

# Abstracts

## 1. Bernhard T. Leube

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### Exploitation of different metal-sulphur frameworks for lithium ion transport

The development of solid lithium ion conductors is a crucial step towards all-solid lithium ion batteries. These could benefit from increased safety, improved compatibility to new anode and cathode materials and increased long-term cyclability. Sulphide based materials such as  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  and the Li-Argyrodites  $\text{Li}_6\text{PS}_5\text{X}$  (X= Cl, Br, I) are among the best Li conductors known. This talk will present recent work two classes of new lithium containing metal sulphides which can be distinguished regarding the sulphide anionic sublattice.

It has been reported that the high entropy rock salt  $(\text{MgCoNiCuZn})_{1-x-z}\text{Ga}_y\text{Li}_x\text{O}$  gives rise to superionic  $\text{Li}^+$  mobility ( $> 10^{-3}$  S/cm) at RT.<sup>[1]</sup> Sulphide based materials are considered to be superior lithium ion conductors due to higher polarizability of sulphur compared to oxygen. Therefore new entropically stabilised sulphide based rock salt phases with a cubic close packed (ccp) sulphur sublattice were synthesised and analysed regarding structure and electrochemical properties.

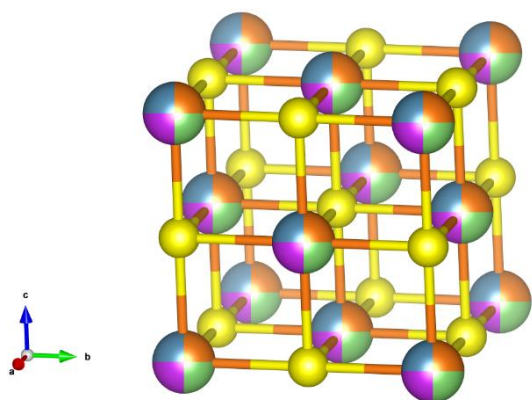


Figure 1: Proposed crystal structure of a high-entropy rock salt with random cation occupancy

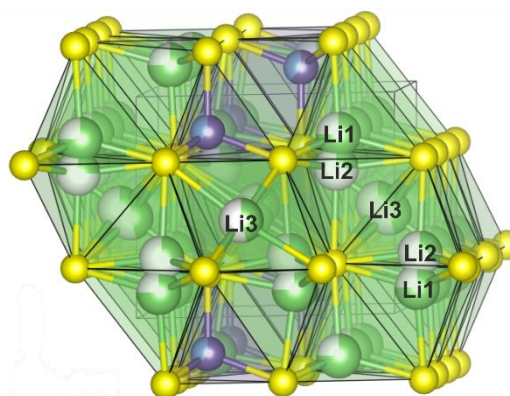


Figure 2: Crystal structure of  $\text{Li}_{4.4}\text{Al}_{0.4}\text{Ge}_{0.6}\text{S}_4$ .

The second part of the talk will focus on materials with hexagonal close (hcp) sulphur packing, such as  $\text{Li}_5\text{AlS}_4$ ,  $\text{Li}_4\text{GeS}_4$ ,  $\text{Li}_4\text{SnS}_4$  or  $\text{Li}_3\text{PS}_4$ . Explorative synthesis was carried out in the  $\text{Li}_5\text{AlS}_4$ - $\text{Li}_4\text{GeS}_4$  and the hcp based phase  $\text{Li}_{4.4}\text{Al}_{0.4}\text{Ge}_{0.6}\text{S}_4$  was isolated. The crystal structure of this novel phase was solved and further investigation showed that a new structural family of sulphide based materials  $\text{Li}_{4.4}\text{M}_{0.4}\text{M}'_{0.6}\text{S}_4$  ( $M = \text{Al}^{3+}$ ,  $\text{Ga}^{3+}$  and  $M' = \text{Ge}^{4+}$ ,  $\text{Sn}^{4+}$ ) is accessible. AC-impedance spectroscopy and  $^7\text{Li}$  dynamic NMR showed high lithium mobility  $\sim 4 \times 10^{-5}$  S/cm and chemical stability was tested against lithium metal. A combination of variable temperature  $^7\text{Li}$  solid state nuclear magnetic resonance spectroscopy and *ab initio* molecular dynamics calculations on selected phases showed that two dimensional diffusion with a low energy barrier of 0.17 eV is responsible for long-range lithium transport. The diffusion pathways are mediated by the disordered vacancies while the ordered vacancies do not contribute to the conductivity. This new structural family of sulfide  $\text{Li}^+$  ion conductors offers insight into the role of disordered vacancies on  $\text{Li}^+$  ion conductivity mechanisms in hexagonally close packed sulfides that can inform future materials design.

