Structure and thermodynamics of oxides/carbides/nitrides/borides at high temperatures

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The 2nd Structure and Thermodynamics of Oxides/carbides/nitrides/borides at High Temperature (STOHT2) conference took place at Arizona State University from Oct. 4–7, 2022. This article provides a snapshot of the meeting, including a look at currently used experimental and computational techniques, their key limitations, and possible future directions for research.

Humankind has an innate appetite for exploration, energy, and speed. These areas all require materials that operate in extreme environments, for example, temperatures above 1,500°C.

While exploring the universe can be cold (about –270°C in deep space), reentry into a planet's atmosphere can be hot (about 1,500°C on Earth). Energy production through nuclear fission can reach temperatures of up to about 1,700°C and even higher for nuclear fusion, while nuclear thermal propulsion systems require temperatures up to about 2,800°C to provide thrust to propel next-generation spacecrafts to Mars and beyond. When traveling at hypersonic speeds on Earth, leading edges can reach temperatures of about 2,700°C at Mach 8.

High-temperature thermal barrier systems as well as high-temperature environmental barrier coatings are required to protect both people and equipment on board from these high temperatures. To effectively design high-temperature material systems, one must have a clear understanding of both their thermodynamic properties and atomic structure. Understanding thermodynamics is essential to determining the longevity (stability) of a system in its operating environment, while atomic structure influences the desired material properties (e.g., mechanical, thermal, electrical, optical). There is a direct interplay between thermodynamics and atomic structure, and thus both need to be understood in the design of next-generation high-temperature materials.

This need for high-temperature material systems led researchers to organize the 1st Structure and Thermodynamics

of Oxides at High Temperature (STOHT1) conference, which was held at the University of California, Davis, in 2016. After several delays due to the COVID-19 pandemic, the 2nd Structure and Thermodynamics of Oxides/carbides/nitrides/borides at High Temperature (STOHT2) conference at Arizona State University took place from Oct. 4–7, 2022 (Figure 1).

The core goal of the STOHT2 meeting was to bring together both high-temperature experimental and computational experts to discuss (i) current state-of-the-art high-temperature techniques and methodologies, (ii) key experimental and computational high-temperature limitations, and (iii) directions to overcome these limitations.

The meeting began with a CALculation of PHAse Diagram (CALPHAD) workshop that focused on FactSage, PyCalphad, and Extensible Self-optimizing Phase Equilibria Infrastructure (ESPEI). The remaining three days focused on a series of invited 40-minute presentations, with 10 minutes of questions and answers from experts in experimental and computational thermodynamics and material structures.

This article provides a snapshot of the meeting and our take on the currently used experimental and computational techniques, their key limitations, and possible future directions for the study of the structure and thermodynamics of oxides/carbides/nitrides/borides at high temperatures. In line with the spirit of the *ACerS Bulletin,* citations throughout are not exhaustive and are used to highlight key bodies of work from authors at the STOHT2 meeting.

Current state-of-the-art high-temperature techniques and methodologies

There is a broad range of techniques available that enable the collection and processing of all-important high-temperature thermochemical and thermophysical data. These techniques can be separated into (i) commercial high-temperature characterization systems, (ii) high-temperature levitation, (iii) combined extreme environment testing, and (iv) computational techniques.

Commercial high-temperature characterization systems

Commercially, there is a wide variety of high-temperature techniques to probe thermochemical and thermophysical properties up to about 2,800°C. For example, Netzsch designed a laser flash apparatus (LFA 427) that can measure thermal diffusivity up to 2,800°C. This instrument, combined with the Netzsch dilatometer (DIL 402) and differential scanning calorimeter, enables thermal conductivity measurements as a function of temperature. These thermophysical properties are of great importance for the development of next-generation hypersonic platforms.

