRIM-S13-027-2017) Effects of in situ amorphous graphite coating on ablation resistance of SiC fiber reinforced SiBCN ceramics in an oxyacetylene flame

D. Li*[1]; D. Jia[1]; Z. Yang[1]; X. Duan[1]; Y. Zhou[1]

1. Institute for Advanced Ceramics, School of Materials Science and Engineering, Harbin Institute of Technology, China

The effects of in situ amorphous graphite coating on ablation behavior of SiC fiber reinforced SiBCN ceramics in an oxyacetylene flame are explored. The ablation products for both the monoliths and composites are similar comprised of amorphous SiO_2 and cristobalite. The ablation resistance stems from formation of dense, passivating oxide scale of B_2O_3 containing amorphous SiO_2. In different ablation stages, the ablation rates are synergistically controlled by various mechanisms. SiC fiber and interfacial structure degradation both deteriorate ablation resistance. The crystallization of the SiC fibers leading to strength reduction is the main reason for poorer performance vs. monoliths.

PACRIM Symposium 18: Microwave Dielectric Materials and Their Applications

Microwave Dielectric Materials and Their Applications II

Room: Kohala 2
Session Chairs: Hitoshi Ohsato, Nagoya Industrial Science Reserach Institte; Heli Jantunen, University of Oulu

1:15 PM

(PACRIM-S18-008-2017) Ultra low sintering temperature ceramics and their utilization for electronics applications (Invited)

H. M. Jantunen*[1]

1. University of Oulu, Microelectronics Research Unit, Finland

Over 170 different ultra low sintering temperature ceramics have been developed so far. These include compositions that can be sintered below 700 °C with excellent electrical properties especially for high frequency applications. Compositions that need no thermal sintering have also been introduced as well as material families with different dielectric properties that can be cofired together and with embedded electrodes. In this paper all published compositions are surveyed and their feasibility for different electronics and telecommunication applications are studied. In addition, the first real applications fabricated so far are presented showing the advantages available with ultra low sintering temperature ceramics.

1:45 PM

(PACRIM-S18-009-2017) Hexagonal M-type microwave ferrite layers integrated in LTCC modules (Invited)

J. Topfer*[1]

1. Ernst-Abbe-Hochschule Jena, Germany

Future satellite communication technologies require microwave ferrites integrated in LTCC multilayer components for applications in the K_a-band (26-40 GHz). Substituted hexagonal M-type Ba-ferrites $BaSc_xFe_{12-x}O_{19}$ exhibit significant potential as self-biasing microwave ferrites. Sc-substituted Ba ferrites with $0 \leq x \leq 2$ were prepared by the mixed oxide route. Static magnetic measurements show that both the saturation magnetization and coercivity decrease with concentration of scandium. This indicates a reduction of the anisotropy field with substituent concentration. The resonance frequency shows a systematic shift with x and resonance in the K_a-band is observed at x=0.5. The sintering behavior of the ferrites was modified by glass additions and densification at 900 °C was achieved. Ferrite tapes with x = 0.5 were co-fired with LTCC tapes and the integration of ferrite layers in LTCC multilayer modules was tested. Alternatively, ferrite layers were screen-printed onto alumina substrates and fired at 850 – 900°C. Anisotropic ferrite layers were obtained by drying the films in a magnetic field. The film texture was characterized using XRD and EBSD. Ferrite films were also printed onto LTCC tapes and post-fired or co-fired. The potential of such oriented hexagonal ferrite layers as integrated self-biased ferrite layers in microwave components was evaluated. Integrated microwave circulators were built and tested.

2:15 PM

(PACRIM-S18-018-2017) Empirical Modeling of the Structural Effects of Vacancies in Perovskites (Invited)

R. Ubic*[1]; K. Tolman[1]

1. Boise State University, USA

Structural distortions in perovskites are commonly due to either second-order Jahn-Teller (SOJT) effects or antiferrodistortive instabilities which give rise to many functional properties; therefore, empirical models for composition-structure relationships are useful in both the lab and industry, yet few exist for perovskites containing extrinsic defects or cation ordering. In this work, various perovskites in several homologous series were characterized and used to derive empirical models which can be used to predict the effects of compositional variations on industrially important perovskites. In particular, while B-site cation ordering causes an overall volume shrinkage with respect to the disordered analogue, A-site order results in an unexpected volume increase. Both results have been verified via density functional theory. It is also possible to quantify the effect of SOJT distortions in Pb-containing compounds and calculate the degree of tetragonal distortion – all from just Shannon ionic radii data. These structural predictions can be linked to properties, specifically polarization, which may lead to further composition-structure-property predictions.

2:45 PM

(PACRIM-S18-011-2017) Stereolithographic Additive Manufacturing of Diamond Photonic Crystals with Alumina Micro Lattices (Invited)

S. Kirihara*[1]

1. Osaka University, Joining and Welding Research Institute, Japan

Photonic crystals with micro ceramic lattices were fabricated by using stereolithographic additive manufacturing. Periodic arrangements in dielectric constants can diffract electromagnetic wave with micrometer order wavelengths and exhibit forbidden gaps in terahertz frequency rage. Alumina photonic crystals with diamond structures of 300μm in structural period were formed successfully to open the band gaps for all crystal directions through isotropic diffractions. In the stereolithography, alumina nanoparticles were dispersed in to photo sensitive liquid resins at 50 % in volume fraction to obtain thixotropic slurries. An ultraviolet laser beam of 355 nm in wavelength was adjusted at 10 μm in spot diameter and scanned on the applied resin surface. Irradiation power was increased at 800 mW for layer by layer joining through dewaxing the resin matrix and sintering the ceramic particles. By using computer aided design, manufacture and evaluation, air cavities were introduced into the diamond photonic crystals to modulate the resonance modes. The structural misfits can localize the terahertz waves strongly through multiple reflections. These terahertz wave cavities will be expected to be used in various types of novel sensors through synchronizing and harmonizing with vibration modes of various biochemical molecules.

3:30 PM

(PACRIM-S18-012-2017) Microwave dielectric properties of direct casted TiO_2 added indialite/cordierite glass ceramic substrate (Invited)

J. Varghese[1]; H. Ohsato*[2]; V. Leite[3]; M. T. Sebastian[1]; H. Jantunen[1]

1. University of Oulu, Microelectronics Research Unit, Finland
2. University of Oulu (Finland) and Department of Research, Nagoya Industrial Science Research Institute, Japan
3. University of Oulu (Finland) and Department of Physics, Valley of Acarau University, Brazil

Materials with high Qf and low dielectric constant ε_r are innovative fifth generation materials for millimeter-wave communications such as non-condensed ultra-high data transfer digital wireless communication and high frequency radar for the pre-crash safety systems. Indialite/cordierite ($Mg_2Al_2Si_5O_{18}$) glass ceramics are suitable candidate for millimeter-wave materials, because of high Qf of > 200,000 GHz and low ε_r of 4.7. The addition of TiO_2 facilitates volume crystallization preventing the cracking by surface crystallization and lower temperature coefficient of the resonance frequency (TCf) close to near zero. The original pure raw materials (MgO, SiO_2, Al_2O_3, and TiO_2) melted at 1550 °C is poured on a graphite plate and pressed by another graphite plate for making glass plate by a direct casting method. The glass plate is immediately bedded in a sagger heated at about 500 °C, and the sagger is kept in a furnace for crystallization at 1200 °C for 10h. The microwave dielectric properties of 10 wt% added indialite/cordierite glass ceramics has ε_r of 5.6, and tanδ of 0.0002 at 5 GHz.

4:00 PM

(PACRIM-S18-013-2017) TiO_2 microspheres as flexible building blocks for dielectric composites (Invited)

C. Elissalde*[1]; J. Lesseur[1]; M. Albino[1]; U. Chung[1]; M. Sindler[2]; L. Fourier[1]; D. Bernard[1]; P. Mounaix[2]; C. Kadlec[3]; T. Fournier[4]; R. Czarny[5]; N. Penin[1]; J. Heintz[1]; M. Maglione[1]

1. ICMCB-CNRS, France
2. IMS-University Bordeaux, France
3. Institute of Physics-Academy of Science, Czech Republic
4. Plateforme Canoe-Université de Pau et des pays de l'Adour, France
5. Thales Research and Technology France, France

Thanks to high permittivity value, moderate dielectric losses and high dielectric breakdown, TiO_2 based dielectric materials are widely used in electronic components such as capacitors, resonators, filters. Many approaches have been proposed to improve the dielectric performances of TiO_2 ceramics through structure, microstructure and defects control. Here we present an original approach combining spray -drying and sintering to prepare calibrated TiO_2 microspheres (size 10-50 μm). These initial building blocks can be used to build new 3D multi-materials with a high flexibility of design allowing thus to aim a wide range of applications. First, the processing steps of TiO_2 microspheres will be described including the key atomization parameters to control their size, shape and microstructure. Sintering was optimized and the density of the microspheres was probed using 3D tomography analysis. In a second part, three illustrations of the use of TiO_2 microspheres will be presented: i) all dielectric composites with tunable properties, ii) 3D THz metamaterials for the mm and THz frequency ranges and iii) polymer matrix composites suitable for 3D additive manufacturing to achieve microwave subwavelength structured components. Whatever the aimed application, the common goal is to propose a flexible route to design composites while controlling both permittivity and losses in a large frequency range.

4:30 PM

(PACRIM-S18-014-2017) $SrLa(R_{0.5}Ti_{0.5})O_4$-Based (R = Mg, Zn) Microwave Dielectric Ceramics with Complex K_2NiF_4-Type Layered Perovskite Structure (Invited)

L. Li*[1]; G. Ren[1]; J. Zhu[1]; B. Liu[1]; X. Chen[1]

1. Zhejiang University, School of Materials Science and Engineering, China

Dense $SrLa(R_{0.5}Ti_{0.5})O_4$ (R = Mg, Zn) ceramics were prepared by a standard solid state reaction method, and the single phase with complex K_2NiF_4-type layered perovskite structure was revealed by XRD. Significantly improved dielectric constant was obtained in $SrLa(R_{0.5}Ti_{0.5})O_4$ ceramics compared to the analogues $SrLaAlO_4$ and $SrLaGaO_4$, which is attributed to the increasing normalized bond lengths of Sr/La-O(1) and Sr/La-O(2a) bonds and the higher polarizability of $(R_{0.5}Ti_{0.5})^{3+}$. Besides, τ_f converts to a positive value with the increase of dielectric constant. The following microwave dielectric properties were obtained in the dense ceramics: $\varepsilon_r = 25.5$, Qf = 72,000 GHz, $\tau_f = 29$ ppm/°C for $SrLa(Mg_{0.5}Ti_{0.5})O_4$, and $\varepsilon_r = 29.4$, Qf = 34,000 GHz, $\tau_f = 38$ ppm/°C for $SrLa(Zn_{0.5}Ti_{0.5})O_4$. Furthermore, the stability of K_2NiF_4-type structure in $MLnBO_4$ compounds was discussed in relation to the tolerance factor of perovskite layer and the radius ratio of M^{2+} and Ln^{3+}, based on which near-zero τ_f values are expected to be obtained in $SrLa(R_{0.5}Ti_{0.5})O_4$-$SrLaAlO_4$ unlimited solid solutions. This has been proven in the following work, and good combination of microwave dielectric properties were obtained as following: $\varepsilon_r = 23.5$, Qf = 102,000 GHz, $\tau_f = -3.4$ ppm/°C for $SrLa[Al_{0.5}(Zn_{0.5}Ti_{0.5})_{0.5}]O_4$, and $\varepsilon_r = 22.2$, Qf = 89,100 GHz, $\tau_f = -0.1$ ppm/°C for $SrLa[Al_{0.35}(Mg_{0.5}Ti_{0.5})_{0.65}]O_4$.

PACRIM Symposium 20: Crystalline Materials for Electrical, Optical, and Medical Applications

Scintillator II

Room: Kohala 1
Session Chair: Nerine Cherepy, Lawrence Livermore Nat'l Lab

1:15 PM

(PACRIM-S20-047-2017) Growth and characterization of Eu-activated halide scintillators (Invited)

E. Bourret*[1]; T. Shalapska[1]; D. Perrodin[1]; G. Bizarri[1]; A. Tremsin[2]

1. Lawrence Berkeley National Laboratory, USA
2. University of California at Berkeley, USA

New classes of mixed and complex scintillators rely on Eu as activator that yields efficient scintillation under x-ray and gamma excitation. In this presentation we will discuss the impact of the presence of Eu on the growth of these halides. For example, the Eu halides used in the growth process are particularly reactive and can react with the crucible materials introducing unwanted contamination. The concentration of Eu impacts the physical properties of the melt and Eu is also shown to be mobile in the crystal at temperatures close to the melting point. These factors were key to optimization of the growth process. The methods used to characterize and control these effects will be presented.

1:45 PM

(PACRIM-S20-048-2017) Multi-Ampoule Growth of Large Diameter Scintillator Crystals (Invited)

M. Zhuravleva*[1]; A. Lindsey[1]; M. Loyd[1]; L. Stand[2]; Y. Wu[1]; M. Koschan[2]; C. Melcher[1]

1. University of Tennessee, Scintillation Materials Research Center, and Department of Materials Science and Engineering, USA
2. University of Tennessee, Scintillation Materials Research Center, USA

The goal of this work is to demonstrate large-scale crystal growth of novel scintillators suitable for use in nuclear non-proliferation applications, e.g. hand-held gamma-ray detectors. In order to accurately identify signatures of radioactive materials, scintillators must be available in sizes beyond the laboratory scale (> 1 in^3) and possess high light output and energy resolution of 2% at 662 keV. This presentation reviews several successful high-performance scintillators such as $KCaI_3$:Eu, $K(Ca,Sr)I_3$:Eu, and KSr_2I_5:Eu that approach the requirements. To demonstrate cost-effective growth technology, we developed the Multi-Ampoule Growth Station (MAGS). It utilizes the vertical Bridgman method, where up to five Ø2” crystals can be grown in parallel and simultaneously. Growth parameters for producing crack-free large diameter crystals were first developed in conventional single-bore furnaces and then implemented in MAGS. Multiple crystals measuring Ø1.5” x 1.5” were grown in the same run and their gamma-ray spectroscopic performance was evaluated. The attained energy resolution for Ø1.5” x 1.5” boules of 3.7-4% at 662 keV is comparable to equal sized commercially available SrI_2:Eu and $CeBr_3$ scintillators and surpasses that of NaI:Tl standard.

2:15 PM

(PACRIM-S20-049-2017) Improved Alkali-Halide Scintillators with Divalent Rare-Earth Activators: The Elimination of Suzuki-Phase Precipitates (Invited)

L. L. Boatner*[1]; E. P. Comer[1]; G. W. Wright[1]; J. O. Ramey[1]; R. A. Riedel[1]; G. E. Jellison[1]; J. A. Kolopus[1]

1. Oak Ridge National Lab, Material Sciences and Technology, USA

Monovalent alkali-halides activated with relatively low levels of Tl or Na are widely used as inorganic scintillators, and their applications include the fields of nuclear non-proliferation, homeland security, defense threat reduction, medical imaging, and nuclear and space physics, among others. The applications of Eu-activated alkali halide scintillators, however, have been more restricted due to the non-uniform segregation of the divalent Eu dopant during the melt growth of single crystals of the alkali halide host. This leads to the formation of unwanted phases (i.e., Suzuki Phase precipitates) in the host crystals thereby limiting the amount of Eu activator that can be incorporated in the scintillator. Eu activator concentrations in excess of ~0.5% generally result in the formation of Suzuki Phase precipitate particles that scatter the scintillation light and adversely affect the optical transmission – often to the point of opaqueness. We have developed a method of successfully removing the Suzuki Phase precipitates to produce significantly increased optical clarity and improving, for example, the neutron detection performance of Eu-activated LiI single-crystal scintillators.

2:45 PM

(PACRIM-S20-050-2017) Design, growth and characterization of directionally solidified eutectics for scintillator application

A. Yoshikawa*[1]

1. IMR, Tohoku University, Japan

As eutectic crystals consist of at least two different crystals, it can have two or more properties in the one body. The directionally solidified eutectic (DSE) systems have been discovered in various materials for many applications. In this talk, mainly two approaches to develop the scintillators using the DSE system will be reported. One is the neutron scintillator using a eutectic body composed of lithium containing crystal and scintillation crystal. Lithium containing crystal plays a role to react with neutron and generates alpha particle. The alpha particle reacts with the scintillation crystal and will give scintillation light. Another attempt is the submicron-diameter phase separated scintillator fibers (PSSFs). They possessed both the properties of an optical fiber and a radiation-to-light conversion. The PSSFs were fabricated using a DSE system. In PSSFs, the light emitted from the scintillator fibers is confined and transported along the fiber direction by a total reflection mode, so that high-resolution radiation imaging can be achieved. As the example, LiF based eutectic scintillator and PSSFs such as CsI/NaCl and GAP/α-Al_2O_3 will be mainly discussed in the talk.

PACRIM Symposium 21: Solid Oxide Fuel Cells and Hydrogen Technologies

SOFC Technologies

Room: Queen's 4
Session Chair: Fatih Dogan, Missouri University of Science and Technology

1:30 PM

(PACRIM-S21-001-2017) Solid Oxide Fuel Cells: A Multi-Fuel and Multi-Functional Technology (Invited)

P. Miranda*[1]; N. Q. Minh[2]

1. Coppe-Federal University of Rio de Janeiro, Metallurgy and Materials Engineering, Brazil
2. University of California, San Diego, USA

Solid oxide fuel cells have been considered for a broad spectrum of power generation applications. Significant progress has been made in the development of the SOFC for practical uses; however, further developments are needed in the three key drivers (cost, performance and reliability) to enable commercialization of the technology. The key features differentiating the SOFC from other types of fuel cell are its multi-fuel and multi-functional capabilities. These features provide the possibility for various practical applications based on similar cell architectures and component designs and/or materials, creating valuable synergy, shortening development cycle and accelerating market introduction. For multi-fuel capability, the SOFC is capable of operating efficiently on a variety of fuels including direct utilization of anhydrous carbonaceous fuels, referred to as direct SOFC, DSOFC. For multi-functional, the SOFC can operate in reverse (electrolysis) mode to produce hydrogen/oxygen/syngas from water, carbon dioxide and mixtures of water and carbon dioxide, referred to as a solid oxide electrolysis cell, SOEC. The SOFC can convert hydrocarbons to selected chemicals and cogenerate electricity, referred to chemical/cogeneration SOFC, CSOFC. This paper provides an overview of DSOFCs, SOECs and CSOFCs and discusses materials selection and operation characteristics in these three operating modes.

2:00 PM

(PACRIM-S21-002-2017) Portable power generation based on micro-tubular SOFCs (Invited)

M. Awano*[1]; Y. Fujishiro[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Inorganic Functional Materials Research Institute, Japan

Solid oxide fuel cells (SOFCs), as a promising future electric power generation technology, has remarkably increased their worldwide interest in recent years due to not only their high electrical efficiency but also multi-fuel capability. AIST focused on the development of materials for electrodes and electrolyte of SOFCs that can lower the operating temperatures under 600°C and the development of manufacturing process technology for sub-millimeter tubular cells as well as for integration of such cells in the micro level. By the development of high performance materials and parts for reactors and manufacturing technologies for the integration of micro reactor modules, we had achieved cell performance of 2W/cm^2 power density at around 600°C, which is the world's highest power density among SOFCs with ceria based electrolyte. Durability for quick start-up operation within 2 minutes and repeating start-up and shut-down operation was revealed. Furthermore, the new fine fabrication technology for functional ceramic components, and the prototype on-hand size module of 200W-class, power generation efficiency of over 40%, had been fabricated and established for its high performance and durability applicable as various distributed power generators.

2:30 PM

(PACRIM-S21-003-2017) Sinterability and conductivity of bismuth, iron and manganese-doped ceria ceramics

C. Chiu*[1]; Y. Chen[1]; W. Wei[1]

1. National Taiwan University, Materials Science and Engineering, Taiwan

Our previous work found the interface reaction between a cathode $(Bi,Sr)(Mn,Fe)O_{3-d}$ and 8 mol% yttria stabilized ZrO_2. The possible solution for this is using a reaction barrier in SOFC. In this study, two types of (Bi, Mn, Fe)-doped ceria were synthesized. Bi_2O_3, Mn_2O_3 and Fe_2O_3 doped in ceria ($Bi_{0.2-2x}Mn_xFe_xCe_{0.8}O_{2-\delta}$) are synthesized either by ethylene diamine tetra acetic acid (EDTA)-citric complexing method or adapted Bi_2O_3 as a liquid phase by adding to a (Mn, Fe) co-doped ceria. The effects of the dopants on the sintering behavior, electric conductivity, microstructure of the ceria-based powders are studied using X-ray diffraction (XRD) for phase analysis, scanning electron microscopy (SEM) for microstructural characterization. The results show that all powders were calcined over 700 °C to assure a single phase of fluorite structure. The made $Bi_{0.07}Mn_{0.07}Fe_{0.07}Ce_{0.79}O_{2-\delta}$ has a better sinterability to get a relative density up to 95% T.D. than the other case if they are sintered at 1250 °C, and show an average grain size of the doped ceria 7μm. The sintered $Bi_{0.07}Mn_{0.07}Fe_{0.07}Ce_{0.79}O_{2-\delta}$ in bulk or thin film shows a fluorite phase. The optimized sintering temperature is falling in the 1250-1350 °C range. The results show the sintering density decreases after sintering at the temperatures higher than 1400 °C. It might be due to the evaporation of bismuth species from the ceria.

2:45 PM

(PACRIM-S21-004-2017) Development of a SOFC/Battery-Hybrid System for Distributed Power Generation in India (Invited)

T. Pfeifer*[1]; A. Chakradeo[2]; N. Ahire[2]; M. Barthel[1]; C. Dosch[1]; R. Näke[1]; M. Hartmann[1]

1. Fraunhofer IKTS, Germany
2. h2e Power Systems, Pvt. Ltd., India

Contracted by h2e Power Systems based in Pune, India, IKTS has developed a 1 kW SOFC power generator. The system is based on CFY stacks, incorporating ESC with Scandia-doped Zirconia electrolytes. CFY-stacks have proven to be robust and reliable, showing degradation rates below 0.6 % per 1.000 hours during endurance operation over 20.000 hours and a cyclization capability of more than 120 near-system cycles under full RedOx-conditions. For the SOFC power generator a CFY stack was integrated into a HotBox-module following a novel design concept. Aside from compactness, a simple and robust, yet highly efficient system concept was set as the primary development goal. To meet these requirements, several system design decisions were implemented, which led to a water-less SOFC system with a net electrical efficiency above 40 %. In 2015, two Proof-of-Concept prototype systems were commissioned at IKTS. One of the prototypes was installed at the customer's site in Pune, India, for test and demonstration purposes. In Project Phase II, three improved demonstration prototypes were built in 2016 for initial demonstration projects and field trials. At the same time, the technology transfer was initiated, in order to enable for a local manufacturing and deployment of SOFC systems in India. The project presentation will outline the development approach, system concept, and major technical achievements.

SOFC Electrolytes and Electrodes

Room: Queen's 4
Session Chair: Masanobu Awano, AIST

3:30 PM

(PACRIM-S21-005-2017) Innovative low-temperature powder synthesis process for SOFCs materials (Invited)

Y. Yamaguchi*[1]; H. Shimada[1]; H. Sumi[1]; T. Yamaguchi[1]; K. Nomura[1]

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

In this study, the SOFCs material were prepared by the novel developed low-temperature solid state synthesis. Using the starting material including alkaline or earth alkaline hydroxides and metal oxide gels, some perovskite oxides can be obtained at temperature range of 20-100°C. This synthesis was based on the acid-base reaction between transition-metal oxide gels and hydroxides. Particularly, this process can provide the highly crystallized complexed oxides in spite of low-temperature synthesis around room temperature. In addition, these powders were obtained with fine particle size. This synthesis method can produce a large amount of powder For example, powders of barium zirconate type electrolyte materials could be obtained by leaving the mixture of barium hydroxide octahydrate and zirconium oxide hydrous gel at 100°C, and it could be used as a proton-conducting electrolytes.