[1]: D. Beradran, S. Franger, A. K. Meena and N. Dragoe, *J. Mater.Chem. A*, 2016, **4**, 9536.

## **2. Wirat Lerdprom**

*Centre for Advanced Structural Ceramics, Imperial College London*

### **SPS, Microwave, Flash sintering; do they really work for porcelains?**

This presentation describes the use of spark plasma, microwave, and flash sintering on porcelain and the impact of each on its densification, phase evolution and physicomechanical properties. Densification behaviour, mullite formation, and physicomechanical properties in the studied processes were different. For example, the pressure applied on SPS induced 10-times greater densification rate compared to conventional sintering of porcelains, and mullite became oriented perpendicular to the applied pressure. Mullite formation, in addition, was altered by microwave energy and flash sintering also conferring unique morphologies. Physicomechanical properties of the porcelains produced under different sintering routes were similar. Energy consumption and sintering process capability will also be addressed.

## **3. Matt Porter**

*University of Birmingham*

### **High-Temperature Ceramic Matrix Composites using Microwave Enhanced Chemical Vapour Infiltration**

High-temperature ceramic matrix composites, specifically SiCf/SiC, have been identified as candidates to operate in the hostile aero-thermo-chemical environments experienced in service without compromising structural integrity, whilst keeping mass at a premium. Chemical vapour infiltration (CVI), is an effective manufacturing route capable of creating near fully dense CMCs with a refined microstructure with no preform degradation and residual stress. CVI's challenges, however, are threefold; i) processing is typically 2 – 3 months; ii) premature surface pore closure occurs prevents greater than 90% densification; iii) associated costs and therefore product are expensive. Microwave energy (MCVI) has been proposed as a potential solution to heat the SiC fibre preform for CVI; it produces an inverse temperature profile, which initiates densification at the centre of the sample, thus avoiding premature porosity closure. It is expected that the use of MCVI could yield near fully dense products in as little as 72 – 96 hours.

#### 4. Shunsuke Murakami

*Department of Materials Science and Engineering, University of Sheffield, Sheffield S1 3JD, UK*

##### **Optimising dopants and properties in BiMeO<sub>3</sub>-doped (Me = Al, Ga, Sc, Y, Mg<sub>2/3</sub>Nb<sub>1/3</sub>, Zn<sub>2/3</sub>Nb<sub>1/3</sub>, Zn<sub>1/2</sub>Ti<sub>1/2</sub>), lead-free BaTiO<sub>3</sub>-BiFeO<sub>3</sub> based piezoelectrics**

A crystallochemical framework is proposed based on electronegativity difference ( $e_n$ ) and tolerance factor ( $t$ ) for BiMeO<sub>3</sub> dopants to optimise the piezoelectric and electrostrictive response in BaTiO<sub>3</sub>-BiFeO<sub>3</sub> based ceramics. Compositions in the series 0.05Bi(Me)O<sub>3</sub>-0.25BaTiO<sub>3</sub>-0.70BiFeO<sub>3</sub> (BMe-BT-BF, Me: Y, Sc<sub>1/2</sub>Y<sub>1/2</sub>, Mg<sub>2/3</sub>Nb<sub>1/3</sub>, Sc, Zn<sub>2/3</sub>Nb<sub>1/3</sub>, Zn<sub>1/2</sub>Ti<sub>1/2</sub>, Ga, and Al) were fabricated using solid state synthesis. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) revealed that only Bi(Mg<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> and BiScO<sub>3</sub> dopants, which lie in a narrow range of  $e_n$  vs.  $t$ , form homogeneous ceramics, reflected in their superior piezoelectric coefficients ( $d_{33} \sim 145$  pC/N).