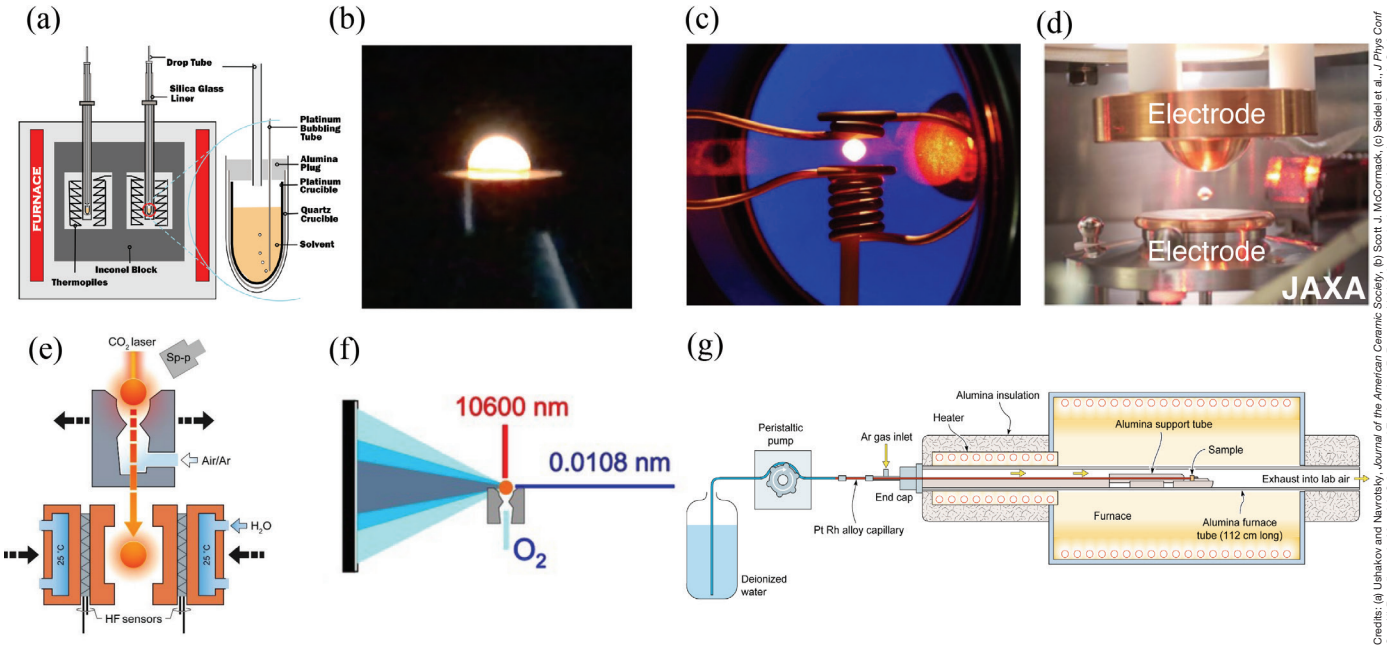
Setaram has a high-temperature differential thermal analyzer (Setsys) that can operate at temperatures up to 2,500°C and a differential scanning calorimeter (Labsys) that operates to 1,600°C and uses highly sensitive 3D sensors for reliable heat capacity measurements. Setaram also offers a high-temperature Calvet calorimeter (Alexsys, Fig. 2a) that can be used to measure enthalpy of formation and enthalpy of mixing of refractory materials.

Costa et al. used the Setaram MHTC 96 calorimeter to determine rare earth silicate and zirconate stabilities with respect to $CaO–MgO–Al_2O_3–SiO_2$ melts,[1] which is of great importance for next-generation barrier coatings that protect jet engines against volcanic ash, sand, and similar threats. Using the Setaram Alexsys systems, Hayun et al. measured formation enthalpies of multicomponent ($n > 5$) metallic alloys,[2] and Goncharvo et al. measured formation energies of uranium mononitride compositions for thermal nuclear propulsion fuel applications.[3] These properties are all essential for the CALPHAD method and are thus required to push our understanding of phase equilibria to high temperatures.

Other companies offer even higher temperature commercial systems. For example, the conical nozzle levitator system (CNL, Fig. 2b) by Materials Development Inc. (Evanston, Ill.) levitates samples in a gas stream, enabling containerless measurements. The CNL can be coupled with a carbon dioxide laser (400 W, 10.6 µm) to heat levitated samples to about 3,400°C, with a dual

Credit: Sergey Ushakov

Figure 1. (Top) Attendees and presenters from the STOHT2 conference. Left to right: Brandon Buckland, Heng Wang, Joerg Neuefeind, Zi-Kui Liu, Wenhao Sun, Philip Spencer, Richard Otis, and Scott McCormack. (Bottom) Students and presenters from the STOHT2 conference. Clockwise starting at top (royal blue shirt): Fox Thorpe, William Rosenberg, Stuart Ness, Nakeshma Cassel, Shivani Srivastava, Randi Swanson, Manuel Loffler, Wenhao Sun, and Mark Asta.