4:00 PM

(PACRIM-S21-006-2017) Improvement in electrochemical performance of proton-conducting solid oxide fuel cells by controlling Ni interdiffusion during co-sintering process (Invited)

H. Shimada*[1]; T. Yamaguchi[1]; H. Sumi[1]; Y. Yamaguchi[1]; K. Nomura[1]

1. National Institute of Advanced Industrial Sience and Technology (AIST), Japan

Solid oxide fuel cells (SOFCs) using proton-conducting ceramics as electrolyte material, called proton-conducting SOFCs, have attracted much attention for wide temperature range operation perovskite-type material such as $Ba(Zr,Ce)O_3$ (BZC) exhibits high protonic conductivity and chemical stability Currently, due to high power density, the majority of cell configurations are anode-supported type. Anode-supported cells (ASCs) are fabricated via co-sintering NiO-based anode and an electrolyte. Although interdiffusion of Ni from the anode into electrolyte during co-sintering process improves the sinterability of electrolyte, Ni interdiffusion causes a decrease in protonic conductivity. In the present study, the electrochemical performance of ASCs with BZC electrolyte were fabricated via a co-sintering process. Then, Ni interdiffusion was quantitatively characterized by EPMA and electrochemical performance of ASCs was evaluated.

4:30 PM

(PACRIM-S21-007-2017) Microstructure-Performance Correlations in LSM-Based Solid Oxide Fuel Cell Cathodes

N. Hilli[1]; C. Cooper[1]; T. R. Dietrick[1]; Z. Liu[2]; R. Goettler[2]; A. H. Heuer[1]; M. R. De Guire*[1]

1. Case Western Reserve University, Materials Science and Engineering, USA
2. LG Fuel Cell Systems Inc., USA

During long-term operation, SOFC cathodes of lanthanum strontium manganite (LSM, $(La_{1-x}Sr_x)_{1-y}MnO_{3\pm\delta}$) and yttria-stabilized zirconia (YSZ) exhibit microstructural changes that may contribute to a decrease in cell performance: * Changes in phase fractions and their distribution across the cathode; * Changes in (total and active) three-phase boundary (TPB) density; * Formation of free manganese oxides (MnOx); * Phase chemistry, particularly Mn content in LSM and YSZ This research program implemented an accelerated testing protocol (1000 °C, 780 mA cm^{-2}) in an effort to gather performance data in time frames of e.g. 500 h that are relevant to much longer-term normal cell operation. Testing under accelerated and conventional conditions was carried out on electrolyte-supported (8YSZ, $Zr_{0.92}Y_{0.08}O_{3-\delta}$) button cells with LSM cathodes of differing levels of excess Mn. Durability testing was carried out, with periodic linear-sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) measurements. Post-test microstructural analysis consisted of transmission electron microscopy (TEM) with energy-dispersive x-ray spectroscopy (EDXS), focused ion-beam scanning electron microscopy (FIB-SEM) and 3-D reconstruction (3DR). Changes in area specific resistance (ASR) are analyzed along with microstructural changes to obtain insights into long-term cathode degradation mechanisms.

4:45 PM

(PACRIM-S21-008-2017) Experimental Phase Diagram Studies in the La-Sr-Ga-Mg-Ni-O System for Solid Oxide Fuel Cells

G. Soydan*[1]; E. Kondakci[1]; A. Demirkesen[1]; N. Solak[1]

1. Istanbul Technical University, Metallurgical and Materials Engineering, Turkey

Strontium and magnesium doped lanthanum gallate (LSGM) perovskite-type compounds are considered as promising solid electrolytes for intermediate temperature fuel cell (IT-SOFC) applications. The cermet-type anode and nickelate-type cathode materials are used as electrodes. In recent experimental works show that the performance of nickelate type cathode can be improved by alkaline earth metal oxide doping such as MgO, CaO and SrO. In our previous studies, the ternary La_2O_3-XO-NiO (X=Mg, Ca, Sr) oxide system has been investigated. However, there is no experimental or computational studies in high order systems. In order to build chemically stable fuel cells, not only the thermodynamic stability of the electrolyte and electrodes themselves, but also the reactivity between component materials should be well established. The work aimed to investigate high order phase equilibria in the La_2O_3-SrO-MgO-NiO and La_2O_3-SrO-Ga_2O_3-NiO oxide system in order to investigate thermodynamic stability of doped La_2NiO_4 ternary compound and reactivity between electrodes and electrolyte.

5:00 PM

(PACRIM-S21-009-2017) The effect of powder characteristics on initial performance of SOFC cathode

L. Ge*[1]; B. Ingram[1]; J. Carter[1]

1. Argonne National Lab, Chemical Science and Engineering, USA

Lanthanum strontium cobalt ferrite (LSCF) perovskite has been identified as promising cathode candidate for intermediate temperature (IT) solid oxide fuel cell (SOFC) applications, due to its mixed ionic and electronic conductivity at operating temperatures (500-700 °C). In particular, A-site deficient LSCF has shown better electrochemical performance compared to its stoichiometry counterpart. However, non-uniformity in electrical, electrochemical, and morphological characteristics found in different powders used for fabricating cell and stack components has been a continuing challenge for SOFC manufacturers. In this study, a wide variety of physical and chemical characterizations on $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-d}$ powders were performed to investigate the correlation between the initial electrochemical performance and materials properties. This effort will help in defining tolerances of key materials properties for optimal cell performance.

PACRIM Symposium 22: Direct Thermal to Electrical Energy Conversion Materials and Applications

Oxides and Sulfides

Room: Queen's 6
Session Chairs: Thierry Caillat, NASA Jet Propulsion Laboratory; Takao Mori, National Institute for Materials Science (NIMS)

1:15 PM

(PACRIM-S22-009-2017) Enhancing the performance of $SrTiO_3$-based thermoelectrics by A-site vacancies, metallic inclusions and additions of graphene (Invited)

D. Srivastava[1]; F. Azough[1]; C. Norman[1]; Y. Lin[1]; K. Simpson[2]; M. Robbins[2]; I. Kinloch[1]; E. Guilmeau[3]; D. Kepaptsoglou[4]; Q. Ramasse[4]; R. Freer*[1]

1. University of Manchester, Materials, United Kingdom
2. European Thermodynamics, United Kingdom
3. CNRS CRISMAT, France
4. SuperSTEM, United Kingdom

Ceramics of $SrTiO_3$, with additions of La and Nb, have been prepared by the mixed oxide and chemical routes and sintered under reducing conditions, giving products of 90-98% theoretical density. The presence of La and Nb generated 13.4% A-site vacancies. Both carrier concentration and carrier mobility increased with sintering time, giving a maximum Figure of Merit (ZT) of 0.25. Selective additional doping by La or Nb led to the creation of additional carriers and reduced electrical resistivity. Together these led to enhanced ZT values of 0.345 at 1000 K. When the ceramics were prepared with inclusions of Cu or Fe there were further increases in carrier concentration and carrier mobility. Both types of metallic inclusions were beneficial, increasing ZT to 0.36 at 900 K for the Cu-containing samples and to 0.38 at 1000 K for the Fe-containing samples. Nanocomposites of $(LaSr)TiO_3$, with 0.6 wt % graphene, exhibited greatly enhanced electrical conductivity and reduced thermal conductivity, giving a ZT = 0.42 at room temperature and 0.36 at 750 °C, A preliminary 7-couple device had a Seebeck coefficient of ~1500 μV/K and an open voltage of 600 mV at 219 °C.

1:45 PM

(PACRIM-S22-010-2017) Ultra-low Thermal Conductivity in β-Pyrochlore Oxides with a Rattler-in-a-Cage Crystal Structure

M. Ohtaki*[1]; K. Mizuta[1]; K. Suekuni[1]

1. Kyushu University, Interdisciplinary Graduate School of Engineering Sciences, Japan

Materials with a smaller atom in an oversized cage-like structure such as filled skutterudites and clathrate compounds are interested in as a promising candidate for thermoelectric materials. In these materials, an anharmonic thermal vibration called the "rattling" motion of the centered atom in the cage is believed to scatter phonons efficiently. We have reported that the unconventional relation between the size of the A cations and the thermal diffusivity for β-pyrochlore type (defect pyrochlore) oxides $ATaWO_6$ (A = K, Rb, Cs), which suggested enhanced phonon scattering by the rattling behavior. Unfortunately, these oxides were insulating. In this work, we investigated the crystal structure and the thermoelectric properties of defect pyrochlore oxides $AFe_{0.33}W_{1.67}O_6$ (A = K, Rb, Cs; hereafter denoted by KFW, RFW, CFW) with better electrical properties than those of $ATaWO_6$. The oxides with smaller A cations indicated larger displacement from the center position of the cage with the larger isotropic displacement parameter. The Raman spectra of the samples were found to have the peaks implying the translational modes of the A-site cations as "rattling mode". The thermal conductivity showed the order of CFW < RFW over the whole temperature range, unlike $ATaWO_6$. However, their values were below 1.0 W/m K, being extremely low among oxides, and lower than that of ATaWO6 (A = Rb, Cs).

2:00 PM

(PACRIM-S22-011-2017) Recent Progress in Complex Thermoelectric Sulphides (Invited)

E. Guilmeau*[1]; T. Barbier[1]; P. Lemoine[2]; O. Lebedev[1]; C. Bourgès[1]; V. Nassif[3]; B. Malaman[4]

1. CNRS CRISMAT, France
2. Institut des Sciences Chimiques de Rennes (ISCR), France
3. Institut Laue Langevin, France
4. Institut Jean Lamour, France

Recently, copper-containing ternary sulphides have been attracting much attention for thermoelectric applications because most of the main components comply with the actual requirements of low cost, earth abundant, and less toxicity. A non-exhaustive list includes p-type tetrahedrite $Cu_{12}Sb_4S_{13}$ (ZT ~ 0.8 @ 700K), colusite $Cu_{26}V_2Sn_6S_{32}$ (ZT ~ 0.56 @ 663K), bornite Cu_5FeS_4 (ZT ~ 0.55 @ 550K), Cu_2SnS_3 (ZT ~ 0.56 @ 750K), Cu_2ZnSnS_4 (ZT ~ 0.35 @ 700K) or n-type $Cu_4Sn_7S_{16}$ (ZT ~ 0.21 @ 700K). A common feature of tetrahedrite, colusite, bornite and $Cu_4Sn_7S_{16}$ phases is their intrinsically low thermal conductivities k originating from high structural complexities, i.e. large number of atoms per unit cell and large Grüneisen parameter. In addition, low-energy vibration mode of Cu atom out of the $[CuS_3]$ triangular planar unit in tetrahedrites explains its ultra low thermal conductivity. In this presentation, recent progress in thermoelectric complex sulphides will be presented, more especially in the Cu-Sb-S, Cu-Sn-S and Cu-Fe-S systems. Synthesis and processing of bulk compounds by mechanical alloying and Spark Plasma Sintering will be reported. Structural analysis by means of X-ray/neutron powder diffraction and transmission electron microscopy is discussed, together with electrical resistivity, Seebeck coefficient and thermal conductivity measurements in different series of compounds.

2:30 PM

(PACRIM-S22-012-2017) Cu_2SnS_3 as Novel p-type Thermoelectric Materials (Invited)

Y. Wang*[1]; L. Pan[1]; H. Zhao[1]; X. Xu[1]; R. Tian[2]; K. Koumoto[2]

1. Nanjing Tech University, College of Materials Science and Engineering, China
2. Toyota Physical and Chemical Research Institute, Japan

Thermoelectric materials can directly generate electricity from waste heat and thus are expected to serve as an important role in future energy solution. It is still a challenge to develop high performance environmentally friendly thermoelectric materials consisting of nontoxic and naturally abundant elements. We hereby report on the transport properties of a diamond-like ternary sulfide of Cu_2SnS_3 as a promising phonon-glass-electron-crystal. Through hole-doping at the Sn-site, the monoclinic structure for pristine compound transformed into cubic and tetragonal, leading to a random cation occupation. High power factor of ~0.9 $mWm^{-1}K^{-2}$ was achieved, about 20 times of the pristine one, which is favored by the 3-dimensional network of Cu-S bonding for charge carriers in these structures. More importantly, microstructure analysis showed an ultrafine mosaic nanostructure due to different cation ordering, which, together with the effect of cation disordering, greatly enhanced the phonon scattering to suppress the lattice thermal conductivity to close to the theoretical minimum of ~0.3 $Wm^{-1}K^{-1}$. As a result, a high dimensionless figure of merit, zT, of ~0.85 has been achieved at 723 K, which is one of the highest so far among sulfide thermoelectrics.

3:00 PM

(PACRIM-S22-013-2017) Excess Sn in $Cu_4Sn_7S_{16}$ responsible for the modification in band structures and reduction in lattice thermal conductivity

T. He[2]; N. Lin[2]; Z. Du[1]; Y. Chao[2]; J. Cui*[1]

1. Ningbo University of Technology, School of Materials and Chemical Engineering, China
2. Taiyuan University of Technology, China

In this work we have investigated the band structures of ternary $Cu_4Sn_{7+x}S_{16}$ (x=0-0.5) compounds with an excess of Sn, and examined their thermoelectric (TE) properties. The first principle calculation reveals that the excess Sn, which exhibits Sn^{2+} preferential to the intrinsic Cu vacancies, unpins the Fermi level (F_r) and allows it to move towards the conduction band minimum (CBM). Accordingly, the Hall carrier concentration (n_H) enhances by about two orders of magnitude with the x value increasing from x=0 to x=0.5. Moreover, the lattice thermal conductivity (κ_L) reduces significantly, which is in a good agreement with the estimation using Callaway model. As a consequence, the dimensionless TE figure of merit (ZT) of the compound $Cu_4Sn_{7+x}S_{16}$ with x=0.5 reaches 0.41 at 863 K. This value doubles that of the stoichiometric $Cu_4Sn_7S_{16}$, proving that the excess Sn in $Cu_4Sn_7S_{16}$ is beneficial to improve the TE performance.

3:15 PM

(PACRIM-S22-014-2017) Spherical Aberration Corrected TEM for Thermoelectric Materials

J. He*[1]

1. Southern University of Science and Technology, Shenzhen Key Laboratory of Thermoelectric Materials and Department of Physics, China

The presentation will start with a brief and realistic coverage of the emerging and maturing themes in the context of energy sources, efficiency, charge storage and distribution. It will illustrate two examples of emerging excitements in nanostructured materials and systems for thermoelectric materials. It will highlight the role of advanced and classical electron microscopy in unravelling the hierarchical architecture of the constituents and their intimate interplay in governing key phenomena in energy conversion. For BaCuSeO, we investigate the microstructural reason of the thermal conductivity in Ba- heavily doped BiCuSeO through scanning transmission electron microscopy (STEM). We found a large amount of nanoscale Bi-rich precipitates dispersed widely in BiCuSeO matrix grains; besides, for the first time, we provide visual evidence of Ba substituting Bi atoms in Bi-O layers. Combined with DFT calculations, we conclude that intrinsic lattice vibration anharmonicity, together with Ba-Bi alloying and excess Ba-rich precipitation, is responsible for the observed low lattice thermal conductivity in experiments.

New Materials and Modules

Room: Queen’s 6
Session Chairs: Robert Freer, University of Manchester; Emmanuel Guilmeau, CNRS CRISMAT

3:45 PM

(PACRIM-S22-015-2017) Bottom-up Nanostructuring for Enhanced Thermoelectric Performance (Invited)

T. Mori*[1]

1. National Institute for Materials Science (NIMS), Japan

We have achieved selective scattering of phonons and thereby critical enhancement of TE properties through nanostructuring: both a) mechanical and b) bottom-up methods. For example, previously, quick, inexpensive, bottom-up wet processes were found to fabricate nanosheets of telluride thermoelectric materials leading to enhanced ZT. We have also recently discovered a bottom-up nanostructuring method leading to a 100% enhancement (i.e. ZT~1.6) in “empty” rare earth-free skutterudites. This is achieved by co-doping the Sb cages of $CoSb_3$ and utilizing phase diagrams to create surprising controlled and effective porosity in the materials. Fabrication of nanocomposites with partial metallic networks in borides has been shown a route to overcome the traditional trade-off between electrical conductivity and Seebeck coefficient leading to large TE enhancement. Characterization of thermal properties on the nanoscale will also be presented; focused picosecond laser thermoreflectance and in-situ TEM thermal probe development. This work is supported by CREST, JST.

4:15 PM

(PACRIM-S22-016-2017) Phonon scattering by dense dislocation arrays for high performance thermoelectrics

S. Kim*[1]

1. University of Seoul, Department of Materials Science and Engineering, Republic of Korea

The widespread use of thermoelectric technology is constrained by a relatively low conversion efficiency of the bulk alloys, which is evaluated in terms of a dimensionless figure of merit (zT). The zT of bulk materials can be improved by reducing lattice thermal conductivity through grain boundary and point-defect scattering, which target low- and high-frequency phonons. Here, we demonstrate that dense dislocation arrays formed in grain boundaries by liquid-phase compaction process (that utilizes excess Te liquid druing sintering) in $Bi_{0.5}Sb_{1.5}Te_3$ effectively scatter midfrequency phonons, leading to a substantially lower lattice thermal conductivity at room temperature and higher (>300K). Full-spectrum phonon scattering with minimal charge-carrier scattering dramatically improved the zT to 1.86 ± 0.15 at 320 kelvin. In addition, lattice thermal conductivity at low temperature (<200K) were also measured and compared, where other phonon scattering mechanisms like Umklapp and point-defect scatterings are less dominant, in order to clarify the influence of dislocation arrays.

4:30 PM

(PACRIM-S22-017-2017) Reduction of electron scattering and enhancement of thermoelectric performance in texture-controlled $Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}$

T. Kanno*[1]; H. Tamaki[1]; H. K. Sato[1]; Y. Miyazaki[2]

1. Panasonic Corporation, Advanced Research Lab., Japan
2. Tohoku University, Department of Applied Physics, Japan

Recently, Zintl phase material $Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}$ was found to exhibit excellent thermoelectric figure of merit (ZT ~ 1.5 at 716 K). The previous study revealed that excess Mg along with Te doping plays an important role to realize good n-type transport, and partial substitution of Sb with Bi works well to reduce the lattice thermal conductivity down to its minimum limit. In terms of the electron transport, the temperature dependence of the hall mobility suggests that the ionized impurity scattering mainly limits the electronic conduction at < 500 K. Here, we investigated fabrication processes and optimized material texture to reduce the electrical resistivity. We adopted the similar fabrication process to the previous report: ball-milling of elemental powders and spark plasma sintering. We mainly changed the sintering temperature to control the grain size. We found that the electrical resistivity effectively reduces as the average grain size increases from submicron to ~ 10 μm, while the lattice thermal conductivity does not vary. The figure of merit at 473 K significantly increases from 0.74 to more than 1. The present study suggests that, at the lower temperature, electron scattering mainly occurs across grain boundaries, and phonon transport is governed by another fluctuation introduced by Bi substitution.

4:45 PM

(PACRIM-S22-018-2017) Development of Earth Abundant Complex Zintl Phases for Thermoelectric Space Power Generation Applications

S. Bux*[1]; S. Ohno[2]; S. Chanakian[1]; K. Lee[1]; M. Wood[2]; Y. Hu[3]; H. Musunuri[1]; U. Aydemir[2]; D. Uhl[1]; B. Li[1]; J. Snyder[2]; S. Kauzlarich[3]; J. Fleurial[1]

1. Jet Propulsion Laboratory/California Institute of Technology, USA
2. Northwestern University, USA
3. University of California, Davis, USA

Since the 1960's, the state-of-the-art power systems for space applications have typically been based up on either Si-Ge alloys or PbTe and TAGS materials. Although reliable and robust, the thermal-to-electric energy conversion efficiency of these systems remains fairly low at only 6.5%. A factor of 2 improvement in conversion efficiency is highly desirable to support future space missions. In recent years, complex Zintl phases such as n-type $La_{3-x}Te_4$ and p-type $Yb_{14}MnSb_{11}$ have emerged as practical high efficiency, high temperature thermoelectric materials with peak ZTs of 1.2 at 1275K. Recently, JPL and collaborating institutions have investigated a series of promising p-type Zintl phases. The new Zintl phases include p-type $Ca_9Zn_{4+x}Sb_9$, n-type Mg_3Sb_2 and p-type $Yb_{14}MgSb_{11}$ and their performance is competitive to that of filled skutterudites with ZTs greater than 1 at 875K. Additionally, preliminary measurements indicate that these new high performance Zintl phases have higher thermal stability and are better thermomechanically matched to the higher temperature segments, thereby facilitating device fabrication and performance. We will present an overview of recent research efforts at JPL and collaborating institutions on the thermoelectric properties of these new materials as well as provide a first assessment of their suitability for infusion into advanced TE devices.

5:00 PM

(PACRIM-S22-019-2017) Skutterudite-Based Thermoelectric Technology for Integration into a Proposed eMMRTG for Space Power Applications (Invited)

T. Caillat*[1]

1. NASA Jet Propulsion Laboratory, USA

The overall objective of the Skutterudite Technology Maturation (STM) project at NASA's Jet Propulsion Laboratory (JPL) is to advance JPL-developed skutterudite (SKD) technology to a point where it can be considered for use in a proposed enhanced Multi-Mission Radioisotope Thermoelectric Generator (eMMRTG). The goal is to be prepared for potential flight unit development readiness by end of FY2018. Conversion efficiency values on the order of 9% have been demonstrated for SKD-based un-segmented couples when operating at a hot junction of 600C and a cold junction of 200C. This represents ~ a 25% improvement over the conversion efficiency of PbTe/TAGS MMRTG couples at beginning-of-life (BOL). The STM project entered its third year at the beginning of FY16. During the first two years of the project, JPL and Teledyne Energy Systems Inc. (TESI) have collaborated to transfer the technology to TESI, to develop the manufacturing capabilities for SKD TE materials and couples at TESI, and to demonstrate their initial performance and initiate a lifetime performance prediction. Significant progress has been made towards those goals, and this paper will summarize this progress as well as the remaining challenges to fully mature this technology.

5:20 PM

(PACRIM-S22-020-2017) Development of High Performance Thermoelectric Modules for Harvesting Waste Heat (Invited)

N. Van Nong*[1]

1. Technical University of Denmark, Department of Energy Conversion and Storage, Denmark

In this talk, our development of high performance thermoelectric (TE) modules for harvesting waste heat is presented. The presentation will focus on the results of some newly achieved high performance TE power generation modules using our recent developed TE materials based on intermetallic compounds, oxides, and their segmentation. Some challenges on the contacts in TE modules will be addressed. A maximum conversion efficiency of 11% was obtained with skutterudite TEG module at the hot side and cold side temperatures of 600 °C and 140 °C, respectively. Furthermore, a new flexible TEG module has also been successfully demonstrated using Bi_2Te_3 materials. Finally, our investigation on the long-term stability of the TE modules under large temperature gradients will be also presented and discussed.

5:40 PM

(PACRIM-S22-021-2017) Flexible Thermoelectric Generators Using Organic Materials by Printing Process (Invited)

S. Cho*[1]

1. Korea Research Institute of Chemical Technology, Division of Advanced Materials, Republic of Korea

Thermoelectric energy conversion is an attractive and environmentally friendly way to recover energy from industrial waste heat or natural heat because of its potential for improving the energy efficiency. As thermoelectric materials, organic materials have unique advantages, such as cost effectiveness, low intrinsic thermal conductivity, high flexibility, and amenability to large area applications. Therefore, organic conducting polymers, which possess good electrical conductivity, have been actively researched. Herein, we present a convenient method for enhancing the thermoelectric properties of inorganic-based nanostructures coated with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (PEDOT:PSS hybrid) by simple chemical treatment. Significant enhancement of the electrical conductivity of PEDOT:PSS hybrids was achieved by simple chemical treatment with H_2SO_4. The power factor of the developed materials could be effectively tuned over a very wide range depending on the concentration of the H_2SO_4 solution used in the chemical treatment. The power factors of the developed thermoelectric materials were optimized to $284\ \mu W\ m^{-1}K^{-2}$. Using the BiTe-PEDOT:PSS hybrids, a flexible thermoelectric generator that could be embedded in textiles was fabricated by a printing process. This thermoelectric array generates a thermoelectric voltage of 2 mV using human body heat

PACRIM Symposium 24: Photovoltaic and Related Materials and Technologies

Photovoltaic Materials and Technologies I

Room: Queen's 5

Session Chairs: Tohru Sekino, Osaka University; Federico Rosei, INRS; Alberto Vomiero, Lulea University of Technology

1:15 PM

(PACRIM-S24-001-2017) Amorphous Oxide Semiconductor Thin Film for OPV with an Energy-Efficient Beneficial Coating Process (Invited)

T. Sugahara*[1]; S. Cong[1]; M. Karakawa[2]; K. Suganuma[1]

1. Osaka University, Japan
2. Kanazawa University, Japan

An effective metal oxide coating with solution processes as deposited at the low temperature is a great challenge, but is required to realize low cost, environmentally friendly, and low energy consumption manufacture of electronic devices and modules. Herein we report semiconductor of the physical and the chemical properties evaluation of thin film as deposition solution coating oxide thin films. Characterization of the films revealed them to be mainly composed of amorphous oxide. The films were applied to organic photovoltaic cells to evaluate the semiconductor properties by using thin film. The films were found to work well as a buffer layer of organic photovoltaic cell at the interface between organic layer and metal electrode. The presented low-temperature solution process without the additional any decomposition energy is expected to make a significant contribution to the realization of flexible and cost-effective solution processed device fabrication.