The promising initial properties of Bi(Mg<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> doped compositions prompted further studies on 0.05Bi(Mg<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub>-(0.95-x)BaTiO<sub>3</sub>-xBiFeO<sub>3</sub> (BMN-BT-BF,  $x = 0.55, 0.60, 0.63, 0.65, 0.70,$  and  $0.75$ ) ceramics. It was revealed that BMN-BT-BF transformed from relaxor-like to ferroelectric behaviour with an increase in  $x$  and the largest strain was 0.41% at 10 kV/mm for  $x = 0.63$ , at the point of crossover from relaxor to ferroelectric.

#### 5. Rebecca Smith

*University of St. Andrews*

##### **Quantum criticality in tetragonal tungsten bronze K<sub>3</sub>Li<sub>2</sub>Ta<sub>5</sub>O<sub>15</sub>.**

Quantum criticality is known<sup>1</sup> in perovskite SrTiO<sub>3</sub>, with a ferroelectric transition at 0 K. This work expands quantum criticality away from perovskites to K<sub>3</sub>Li<sub>2</sub>Ta<sub>5</sub>O<sub>15</sub> in tetragonal tungsten bronze structures, with a  $T_c = 7$  K.<sup>2</sup>

K<sub>3</sub>Li<sub>2</sub>Ta<sub>5</sub>O<sub>15</sub> ceramics were synthesised under various conditions. The amount of K and Li within the 4ml closed crucibles affect the orthorhombic distortion and other properties. The volatility of K and Li at the sintering temperatures are likely to explain these differences.

On the “stoichiometric” K<sub>3</sub>Li<sub>2</sub>Ta<sub>5</sub>O<sub>15</sub> ceramics, further property analyses have been undertaken by various methods including variable temperature structural analysis, dielectric data, and resonant ultrasound spectroscopy. Extrapolating the dielectric data using the empirical Vogel-Fulcher equation suggests that a degenerate ground state occurs at absolute zero, required for quantum criticality.

1: S. E. Rowley et al., *Nat. Phys.*, 2014, **10**, 367–372.

2: T. Fukuda, *Jpn. J. Appl. Phys.*, 1970, **9**, 599–606.

## **6. William Rowlands**

*University of Loughborough*

### **Additive Manufacturing of Advanced Ceramics for Demanding Applications**

Demand is high for lightweight ceramics in the aerospace and automotive heaters. By application of additive manufacturing components can be manufactured in more complex geometries than with conventional methods to reduce the overall weight while improving functionality. This project deals with the investigation of the fabrication of a PTC ceramic heating element relevant to the industrial sponsor products. The aim is to potentially replace one or more conventional component manufacturing methods with additive techniques and to achieve single stage multi-material additive manufacture of heater components. Additive manufacturing combined with rapid field assisted sintering can greatly reduce the cost and time to create functional ceramic components.

High solids loading aqueous PTC material pastes were formulated for use with the micro-extrusion 3D printing process. Various experimental parameters were investigated for their role in determining the rheological characteristics to achieve optimally printed samples. The rheology could be controlled to leave extruded ceramic layers that blend together well leaving seamless layers, or stiffer extrusions for bridging and functionally porous samples. Calcination of PTC precursors was undertaken after printing, leading to highly dense final components with designed pores based on need. Impedance spectroscopy was used to determine the resistivity of the samples and infrared imaging to determine the heating characteristics. A number of techniques (SEM, XRD, EDX) were used to characterise the material and components along the processing stages.