Credits: (a) Ushakov and Navrotsky, *Journal of the American Ceramic Society*; (b) Scott J. McCormack, (c) Seidel et al., *J Phys Conf Ser*; (d) Paradis et al., *Materials Science and Engineering: R: Reports*; (e) Ushakov et al., *Journal of the American Ceramic Society*; (f) Ushakov and Navrotsky, *Journal of the American Ceramic Society*; and (g) Golden and Opila, *J Eur Ceram Soc*

Figure 2. (a) High-temperature oxide drop solution calorimeter,[29] (b) conical nozzle levitator equipped with 400 W carbon dioxide laser, (c) electromagnetic levitator,[4] (d) electrostatic levitator,[6] (e) drop-and-catch calorimeter,[12] (f) high-temperature levitator coupled with X-ray diffraction,[29] and (g) steam-jet furnace.[24] Each figure reproduced with permission from respective journals and/or authors.

carbon dioxide and ytterbium fiber laser (500 W, 1.06 μm) to about 3,700°C (unpublished communication, achieved on a molten HfO_2 with diameter 2.5 mm), and with a calorimeter.

High-temperature levitation

The levitation techniques coupled with laser heating include electromagnetic levitation (EML, Fig. 2c);[4] electrostatic levitation (ESL, Fig. 2d);[5,6] aerodynamic levitation,[7] which includes the previously mentioned CNL; and acoustic levitation.[8] For most levitation techniques, the typical samples are about 2–5 mm diameter spheroids.

These techniques can achieve the highest temperatures while maintaining sample purity, which is essential for accurate thermochemical and thermophysical measurements. Using a CNL with uniaxial laser heating, ceramic spheroids at about 3,000°C can have temperature gradients up to about 500°C/mm (depending on processing), which can be reduced to about 15°C/mm if the sample is a perfect sphere that spins on all axes. When molten, temperature gradients are reduced to about 5°C/mm through convection.[9] Temperature gradients can also be reduced by using multiple lasers to heat from the sample top and bottom simultaneously.

Electromagnetic levitation, which can be used for electrically conductive carbides, nitrides, and borides, provides bulk heating by induction, which reduces the thermal gradient, allows the levitation of larger samples, and is not limited to spheroids. Levitation melting of an 8 mm sample of uranium carbide in EML was demonstrated by Knights et al. in 1971 using induction heating only.[10] However, so far, EML is applied mostly to metal alloys. EML has been combined with laser heating, and this approach was used to preheat semiconductors for levitation or for pulsed laser calorimetry.[11]

High-temperature levitation experiments can be coupled with noncontact diagnostics that enable property measurements at temperatures limited only by sample evaporation. Examples include thermal expansion, heat capacity, thermal diffusivity, and thermal conductivity measurements.

Thermal expansion or density variation as a function of temperature can be measured using high-speed cameras that take advantage of edge detection to determine volume. Through incorporation of a pulsing laser, the heat capacity, thermal diffusivity, and thermal conductivity can also be extracted. Fukuyama et al. performed such measurements on several materials at high temperatures.[11] Additionally, levitating molten samples can be pulsed mechanically, causing them to oscillate. By observing this oscillation using high-speed cameras, high-temperature surface tensions and viscosity can be extracted.[5]

An ESL system was incorporated into the International Space Station because near zero gravity measurements can lead to enhanced accuracy in viscosity and surface tension measurements. This project is being led by the Japan Aerospace Exploration Agency.

A drop-n-catch calorimeter (DnC) was developed in Navrotsky's group at Arizona State University in collaboration with Materials Development Inc. (Fig. 2e).[12] DnC combines a splitable nozzle aerodynamic levitator with laser heating and a calorimeter operating at room temperature. Fusion enthalpies are obtained from measurements on the samples heated to above and below their melting points before the drop. The DnC uses samples several orders of magnitude smaller in size than those used for conventional drop calorimetry up to the 1970s.[12] The calorimeter design and software were further improved by Materials Development Inc. and are now commercially available.