1:40 PM

(PACRIM-S24-002-2017) Energy-Related Phenomena in Metal Nanostructures with Hot Spots: Generation of Hot Plasmonic Electrons and Heat (Invited)

A. Govorov*[1]; L. Besteiro[1]

1. Ohio University, Physics, USA

Plasmons in large nanostructures mostly consist of electrons with small excitation energies. Nevertheless, we show that, under certain conditions, plasmonic nanocrystals are able to generate large numbers of high-energy electrons. The efficiency of generation of energetic plasmonic carriers in metal nanostructures strongly depends on their design and material composition. In particular, we demonstrate that the hot-electron generation becomes especially efficient in plasmonic nanostructures with electromagnetic hot spots. Theoretically, we use the Kinetic DFT to treat the problem of generation of energetic plasmonic electrons. This theory is based on the kinetic equation of motion for the density matrix and the Kohn-Sham one-particle wave functions. The energy distribution of optically-excited plasmonic carriers is strongly size-dependent. In large nanocrystals, most excited carriers have very small excitation energies. Nanostructures with small sizes or with hot spots generate unusually large numbers of energetic electrons, which can be observed using optical spectroscopies. Along with high-energy plasmonic electrons, which can be used for energy applications, plasmonic nanocrystals and resonant metastructures are able to efficiently generate heat energy and high temperatures confined in small volumes.

2:05 PM

(PACRIM-S24-003-2017) Scanning near field optical microscopy applications in plasmonic solar cell design (Invited)

G. Fanchini*[1]

1. University of Western Ontario, Physics and Astronomy, Canada

In our talk, we review a set of near-field optical techniques suitable to investigate plasmonic nanomaterials for solar cells, including the development of three-dimensional (3D) SNOM methods undertaken by our group to image the electromagnetic radiation scattered by arrays of metal nanostructures. Specific examples include the analysis of the nano-optical response of organometallic-polymer nanocomposites comprising molecular gold nanoclusters to be used in plasmonic solar cells and the design of plasmonic solar cells incorporating random arrays of copper nanoparticles (Cu-NPs) as an absorption enhancement layer. Constructive interference of forward-scattered plasmonic waves can be obtained at tunable distances from the surface of random arrays of Cu-NPs, which depend on the particle diameter in the the 10-100 nm diameter range, but is typically too large to use Cu-NPs in contact of the active layer for light harvesting in thin organic solar cells. Using a 200 nm transparent spacer between the system of Cu-NPs and the solar cell active layer, we demonstrate that forward-scattered light can be conveyed in 200 nm thin film solar cells. This architecture increases the photoconversion efficiency by a factor of 3 and demonstrates the added value of 3D-SNOM in predicting the properties-performance relationship in plasmonic solar cells, towards efficient design of light management in the near field.

2:30 PM

(PACRIM-S24-004-2017) Composite nanostructures for high-efficiency excitonic solar cells (Invited)

A. Vomiero*[1]

1. Lulea University of Technology, Engineering Sciences & Mathematics, Sweden

The typical photoanode in excitonic solar cells is composed of a wide band gap semiconductor, which acts as electron transporter for the photoelectrochemical system. Modulation of the composition and shape of nanostructured photoanodes is key element to tailor the processes regulating charge dynamics and, ultimately, to boost the efficiency of the device, by favoring charge transport and collection, while reducing charge recombination. We investigated light harvesting, exciton separation and charge injection and transport in several systems: (i) TiO2 nanoparticles / ZnO nanowires; (ii) Multiwall carbon nanotubes (MWCNTs) / TiO2 nanoparticles; (iii) TiO2 nanotubes; (iv) Hierarchically self-assembled ZnO sub-microstructures. Both dye molecules and semiconducting quantum dots were applied as light harvesters. Possible tailoring of structure and morphology of the photoanodes and of the quantum dots, and their implication in improving the functional properties of these kinds of solar cells will be discussed in detail.

2:55 PM

(PACRIM-S24-005-2017) Paper-based platforms for solar-powered opto-electronic devices

E. Fortunato*[1]; R. Martins[1]; H. Aguas[1]; A. Vicente[1]

1. FCT-UNL, Materials Science, Portugal

Presently, the development of non-wafer-based photovoltaics allows supporting thin film solar cells on a wide variety of low-cost recyclable and flexible substrates such as paper; thereby extending PV solutions to a broad range of consumer-oriented indoor disposable applications where autonomous energy harvesting is today a bottleneck issue. Here, we show a proof-of-concept of the pioneering production of thin-film amorphous silicon (a-Si:H) photovoltaic cells with efficiencies of 3.4% to 4%, by plasma enhanced chemical vapor deposition (PECVD), on paper and packaging cardboard commonly used in the food and beverage industry. Such accomplishment put us one step closer to this revolution, by providing a flexible, renewable and extremely cheap autonomous energy packaging system. Moreover, such Si thin films take advantage of their good performance at low-light levels, which also makes them highly desirable for cheap mobile indoor applications.

3:25 PM

(PACRIM-S24-006-2017) Colloidal heterostrucutred quantum dots for liquid junction solar cells (Invited)

H. Zhao*[1]

1. INRS, EMT, Canada

Colloidal core/shell QDs have attracted much attention due to their unique size-tunable optical properties. In this talk, we focus on the synthesis of colloidal core@shell QDs including the PbS@CdS, and CdSe/CdS, the investigation the photoelectron transfer rate from QDs to wide bandgap semiconducting mesoporous films and further fabrication of solar cells. The as-synthesized QDs were loaded into the mesoporous metal oxide thin film by a link-assisted methods. The different electron affinity of the oxides, the core size and the shell thickness allow to fine tune the electron injection rate by determining the width and height of the energy barrier for tunneling from the core to the oxide. Theoretical modeling using the semi-classical approximation provides an estimate for the escape time of an electron from the QD 1S state, in good agreement with experiments. The results demonstrate the possibility of obtaining fast charge injection in core/shell QDs stabilized by an external shell. Furthermore we report the application of core/shell QDs for QDSCs. The highest photoconversion efficiency of ~5% for "giant" core/shell QDs and

~3% for PbS/CdS QDs. The success in using such core/shell QDs paves the way to realize high efficiency and cost-effective solar cell for renewable and clean energy production.

3:50 PM

(PACRIM-S24-007-2017) Path Toward Ultra-High Efficiency Thin Silicon Photovoltaics (Invited)

N. P. Kherani*[1]

1. University of Toronto, Electrical & Computer Engineering, Canada

Commensurate maximization of optical absorption and complete extraction of photogenerated carriers are primary factors that influence attainment of maximal photovoltaic conversion efficiency. Photonic crystals, periodic nanostructures that exhibit various propagation modes and resonances, provide an opportunity for control over reflection, transmission and trapping of light in a given device construct and hence maximum photogeneration. Equally important are highly passivated interfaces along with bulk material quality and current extracting junction quality and design. This talk will examine various photonic constructs in crystalline silicon in relation to light trapping and photogeneration. The role of passivation in relation to current extraction will be explored. Recent developments of novel optically transparent passivation material will be presented. The integration of these along with high quality junctions toward the attainment of ultra-high efficiency thin crystalline silicon photovoltaics will be discussed.

4:15 PM

(PACRIM-S24-009-2017) Photovoltaic perovskites (Invited)

R. Nechache*[1]

1. Ecole de technologie Superieure, Electrical Engineering, Canada

Since the discovery of the bulk photovoltaic (PV) effect in ferroelectrics, there has been a growing interest in perovskite materials for energy related applications, including PV and water splitting. In such materials, the spontaneous polarization-induced electric field promotes the required separation of photo-excited carriers and allows photovoltages higher than their bandgap, which lead to efficiencies that can exceed the maximum possible in a semiconductor p–n junction solar cells. Bi_2FeCrO_6 (BFCO) is highly promising because it exhibits a conversion efficiency of about 8.1% in thin film form. Other perovskites can be hybrid, if the cation A is replaced with an organic radical. This is the case for halide perovskite compounds (CH3NH3PbX), with X=Br, Cl, I, found recently to possess excellent light absorbing properties in the visible-near infrared spectrum. The use of these materials in solar cells had led to a rapid increased of the photovoltaic conversion efficiency (PCE) in the last year up to about 20 %. The combination of the relatively high PCE with the low cost technologies makes perovskite photovoltaic solar cells very attractive for future development. We will present, the controlled growth and characterization of BFCO thin films and nanostructures via pulsed laser deposition and physical vapor transport technique. The optimization of PV properties of such systems and the performance of their related devices will be also discussed.

4:40 PM

(PACRIM-S24-010-2017) Novel Synthesis Method of Transparent Conductive Oxides (TCO) Nanoink (Invited)

A. Muramatsu*[1]

1. IMR Tohoku University, Institute of Multidisciplinary Research for Advanced Materials, Japan

Generally, thin film of indium-tin-oxides (ITO) as Transparent Conductive Oxides has been prepared by the PVD process with ITO target, but only 20% of ITO yielded from the target is deposited on the substrate. Namely, about 80% ITO is exhausted by the deposition elsewhere far from the substrate. Hence, the recycling process of indium is limited so that ca 20 % ITO of the starting material is lost without any recovery. Even if the recycling of ITO has been carried out in this process, we should prepare ITO target of 5 times more than apparent use of ITO on film. If we change it to printing process from the sputtering, the reduction in ITO use is expected as ca. 50%, considering the increase in film thickness by printing. Our target technology also includes ITO nanoink for our research project. As a result, monodispersed ITO nanoparticles (NPs) with a cubic shape were successfully synthesized with use of quaternary ammonium hydroxide-assisted metal hydroxide organogels. These NPs have perfect uniformity in size with beautiful shape, and perfect single crystalline structure including Sn. As we were attempted to make thin film with ITO nanoink, it was successfully fabricated below 200 nm in thickness and the resistivity was drastically decreased below 1.0×10^{-2} W cm after heat treatments.

PACRIM Symposium 30: Glasses and Ceramics for Nuclear and Hazardous Waste Treatment

Waste Form Simulations

Room: Kona 1
Session Chairs: Yaohiro Inagaki, Kyushu University;
Charles Crawford, Savannah River National Laboratory

1:15 PM

(PACRIM-S30-028-2017) Mesoscale phase-field modeling of radioactive species extraction in hierarchical waste form materials

S. Hu*[1]; Y. Li[1]; C. Henager[1]; T. M. Besmann[2]; A. Grandjean[3]

1. Pacific Northwest National Lab, USA
2. University of South Carolina, USA
3. The French Alternative Energies and Atomic Energy Commission (CEA), DEN, DTCD, SPDE, Laboratoire des Procédés Supercritiques et de Décontamination, France

Hierarchical materials containing multiscale porosity are promising candidates for improving the performance of radioactive waste containment matrices. Understanding the effect of multiscale porous structures and chemistry on diffusion, extraction kinetics, and capacity for radioactive species and or clusters is of importance in designing advanced waste form materials. In this work we will present a mesoscale phase-field model of microstructure evolution in multicomponent and multiphase porous structures. Diffusion, interface reactions, and heterogeneous thermodynamic and kinetic properties will be accounted for in the model. The developed model is generic so that it can be applied to hierarchical structures such as multiscale porous zeolites, salt inclusion materials, and metal organic frameworks for design and optimization of microstructures and properties of interest. As an application of the model, we simulate the effects of microstructure and thermodynamic properties on the behavior of radioactive species in contact with a multiscale porous zeolite to demonstrate the model's abilities to capture anisotropic diffusion and absorption kinetics. This work was supported as part of the Center for Hierarchical Waste Form Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-SC0016574.

1:30 PM

(PACRIM-S30-029-2017) Modelling Heat Production by Fukushima Wasteforms

M. J. Rushton*[1]; D. Pletser[1]; L. Vandeperre[1]; W. E. Lee[1]

1. Imperial College, Materials, United Kingdom

Following the 2011 accident at the Fukushima Daiichi nuclear power plant, large volumes of water were injected into the reactor cores to cool them. A significant issue in the remediation of the Fukushima site is the treatment of this effluent water. As a result, sophisticated treatment plants have been used to remove radionuclides from the water using ion exchange media. This has left large amounts of high dose spent adsorbents (HDSAs) with many containing substantial quantities of ^{137}Cs and ^{90}Sr causing significant heat generation. In addition, hydrogen production from radiolysis of entrained water means that immobilisation would greatly aid in their safe long-term management. Here the heat generated by several HDSA waste form concepts is predicted for different ^{137}Cs and ^{90}Sr loadings. These are based around glass and glass composites using low temperature (< 900K) lead borate and lead borosilicate matrices and are compared with a higher temperature sodium borosilicate (~1400K). Compositional effects on waste temperature such as self-shielding due to Pb are discussed in the context of package design. Predictions are made using the Geant IV radiation transport toolkit in conjunction with finite element modelling to predict waste form temperatures as a function of time, shape and composition. It is hoped that these data will guide the choice of waste form and the storage and disposal strategy for the Fuskushima HDSAs.

Immobilization of Challenging Species

Room: Kona 1
Session Chairs: Yaohiro Inagaki, Kyushu University;
Charles Crawford, Savannah River National Laboratory

1:45 PM

(PACRIM-S30-031-2017) Sequestration and Capture of Radioiodine in Lead Vanadium Iodoapatite Phases

E. V. Johnstone*[1]; D. Bailey[1]; N. C. Hyatt[1]

1. University of Sheffield, Materials Science and Engineering, United Kingdom

Due to its volatile nature and radiotoxicity, radioiodine, e.g.^{129}I and ^{131}I, has been a long-standing problem in the nuclear industry for reprocessing and disposal of spent nuclear fuel (SNF). In the fuel, radioiodine typically forms as gaseous bubbles dispersed in the fuel grains, however, at higher burn-ups it also precipitates with Ag and Pd. These robust precipitates have been observed in the undissolved solids during reprocessing. Whereas the direct disposal of MI_2 (M = Pd, Ag) metal salts has been suggested, their integration into other stable matrices, such as ceramics, has also been proposed. The lead vanadium iodoapatite phase, i.e., $Pb_{10}(VO_4)_6I_2$, has been shown to be an ideal matrix for radioiodine disposal due to its chemical and radiation durability, its ability to structurally accommodate the large I anion, and its relatively low formation temperature. In this work, the use of MI_2 salts was investigated for the synthesis of $M_xPb_{10-x}(VO_4)_6I_2$ apatite phases. These compounds were synthesized in the solid-state and characterized by a variety of physicochemical techniques in order to determine their structural and chemical properties. The use of $M_xPb_{10-x}(VO_4)_6I_2$ as radioiodine waste forms will be discussed in the context of other proposed waste form phases for radioiodine.

2:00 PM

(PACRIM-S30-032-2017) Silver Tellurite Glasses for Immobilization of ^{129}I from Reprocessing

C. Lee*[1]; J. Pyo[1]; H. Park[2]; J. Yang[2]; J. Heo[1]

1. Pohang University of Science and Technology(POSTECH), Department of Advanced Nuclear Engineering, Republic of Korea
2. Korea Atomic Energy Research Institute, Republic of Korea

Radioactive ^{129}I has a long half-life (~1.57 x 10^7 yrs), high solubility and mobility in water with a high volatility. Therefore, ^{129}I waste treatment is one of the most significant issues in waste management. During the reprocessing, ^{129}I appears in a gaseous state and trapped by a Ag activated zeolite filter in the off-gas treatment system. Ag can be bonded to I and form AgI and they have low solubility in water. Silver tellurite glasses were developed to immobilize radioactive ^{129}I wastes. A glass with the composition of $54TeO_2 - 24Ag_2O - 5Bi_2O_3 - 19AgI$ (mol%) was melted at 700 ºC for 30 min under ambient atmosphere. 96 % of iodine remained after the melting and the total waste loading was 11.21 wt.%. Normalized elemental releases from PCT were below US regulation (2g/m^2). Glass transition temperature (165 °C) was well above predicted temperature (100 °C) in a waste disposal site. Iodine K-edge XAS results indicate that oxidation state of iodine in silver tellurite glass is -1 and iodine is surrounded by four Ag ions forming IAg4 tetrahedron.

2:15 PM

(PACRIM-S30-033-2017) Proposed Mechanism of Re Incorporation into Glass during Vitrification of Low-Activity Waste

D. Kim*[1]; T. Jin[1]; J. George[1]; A. A. Kruger[2]

1. PNNL, USA
2. DOE ORP, USA

Technetium-99 is one of the most challenging radionuclides to manage during vitrification of low-activity waste (LAW) at the U.S. DOE's Hanford site because of its high volatility and thus low retention in glass. Crucible melting tests with simulated LAW glass feeds (simulated liquid waste + additives) spiked with Re (surrogate for Tc-99) have been performed to investigate the effects of feed makeup on Re behavior during the melting process. Three separate series of feed variation tests have been completed: (i) effect of feed composition using two baseline glass feeds (designed for tank wastes AN-102 and AZ-102) that showed an extreme difference in Re retention when tested in a small-scale melter, (ii) effect of sulfate concentration, and (iii) effect of reducing agent. The slurry feeds were dried, heated to 400–1100°C, and air quenched. The heat-treated samples were leached with deionized water to separate water-soluble salts from the glass-forming melt. The results of chemical analyses of leach solution and remaining solids were used to identify the soluble and insoluble phases and to quantify Re partitioning into these phases. Preliminary mechanism proposed to explain how the feed variations affect the Re incorporation into glass-forming melt and potential methods to increase Tc-99 retention in glass during LAW vitrification will be discussed.

2:30 PM

(PACRIM-S30-034-2017) Understanding Volatilization of Rhenium during Vitrification of Low-Activity Waste

J. George*[1]; D. Kim[1]; T. Jin[1]; M. J. Schweiger[1]; A. A. Kruger[2]

1. Pacific Northwest National Lab, USA
2. Department of Energy Office of River Protection, USA

Volatile loss of radioactive components such as ^{137}Cs, ^{129}I, and ^{99}Tc are a concern during vitrification of low-activity waste (LAW) at the U.S. Department of Energy's Hanford Site in Washington State. As LAW slurry feeds are heated, salt phases segregate from early glass forming melts and Re (a non-radioactive surrogate for ^{99}Tc) partitions to the salt phase. Previous experiments show that changing slurry feed components will alter the composition of salt phases at varying temperatures and can significantly affect Re retention in the final glass melt. We investigated volatilization behavior of sodium, potassium, and cesium perrhenate salts in the presence of other salts, including sulfates, borates, and nitrates by differential thermal analysis and thermogravimetric analysis (DTA/TGA) methods. These results are compared to observations made regarding Re retention during melting of LAW slurry feeds.

2:45 PM

(PACRIM-S30-035-2017) Rhenium Partitioning during Melting of Simplified Nitrate-Containing Low-Activity Waste Glass Feed

T. Jin*[1]; B. L. Weese[1]; D. Kim[1]; M. J. Schweiger[1]; A. A. Kruger[2]

1. Pacific Northwest National Laboratory, USA
2. US Department of Energy, Office of River Protection, USA

During melting of Hanford low-activity waste (LAW) glass feeds, partitioning of ^{99}Tc (the major radionuclide of concern) into different salt phases at temperatures below 800°C is a key factor affecting the volatile loss of ^{99}Tc. Previous studies with simulated LAW glass feeds identified nitrate and borate as the two major molten salt phases. Simplified LAW glass feeds, containing sodium nitrate spiked with Re (at ~ 1000 ppm in glass) as simulant waste and silica/boric acid as glass forming additives, were developed to investigate the partitioning of Re (a nonradioactive surrogate of ^{99}Tc) into those phases. The feed samples were batched in slurry, dried, heated to different temperatures between 500 and 900°C, and then quenched. The micro-structure of the reacting feed samples was analyzed by scanning electron microscope. The distribution of Re, B, N, Na, and Si in the reacting feed samples were mapped by secondary ion mass spectroscopy and electron probe micro analyzer wavelength dispersive spectroscopy. The qualitative elemental mapping revealed that the nitrate-rich and borate-rich phases tended to separate and Re was preferentially associated with nitrate rich phases. The effect of temperature on partitioning of Re at elevated temperatures and its implication to the mechanism of Re incorporation into glass will be discussed.

3:00 PM

(PACRIM-S30-048-2017) High-density $Li_5La_3Ta_2O_{12}$ ceramics for ion-selective fission waste processing

H. J. Brown-Shaklee*[1]; M. Blea-Kirby[1]; J. Greigo[1]; M. Rodriguez[1]; J. Ihlefeld[1]; E. Spoerke[1]

1. Sandia National Laboratories, Electronic, Optical and Nano Materials, USA

Ionic conductivity in ceramics is influenced to a significant degree by total porosity. For separation of fission waste by ion-selective electrochemistry, it is extremely critical that high-density ion-selective ceramics can be made. In this case, Cs^+ ions must be selectively screened at a solid electrolyte by leveraging selective Li-ion conduction through a dense ceramic without Cs^+ conduction through interconnected pore networks. Here, we describe the critical processing methods that we used to achieve >95% theoretical density $Li_5La_3Ta_2O_{12}$ (LLTO) lithium ion conducting garnet. All LLTO in this study was densified via pressureless sintering in controlled atmospheres which enabled control of stoichiometry. We will describe the phase space around the LLTO garnet and describe mechanisms for stabilization of the garnet phase at the high temperatures required for densification. Finally, we will show that the ion conductivity of these dense garnet ceramics exceed that measured for pressureless sintered LLTO and associated Li-ion conductors by other groups. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

PACRIM Symposium 32: Nanostructured Bioceramics and Ceramics for Biomedical Applications

Nanostructured Bioceramics III

Room: Monarchy
Session Chairs: Kohei Soga, Tokyo University of Science;
Shiow-Kang Yen, Department of Materials Science and Engineering;
Antonio Feteira, Sheffield Hallam University

1:15 PM

(PACRIM-S32-016-2017) Electrospinning for Cell Fiber Fabrication: Effects of Process Parameters on Fiber Quality (Invited)

H. Sun[1]; Q. Zhao[1]; M. Wang*[1]

1. The University of Hong Kong, Department of Mechanical Engineering, Hong Kong

There is growing interest in cell-encapsulated fibers ("cell fibers") for regenerative biology and medicine. In tissue engineering, cell fibers can be used to fabricate biomimetic cell-scaffold constructs for enhancing human body tissue regeneration. Continuous generation of cell-laden hydrogel fibers is shown recently. In this study, coaxial electrospinning (coaxial-ES) was investigated for continuously fabricating structurally stable hydrogel cell fibers. Using coaxial-ES, fibroblasts (1×105~1×106 cells/mL in final fibers) were encapsulated in crosslinked alginate hydrogel fibers. In coaxial-ES, inner capillary of coaxial spinneret was fed with a blended liquid made by mixing a fibroblast suspension (in PBS; at different cell densities) and a sodium alginate (Na-alginate) aqueous solution and outer capillary was fed with a CaCl2 aqueous solution for crosslinking Na-alginate to Ca-alginate hydrogel during coaxial-ES. The applied voltage in coaxial-ES was kept low (1~3 kV) to achieve high cell viability and properties. At 1, 2 and 3 kV voltages, cell fibers had diameters of 500, 400 and 350 nm and exhibited smooth fiber structure. Cells were generally evenly distributed in cell fibers. Using parameters outside optimal conditions, either cell fibers could not be continuously produced or cell fibers did not possess desired properties. In vitro tests revealed high cell viability in fibers.