## **7. Stephanie M. Thornber**

*National Nuclear Lab (NNL)*

### **Zirconolite Glass-Ceramics for Plutonium Immobilisation in the UK: From PhD to Industry**

The UK has around 140 tonnes of separated civil plutonium oxide ( $\text{PuO}_2$ ) stored at the Sellafield site. Whilst the current UK government policy is to fabricate the  $\text{PuO}_2$  material into fuel, a significant fraction of the stockpile material may not be suitable. Therefore an alternative immobilisation treatment route is required. Zirconolite ( $\text{CaZrTi}_2\text{O}_7$ ) ceramic and glass-ceramic materials are being developed as potential host materials for the immobilisation of Pu into stable forms for long-term storage and geological disposal. Zirconolite ( $\text{CaZrTi}_2\text{O}_7$ ) is a naturally occurring ceramic mineral that readily accommodates Pu into its structure and has been shown to have excellent durability and radionuclide retention properties. Zirconolite glass-ceramics partition Pu into the durable ceramic phase and accommodate impurities in the glass phase.

The UK's Nuclear Decommissioning Authority (NDA) has identified hot isostatic pressing (HIPing) as a leading option for the consolidation of ceramic and glass-ceramic materials for the immobilisation of the stockpile  $\text{PuO}_2$  material. Hot isostatic press applies high temperatures and pressures to the workpiece producing high density, hermetically sealed ceramic / glass-ceramic wastefoms ready for long-term storage.

This work looks at the development of zirconolite glass-ceramics for successful immobilisation of Pu materials utilising hot isostatic pressing as the consolidation technique. Formulation and process

optimisation led to waste incorporation investigations using inactive and radioactive surrogates. Results from surrogate studies led to the fabrication and consolidation of PuO<sub>2</sub> loading zirconolite glass-ceramic samples.

This work is directly applicable to current industrial projects underway within the nuclear industry, including the development of a small scale radioactive hot isostatic press facility at the National Nuclear Laboratory designed for fabrication of small scale PuO<sub>2</sub> loaded HIP samples.

## **8. Chao Yun**

*University of Cambridge*

### **Self-assembled oxide films with tailored nanoscale ionic and electronic channels for controlled resistive switching**

Resistive switches are non-volatile memory cells based on nano-ionic redox processes that offer energy efficient device architectures and open pathways to neuromorphics and cognitive computing. Self-assembled SrTiO<sub>3</sub>-Sm:CeO<sub>2</sub> (STO-SDC) vertically heteroepitaxial nanocomposite (VHN) shows much enhanced forming-free resistive switching on/off ratio, high reproducibility as well as good retention and endurance. It was found that the ionic conduction channel (which is in the Sm:CeO<sub>2</sub> nanocolumns) and the electronic conduction channel (which is in the STO-SDC vertical interface) influence and enhance the resistive switching separately: the former can be tuned by Sm doping and the latter can be tuned by crystallinity. Simultaneous tuning enables a dramatic enhancement of the performance.

## **9. Rowena H. Brugge**

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### **Local chemical degradation processes and ionic transport in all-solid-state batteries**

All-solid-state batteries are considered as the most promising and safest choice in the development of the next generation of metal ion-based batteries with high energy density. Solid ceramic electrolytes with garnet-like structures have a wide electrochemical and chemical stability and have been lately reported to surpass the required 1 mS·cm<sup>-1</sup> room temperature conductivity for their successful implementation in lithium ion batteries. However, problems with degradation processes, high polarisation resistance with metal electrodes and dendritic-driven cell failure need still to be understood and solved.

In this work, a combination of surface sensitive chemical analysis techniques and electrochemical measurements are used to correlate chemical degradation processes with electrochemical performance in Li/Garnet half cells. The dynamic nature of the metal/electrolyte interface, and the role of local chemical environments on the alkaline-metal ionic transport kinetics and critical current densities for dendrite formation are demonstrated.