Levitation-based high-temperature environments are now available in the user programs at several national synchrotron and neutron facilities. In the United States, CNL is in operation at beamline 6-ID-D at Argonne National Laboratory's Advanced Photon Source (Fig. 2f). ESL and CNL systems are available at beamline 1B (NOMAD) at Oak Ridge National Laboratory's Spallation Neutron Source. A hyperbaric EML system is also proposed as one of the environments for neutron diffraction.[13] In Japan, CNL is available at beamline BL04B2 at Super Photon ring-8 GeV (SPring8). These in-situ high-temperature X-ray and neutron diffraction experiments have been used to observe phase transformations,[14] phase diagram construction,[15,16] thermal expansion measurements,[17,18] and liquid local structure measurements,[19–21] to name a few.

Gallington et al. demonstrated that molecular dynamics techniques based on machine learning and density functional theory can be coupled with in-situ scattering local structure data to build interatomic potentials.[22] This approach was applied to amorphous and molten HfO_2.

Yashima et al. implemented the maximum entropy method, which allows researchers to obtain more detailed electron densities from diffraction data, to map atom transport pathways in oxides.[23] To date, this technique has not been applied to in-situ high-temperature diffraction data collected via levitation techniques. The maximum entropy method will be useful in studying lambda transitions in refractory oxides and carbides to better understand sublattice melting phenomena at the highest of temperatures.

Combined extreme environment testing

Coupling other extreme environments with high-temperature testing is required to best study materials under their operating conditions.

For example, environmental barrier coatings are required for next-generation aircraft engines to ensure stability in chemically corrosive environments. The Opila group designed a high-temperature furnace that injects high-velocity hot water (Fig. 2g) to simulate the effects of steams on degradation of the ceramics.[24] Oxyacetylene torch testing as well as arc jet testing are used to simulate atmospheric reentry conditions.[25]

High-temperature mechanical testing setups that use four-point bend tests exist within the Fahrenholtz and Hilmas lab at Missouri University of Science and Technology. The temperature limits of these mechanical systems are limited by the eutectics of the graphite grips with the material being tested. Because of this limitation, diborides can only be tested up to about 2,300°C. New sintering techniques take advantage of electric fields to enhance densification.[26] Close examination of these systems led to the observation of interesting grain boundary phase transitions.[27] Now there is a push to incorporate surface effects into phase equilibria and the construction of grain boundary and nanophase phase diagrams.[28]

Computational techniques

Recent progress in developing first-principles methods has led to successful high-temperature discoveries.

To compute high-temperature materials properties, density functional theory (DFT) can be used on two levels: with lattice dynamics quasiharmonic approximation to calculate free energies of reactions at relatively low temperatures; and in conjunction with molecular dynamics (MD) techniques to obtain data at high temperatures, e.g., in the study of molten salts (Fig. 3e).[30] In addition, DFT and MD simulations generate a large amount of data, which are crucial to CALPHAD modeling and machine learning.

The CALPHAD method employs computational thermodynamics to predict materials properties of multicomponent systems. CALPHAD allows one to combine thermodynamic data from experiment or computation with data on phase equilibria in multicomponent systems to develop predictions for complex systems or locate the range of possible compositions for desired crystal structures. The reliability of these predictions depends on the thermodynamic description of all phases (stable, metastable, and unstable), across the entire compositional range, not only in the range of their stability or of technological interest.

Machine learning approaches can expedite the searches and prediction of properties. The Materials Genome Initiative resulted in the development of several materials databases, including the Materials Project, led by the Ceder and Persson group at UC Berkeley; Automatic Flow (AFLOW), led by the Curtarolo group at Duke University; and Open Quantum Materials Database (OQMD), led by Chris Wolverton at Northwestern University. Machine learning models were built from such databases to predict materials characteristics, especially refractory-materials-related high-temperature properties.

Experimental and computational high-temperature limitations

To date, the key limitations of high-temperature experimental and computational tests are (i) environment control in high-temperature experiments to prevent unwanted reactions, (ii) controlling and measuring temperature with high accuracy, (iii) database limitations, (iv) high-temperature computation, and (v) integrating physics with machine learning.

Environment control

When at high temperatures, everything reacts with everything. Material systems that may remain in the metastable states indefinitely at room temperature have sufficient energy at higher temperature to achieve their equilibrium states, overcoming kinetics barriers.

In general, furnaces that operate above 1,800°C are graphite furnaces. Samples can become contaminated with carbon in these furnaces. There are ways to reduce contamination, such as sample encapsulation using other materials like tungsten, but even those can react. Here high-temperature levitation really shines, as it is containerless and the sample is shielded by its surrounding levitation gas.