1:45 PM

(PACRIM-S32-017-2017) Micro/nanostructured silica coatings modulate dental tissue attachment and orientation on ceramic implants (Invited)

D. Hansford*[1]; A. Peleaz-Vargas[2]; A. Carvalho[3]; D. Gallego-Pérez[1]; N. Higuita-Castro[1]; L. Grenho[3]; M. Laranjeiro[3]; M. P. Ferraz[4]; M. Fernandes[3]; F. Monteiro[3]

1. The Ohio State University, USA
2. Universidad Cooperativa de Colombia, Facultad de Odontología, Colombia
3. Universidade do Porto, Instituto de Engenharia Biomédica, Portugal
4. Universidade Fernando Pessoa, Centro de Estudos em Biomedicina, Portugal

Ceramic implants are of great interest for dental applications due to their chemical stability and aesthetic appeal, but their limited attachment to dental tissue has prevented their widespread use. Thin film sol-gel silica was used as a coating on zirconia, alumina, porcelain, 316L stainless steel, and titanium, demonstrating a uniform cellular response independent of the underlying implant material, with strong adhesion to all implant materials. The use of silica with engineered nanostructures via precision replica molding greatly enhanced the attachment and guidance of tissues to dental ceramics. Enhanced bioactivity of the ceramic implants was demonstrated through enhanced cellular attachment and guidance of human bone-derived mesenchymal stem cells, gingival fibroblasts, and microvascular endothelial cells. Intracellular staining and PCR indicated expected increases in metabolic activity, ALP activity, and gene expression for enhanced osteogenic differentiation in the hBDMSCs, with enhanced metabolic activity for the fibroblasts and endothelial cells on the nanostructures. Studies also showed that the coatings were blood compatible and reduced the bacterial adhesion compared to zirconia. These results demonstrate that nanostructured silica coatings show great promise for enhancing the performance of dental ceramic implants to overcome their current limitations.

2:15 PM

(PACRIM-S32-018-2017) Fluorescent Ceramic Nanoparticles for Biophotonics in the Second Biological Window (Invited)

K. Soga*[1]; M. Kamimura[1]

1. Tokyo University of Science, Dept Mater Sci & Tech, Japan

The use of the near infrared wavelength range between 1000 and 2000 nm is attracting interests of the uses of biophotonics because of the most transparency of the biological objects in the range. For example, observation depth of fluorescence in vivo imaging with wavelength below 1000 nm (i. e. visible and the NIR I) is limited within several millimeters, while that in the above range (NIR II: Second Biological Window) has been proved to be several centimeters. The authors have developed both of the fluorescent materials and imaging systems for the NIR II imaging for a decade. One of the candidate fluorescence probe is made of rare-earth doped ceramic nanoparticles (RED-CNP). The paper will review and update the design and processing of the RED-CNP for the biophotonics. Also, more recent studies made “nanothermomtry” in biological systems by using the ratiometry of the fluorescence bands in the NIR II with the RED-CNP. Materials design and some demonstrative works of the fluorescence nanothermometry in the NIR II will also be reported.

2:45 PM

(PACRIM-S32-019-2017) New Bioactive and Multifunctional Magnetic Nanoparticles: A Potential Revolution in Nanomedicine (Invited)

A. Tampieri*[1]; M. Sandri[1]; M. Montesi[1]; S. Panseri[1]; S. Sprio[1]; M. Iafisco[1]; A. Adamiano[1]

1. National Research Council of Italy, Institute of Science and Technology for Ceramics, Italy

The use of smart nanoparticles into more effective and targeted therapies against degenerative pathologies is today limited by: i)low biodegradability and biocompatibility; ii)uncontrolled drug release; iii)limited cell-target specificity; iv)low efficiency in crossing biological barriers. A novel magnetic apatitic nanoparticle (FeHA) has been recently developed, through controlled substitution of Ca^{2+} ions with $Fe^{2+/3+}$ ions, with specific Fe/Ca and Fe^{2+}/Fe^{3+} ratios. Fe-HA exhibits excellent biocompatibility and biodegradability, and intrinsic superparamagnetic properties that enable remote activation by magnetic signals. The new nanoparticles allow selective cell internalization and targeting, and translation of magnetic cell-based therapies from laboratory to clinical studies. This approach also enables the forced 3-D colonisation of scaffolds by cells to enhance/shorten regeneration critical size tissue defects. Besides, Fe-HA can be used as effective contrast agent in MRI imaging, for live monitoring of injected cells/biomolecules such as anti-cancer drugs, proteins, nucleic acids, and drive them to targeted tissues for on-demand activation and release thus opening brilliant perspective in personalised medicine applications. Due to its unique multifunctional features, FeHA can replace SPIONs for a number of breakthrough applications in regenerative medicine and theranostics.

3:15 PM

(PACRIM-S32-020-2017) Porous Geltin-Hydroxyapatite Composite Microspheres as Doxorubicin Carriers for Osteosarcoma Treatments: In-vitro Study

S. Yen*[1]; Y. Lai[2]; C. Lin[3]; Y. Liang[1]

1. National Chung Hsing University, Department of Materials Science and Engineering, Taiwan
2. China Medical University Hospital, Physical Medicine and Rehabilitation, Taiwan
3. Taichung Armed Force General Hospital, Department of Orthopaedic Surgery, Taiwan

In this study, we attempt to prepare porous geltin-hydroxyapatite (Gel-HAp) composite microspheres by hydrothermal methods for doxorubicin(DOX) loading in the osteosarcoma treatment. The related characterization was carried out by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), electron microscopy (EM), thermalgravimetry analysis (TGA) and specific surface area/porosimetry & chemisorption analyzer, to observe their crystalline phase, composition, morphology, chemical bonding, thermal stability and pore distribution. The results indicate that the morphology of composite microspheres is porous structure with specific surface area 158.6 m^2/g, pore size from 3 to 150 nm, and pore volume 0.492 cm^3/g. Due to the high specific surface area and great pore volume, the DOX loading can be up to 40% and the releasing can last for more than two months after chitosan was added in the DOX solution. Besides, the MTT Assay was carried out to analyze the effect of DOX loaded composites on the osteosarcoma viability. In general, it is concluded tha the high drug-loaded and injectable Gel-HAp microspheres have been successfully prepared to achieve DOX sustaining release, retarding the proliferation of G-292 cell efficiently.

3:45 PM

(PACRIM-S32-021-2017) Big Health Advances with Small Materials: 20 Years of Commercializing Medical Devices Using Nanotechnology (Invited)

T. Webster*[1]

1. Northeastern University, USA

There is an acute shortage of organs due to disease, trauma, congenital defects, and most importantly, age related maladies. The synthetic materials used in tissue engineering applications today are typically composed of millimeter or micron sized particles and/or fiber dimensions. Although human cells are on the micron scale, their individual components, e.g. proteins, are composed of nanometer features. By modifying only the nanofeatures on material surfaces without changing surface chemistry, it is possible to increase tissue growth of any human tissue by controlling the endogenous adsorption of adhesive proteins onto the material surface. In addition, our group has shown that these same nanofeatures and nano-modifications can reduce bacterial growth without using antibiotics, which may further accelerate the growth of antibiotic resistant microbes. Finally, nanomedicine has been shown to stimulate the growth and differentiation of stem cells, which may someday be used to treat incurable disorders, such as neural damage. This strategy also accelerates FDA approval and commercialization efforts since new chemistries are not proposed, rather chemistries already approved by the FDA with altered nanoscale features. This invited talk will highlight some of the advancements and emphasize current ceramic nanomaterials approved by the FDA for human implantation.

4:15 PM

(PACRIM-S32-022-2017) Comparison of the mechanical properties and restorative quality of three commercial dental prosthetic materials

A. Feteira*[1]; A. Kounga[2]

1. Sheffield Hallam University, United Kingdom
2. Institut Straumann AG, Switzerland

The influence of phase assemblage on the underlying mechanical properties of three different commercial dental materials: the newly developed N!CE™ (lithium disilicate reinforced lithium aluminosilicate, Straumann, Institut Straumann AG); IPS e.max®CAD (lithium disilicate, Ivoclar Vivadent AG. Liechtenstein) and Vita Suprinity® (zirconia reinforced lithium silicate ceramic (ZLS), VITA Zahnfabrik, DeguDent GmbH and Fraunhofer-Institut for Silicate Research ISC) was investigated. In the partially crystallised state the highest strength (300 MPa) is exhibited by N!CE™ due to the coexistence of lithium disilicate and lithium aluminosilicate needles. In the fully crystallised state the highest strength (550 MPa) is exhibited by IPS e.max® CAD. N!CE™ shows the largest fracture toughness in both partially and fully crystallised. The time to mill a crown from partially crystallised state is ~21 minutes for all materials, however in the fully crystallised state this time increases to ~30 minutes for N!CE™ and Vita Suprinity®, whereas IPS e.max® CAD could not be milled.

4:30 PM

(PACRIM-S32-023-2017) Direct-Writing of 3D Scaffolds from Bioactive Glasses (Invited)

L. Hupa*[1]; S. Eqtesadi[1]; A. Motealleh[2]; P. Miranda[2]

1. Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Finland
2. Universidad de Extremadura, Escuela de Ingenierías Industriales, Spain

Intense research efforts are paid to manufacture amorphous or partly crystalline tissue engineering scaffolds from bioactive glasses. Tailored external geometry, specified pore volume fraction, pore size and pore interconnectivity are paramount properties for the scaffolds. Further, the mechanical properties and their change upon the implantation must fulfill the strength requirements in the application. We compare scaffolds manufactured from three well-known glasses, Bioglass 45S5, BonAlive S53P4, glass 13-93 and one experimental composition, 1-06 through robocasting. Robocasting is an extrusion-based, direct writing technique in which glass particle containing paste –like suspensions, inks, with tailored rheological properties are used to build the desired 3D structures. Robocasting provides a means to improve the mechanical performance of scaffolds by providing a much greater level of control over pore architecture and more regular strut morphologies than in conventional techniques. After the printing, the scaffolds are thermally treated to remove any organic additives in the ink and to consolidate the particulates into strong struts. The compositions of glasses 13-93 and 1-06 have been optimized to allow viscous flow sintering while 45S5 and S53P4 partly crystallize during the thermal treatment. We discuss in detail the in vitro properties and mechanical strength of these amorphous and glass-ceramic scaffolds.

Friday, May 26, 2017

GOMD Award Lectures

Varshneya Glass Technology Lecture

Room: Kona 5

8:35 AM

(GOMD-PL-005-2017) Volume holographic elements in photo-thermo-refractive glass: Features and applications (Invited)

L. Glebov*[1]

1. University of Central Florida, CREOL, USA

This presentation summarizes the results of volume holographic elements development for spectroscopy and fine laser control that were performed by research teams of Photoinduced Processing Laboratory at CREOL/UCF and OptiGrate Corp. in collaboration with numerous researchers from different countries. This survey includes mechanisms of refractive index change and origin of induced absorption and scattering in photo-thermo-refractive (PTR) glass and basics of holographic elements recording in this material. The main types of holographic optical elements recorded in PTR glass are: reflecting and transmitting volume Bragg gratings (VBGs), longitudinal and transverse chirped Bragg gratings (CBGs), monolithic solid state lasers with VBGs imprinted in gain elements, tunable and achromatic holographic phase masks (HPMs), and complex holographic elements such as lenses or curved mirrors. Applications of those elements for conventional and Raman spectroscopy, spectral and angular mode selection in different types of lasers, mode conversion by complex VBGs and holographic phase masks, spectral and coherent beam combining, ultrashort laser pulses stretching, compression and shaping, and monolithic solid state lasers with distributed Bragg reflector (DBR) and distributed feedback (DFB) are described.

GOMD Symposium 1: Fundamentals of the Glassy State

Glass under Pressure

Room: Kona 4

Session Chair: Atsunobu Masuno, Hirosaki University

9:45 AM

(GOMD-S1-109-2017) Pressure induced structural changes in glassy materials (Invited)

A. Zeidler*[1]; P. Salmon[1]

1. University of Bath, Department of Physics, United Kingdom

A prerequisite for designing glassy materials with new functional properties is an understanding of the structure, and the evolution of this structure under different state conditions. Here, pressure can be used as a tuneable parameter, and can induce abrupt structural changes as in polyamorphic transitions. The behaviour of glass under pressure is important for understanding phenomena such as crack formation and propagation, where pressures in the GPa regime are readily encountered. High pressures can also be used to form permanently densified glassy materials with altered mechanical and optical properties. But what are the mechanisms by which glass networks collapse under load? Can atomistic models be developed that have predictive capabilities? We have investigated the structures of a range of oxide and chalcogenide glasses by in situ high-pressure neutron diffraction. The results are combined with those obtained from other experimental techniques in order to deduce the mechanisms of structural transformation, and to develop realistic molecular dynamics models. In the case of oxide glasses, we have found that the oxygen-packing fraction is a crucial parameter in determining when the pressure-induced transformations of a network topology are likely to occur.

10:15 AM

(GOMD-S1-110-2017) Elastic/plastic transformation of vitreous silica under pressure (Invited)

B. Ruffle*[1]

1. Montpellier University, Physics Department, France

In spite of great experimental efforts, the nature of the pressure-induced transformations in amorphous solids is not yet adequately understood. The talk will focus on the thermodynamic properties of vitreous silica submitted to high pressures in a diamond anvil cell as obtained directly from Brillouin Light Scattering experiments or indirectly from standard relations. The analysis reveals non-negligible differences between static and dynamic compressibilities which are mostly related to the existence of thermally activated relaxational processes. Estimate of the residual densifications after complete cycles of compression/decompression is discussed and compared to literature data.

10:45 AM

(GOMD-S1-111-2017) Elastic anomaly and mechanism of densification in the ternary SiO_2-Na_2O-Al_2O_3

D. de Ligny*[1]; M. Cicconi[1]; A. Veber[1]; A. Cornet[2]; C. Sonneville[2]; V. Martinez[2]; M. Christine[2]; B. Champagnon[2]

1. University Erlangen-Nürnberg, Materials Sciences and Engineering, Germany
2. University Lyon1, Institut Lumière Matière, France

The elastic anomaly of silica glass corresponds to a decrease of the bulk modulus around 2GPa. It is associated with a low atomic packing density, a high permanent densification rate and a relatively low Poisson's ratio. A first understanding of this anomaly was associated with the folding of silica six membered rings. Glasses presenting this elastic anomaly are expected to present a better crack resistance since a part of the energy can be dispersed by this ring folding process and or by the increase of the packing density by permanent densification. For many years, this elastic anomaly was only shown for pure silica. However, recent studies show that it could extend to many different compositions of alumino silicates as Albite $NaAlSi_3O_8$ or Anorthite $CaAl_2Si_2O_8$ glasses. These new data challenge our thinking about the elastic anomaly origin. It seems then that the six membered silica rings can be partially substituted by Alumina. As to test that a set of sodo alumino silicate glasses were synthesized and studied in situ at high pressure by both Raman and Brillouin spectroscopies. The composition dependence of the elastic anomaly can then be determined. The structures responsible of the elastic anomaly are conserved even when half of the Si is substituted by Al in fully polymerized glasses.

11:00 AM

(GOMD-S1-112-2017) Polyamorphism in lithium borate glasses

G. Lelong*[1]; C. J. Sahle[2]; V. Giordano[3]; E. de Clermont[1]; L. Cormier[1]

1. UPMC, IMPMC, France
2. European Synchrotron Radiation Facility, France
3. Institut Lumière Matière, France

During compression, changes in the structure of amorphous materials can be discontinuous, a phenomenon referred to as polyamorphism. Recent non-resonant inelastic X-ray scattering (NRIXS) studies showed that borate glasses exhibit pressure-induced coordination transformation, with the conversion of three-fold coordinated boron ($^{[3]}B$) into four-fold coordinated boron ($^{[4]}B$)[1]. We have recently carried out a successful in-situ NRIXS measurement on ID20 on both glassy $LiBO_2$ and $Li_6B_4O_9$ at high pressure in a diamond anvil cell up to 30 GPa. These two glasses show at room pressure an increasing degree of depolymerisation of the borate network accompanied by an increase number of non-bridging oxygens (NBO). While the network structure is usually described in terms of connections between the basic structural units (BO_3 and BO_4), the non-bonding O sites reflect the network topology and degree of network polymerization. During the compression, we were able to measure both the B and O K-edges, and then monitor the $^{[3]}B$ to $^{[4]}B$ conversion and the recombination of the NBOs as a function of pressure. The evidenced effect of the NBOs goes along with the effect of the network-modifying cations, showing that the composition and the polymeric state of the initial glass control the pressure-induced structural modifications.

11:15 AM

(GOMD-S1-113-2017) The Elastic Limit of Silicate Glasses Using Molecular Dynamics

S. Goyal*[1]; V. Subramanian[1]

1. Corning Incorporated, USA

Glass reacts to extreme stress by undergoing elastic and irreversible deformation. Irreversible deformation can occur in glass via densification, isochoric shear flows or a combination of these two. Such extreme stresses are observed during indentation and scratch of glass, which are commonly encountered during usage of cover glasses in mobile devices. To understand these deformations, we need to characterize the elastic limit and post yielding behavior of glass. The elastic limit is defined as the region in stress and strain space within which the material response is elastic. Typically the elastic limit is bound by the yield surface and the fracture loci and these individual regions need to be determined. Post yielding, the material behavior is elasto-plastic with evolving yield surfaces being observed in metals. This talk focuses on our recent work in developing a framework for accurately characterizing the elastic limit for silicate glasses in stress and strain space. We have used molecular dynamics as our tool as it samples a length scale that allows us to model bulk behavior and is accurate enough to exhibit complex changes in structures as a function of compositions. The initial yield surface and the fracture loci were characterized to obtain the elastic limit. Such information can potentially be used to build accurate continuum scale constitutive models for glasses to predict indentation and scratch behavior.

11:30 AM

(GOMD-S1-114-2017) Diffusion of water in silica: Influence of moderate stresses

S. Wiederhorn*[1]; G. Rizzi[2]; M. J. Hoffmann[2]; T. Fett[2]; S. Wagner[2]

1. National Institute of Standards and Technology, USA
2. Karlsruhe Institute of Technology, Germany

In earlier work, we studied the diffusive transfer of water into silica glass in the absence of externally applied stresses, or swelling effects. Here, we investigate the effect of stresses on the swelling process. By taking into account the co-action of water penetration into the surface of silica glass and the development of swelling stresses in the water-penetrated zone, several experimental findings in the literature can be predicted and interpreted. In detail, these are an apparent decrease of the diffusivity with time, an increase of water solubility under compressive loading and the opposite effect under tensile loading. Moreover, the reversal of these effects at longer times can be shown to be a direct consequence of the effect of stress on the equilibrium constant for the silica/water reaction.

11:45 AM

(GOMD-S1-115-2017) Modifier-Free Al_2O_3-B_2O_3-P_2O_5-SiO_2 Glasses under Pressure

M. M. Smedskjaer*[1]; S. Kapoor[1]; X. Guo[2]; R. Youngman[2]; C. L. Hogue[2]; J. C. Mauro[2]; S. Rzoska[3]; M. Bockowski[3]; L. R. Jensen[4]

1. Aalborg University, Department of Chemistry and Bioscience, Denmark
2. Corning Incorporated, USA
3. Institute of Physics Polish Academy of Sciences, Poland
4. Aalborg University, Department of Mechanical and Manufacturing Engineering, Denmark

SiO_2, P_2O_5, B_2O_3, and Al_2O_3 are all well-known network formers in glassy solids, but the structure and properties of mixed Al_2O_3-B_2O_3-P_2O_5-SiO_2 glasses without the presence of network modifiers are poorly understood. The relatively low atomic packing density of these glasses should favor network densification when subjected to high local stress (e.g., indentation) at room temperature, and it is therefore interesting to examine their structural response to high pressure treatment. In the present study, we investigate the pressure-induced changes in volume, structure, and mechanical properties (hardness and crack resistance) of two Al_2O_3-B_2O_3-P_2O_5-SiO_2 glass series with varying Si/P and Si/B ratio, respectively. The glasses are isostatically compressed at 1 or 2 GPa at the glass transition temperature, enabling permanent densification of bulk sample specimens. We discuss the pressure-induced changes in glass properties in relation to the structural changes quantified through Raman and ^{11}B, ^{27}Al, and ^{31}P NMR spectroscopy.

GOMD Symposium 4: Glass Technology and Crosscutting Topics

Challenges in Glass Manufacturing III

Room: Waikoloa 3
Session Chairs: Irene Peterson, Corning Incorporated; Deborah Baker, Corning Incorporated

8:30 AM

(GOMD-S4-062-2017) Latest milestones of Glass Technology Improvements in Sisecam (Invited)

H. Sesigur*[1]

1. Sisecam, Research and Technology Center, Glass Technology Directorate, Turkey

Today glass can be thought as a fully developed technology with its two century research past, but there is still much to be discovered. The past years witnessed tremendous amount of development studies on this technology performed by both industry and academia, resulting few revolutionary developments but mostly evolutionary improvements in order to advance glass manufacturing process for better quality, protected environment and lower cost. Melting kinetics, sulfate chemistry and fining mechanism are the main building blocks of glass production technology and the mostly studied topics in order to have an optimum glass quality, fuel consumption, emission level and cost. The effect of batch composition as well as the other affecting parameters of melting and fining processes, such as the oxidation state, basicity, temperature and water content, have to be optimized in order to take no risk in the final glass quality. Sisecam which is a 80 years old glass manufacturing company, initiated its corporate R&D activities in the field of glass technology 40 years ago. This presentation reveals an overview of the recent work on melting kinetics and fining process taking place in SLS glasses. Examples of practical experiences as well as experimental investigations of Sisecam will also be conveyed in detail.

9:00 AM

(GOMD-S4-063-2017) Solubility of CO_2 and structure analysis of Na_2O-(ZnO/RE_2O_3)-SiO_2 glass melts

T. Yano*[1]; T. Naito[1]; T. Kishi[1]; N. Matsushita[1]

1. Tokyo Institute of Technology, Department of Materials Science and Engineering, Japan

Dissolution of gases into high-temperature glass melts is one of the important phenomena in the melting process because it directly correlates with the quality of glass products. In the vitirification process, various gas species are produced by the reactions of batch materials, and some ones also come from the atmosphere created by the combustion of the burner flame in the melting furnace. CO_2 gas is one of the major species and its solubility is indispensable to consider the phenomena of bubbles in the glass melt. It is known to have deeply correlating with the glass compositions, but the relation with the structure of glass melts has not been understood well yet. In this study, solubility of CO_2 gas in the silicate glass melts has been measured at the temperature, 1400 ºC, and the effects of the addition of rare earth metal oxides (RE_2O_3) and zinc oxide (ZnO) are evaluated. CO_2 gas-saturated Na_2O-(ZnO or RE_2O_3)-SiO_2 glass samples at 1400 ºC are prepared, and then subjected to the measurement of gas analyzer using FT-IR spectrometer. In order to understand their melt structures, high-temperature Raman spectroscopy is applied, and the spectra are collected from the melts at the temperature around 1400 ºC. From these experimental results, the compositional dependence of the solubility of CO_2 gas is considered from the point of view of the structural changes induced by the addition of RE_2O_3 or ZnO.

9:15 AM

(GOMD-S4-064-2017) Nucleation and growth of bubbles during glass cullet melting

D. Boloré*[1]; F. Pigeonneau[1]

1. Saint-Gobain Recherche, France

In an industrial furnace, bubbles generated during the batch reaction are well-known: mainly CO_2 bubbles during the melting and SO_2/O_2 bubbles during the fining. In order to use more and more recycled glass for the production of new glass sheets or bottles, it is necessary to understand what differences exist on the bubble behavior. Without chemical reactions between raw materials, the only available gases are dissolved in the glass cullet. Using High-Temperature Observation and image analysis coupled with Evolved Gas Analysis, we exhibit several situations depending on the conditions of the glass production and on the glass composition. We show that the nucleation process can follow a Poisson behavior and that coalescence has a strong effect on the spatial distribution of the resulting bubbles. Using Voronoï tessellations to follow the spatial distribution of the bubbles, it is possible to estimate the number of coalescence events. The growth rate of the bubbles is also measured and follows a diffusion process which can be modelled. Glass redox state and industrial conditions of glass production are responsible for differences in the growth rates of bubbles. This presentation tries to show that image analysis bring a new insight of the reactions occurring in melted glasses and that thermodynamic values such as diffusivities, solubilities could be estimated through this approach.

Challenges in Glass Manufacturing IV

Room: Waikoloa 3
Session Chairs: Irene Peterson, Corning Incorporated;
Jennifer Rygel, Corning Incorporated

9:45 AM

(GOMD-S4-065-2017) Heat flow from molten glass to glass batch through foam layer (Invited)

P. Hrma*[1]; S. Lee[1]; R. Pokorny[2]; B. McCarthy[1]; D. Dixon[1]; W. Eaton[1]; M. J. Schweiger[1]; A. A. Kruger[3]

1. Pacific Northwest National Laboratory, USA
2. Laboratory of Inorganic Materials, Joint Workplace of the University of Chemistry and Technology Prague and the Institute of Rock Structure and Mechanics of the ASCR, v.v.i., Czech Republic
3. U.S. Department of Energy, Office of River Protection, USA

The rate of glass melting depends on the heat flow to the glass batch. In an electric melter, the heat for melting is delivered from molten glass to the cold-cap bottom, where it is transferred through a thermally insulating layer of viscous foam. To obtain data indispensable for understanding the batch-to-glass conversion process and its mathematical modeling, glass batch properties, such as chemical and phase composition, densities, heat conductivity, reaction heats, heat capacity, and porosity, are determined as functions of temperature using various experimental techniques, including XRD, SEM-EDS, TGA, DSC, EGA, and X-ray CT. The laboratory-scale melter allows direct observation of the cold cap structure. Batch foaming is investigated with the expansion test in which wall effects are avoided while observing changes in porosity and, if the x-ray CT is applied, the bubble size distribution. Rheometry is used to study the evolution of mechanical properties from the stiff sintered batch to viscous foam. The interface between cold cap bottom and the glass melt below is a challenging area for both experimental observation and mathematical modeling. Apart from the batch conversion process that occurs within the cold cap, this area is affected by the melt convection. Mathematical model of the entire melter, validated both by round robin test and experimental verification, will allow full understanding this interaction.

10:15 AM

(GOMD-S4-066-2017) The rate-controlling step of the industrial batch-to-melt conversion

R. Conradt*[1]

1. RWTH Aachen University, GHI, Germany

The batch-to-melt conversion is the first high-temperature step of industrial glass melting. Its power demand constitutes the major part of the overall intrinsic power demand of the process. The influence governing its time demand is, however, not clear. It may consist in the nature of heat transfer to the batch, or heat transport within the batch, or the rate of local chemical reactions. Although FEM models of glass melting tanks rest on the assumption that chemical turnover instantaneously follows heat transport, the nature of the rate-controlling step is in fact unknown. Experiments at the lab scale are presented which reveal the nature of the rate-controlling step. It turns out that different mechanisms are rate-controlling at different temperature levels. Results from campaigns performed at the industrial scale on batches yielding identical glass compositions are presented, comprising three different scenarios or cases. Case 1 refers to campaigns performed on identical batches melted in slightly different furnaces of the same basic design. Case 2 refers to batches with distinctly different intrinsic energy demand, melted in the same furnace. Case 3 refers to batches with identical intrinsic energy demand, however, with a distinctly different kinetics of chemical turnover, again melted in the same furnace. It is show how the features of the batch-to-melt turnover influence the performance of a furnaces.

10:30 AM

(GOMD-S4-067-2017) Modeling of batch to glass conversion during waste glass melting: Evaluation of feed and foam heat conductivity and prediction of melting rate

R. Pokorny*[1]; M. Hujova[1]; J. Klouzek[1]; D. P. Guillen[2]; M. J. Schweiger[3]; P. Hrma[3]; A. A. Kruger[4]

1. University of Chemistry and Technology Prague, Czech Republic
2. Idaho National Lab, USA
3. Pacific Northwest National Lab, USA
4. US Department of Energy, Office of River Protection, USA

The cost and schedule of nuclear waste treatment and immobilization is greatly dependent upon the rate of glass production during vitrification. To address this issue, we have developed in recent years a mathematical model of the cold cap, which incorporates the dynamic behaviour of the foam layer, formed by gas-evolving reactions in the later stages of the batch-to-glass conversion process. In this contribution, we will present this batch-to-glass transition model, and talk about its recent improvements. One of the important, yet not well described parameter is the temperature dependent heat conductivity of the glass batch as it sinters, turns into primary foam, and later forms a bubble free glass. A combination of experimental methods (heat conductivity measurements, foam expansion experiments, X-Ray tomography, etc.) and theoretical models (heat transfer in hetero-phase media) was employed to obtain the effective heat conductivity of the batch as a function of temperature. In the second part of the talk, we will also examine the results of the cold cap model obtained for five different melter feeds, which exhibit pilot-scale melting rates in the range of 550-1900 kg m^{-2} day^{-1} at the same processing conditions.

10:45 AM

(GOMD-S4-068-2017) Complete set of spectral characteristics of semi-transparent bodies for accurate description of heat transfer by radiation

O. Prokhorenko*[1]

1. L.G.P. International, USA

Progress in computer modeling of various physical processes, and technological operations should in particular, with improvement of accuracy of solution thermal sub-tasks. As heat transfer in semi-transparent bodies is carried out by radiation, an accurate solution of quite a few tasks is not possible without actual data on spectral absorption, reflection, emissivity, and, also, index of refraction. In the present paper the problem of variations of those important optical characteristics with glass composition, and temperature is considered. The future work will be devoted to investigation of dependences of optical properties of glass obtained by rapid cooling (at tempering, continuous fiber drawing, beads cooling, spin process, etc.) on their thermal history.

PACRIM Symposium 01: Characterization and Modeling of Ceramic Interfaces: Structure, bonding, and Grain Growth

Microstructure Evolution

Room: Kohala 3
Session Chairs: Naoya Shibata, The University of Tokyo;
Sung-Yoon Chung, Korea Advanced Institute of Sci. & Tech. (KAIST)

9:00 AM

(PACRIM-S1-019-2017) Diffuse Interface Modeling of Sintering, Grain Growth and Coarsening in Ceramics: Application to Additive Manufacturing

F. Abdeljawad*[1]; D. Bolintineanu[2]; D. Kammler[2]; H. J. Brown-Shaklee[1]; A. W. Cook[1]

1. Sandia National Laboratories, Materials Science & Engineering Center, USA
2. Sandia National Laboratories, USA

The direct write additive manufacturing (AM) technique has emerged as a powerful technology for building objects with complex geometries by adding material layer-upon-layer. Materials processed via AM exhibit microstructures that are greatly influenced by the AM process parameters and several coupled phenomena. Herein, based on a diffuse-interface model we examine sintering, grain growth and coarsening in ceramic materials processed via direct write. The model is capable of accounting for bulk thermodynamics, free energies of grain boundaries (GBs) and free surfaces, and capturing various mass transport mechanisms (surface, GB, bulk, evaporation); all of which can be obtained from atomistic calculations. We present quantitative analysis of the interplay of the aforementioned processes along with the roles of particle size/distribution, equilibrium dihedral angle, and spatial arrangement of filaments on the evolution of the grain microstructure, solid phase, inter- and intra-filament porosity. Finally, we discuss further extensions aimed at incorporating anisotropy in interfacial properties and role of gradients in the temperature field.

9:15 AM

(PACRIM-S1-020-2017) Space-, Time-, and Temperature-Resolved Hyperspectral Raman Imaging of High-Temperature Sintering Reactions in Kaolinite-Based Ceramics

K. Stange*[1]; C. Lenting[1]; T. Geisler[1]

1. Rheinische Friedrich-Wilhelms-Universität Bonn, Steinmann-Institut für Geologie, Mineralogie und Paläontologie, Germany

Sintering reactions of clay bodies have previously been studied by numerous experiments that involve quenching to RT and analyzing the reaction product by different techniques. In this study, green bodies containing kaolin and calcite, were progressively fired in air at various temperatures from RT to about 1060°C. For the first time, mineral reactions and textural relationships were studied in situ as a function of temperature, time, and space with a few micrometer resolution by hyperspectral Raman imaging. Gehlenite, wollastonite, and pseudowollastonite could be identified as new phases during sintering, and their textural evolution could be followed with temperature and time. Gehlenite was first observed at a temperature of 660°C. From 800°C wollastonite formed at the direct contact to gehlenite, whereby at temperatures higher 990°C wollastonite seems to be gradually replacing gehlenite. The crystallization of pseudowollastonite was observed already ~290°C below the accepted critical temperature (~1125°C) for the wollastonite-to-pseudowollastonite transformation, suggesting that pseudowollastonite can form metastably. The results of this study demonstrate that hyperspectral Raman imaging is a powerful method to study in situ phase transitions and recrystallization processes at grain boundaries during high-temperature sintering of ceramic.

9:45 AM

(PACRIM-S1-021-2017) Anti-thermal grain growth in perovskite ceramics (Invited)

W. Rheinheimer*[1]

1. Karlsruhe Institute of Technology, Institute for Applied Materials, Germany

Several perovskite ceramics are known to show non-Arrhenius grain growth. In particular for strontium titanate a grain growth transition was documented with decreasing grain growth rates with increasing temperature. Other materials as barium titanate, lithium lanthanum titanate and barium-strontium-titanate indicate grain growth transitions as well. The growth transitions are coupled to bimodal microstructures and seem to be caused by the existence, coexistence and transition of different grain boundary types. This talk gives a review on the details of the grain growth transitions in perovskites. A simple mean field approach and standard grain growth experiments are compared with phase-field simulations of grain growth. Important parameters such as atomistic boundary structure, segregation effects, wetting transitions, faceting, grain boundary stoichiometry, space charge and interfacial drag effects are discussed with respect to their impact on grain growth in perovskites. A summary of open questions and future directions is given.

10:15 AM

(PACRIM-S1-022-2017) Electric Field Effects on Grain Boundary Formation and Grain Growth (Invited)

K. van Benthem*[1]

1. University of California, Davis, Materials Science and Engineering, USA

The application of electrostatic fields during sintering was previously reported to enhance consolidation of materials during electric field assisted sintering, including spark plasma sintering (SPS) and flash sintering. While these techniques are frequently employed for the synthesis of a wide variety of microstructures with sometimes unprecedented properties, a fundamental understanding of electic field effects on the atomic-scale mechanisms for grain boundary formation and grain growth has not yet been achieved. In this presentation we review systematic experimental studies de-coupling the effects of heating and applied electrostatic fields. In situ transmission electron microscopy was carried out to directly verify that electric fields accalerate densification of stabilized ZrO_2 at lower temperatures. Furthermore, accalerated grain growth in $MgAl_2O_4$ was observed i nthe presence of externally applied electric fields. Both of these observations can be ratioanlized with a lowering of the Gibbs Free Energy for defect formation. More recent investigations of bicrystal formation in $SrTiO_3$ reveal a significant modifcation of the grain boundary core structrues due to an applied electric field, which appears consistent with previous observations.

PACRIM Symposium 04: Polymer-Derived Ceramics (PDCs) and Composites

Applications of PDCs I

Room: King's 3
Session Chair: Enrico Bernardo, University of Padova

8:30 AM

(PACRIM-S4-025-2017) Applications of preceramic polymers – polysilazanes as high-performance coating binders and beyond (Invited)

I. Zenz*[1]

1. Merck KGaA, Performance Materials - Functional Materials, Germany

Polysilazanes are silicon polymers belonging to the group of preceramic polymers. We as the only supplier of these polymers are offering them with a variety of different functionalities to be employed in various applications, making use of their characteristic polymer to ceramic transformation via crosslinking and subsequent pyrolysis/annealing. Our focus with organic and inorganic polysilazanes is on coating applications around mobility, architecture and industrial as well as further areas of interest. Polysilazanes transform into dense glass-like silicon dioxide films or ceramic layers upon curing and exhibit specific properties such as high-temperature stability, improved anti-scratch protection and weathering resistance on a wide range of different substrates such as metals, glass, plastics, composites or wood. This makes them a perfect choice as coating binders in many high-value applications. Polysilazanes are in our view a great technology platform, as these liquid polymers can conveniently be modified in many different ways in order to produce a spectrum of ceramic films or materials with customized chemistry and connected specific physical and technical parameters. Also curing conditions such as temperature, moisture and curing atmosphere have a profound impact on the properties and areas of application of polymer derived ceramics.

9:00 AM

(PACRIM-S4-026-2017) In-situ pyrolyzed polymer derived ceramic composite coatings on ablative substrates

K. Wang*[1]; W. Han[2]; Z. Zhang[2]; S. Kuang[1]

1. Aerospace Research Institute of Materials and Processing Technology, China
2. Institute of Chemistry, Chinese Academy of Sciences, China

Recent research on polymer derived ceramic (PDC) composite coatings was mostly focused on material systems deposited on metallic substrates like stainless steel, nickel-based alloy, etc. Typically, they were crosslinked and pyrolyzed (at high temperatures) before application. Here we report our work on PDC composite coatings designed for ablative polymer matrix composite (PMC) substrates, processed below 200C and capable of being in-situ pyrolyzed during high temperature services. Technical challenges for the coating to survive harsh environment (heat and flow) on top of ablative, i.e., recessive, substrates are presented. Substrate's oxidation-resistant properties and ablative surface quality were also shown to be significantly improved by successfully employing such PDC composite coatings with enhanced 'coating—substrate' interfacial strength: an arc-jet test (maximum hot surface temperature > 1400C, total time 1000 s) results demonstrate that recession depth of the same substrate material can be reduced from 0.48-0.90 mm to nearly none, and ablation test with high heat flux density (~6000 kW/m^2) indicates that the linear recession rate decreases to roughly 1/3.

9:15 AM

(PACRIM-S4-027-2017) Polymer-derived ceramic corrosion resistant layers with glass fillers

I. Petrikova[1]; M. Parchoviansky[1]; M. Lenz-Leite[2]; G. Motz[2]; D. Galusek*[1]

1. IIC SAS, Joint Glass Centre, Slovakia
2. University of Bayreuth, Germany

From economic point of view the ferritic stainless steel AISI 441 is a suitable material for a variety of applications. However, the corrosion and oxidation performance of the steel is not sufficient for a long-term operation at higher temperatures. Polymer derived ceramic (PDC) polysilazane-based double layer composite coatings on steel substrates consisting of a PDC bond-coat, and a PDC-based top-coat containing ceramic passive (ZrO_2) and active ($ZrSi_2$) fillers, as well as a specially tailored passive glass fillers with high melting temperature were developed. The corrosion (aqueous environment up to 200 °C) and oxidation (oxygen, air, water vapor up to 1100 °C) behavior of the coated and uncoated steel was evaluated. The corrosion under hydrothermal conditions resulted in partial oxidation of the uncoated steel substrate, whereas the coated sample was protected by the PDC coating. The high temperature oxidation behavior in a flow-through oxygen atmosphere was investigated at the temperatures of 900 °C, 1000 °C and 1100 °C. Beneficial effect of the PDC coating was observed at the temperature of 900 °C, demonstrated by marked reduction of the weight gain of coated steel after 196 h of exposure to flowing oxygen. At higher temperatures the protective action of the PDC coat was not observed, and a thick layer of corrosion products was formed at the steel/coating interface.

9:30 AM

(PACRIM-S4-028-2017) Polymer-derived thermal barrier coating system on steel for application up to 1000 °C

G. Barroso*[1]; W. Krenkel[1]; G. Motz[1]

1. University of Bayreuth, Ceramic Materials Engineering, Germany

The processing of thermal barrier coatings (TBCs) by conventional techniques, like thermal spraying and PVD, have limitations related to high costs and size/shape of the parts to be coated. The polymer-derived ceramic technique is proposed to realize a simple, cost-effective and versatile processing of TBCs. The processing consists in the deposition of the coating slurry containing the preceramic polymer and selected fillers by simple lacquer methods. A subsequent thermal treatment converts the precursor into a ceramic material. In this work, $ZrSi_2$ and YSZ were used as active and passive fillers in combination with an (organo)silazane to obtain a coating system with low thermal conductivity and stability up to 1000 °C. The composite coatings were applied onto steel sheets and on the inside of steel pipes (AISI 441), primarely coated with a PHPS bond-coat. Pyrolysis of the top-coat was conducted in air at 1000 °C. The developed coating system was characterized regarding conversion behavior, microstructure, porosity, adhesion, thermal properties and durability. The results show that the TBCs prepared by PDC processing have a great potential for the application in exhaust systems. Coatings with thickness of 50 μm and excellent microstructure for thermal barrier applications were obtained, resulting in pull-off adhesion strength above 20 MPa and thermal conductivity as low as 0.5 W(mK)$^{-1}$.

9:45 AM

(PACRIM-S4-029-2017) Effect of ion implantation on precursor polymers for synthesis of carbon material with catalytic performance

A. Idesaki*[1]; M. Sugimoto[1]; S. Yamamoto[1]; T. Yamaki[1]

1. National Institutes for Quantum and Radiological Science and Technology (QST), Quantum Beam Science Research Directorate, Japan

Nitrogen-containing carbon material, which shows oxygen reduction reaction (ORR) activity, is expected to be applied for a catalyst for fuel cells alternative to Pt-catalyst. Generally, the N-containing carbon material is synthesized by a method of precursor polymer process; a mixture of phenolic resin and metal-phthalocyanine is carbonizaed in an inert atmosphere. On the other hand, ion implantation for polymeric materials has been adopted for surface modification of electrical properties, wear resistance, and so on, because the ion implantation has advantages of heteroatom-doping and high-energy-deposition at surface. By adopting the ion implantation for the synthesis process of the nitrogen-containing carbon material, it is expected to obtain a N-containing carbon material with high number density of ORR active sites at surface. In this work, effect of ion implantation on changes in chemical bonds of precursor polymer, behavior of graphite structure growth, and ORR activity after carbonization were investigated.

Applications of PDCs II

Room: King's 3
Session Chair: Samuel Bernard, CNRS

10:15 AM

(PACRIM-S4-030-2017) Highly porous silicate bioceramics from preceramic polymers and reactive fillers (Invited)

E. Bernardo*[1]; H. Elsayed[1]; L. Fiocco[1]

1. University of Padova, Dept. of Industrial Engineering, Italy

Highly porous foams, based on akermanite ($Ca_2MgSi_2O_7$) and wollastonite ($CaSiO_3$)–diopside ($CaMgSi_2O_6$) ceramics, may be produced with commercial silicones mixed with $CaCO_3$ and $Mg(OH)_2$ micro-sized particles. An extensive foaming is achieved simply by water release, at 300-350 °C, from decomposition of sodium borate or phosphate hydrated salts, used as secondary fillers and forming liquid phase (favouring ionic interdiffusion) upon firing at 1100°C. Operating with anhydrous salts, silicone-based pastes can be applied also for direct ink writing, leading to 3D reticulated structures, later ceramized as above. Optimized formulations lead to materials with remarkable compressive strength (well exceeding 5 MPa, with a total porosity in the order of 70%) and bioactivity, confirmed by in vivo cell tests. The overall approach may be extended even to Ca-Zn bioactive silicates. In this case, foaming and phase evolution are associated with the use of calcium borate, leading to novel B-doped hardystonite ceramics ($Ca_2Zn_{1-x}B_{2x}Si_{2-x}O_7$).

10:45 AM

(PACRIM-S4-031-2017) Polymer-Derived Ceramic Membranes and Sensors (Invited)

A. Gurlo*[1]

1. Technische Universitaet Berlin, Chair of Advanced Ceramic Materials, Germany

Tunable synthesis of nanocomposites possessing desired functionalities has received considerable attention in the last decades. In the field of the hydrogen economy such materials are applied as catalysts for hydrogen production, hydrogen storage materials, hydrogen separation membranes, and hydrogen sensors. In the present work we report a precursor-based approach towards composite materials composed of polymeric matrix with incorporated nanoscaled metallic, oxide and nitride particles. After thermal treatment under desired conditions (temperature, ambient gas) such polymeric nanocomposites transform into ceramic nanocomposites. Their porosity is tuned by an appropriate choice of thermolysis and annealing conditions. Case studies include the synthesis and characterization of (i) microporous ceramic membranes and (ii) catalytically active nanocomposites.

11:15 AM

(PACRIM-S4-032-2017) Boron-modified Silicon Oxycarbide Composite Electrode for Electrochemical Energy Storage (Invited)

M. Abass[1]; G. Singh*[1]

1. Kansas State University, Mechanical and Nuclear, USA

Heteroatom modification of polymer-derived ceramics is one of the sustainable means of improving their electrochemical energy storage properties as electrode materials. In electrochemical energy storage application, boron is believed to improve the electronic conductivity and chemical stability of SiOC by modifying its nano-domain structure. Herein we report synthesis of freestanding films of boron nitride nanotube (BNNT)-modified silicon oxycarbides (SiOC) ceramic. The composite films were synthesized via vacuum filtration technique with reduced graphene oxide (rGO) as conducting agent. The layer-by-layer configuration ensured uniform dispersion of the ceramic on rGO sheets. Thin films containing varying loading of BNNTs were tested as sodium-ion battery (Na-IB) and supercapacitor electrodes. SiOC containing 0.5 wt % BNNTs (SiOCB-0.5wt.%) displayed optimum electrochemical properties. As observed in this study, superior capacity of SiOCB-0.5 wt % as an electrode material for Na-IB and supercapacitor suggests the existence of an optimum doping level of boron required to enhance desirable properties of SiOC composites.

PACRIM Symposium 06: Synthesis and Processing of Materials Using Electric Currents and Pressures

Electric Currents II

Room: King's 1
Session Chairs: Yasuhiro Kodera, University of California, San Diego; Manshi Ohyanagi, Ryukoku University; Claude Estournes, CIRIMAT

8:30 AM

(PACRIM-S6-010-2017) Progress in Spark Plasma Sintering (SPS) Method and Cost-Effective Technology to Produce Functionally Graded Materials (FGMs) on the Large Scale (Invited)

M. Tokita*[1]

1. NJS Co.,Ltd., SPS R&D Center, Japan

Functionally Graded Materials (FGMs) is being considered in many high-tech and high-performance applications in the field of mold & die, cutting tools, electronics, automotive, clean energy and aerospace industries. The FGMs will always cost more than metallic or ceramic, monolithic or composite alternative materials because of the inherent cost of manufacturing method. The potentials for an industrial use of FGMs are hampered by the lack of an infrastructure for high volume manufacturing facilities. In order to overcome those existing issues, the low cost production systems and processes are desired. The SPS has a high potential to be a major FGMs manufacturing method in the various industries provided the developments necessary, therefore, is now challenging both high-value added small scale and large scale area using by the 5th generation SPS systems with new process. For example, industrially commercialized application on ZrO2/Ti alloy FGMs for Ultra-sonic Homogenizer system developed in Japan will be introduced in this talk. A weldable WC/Ni system FGM having Hv1400-1500 surface hardness was already applied to a screw component of extruding machine and achieved more than 3 times longer life time at economical running cost. The factors influencing the cost for industrialization of SPS method on advanced FGMs are discussed.

9:00 AM

(PACRIM-S6-011-2017) Spark plasma sintering of Diamond/Si_3N_4 composite (Invited)

M. Ohyanagi*[1]; H. Inoue[1]; K. Shirai[1]; Z. Munir[2]

1. Ryukoku University, Japan
2. University of California, Davis, Department of Chemical Engineering and Materials Science, USA

The feature of SPS method includes very short processing time and very high-heating rate compared to the conventional hot-pressing process and hot isostatic pressing, which makes it possible to densify metastable materials by suppressing the kinetic change of the metastable phase. The unique SPS process was developed so that the loading pressure can go up to 1GPa by using a set of specially-modified high pressure die (consisting of inner and outer dies). We describe, herein, the fabrication of 50vol% diamond/Si_3N_4 composite under 1GPa at 1550°C which the condition for the consolidation is thermodynamically not stable for diamond. The key issue is to suppress the transformation of diamond to graphite under relatively high pressure, for short time and just above at the threshold temperature for the graphitization. When the 50vol% diamond/

Si_3N_4 composite was consolidated with 8wt% and 12 wt% of Al_2O_3-Y_2O_3 additives at 1550ºC under 1.0GPa for 5min., the relative density reached 93.5% and 96.2%. The Raman spectrum of the composite showed that most of diamond structure was maintained, but the low intensity of DLC signal was also detected in the composites. The abrasion test for the dense composite of 50vol%diamond/Si_3N_4 with 96.2% of the relative density was performed. The abrasion amount in the denser composite with 12wt% of the additive was much less than that of the composite with 8.0wt% of additive.