Material systems with components that have high vapor pressure can sublimate, making them very difficult to study at high temperatures even when using levitation techniques. To date, most levitation systems are designed for studying metals and oxides and are not designed to study the more refractory and high-temperature carbides, nitrides, and diborides. There is a direct need to

further develop high-temperature levitation to extract property data from these more challenging high-temperature materials.

Controlling and measuring temperature

Temperature control and measurement is challenging at extreme temperatures. High-temperature thermocouples can degrade when operating above 2,400°C due to diffusion across their junction. This degradation can be somewhat overcome by consistent calibration, but this method is not ideal. Pyrometers are the next best tool for measuring temperature, but they come with even higher temperature errors than thermocouples. These errors are predominantly due to thermal gradients and uncertainty in emissivity. As mentioned previously, there are multiple ways to reduce thermal gradients, but it is difficult to eliminate them.

Database limitations (for both CALPHAD and machine learning)

Despite recent rapid developments, databases are still limited in quantity and variety. It requires extensive efforts to build databases, e.g., the SpMCBN database for refractory carbide, nitride, boride, and silicide systems and the newly assessed Zr–B–C–O system.[31,32] In addition, CALPHAD and machine learning models are only as good as the quality of the data they are trained on. Including new data can be time-consuming for CALPHAD and ML as databases grow and evolve.[33] Additionally, integrating data from different sources and approaches is challenging, as they are often subject to different and poorly known systematic errors.

High-temperature computation

High-temperature material properties are often significantly more expensive to compute than properties at 0 K. They require molecular dynamics or other approaches to include entropy effects. The high temperature leads to disordering and defects, which require, in principle, an extensive sampling of the configurational space (Fig. 3b).[34,35] Lattice dynamics quasi-harmonic approximation starts to fail at high temperatures as anharmonic effects grow. Liquid phases are considerably more challenging to model compared to solids.

Integrating physics with machine learning

Machine learning models are only as good as the underlying physical principles on which they are built. Machine learning typically does not come with a straightforward analytical expression, which is both a strength and a weakness. While it greatly increases its applicability, it becomes challenging to integrate physics into the machine learning algorithms. Without the guidance of physics, machine learning models inevitably break physical laws, resulting in unreasonable "predictions."

Directions to overcome these limitations

The innovations required to overcome the limitations discussed above include (i) further development of novel high-temperature systems that push the limitations of composition control, (ii) improved temperature measurements at the highest of temperatures through improved pyrometry, and (iii) new computational methods to simulate high-temperature properties via DFT, ML, and CALPHAD.

Levitation at high pressure has been attempted since the 1990s to improve processing and environmental control. However, existing levitators at synchrotron and neutron facilities still operate only at ambient pressure.

A hyperbaric aerodynamic levitator was constructed by David Lipke (Missouri Science and Technology), and the results of these experiments were presented at the STOHT2 conference. These levitation systems provide novel environmental control that will be essential for characterizing materials in combined extreme environments. The ability to control levitation gas composition in hyperbaric conditions opens an entire new field of high-temperature thermochemistry, where solid–gas reactions can be studied in situ as functions of temperature and pressure.

Of particular interest is reducing sublimation of high-vapor-pressure components, further expanding the composition space that can be studied at the highest of temperatures. Nitrides are a specific material example that will benefit from these types of systems. They sublimate before melting, which makes them extremely difficult to study at high temperatures while accurately controlling their composition. An ESL system with controlled atmosphere was recently able to observe AlN formation in Ni–Al in situ at high temperatures.[39] These sorts of experiments have the potential to provide great insight into in-situ oxidation of high-temperature refractory materials at temperatures, e.g., carbides, nitrides, and diborides.

These comments highlight the need for more levitation systems that can take advantage of atmospheric controls at high temperatures to study reactions in extreme environments. This system can then be coupled with synchrotron and neutron sources to obtain structural information in situ at high temperatures.

Noncontact temperature measurements have always been difficult because the sample surface serves as the sensor. Spectral band or "single-color" pyrometers are currently used on levitators at the beamlines for measurement of the sample temperature. They provide the fastest acquisition time, but they require knowledge of emissivity, which, for a levitating spheroid, will depend on temperature, wavelength, surface curvature, and angle of observation. Surface reduction or oxidation is also often accompanied by drastic changes in emissivity.