9:30 AM

(PACRIM-S6-012-2017) Development of Electric current activated/assisted sintering (ECAS/SPS) (Invited)

Y. Sakka*[1]

1. National Institute for Materials Science (NIMS), Japan

Essentially, SPS exploits the same punch/die system concept as the more familiar hot pressing (HP) process. The well-established advantages of SPS are: (a) low power consumption, (b) the absence of sintering aids, (c) control of the thermal gradient (for functional graded materials (FGMs), (d) selective control of the density in specfied regions, (e) accurate control of the porosity, (f) single step sintering-bonding, (g) particle surface cleaning, (h) high heating rate and (i) near-net-shape capability. In the SPS process, however, the measured temperature is not directly related to the sintering temperature. The combined experimental and FEM simulation analysis permitted to obtain the optimum process and mold design which permitted to have direct control of the final microstructure. The electric conductivity of the material plays a fundamental role on the current and temperature distribution inside the sample. The SPS method was successfully applied to electric conductive ceramics such as pure WC, WC-diamond, (Zr,Hf)B2-systems, MAX phase ceramics, semiconductors such as B4C, B4C compounds, and low electrical conductive ceramics such as transparent alumina, CNT-alumina nanocomposites. Finally, we will summarize future direction and problems of the SPS technology.

10:15 AM

(PACRIM-S6-013-2017) Modification of pulsed electric current sintering conditions for the reduction of processing time

M. Mikami*[1]; K. Kubo[2]; N. Uchiyama[2]; H. Miyazaki[3]; Y. Nishino[3]

1. National Institute of Advanced Industrial Science and Technology, Japan
2. Atsumitec Co., Ltd., Japan
3. Nagoya Institute of Technology, Japan

Pulsed electric current sintering is an effective method of controlling microstructure in sintered material because of its high heating and cooling rate. In various kinds of functional material, transport properties can be controlled by microstructure refinement in order to optimize its performance. Especially for a thermoelectric material, the reduction of thermal conductivity and the improvement of mechanical strength can enhance utility for thermoelectric energy conversion devices. However, typical whole processing time of the pulsed electric current sintering is the order of tens of minutes or longer and it is too long for the mass fabrication at low cost. In this study, in order to reduce the processing time, heating conditions such as amount of current, current flow region, sintering mold were modified according to the finite element simulation. Using the modified sintering process, sintered compact was obtained by current feed within several seconds. The microstructure and transport properties of the sintered compact will be presented.

10:35 AM

(PACRIM-S6-014-2017) Deformable Punch Spark Plasma Sintering for Processing of Fully Dense Nanocrystalline Oxides (Invited)

R. Castro*[1]

1. University of California, Davis, Material Science & Engineering, USA

Fully dense nanocrystalline oxides are extremely difficult to be obtained due to the high stability of isolated pores formed during the finail stage of sintering. While techniques such as Spark Plasma Sintering can improve densification by gplastic yielding, this densification mechanism is hindered by the high stability of the isolated pores. This leaves pores to be eliminated only with some grain growth. From a thermodynamic perspective, grain growth decreases the stability of the pores by changing equilibrium contact angles attainted at the interface between pores and grain boundaries. In this work, we introduce an alternative manner to de-stabilize pores by utilizing a deformable punch in the die. This is designed to complaint at the final stage of sintering, such that grains are forced to slide along and naturally cause a change in the equilibrium angle. Using cemented WC punch, MgAl2O4 nanoparticles with sizes below 5nm were sintered using this technique and the results were fully dense, transparent ceramics, with grain sizes below 10nm. This unprecedented achievement allowed assess of nano-related properties, such as the extension of the Hall-Petch relationship down to those small grain sizes -. We further used the deformable punch to sintering BaTiO3, obtaining a highly transparent sample with grain sizes below 20nm, and has the potential for application in many other systems.

11:05 AM

(PACRIM-S6-015-2017) Synthesis and processing of magnetic nanocomposites through CAPAD

Y. Kodera*[1]; K. Chan[1]; A. Volodchenkov[2]; J. E. Garay[1]

1. University of California, San Diego, Mechanical and Aerospace Engineering, USA
2. University of California, Riverside, USA

A core mission for material scientists is the developing new materials via innovative processing approaches. One example is overcoming thermodynamic limits using kinetics to obtain materials with far from equilibrium (FFE) state. Bulk material with nano-sized grains that possess non-conventional properties is great example. Obtaining FFE bulk materials through powder consolidation approaches, requires the optimizations of the powder synthesis method specifically for the consolidation method and the consolidation method to maintain FFE state as bulk form. This is because an appropriate energy balance (heat) is required; if FFE materials are over heated, they will convert to equilibrium phase/state and exhibit conventional properties. Here we will present results on the chemical synthesis of metastable material/phases and the integration into a consolidated nanocomposite via Current Activated Pressure Assisted Densification (CAPAD). We will show processing of iron oxide/silica hard bulk magnets with coercive fields comparable to typical rare-earth magnets. Also an increase in energy product of ferrite by forming nano-composite with 3d transition metal will be presented.

11:25 AM

(PACRIM-S6-016-2017) Nanostructured zinc oxide by FAST/SPS and cold sintering

J. Gonzalez-Julian*[1]; K. Neuhaus[2]; M. Bernemann[2]; M. Bram[1]; O. Guillon[1]

1. Forschungszentrum Juelich, Germany
2. University of Muenster, Germany

Retention of nanocrystallinity in dense ceramic materials is one of main challenge in material science. To achieve this objective, the sintering temperature has to be strongly reduced in order to avoid unwanted grain growth mechanisms. Different approaches have been largely explored, such as sintering methods assisted by mechanical pressure (Hot pressing), electric field/current (flash sintering) and combination of both (Field Assisted Sintering/Spark Plasma Sintering, FAST/SPS). Recently, one of the most promising approaches is to incorporate a transient liquid phase, typically water, to promote the full densification at low temperature. This method has been observed in FAST/SPS, and also demonstrated in several ceramic materials under high uniaxial pressures, which has been called "cold sintering". In this work, sintering behavior of ZnO with different contents of water will be analyzed using FAST/SPS and cold sintering. Highly dense nanocrystalline ZnO was obtained for maximal sintering temperatures of 400 °C and 250 °C, using graphite and non-graphite tools (to increase the mechanical pressure), respectively. Regarding the cold sintering, ZnO was highly densified keeping the nanostructure at only 250 °C. Sintering behavior, microstructure of the consolidated nanostructures, and the characterization by different techniques such AFM and photoluminescence will be evaluated to reveal the involved mechanisms.

PACRIM Symposium 13: Advanced Structural Ceramics for Extreme Environments

New Materials and Properties

Room: Kohala 4
Session Chairs: Stephan Schmidt-Wimmer, Airbus Defence and Space; Hailong Wang, Zhengzhou University

8:30 AM

(PACRIM-S13-029-2017) Oxidation behavior of porous Si_3N_4 ceramics

H. Liang*[1]; Y. Zeng[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Being an almighty ceramic, Si_3N_4 possess the high performance of high strength, high hardness, good resistance to thermal shock and oxidation, low dielectric constant and dielectric loss. Especially, compared with other engineering ceramics, porous Si_3N_4 ceramics have great advantage over other porous ceramics due to the extensive existence of rod-like grains in the matrix. As a consequence, porous Si_3N_4 ceramics have great potential to be used in various industry sectors. Generally speaking, high temperature and oxidation atmosphere are often encountered when porous Si_3N_4 ceramics are under service. So oxidation of porous Si_3N_4 ceramics should be taken into consideration when they are adopted. However, in spite that the oxidation behavior of dense Si_3N_4 ceramics have been widely studied in the past several decades, those of porous Si_3N_4 ceramics have been rarely concerned. In this investigation, the oxidation behavior of porous Si_3N_4 ceramics were studied in detail including the weight change, phase transformation, residual flexural strength and morphology evolution etc. The oxidation mechanism of porous Si_3N_4 ceramics were also analyzed.

8:45 AM

(PACRIM-S13-030-2017) New Ceramic Material AlB12-AlN: A Combination of High Boron Content, Hardness and Thermal Conductivity

O. Vasiliev*[1]; V. Kartuzov[1]; V. Muratov[1]; P. Mazur[1]; V. Garbuz[1]; Y. Kartuzov[1]

1. Institut for Problems of Materials Sciences NAS of Ukraine, Ukraine

The purpose of the work was to combine in a ceramic material, on the basis of theoretical studies with computer modeling elements, the properties of AlB_{12} (high boron content, hardness, chemical and wear resistance, etc.) and AlN, as softer constituent with high thermal conductivity. AlB_{12} and AlN powders were produced by vacuum-thermal synthesis with CVD elements from the inexpensive raw materials, without elemental boron, and compacted using hot pressing. To vary the ratio of the components in the ceramics, AlB_{12} was separated from AlN by wet chemistry. The result of the synthesis was a mixture of nanopowders (d_a <100 nm) AlB_{12} and AlN. Because of small particle sizes, the temperature of hot pressing was only 1800 °C. Ceramics with 25% AlB_{12} and 75% AlN has hardness of 24 GPa, and retains its values above 16 GPa at loads up to 500 N (Vickers test). There is no interaction between components in the AlB_{12}-AlN system, allowing for the material properties variation according to the mixture rule. This way we estimated the thermal conductivity of the ceramics 100 W/(m*K). In conclusion, a new ceramic composite AlB_{12}-AlN was obtained, which possesses high boron content (neutron absorption), high mechanical properties and thermal conductivity level; the method of its preparation allows for the variation of operational properties by control of the ratio between the components.

9:00 AM

(PACRIM-S13-031-2017) Processing and Properties of ZrB_2-SiCw Composites Sintered by Spark Plasma Sintering

H. Wang*[1]; G. Shao[1]; B. Fan[1]; H. Lu[1]; R. Zhang[2]

1. Zhengzhou University, Materials Science and Engineering, China
2. Zhengzhou Institute of Aeronautical Industry Management, China

The ZrB_2-SiC_w composite powder was synthesized by sol-gel method using zirconium diboride, tetraethoxysilane (TEOS) and activated carbon as starting materials, then densified by SPS at 1700 ℃ under a pressure of 40 MPa for 5 min. The processing parameters including carbon source, the ratio of silicon and carbon, temperature and holding time for the synthesis of ZrB_2-SiCw powers were optimized, and the synthetic mechanism were investigated. Microstructure observations revealed that a large number of crooked SiC whiskers appear on the surface of ZrB_2 particles. Moreover, full dense ZrB_2-SiCw ceramics were achieved by SPS. Both fracture toughness and flexual strength of ZrB_2-SiCw composites were greatly improved with increasing amount of SiC whiskers. ZrB_2-30vol% SiC_w composite showed the highest fracture toughness of 6.1 MPa•$m^{1/2}$ and flexural strength of 350 MPa, which were attributed to the formation of SiC whisker.

PACRIM Symposium 18: Microwave Dielectric Materials and Their Applications

Microwave Dielectric Materials and Their Applications III

Room: Kohala 2
Session Chair: Chonglin Chen, University of Texas San Antonio

8:30 AM

(PACRIM-S18-015-2017) Defect Engineered Complex Oxide Thin Films with Tunable Multiferroic Properties (Invited)

C. Chen*[1]

1. University of Texas San Antonio, Physics, USA

Complex oxides have demonstrated various important physical properties such as various dielectric and unusual magnetic properties. These extraordinary phenomena are highly dependent upon the degrees of the freedom of the charge distribution, spin and orbital status, and the lattice structures. Complex cobalt oxide can exhibit different cobalt and oxygen coordination from tetrahedral, pyramidal to octahedral dependent on the oxygen content in it, leading to various crystal structures with a great flexibility of the oxygen frameworks. Thus, oxygen nonstoichiometry is a very crucial parameter for tuning their physical properties determined by their crystal structure. For instance, $LnBaCo_2O_{5+d}$ (LnBCO, Ln= rare transition metal elements) systems exhibit various unique physical properties because of not only the presence of A-site disordered and A-site ordered structures, due to the close ionic sizes of Ln and

Ba, but also the degree of ordered oxygen vacancy structures. There defect engineered structures result in the formation of the double perovskite structure but also the room temperature ferroelectricity and large magnetoelectric response in the single phase ferromagnetic $LnBaCo_2O_{5+d}$ thin films. These findings open a new avenue for the design and synthesis of room temperature multiferroic materials by tailoring their microstructures to facilitate multiferroic coupling.

9:00 AM

(PACRIM-S18-016-2017) Recycled glass foams for high power microwave terminations (Invited)

R. Benzerga*[1]; V. Laur[2]; R. Lebullenger[3]; L. Le Gendre[1]; G. Lanoë[3]; P. Queffelec[2]; A. Sharaiha[1]

1. IETR - University Rennes 1, France
2. LabSTICC - UBO, France
3. ISCR - University Rennes1, France

With the continuous improvement of people's living standard, the needs in raw materials increase whereas resources drastically decrease. Since early seventies, recycling chains of glass wastes were developed with a great success and glass containers are now widely recycled. But some types of glass compositions, often polluted with heavy metals, pose a tougher problem. Indeed, as hazardous materials, glass wastes from electronic industry (e-wastes) should be treated in specific recycling process. This is particularly the case of cathode ray tubes (CRT) found in older style TV screens and monitors. Foam glass manufacture is a promising mode for re-using CRT glasses: depending on the foaming process, this cellular material combines low density, low thermal conductivity, excellent thermal stability and high rigidity. For this work, we focused our attention on EM absorptive properties of those glass foams based on cathode ray tube cullet. Inorganic additives can be used to reinforce the shielding properties in a specific spectral range. Indeed, when Carbon is used as the foaming agent, high dielectric losses are observed making of these foams a good candidate for EM absorbing applications. In this work, we studied the impact of the load rate and nature of the foaming agent on the density and the microwave behavior of glass foams. The potentiality for microwave absorbing applications of these foams will be discussed.

9:30 AM

(PACRIM-S18-017-2017) High wave absorption properties of $BaFe_{12-x}Zr_xO_{19}$ controlled by Zr^{4+} dependent permittivity and permeability (Invited)

P. Du*[1]; Z. Wang[1]; N. Ma[1]; C. Liu[1]

1. Zhejiang University, Materials Science and Engineering, China

With the extensive use of modern electronic devices, the serious issue of electromagnetic pollution, which will harm the environment and health of human beings, has been triggered. In addition, for use in stealth applications, EM absorbing materials play a vital role against radar detection. Therefore, highly efficient absorbing materials are of high interest to attenuate the unwanted electromagnetic radiation in recent decades. In this work, M-type barium ferrite powders doped with Zr4+ ions (BaFe12 xZrxO19 x = 0–0.4), possessing high permittivity and multi-resonant permeability, were synthesized by the sol–gel process. Controlled by the Zr4+ doped for Fe3+ at the 4f1 sites importantly in the barium ferrite, ε′and ε″ of the ferrite were increased to 7.7–6 and 3.4–1.5 over 18–40 GHz from 5.8–5 and 0.7–0.4 without doping, respectively. Contributed mainly by the enhanced permittivity, the matching thicknesses of the Zr4+ ions doped ferrites were as low as only ~1 mm or below, i.e. 1.5–3 times thinner than those reported recently. Furthermore, a strong reflection loss of ~50 dB and a broad bandwidth of ~12 GHz (RL<-10 dB) could be attained and the absorptivity of electromagnetic (EM) power per unit thickness reached as high as 0.156%/μm. It is consequent that the Zr4+-doped barium ferrites are promising for use as excellent absorbing materials in the wave absorption area.

10:15 AM

(PACRIM-S18-010-2017) Plasma Metamaterials in the Microwave Frequency Range (Invited)

M. Lanagan*[1]; Z. Cohick[1]; S. Antonsson[1]; A. Baker[2]; M. Sarkarat[2]; P. Steve[2]; C. Randall[2]

1. Penn State University, Dept. of Engineering Science and Mechanics, USA
2. Materials Research Institute, USA

Previous work has shown that arrays of conducting rings and rods have a negative index of refraction in the microwave frequency range. Electromagnetic coupling between resonators within an array will steer microwaves in paths that are associated with negative index. The resonant behavior of individual resonators and electromagnetic coupling between resonators can be altered by a plasma. Split-ring and cylindrical dielectric resonators were designed, fabricated and characterized at high power in the microwave frequency range. For the split-ring resonators, silver electrodes were deposited on alumina substrates by screen printing and plasma was generated in the gap of the conducting ring. Degradation of the resonator performance was caused by metal evaporation and the operation life significantly increased with the addition of protective dielectric layers. Ceramic cylinders of titania, calcium titanate and zirconium tin titanate were fabricated and tested in a high power microwave system. Two resonator configurations were also explored. Single cylinders were axially split into two sections and plasma was generated within the gap. Arrays of dielectric cylinders were also explored and plasmas between individual resonators were ignited and sustained. The effects of resonant mode, permittivity, microwave power and plasma formation will be presented.

10:45 AM

(PACRIM-S18-019-2017) Energy storage properties of niobate-based and Barium strontium titanate glass-ceramics by microwave crystallization

J. Zhai*[1]

1. Tongji University, Functional Materials Research Laboratory, School of Materials Science & Engineering, China

In this study, the niobate based and Barium strontium titanate (BST) glass-ceramics were fabricated via controlled crystallization with different crystallization route. Effects of the microwave crystallization and microwave treatment on the microstructure and energy storage properties of the glass-ceramics were systematically investigated. The dielectric breakdown strength (BDS) of the glass ceramics was significantly improved from 561.3 kV/cm to 791.4 kV/cm by the microwave crystallization in BST based glass-ceramics. And it can be further enhanced to 900.0 kV/cm by conventional crystallization combined with microwave treatment. The corresponding energy densities of samples derived from the microwave processes were increased to 1.05 J/cm^3 and 1.13 J/cm^3, respectively, compared with the sample fabricated by the conventional crystallization route (0.47 J/cm^3). The microstructure showed that the grain size increased as the crystallization time prolonged for niobate-based glass-ceramics. The dielectric constant and electric breakdown strength indicated a trend of increasing at first and then reducing with the increase of the crystallization time. The optimization of dielectric constant of 102 and breakdown strength of 1410.81 kV/cm were obtained. The maximum of theoretical energy storage density can reach a value of 8.99 J/cm^3.

11:10 AM

(PACRIM-S18-020-2017) Dielectric Material Measurement of Hypersonic Electromagnetic Windows for High Temperature

Y. Xu*[1]; J. Zhang[1]

1. Beijing Institute of Space Long March Vehicle, China

Complex permittivity measurements for high temperature at Ku band by short waveguide method were obtained. The measurement methodology and considerations for hypersonic electromagnetic windows are described herein, and the measurement and analysis results of some typical dielectric materials from room temperature to 1600 centigrade have been given. The results show that, general before 800-1000 centigrade, the dielectric constant and the loss angle tangent of composite material will decrease with the increase of temperature, due to the presence of the surface water adsorbed and in vivo physical water. When the temperature rose to 1000 centigrade, dielectric constant and loss angle tangent to minimum, which shows that composite materials in the absorbed water volatile completely. When the temperature is above 1000 centigrade, the dielectric constant and loss angle tangent have greatly increased because of the trace impurities introduced in the preparation of composite materials, which will ionize and generate particle conductance with temperature increasing. The measurement methodology and considerations can be used in the study of hypersonic electromagnetic windows.

11:35 AM

(PACRIM-S18-021-2017) Phase-Chemical Structure and Dielectric Characteristics of A/B-Site Modified Titanate Paraelectric $SrTiO_3$ Ceramics

B. Ullah*[1]; W. Lei[1]; X. Wang[1]; G. Fan[1]; W. Lu[1]

1. Huazhong University of Science and Technology, School of Optical and Electronic Information, China

Rare earth ion substitution into the A site of $SrTiO_3$ ($Sr_{(1-x)}Ce_{x}$-$Ti_{(1-0.25x)}O_3$, $0.25 \le x \le 1.0$) ceramic with B-site vacancy compensation were prepared by conventional solid state reaction. The phase-chemical structure, microstructure together with microwave dielectric porperties were investigated systematically. The addition of cerium on A/B-site facilated the formation of impurity phases, oxygen vacancies and structure phase transition from cubic to tetragonal. The chemical structure revealed the existence of mixed valance state of Ti^{3+}/Ti^{4+}, upon oxygen vacancy formation. Increasing, Ce(x) content from x = 0.25 to x = 1.0, whereas ε_r changed from 94 to 39, however, τ_f deceased from + 665 ppm/°C to +10 ppm/°C. Nevertheless, the Q×f value changed from 7341 GHz to 6457 GHz sintered at optimal temperature of 1250 °C for 3 h.

PACRIM Symposium 21: Solid Oxide Fuel Cells and Hydrogen Technologies

SOFC Interconnect

Room: Queen's 4
Session Chair: Kathy Lu, Virginia Tech

9:00 AM

(PACRIM-S21-010-2017) Solid oxide fuel cell interconnect coatings (Invited)

K. Lu*[1]; K. Shen[1]

1. Virginia Tech, USA

Cr-containing metallic interconnects pose performance challenges, including oxidation and Cr diffusion/evaporation, during the long-term operation of solid oxide fuel cells. In our study, CoFe alloy interconnect coatings are deposited by electrodeposition and then oxidization. Higher Co content oxide coatings are more effective in limiting the growth of the chromia scale while all coatings are effective in inhibiting Cr diffusion and evaporation. With the $Co_{0.8}Fe_{0.2}$ oxide coated interconnect, the electrochemical performance of the $Sm_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_3$ cathode is improved. Only 1.54 at% of Cr is detected on the surface of the $Sm_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_3$ cathode while no Cr is detected 0.66 μm or more into the cathode. In addition, a novel Co/Sm-doped CeO_2 (SDC)/Co tri-layer coating has been developed. The Co_3O_4/SDC/Co_3O_4 coating layer can effectively inhibit the Cr diffusion and evaporation and significantly slow the oxidation rate of the interconnect. The ohmic resistance R_Ω, high frequency polarization resistance R_H, and low frequency polarization resistance R_L of the half cell with the Co_3O_4/SDC/Co_3O_4 coated interconnect and $Sm_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_3$ cathode are all smaller than those of the half cell with the bare interconnect. These two coatings have great advantages to be used as a protective layer for the metallic interconnect in SOFCs to improve the cell performance, stability, and durability.

9:30 AM

(PACRIM-S21-011-2017) MAX-phases-based materials as interconnects for hydrogen fuel cells

T. Prikhna*[1]; O. Ostash[2]; A. Ivasyshyn[2]; V. Sverdun[1]; M. Karpets[3]; V. Podhurska[2]; V. Moshchil[1]; T. Cabioch[4]; P. Chartier[4]; L. Jaworska[5]; P. Figiel[5]; T. Zimych[1]; J. Cyboron[5]

1. Institute for Superhard Materials of the National Academy of Sciences of Ukraine, Ukraine
2. Physico-Mechanical Institute of the National Academy of Sciences of Ukraine, Ukraine
3. Institute for Problems in Material Science of the National Academy of Sciences of Ukraine, Ukraine
4. Universite de Poitiers, CNRS/ Laboratoire PHYMAT, France, France
5. The Institute of Advanced Manufacturing Technology, Poland, Poland

Interconnects for hydrogen fuel cells should be stable in hydrogen and oxygen environments, electroconductive and mechanically stable at working temperatures. The obtained dense MAX-phases-based materials of 211 and 312 structural types of Ti,Nb–Al–C systems prepared by hot pressing at 30 MPa are stable in hydrogen and oxidizing environments at 600ºC, are about twice lighter (ρ=4.27 g/cm^3) and more stable in air than Cr-containing Crofer steels widely used as interconnects. The most resistant in air at 600ºCfor 1000 h among the studied materials turned out to be the material contained 73% of Ti_2AlC phase (as Rietveld refinement showed), somewhat less stable were contained 63% of $(Ti_,Nb)_3AlC_2$ and previously oxidized at 1200ºC contained 89% of Ti_3AlC_2 materials. At room temperature Ti_3AlC_2-based materials demonstrated 4.6-5.8 GPa microhardness at 5 N load, 500-570 MPa bending and 700-1300 MPa compression strengths, their fracture toughness attained 10.2±0.4 MPa●√m, and 2.7●10^6 Sm/m electrical conductivity at 20 ºC. The bending strength of Ti_3AlC_2-based material in air at 20°C was 535 MPa, after keeping at 600°C in air and hydrogen it decreased to 490 and 500 MPa, respectively. For $(Ti_,Nb)_3AlC_2$ –based materials the bending strength at 20ºC in air was 480 MPa and increased by 10% after heating at 600°C both in air and in hydrogen. So, the addition of Nb to Ti_3AlC_2 positively influences its refractivity.

9:45 AM

(PACRIM-S21-012-2017) Promising metal matrix composites (TiC/Ni-Cr) for IT-SOFC interconnect applications

Y. Liu*[1]; Q. Qi[1]

1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, Structrural Ceramics Engineering Center, China

As green and clean energy conversion devices, solid oxide fuel cells (SOFCs) have been the subject of intensive research and development around the world. With the advance of cell technology, the operation temperature of SOFC has reduced to intermediate-temperature range, which make it possible to use low cost ferritic stainless steels as SOFC interconnects. However, there are two obvious shortcomings for ferric steel, one is degradation of electrical conductivity for long-term operation temperature caused by the oxidation of metal, and the other is chrome poisoning to the cathode, which lead to severe SOFC performance deterioration. In order to overcome the difficulties, the promising TiC/Ni-Cr materials were development as SOFC interconnects. The 60vol.% TiC/Ni-Cr composites with 98.7% theoretical density were fabricated by pressureless infiltration process. The microstructure and properties, including electrical resistance, CTE, mechanical strength were evaluated and investigated. The appropriate and linear thermal expansion, excellent mechanical and electrical properties obtained demonstrates that the TiC/Ni-Cr composites are feasible for SOFC interconnect applications.

Current Collection, Sealing, Hydrogen Generation

Room: Queen's 4
Session Chair: Fatih Dogan, Missouri University of Science and Technology

10:15 AM

(PACRIM-S21-013-2017) Highly Efficient Current Collection in Solid Oxide Fuel Cells (Invited)

F. Dogan*[1]

1. Missouri University of Science and Technology, Dept. of Materials Science and Engineering, USA

Planar SOFC multi-cell stacks incorporating metallic interconnects generally exhibit average cell performance lower than that observed for out-of-stack cells under similar conditions. It has been suggested that electrode-interconnect, especially cathode-interconnect, contacts (and their ohmic resistances) are the main cause for this observed difference. Properties of silver at elevated temperatures limit its use as a porous electrode or current collector in solid oxide fuel cell (SOFC) configurations. Its relatively low melting temperature (962°C) leads to accelerated densification of silver at operating temperatures of intermediate temperature SOFCs (550°C-800°C). In previous studies, powder based silver composites demonstrated stable microstructures with desirable porosity and electrical conductivity during long-term testing. Although the characterized features of the silver based composites allowed their use as efficient and stable cathode current collectors, they demonstrated limited electrochemical performance as a cathode layer. In this study, nanostructured coatings of various perovskite based cathode materials LSM, LSF, and LSCF were deposited into porous silver composites by infiltration of polymeric precursors to enhance their electrode efficiencies. As a result, novel metal-matrix perovskite nanocomposites were obtained.

10:45 AM

(PACRIM-S21-014-2017) Glass ceramic sealants for CFY based SOFC

A. Rost*[1]; J. Schilm[1]; M. Kusnezoff[1]; A. Michaelis[1]

1. Fraunhofer IKTS, Germany

The operation of solid oxide fuel cells as also electrolyzers require gas tight and long stable sealing materials. Glass ceramic sealings have successfully proofed to reliable seal different stack designs and can be tailored to meet the requirements of the sealing partners as also the joining conditions. Most studies focus on chromium containing ferritic steels like Crofer 22 APU as interconnectors and the formation of undesired chromia species in contact with glassy seals. The formation for chromia depends on the glass composition and the chromium content of the steel (20 – 30 wt.%). A very robust interconnect material is the chromium based the sinter alloy CFY (Plansee SE), with > 93 wt.% chromium. The high chromium content dramatically forces the described formation of chromia based scales. Results of the development of sealing glasses are presented which are adapted to CFY alloy. Therefore, reactive components in the glass seal, like BaO or SrO had to be reduced. However, intrinsic glass properties like crystallization rate and thermal expansion of the glass ceramic as also the joining ability by itself depends on these components. Development of sealing glasses in the system (BaO,CaO)-Al_2O_3-SiO_2 as also testing in a self-developed dual atmosphere test rig and SOFC stacks are presented. Results are discussed in terms of glass properties, electric resistivity, gas tightness, and microstructure at the joining interfaces.

11:00 AM

(PACRIM-S21-015-2017) Hydrogen formation from biogas using electrochemical cell with gadolinium-doped ceria porous electrolyte

Y. Hirata[1]; T. Shimonosono*[1]; K. Ueda[1]; S. Sameshima[1]; K. Yamaji[2]

1. Kagoshima University, Department of Chemistry, Biotechnology, and Chemical Engineering, Japan
2. National Institute of Advanced Industrial Science and Technology, Japan

The electrochemical cell consisting of a gadolinium-doped ceria (GDC, $Ce_{0.9}Gd_{0.1}O_{1.95}$) porous electrolyte, Ni–GDC cathode and Ru–GDC anode was applied for the dry-reforming ($CH_4 + CO_2 \rightarrow 2H_2 + 2CO$) of a real biogas ($CH_4$ 60.0%, CO_2 37.5%, N_2 2.5%) produced from waste sweet potato. The composition of the supplied gas was adjusted to $CH_4/CO_2 = 1/1$ volume ratio. The supplied gas changed continuously into a H_2–CO mixed fuel with H_2/CO = 1/0.949–1/1.312 volume ratios at 1–2 V of applied voltage and 800°C for 24 h. The yield of the mixed fuel was higher than 80%. This dry-reforming reaction was thermodynamically controlled at 800°C. The decrease of heating temperature to 700°C reduced gradually the fraction of the H_2–CO fuel (61.3–18.3%) within 24 h. This result originated from the deposition of carbon over Ni catalyst through the competitive parallel reactions ($CH_4 \rightarrow C + 2H_2$, $2CO \rightarrow C + CO_2$). At 600°C, the H_2–CO fuel based on the Faraday's law was produced by the electrochemical reforming of the biogas.

11:15 AM

(PACRIM-S21-016-2017) Study of water uptake behavior on yttria-doped barium zirconate solid solutions using water adsorption calorimetry

M. Dancini Goncalves*[3]; P. Maram[1]; R. Muccillo[2]; A. Navrotsky[3]

1. University of California, Davis, NEAT, USA
2. IPEN, CCTM, Brazil
3. University of California, Davis, Peter A. Rock Lab and NEAT ORU, USA

Yttria-doped barium zirconate, $BaZr_{1-x}Y_xO_{3-\delta}$ (BZYx), has been extensively investigated due to high proton conductivity at intermediate temperatures and chemical stability, making it a suitable solid electrolyte for solid oxide fuel cells. The BZYx defect chemistry, temperature and pressure govern its water uptake behavior, whose understanding gives insights into the chemical stability of hydrogen bonding in the defects. In this work, we investigated BZYx, with x = 10 to 30 mol% Y, solid solutions in terms of water uptake behavior and enthalpy of absorption as a function of temperature (200, 300 and 400 °C) using water adsorption calorimetry. The isotherms of water absorption show that absorption is maximum at 200 °C and increases with increasing dopant concentration, but decreases when increasing temperature. The total water absorbed by each composition at 0.023 atm and 200 °C corresponds to the amount required to fill the oxygen vacancies, which corresponds to 0.049, 0.094 and 0.127 mols of water for BZY10, BZY20 and BZY30, respectively. The integral enthalpies of absorption increase in the following order BZY10 < BZY20 < BZY30 and with increasing temperature, which could be related to the stability of hydrogen bonds.

PACRIM Symposium 22: Direct Thermal to Electrical Energy Conversion Materials and Applications

Novel Aspects of Thermal-to-Electrical Direct Energy Conversion

Room: Queen's 6
Session Chairs: Lei Miao, Guilin University of Electronic Technology; Maarit Karppinen, Aalto University

8:30 AM

(PACRIM-S22-022-2017) Enhanced Electron Collection in Perovskite Solar Cells Employing Thermoelectric Coaxial Nanofibers (Invited)

N. Wang*[1]

1. University of Electronic Science and Technology of China, School of Microelectrics and Solid-state Electronics, China

As for perovskite solar cells (PSCs), the quest for further improvement of charge transfer and collection motivates us to explore the use of alternative ways to realize the desired goal. Thermoelectric NaCo2O4 nanofibers coated with a thin layer of TiO2 nanoparticles (NaCo2O4/TiO2) are randomly distributed in the m-TiO2 layer as composite photoanodes for PSCs. The existing TiO2 shell is beneficial to passivate NaCo2O4 surface defects to retard interfacial charge recombination. Experimental results in the present investigation reveal that the incorporated NaCo2O4 can convert unwanted heat to thermoelectromotive force, which could promote electron transport and suppress charge recombination thereby enhancing electron collection. Meanwhile, the electron injection efficiency is also found to be significantly improved under the influence of thermoelectromotive force. The device applying 9.1 wt% NaCo2O4/TiO2 demonstrated the best photovoltaic performance with an enhancement of ≈20% in PCE in comparison with pristine one. The synergistic effects of fast electron transport rate, reduced charge recombination, and high efficiencies of electron injection made it possible to increase J sc and further result in an improved overall PCE. This study provides a new way to improve the charge injection and transport for highly efficient PSCs of practical significance.

8:50 AM

(PACRIM-S22-023-2017) Anomalous Photo-Thermoelectric Effects in Tungsten Trioxide Loaded with Platinum (Invited)

H. Irie*[1]

1. University of Yamanashi, Clean Energy Research Center, Japan

Anomalous photo-thermoelectric effects (a photoconductive effect (photoconductivity, s_{photo}) and a photo-Seebeck effect (photo-Seebeck coefficient, S_{photo})) was observed in response to the visible-light irradiation in tungsten trioxide loaded with platinum (Pt/WO_3) in the absence of oxygen after a photochromic reaction, converting WO_3 to protonated WO_3 (H_xWO_{3-y}). Under visible-light irradiation, both s_{photo} and the absolute value of S_{photo} increased. After the irradiation, both values decreased, that is, s and the absolute value of S were smaller than s_{photo} and the absolute value of S_{photo}, respectively. These effects are likely to be due to the photoinduced charge carriers and the accumulated electrons in Pt contributing to the increase in s_{photo}. In addition, electrons are extracted from the W^{5+} state, decreasing the number of W^{5+} in H_xWO_{3-y} and thus contributing to the increase in S_{photo}. After light irradiation, the accumulated electrons in Pt returned to the energetically favorable W^{5+} state, and Pt/H_xWO_{3-y} returned to the initial state. Then both s and S decreased. We suggested that the observed phenomena are caused by the accumulation of electrons in Pt, which is different from the previous explanation of two-carrier contribution to the transport properties for the anomalous phenomena demonstrated in past studies.

9:10 AM

(PACRIM-S22-024-2017) Thermoelectrochemical Cells with Molten Carbonate Electrolytes and Gas Electrodes (Invited)

G. Haarberg*[1]

1. Norwegian University of Science and Technology, Norway

The purpose of this study is to develop thermoelectric cells for utilising waste heat and hot off-gases containing high levels of CO_2 from various electrochemical and metallurgical industries. The use of a molten carbonate electrolyte may offer improved power production compared to commercial thermoelectric converters. The possibilities to combine such a thermoelectrochemical cell with a fuel cell or a batterey will be explored. Experiments to measure thermoelectric potentials were carried out in molten Li_2CO_3-Na_2CO_3 at different temperatures from 400 - 850 ˚C. Reversible electrodes with respect to carbonate ions were established by using gas mixture of O_2 and CO_2. Solid MgO particles were added to the molten electrolyte in order to improve the conditions for thermoelectric conversion. Two identical electrodes of platinum or gold were located at different temperatures for determining the Seebeck coefficient based on potential measurements. Effects of electrode gas flow and content of solid MgO on the measured thermoelectric potentials were studied. Seebeck coefficients in the order of 1 mV/K were obtained in most of the studied molten carbonate electrolytes.

9:30 AM

(PACRIM-S22-025-2017) Sodium Ion Expansion Power Block for Distributed CSP

S. Balagopal*[1]; S. Yee[2]

1. Ceramatec, Inc., USA
2. Georgia Institute of Technology, Mechanical Engineering, USA

Develop and demonstrate a modular sodium ion expansion power block for distributed CSP with an estimated efficiency (η_{te}) of 40%. These generators will be most similar to thermoelectric generators, and the ion expansion engines are considerably more efficient and have a ZT equivalent of 35 compared to a ZT < 3 for the best performing thermoelectric materials. The key to innovation use of NaSelect^{TM} and B-Alumina solid electrolytes, which have high sodium ion conductivities for operation in the dual stage heat engine. An integrated unit with air-cooled design will be built and operated to demonstrate an early TRL 5 maturity level of this technology. Once developed, this technology at scale can realize a system capital cost of <\$900/kW$_e$ with a 10-year lifetime. This modular power block can be deployed for both (i) small scale dish solar (displacing dish Stirling), which is appropriate for the distributed residential scale (2-3 kW$_e$) and (ii) large scale integrated CSP appropriate for the centralized industrial scale.

Carbon/Organic Materials

Room: Queen's 6
Session Chairs: Hiroshi Irie, University of Yamanashi;
Geir Martin Haarberg, Norwegian University of Science and Technology

10:15 AM

(PACRIM-S22-026-2017) Oxide-Graphene Thermoelectric Nanocomposites (Invited)

Y. Lim*[1]; W. Nam[2]; J. Lee[2]; W. Seo[3]

1. Pukyong National University, Department of Materials System Engineering, Republic of Korea
2. Institute for Basic Science (IBS), Center for Nanomaterials and Chemical Reactions, Republic of Korea
3. Korea Institute of Ceramic Engineering and Technology, Energy and Environmental Division, Republic of Korea

We report a strategy for the enhancement of thermoelectric transport properties in oxide nanocomposites. We designed a method for the interface control of oxide nanocomposites using graphene, and fabricated the hybrid nanocomposites of AZO, ITO, and TiO_2 with graphene. Uniform distributions of graphene at the nanograin boundaries were ascertained from the structural point of view, and advantageous effects of the interface control both on the charge and thermal transports were observed in the interface-controlled oxide-graphene nanocomposites from the thermoelectric point of view. Depending on the band alignment between the oxide and graphene, single crystalline (AZO, ITO) or percolated (TiO_2) charge transport could be obtained selectively in the nanocomposites. Meanwhile, the lattice thermal conductivities in all nanocomposites could be reduced thanks to the additional phonon scattering at the oxide-graphene interfaces. Both the reduction in thermal conductivity and the enhancement in electrical conductivity, i.e. "phonon glass-electron crystal", could be realized in the interface-controlled oxide nanocomposites, and this discovery of the structurally nanocrystalline-electrically single crystalline composite demonstrates a new route for enhancing the thermoelectric performance in nanocomposites.

10:45 AM

(PACRIM-S22-027-2017) Flexible thermoelectrics of reduced graphene oxide/nanowires hybrid films on paper (Invited)

L. Miao*[1]; X. Wang[1]; J. Gao[1]; Y. Peng[1]; C. Liu[1]; J. Zhou[1]; Y. Cheng[2]

1. Guilin University of Electronic Technology, School of Material Science and Engineering, China
2. East China University of Science and Technology, School of Chemistry and Molecular Engineering, China

Thermoelectric battery could provide continuous power by conversion the body heat into electricity for wearable electronic devices. However, the expensive price and poor thermoelectric performance of conductive polymers or composites is far from satisfactory. With the reduced dimensionality and size, inorganic materials would become flexible to some degree. Here, we demonstrate that highly-flexible thermoelectric hybrid films based on the reduced graphene oxide (RGO) and tellurium nanowires (Te NWs) / Ag_2Te nanowires layered structure have been fabricated via vacuum filtration either on glass fiber or paper. The electrical conductivity and Seebeck coefficient of RGO/Te NWs hybrid film can reach 978 S/m and 286 μV/K, respectively, pushing the power factor (PF) value up to 80 $\mu W/(mK^2)$ at 40°C, approximately 80 times larger than the pure Te NWs film, possibly due to the combination of high carrier concentration of RGO and high carrier mobility of Te NWs. This work provides a possible access to high-performance and flexible TE films based on RGO sheets and inorganic semiconductors.

11:15 AM

(PACRIM-S22-028-2017) Layer-engineered inorganic-organic hybrid materials for flexible thermoelectrics (Invited)

M. Karppinen*[1]

1. Aalto University, Department of Chemistry, Finland

Layer-engineering of superlattice materials consisting of mutually different nanoscale layers provides us with the means to enhance material's thermoelectric characteristics by suppressing its thermal conductivity without significantly hindering the electrical transport properties. An elegant way to build such multilayered hybrid materials with atomic/molecule level accuracy from thin organic layers and slightly thicker thermoelectric oxide layers is to combine the state-of-the-art thin-film fabrication technique for inorganics, *i.e.* atomic layer deposition (ALD), with its emerging counterpart for the organics, *i.e.* molecular layer deposition (MLD). Here I summarize our recent works on (Zn,Al)O:organic and $(Ti,Nb)O_2$:organic superlattice thin films, and discuss the future potential of the ALD/MLD-fabricated inorganic-organic hybrid materials in thermoelectrics. Most importantly, the technique allows for the fabrication of highly conformal and flexible coatings on e.g. polymers or textiles, thus paving the way towards novel integrated/wearable energy solutions.

11:45 AM

(PACRIM-S22-029-2017) Sub-nanoscale inorganic/organic hybridization-new strategy for flexible thermoelectric device

R. Tian*[1]; C. Wan[2]; Y. Wang[3]; Q. Wei[5]; T. Ishida[5]; A. Yamamoto[5]; A. Tsuruta[4]; W. Shin[4]; K. Koumoto[1]

1. Toyota Physical and Chemical Research Institute, Japan
2. Tsinghua University, China
3. Nanjing Technological University, China
4. National Advanced Institute of Science and Technology, Japan
5. National Institute of Advanced Industrial Science and Technology (AIST), Japan

The demand for flexible thermoelectric materials driven by the integration of wearable electronics has stimulated the development of various organic/inorganic hybrid composites from micro to nano scale. However, the interface between organic and inorganic components has to be carefully engineered to permit good adhesion and efficient charge transport across the boundaries. On the other hand, liquid exfoliation has proven to be an effective and scalable approach to obtain large-scale 2D nanosheets in graphene, boron nitrides, layered perovskites and transition metal dichalcogenides. This also provides fresh insights into the hybridization of inorganics/organics at the sub-nanoscale. Here, we present a liquid-exfoliation-and-self-assembly method to produce TiS_2/organics hybrid superlattice film, which can be either free-standing or deposited onto substrates. Charge transfer occurs when the organic molecules are intercalated into layered TiS_2 to form an intercalation complex, which gives rise to a high electrical conductivity. Meanwhile, it is found that the intercalation of organic molecules can greatly suppress the thermal conductivity and allow the mechanical flexibility. We have also fabricated a prototype flexible thermoelectric module, and the performance of our module will be presented.

PACRIM Symposium 24: Photovoltaic and Related Materials and Technologies

Photovoltaic Materials and Technologies II

Room: Queen's 5
Session Chairs: Giovanni Fanchini, University of Western Ontario; Kylie Catchpole, Australian National University; Oomman Varghese, University of Houston; Sylvain Cloutier, Ecole de Technologie Supérieure (ETS)

8:30 AM

(PACRIM-S24-011-2017) High-performance printable hybrid device architectures (Invited)

S. G. Cloutier*[1]; I. Ka[1]; R. Nechache[1]; L. Gerlein[1]; X. Guo[1]; J. Benavides[1]; T. Charles[1]

1. Ecole de Technologie Supérieure (ETS), Canada

In recent years, there was an extraordinary push to develop new and better low-cost optoelectronic platforms for solar-energy harvesting, lighting & displays and sensing applications. We are proposing to employ a unique electrospinning and co-jetting expertise we have developed for the aerospace industry to explore the fundamental structure-property interrelations in novel hybrid device architectures. We are proposing to take advantage of the unique advantages of electrospinning/co-jetting techniques to explore revolutionary low-cost hybrid device architectures using (1) combinatorial co-jetting of hybrid conjugated polymer-nanocrystal droplets and (2) hybrid carbon nanotube/nanofiber-perovskites glasses. While our preliminary results suggest we have tackled most of the key challenges and identified the key parameters pertaining to the fabrication of these three emerging material systems, we are proposing to focus this presentation on (1) their integration into more complex light-emitting device architectures and (2) the fundamental interrelations between synthesis-structure-properties to eventually achieve all the level of control required to produce the best low-cost device architectures.

8:55 AM

(PACRIM-S24-012-2017) Nanoscale Earth Abundant Materials for Emerging Photovoltaic Technologies (Invited)

O. K. Varghese*[1]; M. Paulose[1]; P. Kaur[1]

1. University of Houston, Department of Physics, USA

Recent innovations in nanomaterials technology facilitated the development of nanostructures of several earth abundant inorganic materials, both oxides and non-oxides, useful for efficient and low cost photovoltaic cells. The paradigm shift created by the use of titanium dioxide nanoparticle films in dye sensitized solar cells later led to the origination of several useful inorganic heterojunction and organic-inorganic hybrid solar cell configurations utilizing various nanoarchitectures. Besides reducing the amount of materials used in the cells, the nanostructures enable the use of low cost earth abundant materials, even those having poor minority carrier diffusion lengths, as electron/hole transport medium or light absorbers or both. Ordered nanostructures have superior properties compared to random networks at least in terms of light utilization and carrier transport. This presentation will give an overview of the roles of the nanostructures of earth abundant materials in enhancing the performance of hybrid solar cells. We have recently demonstrated that anodically grown titania nanotube arrays could not only yield highly efficient perovskite solar cells but also enhance the stability of the cells. In another work we developed a new hybrid cell configuration for utilizing earth abundant materials as light absorbers. The results of these studies will be discussed in detail.

9:20 AM

(PACRIM-S24-013-2017) Biopolymers for solar energy conversion (Invited)

C. Santato*[1]; E. Di Mauro[1]; D. Boisvert[1]

1. Ecole Polytechnque de Montreal, Canada

Melanin is a broad term that indicates pigments of diverse structures and origins. It has different biological functions, such as thermoregulation, photoprotection and metal chelation. Eumelanin is the black-brown subgroup derived at least in part from the oxidative polymerization of L-dopa via 5,6-dihydroxyindole intermediates. In the human skin, eumelanin absorbs and scatters solar radiation. The low cost and the environmental compatibility of the material make the polymer interesting for technologies, e.g. in DSSCs. Eumelanin absorbs in the whole UV-vis region, with a monotonic decrease of absorbance from the UV to the near IR. This unusual behavior has been described with the “chemical disorder model”. Here eumelanin is depicted as a complex polymeric material that contains a range of chemically distinct chromophores that absorb at different wavelengths. Here, we propose a new synthetic approach that allows the direct polymerization of the eumelanin monomers on metal oxide photoanodes, to produce controlled thin layers of melanin-like polymer on metal oxide mesoporous surfaces. Such solid state polymerization allowed a strong control of the thickness and of the composition of the polymer. The great affinity between the carboxylic groups of DHICA and the indolic groups of DHI and DHI and the metal oxide surface assures the required intimate contact to expect significant power conversion efficiencies.