During diffraction measurements on levitated samples, the practical way to overcome uncertainty in surface emissivity and in thermal gradient is by calibration with known or independently measured temperatures of phase transition and melting, which can be observed directly from diffraction patterns.[14] Spectropyrometers, in which ratio of intensities on multiple spectral bands are evaluated, provide emissivity-free temperature measurements and have been commercially available from a small U.S. company called FAR Associates. They are successfully used in lab-based levitators in Navrotsky's group at Arizona State University and in Lipke's group at Missouri University of Science and Technology. Lu et al. in 2009 demonstrated the application of CMOS sensors as three-color 2D pyrometers,[40] but this application is not yet commercialized.

Computational tools and packages were built to automate the processes for CALPHAD and DFT methods, providing

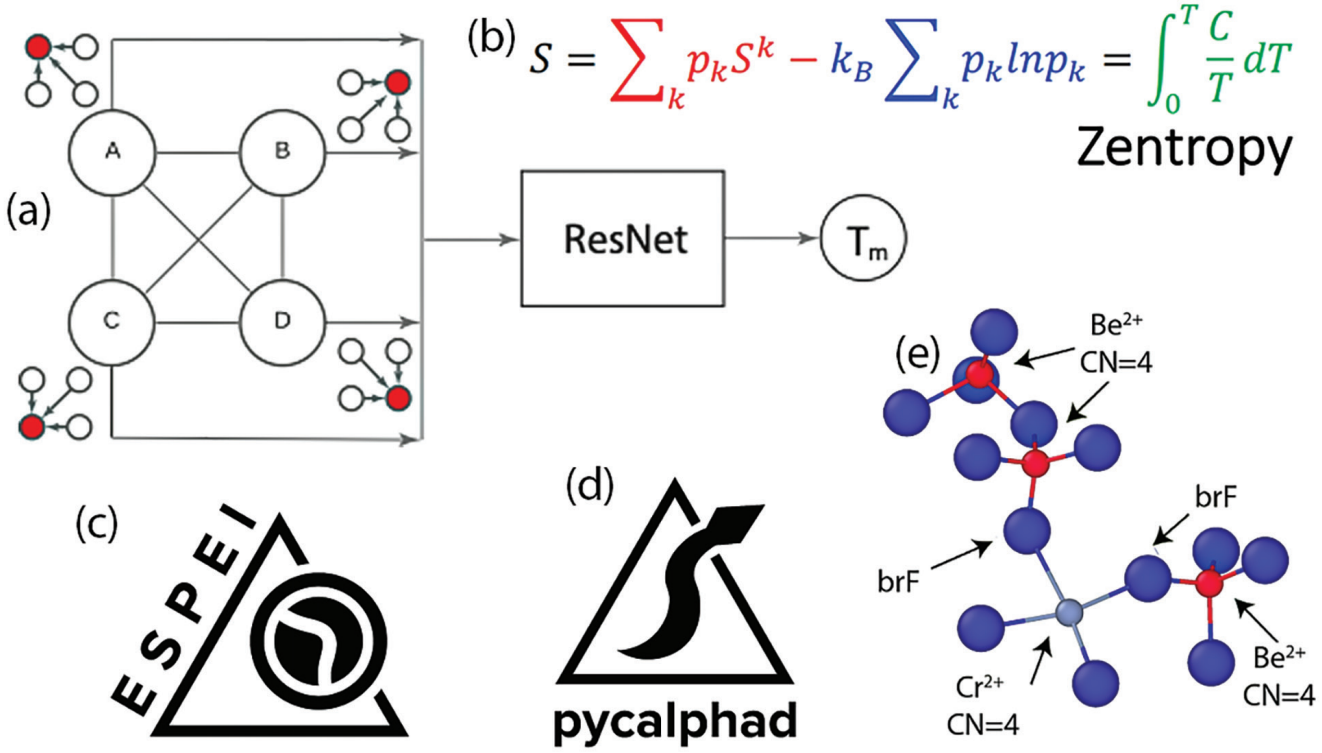


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Figure 3. (a) a graph neural network model for melting temperature prediction,[36] (b) the Zentropy method,[34,35] (c) ESPEI (which uses PyCalphad to develop CALPHAD databases),[37] (d) PyCalphad (which uses the databases for calculations),[38] and (e) molecular dynamics to study chromium in 2LiF-BeF_2.[30] Each figure reproduced with permission from respective journals and/or authors.

frameworks for material property calculations. PyCalphad is a Python library for computational thermodynamics (Fig. 3d),[37] based within the CALPHAD method.[38] ESPEI (Fig. 3c) is a tool for creating and integrating CALPHAD databases,[36] as well as evaluating the uncertainty of CALPHAD models.[37] The Solid and Liquid in Ultra Small Coexistence with Hovering Interfaces (SLUSCHI) package implements the small-cell coexistence method for direct DFT melting temperature calculations.[39,41] All tools and packages are free and open source.