9:45 AM

(PACRIM-S24-014-2017) Polyalkylene Carbonate Binders for Cleaner Burning Thick Film Ag Paste: Comparison to Commercially Available Ag Pastes

P. Ferraro*[1]; S. Hanggodo[1]

1. Empower Materials, USA

Use of clean-burning binder systems in thick film paste formulations for solar cell applications offer advantages of reduced residual carbon, improved conductive feature density, and overall performance and reliability. This paper presents the technical advantages of employing clean-burning polyalkylene carbonates (QPAC®) as the principle binder for thick film Ag paste. Rheological, thermal, structural and electrical characteristics are presented and compared to commercially available Ag solar pastes.

10:15 AM

(PACRIM-S24-015-2017) 5 to 20-Junction Photonic Power Converters: Materials, Designs and Performance (Invited)

K. Hinzer*[1]

1. University of Ottawa, Canada

Photovoltaic devices connected in series can become efficient DC-DC power converters when illuminated by laser or light emitting diodes with over 65% conversion efficiencies [1-2]. Using tailored devices with multiple junctions, 5 to 24 V power signals are obtained. As these are photonic devices, no electromagnetic interference is generated for the optical transmission path in dielectric medium. In this paper, we will present results on the III-V semiconductor material properties required for these devices in the 850 nm range and the role of nanostructures to increase their maximum efficiencies depending on the wavelengths desired. We will discuss the importance of luminescent coupling in the overall device performance. For good-quality materials with sufficiently high internal radiative efficiency (fraction of radiative to total recombination), photon recycling leads to an accumulation of carriers and an increase in photovoltage, while luminescent coupling redistributes photocurrent between the junctions more optimally, reducing the wavelength sensitivity. These two effects lead to devices operating at 65-70% conversion efficiencies. We present modeling and experimental results. We conclude with early system demonstrations of their potential in applications.

10:40 AM

(PACRIM-S24-016-2017) High efficiency perovskite on silicon tandem solar cells (Invited)

K. Catchpole*[1]

1. Australian National University, Australia

A tandem configuration of perovskite and silicon solar cells is a promising way to achieve high efficiency solar energy conversion at low cost. Four-terminal tandems, in which each cell is connected independently, avoid the need for current matching between the top and bottom cells, giving greater design flexibility. A semi-transparent perovskite cell is fabricated with broadband near infra-red transmittance of >80% using optimized sputtered indium tin oxide front and rear contacts. Our semi-transparent cell exhibits much less hysteresis than opaque reference cells. A four-terminal perovskite on silicon tandem efficiency of more than 24% is achieved. We also demonstrate an efficient spectrum splitting perovskite-on-silicon tandem in which the perovskite cell serves two functions: absorbing short wavelengths and eliminating the need for a sophisticated optical splitter. Tandem efficiency of 25.2% has been achieved using a silicon cell with an initial efficiency of 22.4%.

11:05 AM

(PACRIM-S24-017-2017) Eu^{3+}:Ag co-doped zinc-tellurite glass for solar sell applications

J. Amjad*[1]; D. Rajesh[2]; M. R. Dousti[3]; A. de Camargo[2]

1. COMSATS Institute of Information Technology, Lahore, Physics, Pakistan
2. University of Sao Paulo, Brazil
3. Federal University of Alagoas, Maceio, AL, Brazil, Brazil

Zinc-tellurite glasses containing europium ions and silver nanoparticles were investigated structurally and optically. High resolution transmission electron microscopic (HRTEM) measurements confirmed the existence of metal nanostructures inside the glass host with maximum size~10 nm for the sample annealed for ~3h above the glass transition temperature (T_g). Photoluminescence studies were carried while exciting the samples on resonance and slightly away from maximum plasma frequency. On resonance excitation and/or annealing the samples for relative longer durations above T_g, induces the quench in europium luminescence whereas a notable downconversion enhancement was found while using the excitation radiations away from plasmon band maximum. Moreover, Lifetime measurements were also performed to probe any energy transfer mechanism. No significant change in lifetime of the hypersensitive transition $^5D_0$-$^7F_1$ was found excluding the probability of any energy transfer between the two species. The enhancement in the europium luminescence could be attributted to the local field effect of metal nanostructures whereas quenching is understood in terms of the plasmon reabsorption. The enhanced downconversion can be exploited to enhance the efficiency of commercially available semiconductor solar cells

11:20 AM

(PACRIM-S24-018-2017) Interface engineering of multi-layered ZnS-GaP thin films with high visible-light photoactivity

J. Hart*[1]; F. Kurnia[1]; M. Al-Farsi[1]; Y. Ng[2]; N. Valanoor[1]; N. Allan[3]

1. UNSW Australia, School of Materials Science and Engineering, Australia
2. UNSW Australia, School of Chemical Engineering, Australia
3. University of Bristol, School of Chemistry, United Kingdom

Photocatalytic water splitting is a promising method for allowing solar energy to be stored in chemical form. Many potential semiconductors for photocatalysis of water splitting, including TiO_2, have band gaps that are too large for absorption of visible light and hence have low efficiencies under sunlight. By combining two semiconductors together in a solid solution or heterostructure, it can be possible to tune the band gap and hence optimize photocatalytic efficiency. In this work, we show that ZnS-GaP multi-layered thin film photoelectrodes can produce high current densities under visible light. The photocurrent density increases as the number of interfaces between ZnS and GaP in the thin film structure increases, demonstrating that the current is predominantly produced at these interfaces. Through density functional theory calculations, we show that the band gaps of these multi-layered structures depend on the thickness of the ZnS and GaP layers, as well as the crystallographic interfacial plane. The interaction of ZnS and GaP at the interfaces is analyzed to provide insights into the factors that control the band gaps of these mixed semiconductor systems.

11:35 AM

(PACRIM-S24-019-2017) Photovoltaic solar cells based on Sb_2Se_3 nano-rods obtained by magnetron sputtering deposition

G. Liang[2]; H. Ma[1]; Z. Luo[3]; P. Fan[2]; X. Zhang*[1]

1. Université de Rennes I, Lab. Glasses and Ceramics, France
2. Shenzhen University, College of Physics and Energy, China
3. Shenzhen University, College of Chemistry and Chemical Engineering, China

The non-toxic and earth abundant materials based on Sb_2Se_3 has been extensively explored for a wide range of applications including solar energy conversion and thermoelectric device. The Sb_2Se_3 compound with an orthorhombic structure has an inherent anisotropic crystal structure which promotes 1D nano-structure. In addition, the Sb_2Se_3 exhibits a direct band-gap of 1.1-1.3eV with an absorption coefficient around $10^5 cm^{-1}$. Theoretical calculations demonstrated that Sb_2Se_3 based solar cell is a promising candidate for achieving >30% efficiency. Considerable efforts have been devoted to the synthesis of 1D Sb_2Se_3 nanostructure exclusively based on solution processing. In this work, a simple method for fabricating Sb_2Se_3 nano-rods by magnetron sputtering Sb_2Se_3 alloy target is proposed. The thermally induced nano-rods exhibit a well-crystallized structure with a preferred crystallographic orientation of (221) and a stable valence of Sb^{3+} and Se^{2-}. The obtained thin film has a band-gap of 1.32 eV and a high absorption coefficient of $10^5 cm^{-1}$ in visible region. The photo-electrochemical measurements show that the Sb_2Se_3 nano-rods are p-type semiconductors with an excellent photo-response. A photovoltaic solar cell using the Sb_2Se_3 nano-rods film as absorber has been demonstrated with an encouraging power conversion efficiency of 2.11 %. Directions for future improvement will be discussed.

PACRIM Symposium 30: Glasses and Ceramics for Nuclear and Hazardous Waste Treatment

Geopolymer, Glass-Ceramic, and Composite Waste Forms II

Room: Kona 1

Session Chairs: Kevin Fox, Savannah River National Laboratory; Russell Hand, University of Sheffield

8:30 AM

(PACRIM-S30-036-2017) Geopolymers and alternative cemented waste forms (Invited)

J. Provis*[1]

1. University of Sheffield, United Kingdom

This presentation will highlight recent developments - in research and in practice - related to the development and use of geopolymers and other alternative cements for the immobilization of wastes arising from the nuclear fuel cycle. Although many national waste management programs are successfully using Portland cement (and its blends with supplementary cementitious materials) to immobilize large volumes of low and intermediate level wastes, there are several types of waste which are not compatible with the chemistry of Portland cement, and so the development of alternative cementitious binder systems is required. Geopolymers, based mainly on alkali-aluminosilicate chemistry, are one of the classes of cementing system which has been identified to hold great promise in this regard, and have been put into practice in multiple countries. This presentation will link the structure, chemistry and technical characteristics of some of the available alternative cementitious binders which may be of value in the global nuclear industry, with the aim of providing an overview and some specific insight into how these materials may be designed, specified and applied.

9:00 AM

(PACRIM-S30-037-2017) Nano-Engineering of Cementitious Materials towards Improved Nuclear Wasteforms

B. Wang*[1]; N. Krishnan[1]; G. Sant[1]; M. Bauchy[1]

1. University of California, Los Angeles, Civil and Environmental Engineering, USA

Although concrete is commonly used to immobilize nuclear waste, its relatively low performance as a wasteform has restricted its use to simple physical barriers thus far. This has prevented the

immobilization of high-level waste, for which the vitrification process is preferred. Designing cementitious phases showing higher chemical durability, resistance to irradiation, and thermal stability would offer an attractive alternative to traditional borosilicate glasses, with lower costs and more flexible processability. Here, we rely on recent progress in the knowledge of the atomic structure of calcium–silicate–hydrate (C–S–H), the binding phase of concrete, to reveal the "atomic genome" of concrete. We demonstrate that the topology of the atomic network controls the macroscopic properties of C–S–H, including its dissolution rate, fracture toughness, creep modulus, thermal expansion, and resistance to irradiation. This paves the way for the discovery of cementitious phases with tailored properties towards the design of novel wasteforms with improved performances.

9:15 AM

(PACRIM-S30-038-2017) Influence of Aluminum Cations on the Hydration Process of a Brushite Cement for Nuclear Waste Immobilization

P. M. Laniesse*[1]; C. Cau-Dit-Coumes[1]; A. Pascal[1]; A. Mesbah[2]; G. Le Saout[3]

1. CEA, Treatment and Waste Conditioning Department, France
2. ICSM, France
3. Ecole des Mines d'Alès, France

Portland cement is extensively used for the conditioning of low- or intermediate-level radioactive wastes. However, its high alkalinity is a serious obstacle in the case of acidic wastes. This presentation aims at investigating the role of aluminum cations on the hydration process of a brushite cement which might show an enhanced chemical compatibility with acidic wastes, as compared to calcium silicate cements. The binder was a two-component system, consisting of wollastonite and a phosphoric acid solution containing borax, aluminum and zinc. The hydration process was investigated using a specific cell allowing the simultaneous measurement of the elastic modulus and the electrical conductivity during setting. Furthermore, the phase assemblage was characterized by X-ray diffraction, scanning electron microscopy and ^{31}P and ^{27}Al MAS-NMR. Hydration occurred in two main steps. In addition to amorphous silica and an amorphous phase containing phosphate, zinc and aluminum, dissolution of wollastonite successively yielded monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2.H_2O$) and brushite ($CaHPO_4.2H_2O$). At constant Ca/P ratio, the hydration process and the final properties of the paste were strongly influenced by aluminum cations. Increasing its concentration in the solution limited the heat of hydration but significantly improved the mechanical strength of the hardened product.

9:30 AM

(PACRIM-S30-039-2017) Optimum Conditions for Vitrification of Cs-Sorbed Zeolite Waste Generated from Decontamination of Effluents at Fukushima Dai-ichi NPP

Y. Inagaki*[1]; T. Arima[1]; K. Idemitsu[1]; D. Akiyama[2]; N. Sato[2]; A. Kirishima[2]

1. Kyushu University, Department of Applied Quantum Physics & Nuclear Engineering, Japan
2. Tohoku University, Institute of Multidisciplinary Research, Japan

Zeolite adsorbent has been used for decontamination of effluents containing radioactive Cs generated at Fukushima Dai-ichi NPP, and the amount of spent adsorbent has been increasing. One of potential methods to convert the spent adsorbent into passively safe material for storage and disposal is vitrification into borosilicate glass waste form, which can reduce the waste volume and immobilize Cs for long-term. The vitrification conditions, such as glass forming additives and melting temperature, closely affect properties of the vitrified products, such as volume reduction, Cs-incorporation and chemical durability. In the present study, therefore, lab-scale vitrification tests were performed for modified chabazite, the same type of zeolite used at Fukushima Dai-ichi NPP, in order to evaluate relations between the vitrification conditions and the properties of products quantitatively. The chabazite sorbing natural Cs was melted with glass additives to provide vitrified products, and the properties of products were evaluated as a function of the vitrification conditions. The results indicated one of the optimum vitrification conditions is melting at 1100°C for 3 hours with glass additives of 30wt% $Na_2B_4O_7$, which provides the volume reduction ratio of 55-60%, the Cs -incorporation ratio of 95-100% and the initial dissolution rate as low as HLW glass.

9:45 AM

(PACRIM-S30-040-2017) Vitrification of Clinoptilolite using Low Melting Glass Formulations

J. Clarke*[1]; M. C. Stennett[1]; C. L. Corkhill[1]; R. J. Hand[1]; N. C. Hyatt[1]

1. University of Sheffield, United Kingdom

Clinoptilolite is a zeolite mineral that is used for nuclear waste effluent treatment due to its high affinity for certain fission products- for example caesium. As an aluminosilicate, of small particle size (<1mm), clinoptilolite is ideally suited for vitrification, immobilising fission products in a durable wasteform. Sodium borosilicate glass compositions were selected for candidate wasteforms- eight compositions were formulated during the initial trials and four compositions were taken forward for further analysis. The clinoptilolite was ion-exchanged with Cs and vitrified in stainless steel containers, at relatively low temperatures 900-1050°C. Samples were melted statically and with in-situ stirring to study inhomogeneities present in the glass. Samples were characterised using SEM/EDX, XRD, thermal analysis, density, and XANES analysis to obtain information on glass transition temperatures, crystallisation events, secondary phases present and redox conditions. Cs retentions are calculated to assess the volatilisation in these low melting glasses, the glasses are also subject to durability studies to assess Cs retention during glass dissolution and ^{133}Cs NMR is used to study the bonding environment of caesium in the glass.

10:15 AM

(PACRIM-S30-041-2017) Properties of Glass formed by Vitrification of Radioactive Cs sorbed Zeolite and its Cs Evaporation Behavior

D. Akiyama*[1]; N. Sato[1]; A. Kirishima[1]; Y. Inagaki[2]; T. Arima[2]

1. IMRAM Tohoku University, Japan
2. Kyushu University, Department of Applied Quantum Physics & Nuclear Engineering, Japan

A large amount of waste water contaminated by radioactive cesium and etc has been generating at Fukushima Dai-ichi NPS after the severe accident. Zeolite has been used for the decontamination of such water resulting in the increase of large quantity of absorbent wastes. Vitrification method is one of the candidate solidification processes for spent adsorbent. This method can reduce the waste volume and immobilize Cs for long-term. However, some of cesium sorbed by zeolite may volatilize through the vitrification process depending on vitrification conditions. Furthermore, it is important to evaluate the property of waste glass from the stand point of safety assessment for storage and disposal. In this study, the modified chabazite which is a same type of zeolite used at Fukushima Dai-ichi NPS was used as a simulated adsorbent. The chabazite sorbed by radioactive or nonradioactive cesium (^{137}Cs or ^{133}Cs) was melted with glass additives at 1000~1150°C in air. Cesium incorporation ratio at vitrification process was evaluated by either radioactivity measurement using NaI scintillation counter or XRF analysis. The glass transition point of vitrified waste was estimated to be around 580°C by TG-DTA. Cesium incorporation ratio was over 90 % by glass formation at 1100°C. From the results, the glass vitrification method was found to be effective for the sorbent waste treatment.

10:30 AM

(PACRIM-S30-042-2017) Zeolites as an immobilisation matrix for chloride waste salt: Occlusion, HIPing and chemical durability

F. Y. Tocino*[1]; N. C. Hyatt[1]; A. Mason[1]

1. University of Sheffield, Material Science and Engineering, United Kingdom

Different pyromettalurgical processes ("pyroprocesses") have been developed for recovering the actinide elements in spent nuclear fuel by electrotransport through molten salt eutectic (typically LiCl-KCl) to solid and liquid metal cathodes. This waste salt contains alkali-metals, alkaline-earth, rare earth and minor actinides elements and can be considered as a high level waste containing chloride salts. Such chlorides constitute an issue in the production of vitreous waste due to their low solubility and negative impact on the chemical durability. This is why salt occluded zeolites have been identified as potential immobilisation matrices for waste salts. In this study, we will mainly focus on the capacity of retention of the zeolite using a model salt. The wasteform is then sintered using HIP (High Isostatic Pressing) and the leach resistance of the wasteform is then assessed. The aims are to find an easy way of recycling the molten salt for further use in pyroprocessing and to consolidate the final powder using HIPing, in order to produce the most durable waste achievable.

10:45 AM

(PACRIM-S30-043-2017) Vitrification of contaminated soil containing Cs

S. Tan*[1]; R. J. Hand[1]; O. McGann[3]; J. McDonald-Taylor[2]; S. Morgan[4]

1. The University of Sheffield, ISL, Department of Materials Science and Engineering, United Kingdom
2. National Nuclear Laboratory, United Kingdom
3. Glass Technology Service Ltd., United Kingdom
4. Sellafield Ltd., United Kingdom

On a global scale there are significant amounts of soils contaminated by nuclear activities that require treatment. In the UK, some contaminated soils are categorised as intermediate level nuclear waste; currently such soils do not have a treatment and disposal route. As part of an ongoing project to develop a novel small scale melter for waste vitrification (Hazmelt) we have investigated vitrification of contaminated soils, representative of those found on the Sellafield site, by adding additives to form a homogeneous melt at high temperatures and to form a glass product after cooling. The challenges of vitrifying the selected soil include its high silica content (~90 mol%), Cs contamination and organic matters. In this study, two series of glasses have been prepared from simulant contaminated soil with a representative addition of non-active Cs. In series 1, the simulant soil was melted with various amounts of $Na_2B_4O_7$. In series 2, the simulant soil was melted with additions of H_3BO_3, Na_2CO_3 and $CaCO_3$. Homogeneous glasses with acceptable Cs retention have been achieved with up to 70wt% additions of simulant soil. XRD, DTA, Raman, XRF and SEM have been used to assess the structure and properties of the glasses. Chemical durability of the glasses has been determined using PCT-B. The leachates are measured with ICP-OES and the changes in glass composition and structure following the durability tests investigated by SEM and XRD.

11:00 AM

(PACRIM-S30-044-2017) Development of Multiphase Ceramic Waste Forms Using a Melt Process

J. Amoroso*[1]; C. Dandeneau[1]; M. Tang[2]; K. Brinkman[3]

1. Savannah River National Laboratory, USA
2. Los Alamos National Lab, USA
3. Clemson University, USA

The development of next generation nuclear energy necessitates the parallel development of waste treatment strategies and immobilization technologies. Vitrification technology and the resulting glass material is the most widely practiced method for immobilizing nuclear waste throughout the world. Nevertheless, multiphase ceramic waste forms are promising hosts for nuclear waste immobilization as they are thermodynamically more stable than conventional borosilicate glass waste forms and have the potential for increased nominal waste loading limits relative to glass systems. However, ceramic materials are typically processed using solid state reaction routes. A multiphase ceramic produced from a melt-process would provide an opportunity to broaden the available disposal options and lower waste treatment cost. Therefore, research at the Savannah River National Laboratory (SRNL) has been exploring melt-processing ceramic waste forms that are intentionally designed to crystallize into a multi-phase ceramic upon cooling from a melt. Advances in understanding the challenges associated with processing these ceramic waste forms and the effects of the phase assemblage and elemental speciation in the phases on the performance and properties of the waste form will be discussed.

11:15 AM

(PACRIM-S30-045-2017) Ceramic and glass-ceramic wasteforms for actinide disposition

S. Sun*[1]; M. C. Stennett[1]; C. L. Corkhill[1]; N. C. Hyatt[1]

1. University of Sheffield, United Kingdom

Pyrochlore ceramic and zirconolite glass-ceramic wasteforms are the potential host phases for actinide disposition. Composition – processing – structure relations in a series of pyrochlore related wasteforms (prototypically $CaCeTi_2O_7$ and $CaUTi_2O_7$) were emphasized in this work, using Rietveld modelling of powder X-ray and neutron diffraction data and analysis of Ce and U L_3 edge XANES. An almost single phase Ce pyrochlore with composition of $Ca_{0.60}Ce_{0.92}Ti_{2.27}O_7$, was synthesised and the first reliable structure determination made from analysis of neutron diffraction data (space group Fd-3m, a = 10.1462(4) Å). In addition, the synthesis of uranium betafite pyrochlore ceramics, was investigated at 1320ºC in flowing N_2 from $CaTiO_3$, TiO_2, ZrO_2 and U_3O_8 as raw precursors. The betafite phase was obtained in high yield (> 85%) and a mean uranium oxidation state of 4.1±0.1 was determined by XANES and XPS; all U_3O_8 was incorporated into the ceramic host phase. In addition, the radiation and dissolution resistance of the zirconolite glass-ceramics was studied as well. The influence of heavy ion implantation and different solution environments on the morphology and phase evolution was investigated.

11:30 AM

(PACRIM-S30-046-2017) Structural characterization of (Ba,Cr)-hollandites for Cs immobilization

P. Tumurugoti[1]; S. T. Misture*[1]; S. K. Sundaram[1]; J. Amoroso[2]

1. Alfred University, Materials Science and Engineering, USA
2. Savannah River National Lab, USA

Ba-hollandites with compositions $Ba_{1.15-x}Cs_{2x}Cr_{2.3}Ti_{5.7}O_{16}$ ($0 \le x \le 1.15$) intended for immobilization of cesium from nuclear waste were prepared, characterized, and analyzed for Cs retention properties. Sol-gel synthesized powders were used for structural characterization using a combination of X-ray and neutron diffraction. Phase-pure hollandites adapting monoclinic symmetry (I2/m) were observed to form in the compositional range $0 \le x \le 0.4$. Structural models for the compositions: x = 0, 0.15 and 0.25, were developed from Rietveld analysis of powder diffraction patterns. Refined anisotropic displacement parameters (U_{ij}) indicate local disorder of Ba/Cs along the tunnel direction (U_{22} = 0.16 - 0.18 Å^2, U_{11}, U_{33} = 0.001 - 0.01 Å^2). In addition, weak superlattice reflections are also seen in x-ray diffraction patterns. Our data suggests the presence of supercell structures with ordered tunnel cations for the studied phase-pure hollandites. The implications of the structural features on Cs retention are also discussed and are validated by experimental Cs leachability data determined by Product Consistency Tests (PCT).

11:45 AM

(PACRIM-S30-047-2017) Cerium Substituted Zirconolite: 2M and 4M Polymorph Transition

B. Clark*[1]; S. K. Sundaram[1]; S. T. Misture[1]; J. Amoroso[2]

1. Alfred University, USA
2. Savannah River National Lab, USA

Compounds with the formulae $CaZr_{1-x}Ce_{x}Ti_{2}O_{7}$ with x = 0.1-0.5 were synthesized by solid state reaction. Cerium was used as a surrogate for actinide elements. Sintering was carried out via spark plasma sintering (SPS) during which the perovskite phase stabilized due to the reducing conditions during SPS. Zirconolite has superior chemical durability compared to perovskite. A transition from the 2M polymorph to the 4M polymorph (expanded unit cell) in zirconolite was observed with increasing cerium content. The presence of both tri- and tetravalent Ce, contrary to formulation, was confirmed using X-ray absorption near edge spectroscopy (XANES), allowing substitution on both Ca and Zr sites. Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) revealed that the 2M polymorph was dilute in Ce content in comparison to the 4M-zirconolite. High temperature X-ray diffraction (HTXRD) was used to detail the kinetics of perovskite to zirconolite transition. Monolithic chemical durability testing was performed at 90°C for up to 49 days. Minimal Ce was leached from these samples and negligible alteration was observed, exhibiting superior chemical durability over other Ce bearing waste forms.

Author Index

*** Denotes Presenter**

*Denotes Presenter