Ensemble models were built to calculate the uncertainty of ML prediction (Fig. 3a) and detect outliers.[42] A manual review helps resolve the two possible causes for each outlier. Either (i) the data point is wrong due to data issues (so we should correct or remove the data point), or (ii) the data point is correct and thus essential to the mapping (so more sampling is needed to anchor the ML model in the vicinity accurately).

In the synthesis of inorganic materials, reactions often lead to unexpected nonequilibrium kinetic products instead of thermodynamic equilibrium phases. Understanding the competition between thermodynamics and kinetics is a fundamental step toward the rational synthesis of target materials. Building a machine learning model for materials synthesizability requires considering all possible reaction pathways[43]; merely the reactant and product are insufficient.

New computational approaches, such as the small-size coexistence method for melting temperature calculations, were built to compute high-temperature materials properties directly from DFT. For example, the Hf–C–N system was computationally predicted to be the material with the world's highest melting temperature based on DFT MD calculations using the SLUSCHI package.[42,44] This discovery was also later confirmed independently from experiments.

Conclusions

The STOHT2 meeting highlighted how current state-of-the-art experimental and computational methods can be incorporated in tandem to study materials at the highest of temperatures.

High-temperature levitation techniques have shown to be indispensable to the study of structural, thermodynamic, and thermophysical properties at high temperatures. DFT combined with MD offers essential data to guide experiments, and after experimental validation, it can provide experimentally inaccessible data to build CALPHAD-type databases.

Although there are many successes, work remains to be done. At high temperatures (>2,500°C), it can be difficult to control the chemical environment and measure the temperature with high accuracy using thermocouples and pyrometers. Ab initio molecular dynamic computations at high temperatures when quasiharmonic approximations in MD start to fail are time and resource demanding. However, the developed packages, such as SLUSCHI, allow automation of DFT melting temperature calculations.

Thermodynamic analysis is especially relevant for high-temperature materials and processes. However, CALPHAD databases for ceramic materials above 2,000°C are very limited and mostly based on experimental data obtained decades ago.

These challenges have led to opportunities. Coupling levitation with lasers and induction heating with high-pressure

chambers offers the possibility to explore high-temperature environments not previously achievable in controlled experiments. The development of hyperbaric aerodynamic and electromagnetic levitation as sample environments on synchrotron and neutron sources can open new vistas for structural characterization of high-temperature materials and provide experimental data for benchmarking computations and building CALPHAD databases.

In addition to commercially available CALPHAD software and databases, the new generation of free open-source software is becoming available, such as ESPEI. This software allows for uncertainty analysis of phase diagrams to be generated using all available experimental and computational data; the building and optimization of CALPHAD-type databases in a top-down manner in addition to the traditional bottom-up approach; and integration with PyCalphad, which allows for the implementation of new models by the users. Such software advances will undoubtedly democratize CALPHAD and will provide faster integration of new experimental and computational data into the models.

Considering both successes and challenges, the high-temperature materials field has a bright future.

Acknowledgements

The authors would like to acknowledge the workshop presenters, the invited speakers, and poster presenters that attended the STOHT2 conference, in addition to the sponsors.

Regarding workshops, Jean-Philippe Harvey (Ecole Polytechnique de Montreal, Canada) presented at the FactSage workshop. Richard Otis (NASA Jet Propulsion Laboratory, Calif.) and Brandon Boucklund (Lawrence Livermore National Laboratory, Calif.) presented at the PyCalphad & ESPEI workshop.

The invited speakers include (in order of presentation) Alexandra Navrotsky (Arizona State University), Richard Weber (Materials Development Inc., Ill.), Chris Benmore (Argonne National Laboratory, Ill.), Shinji Kohara (Tokyo University of Science, Japan), Joerg Neuefeind (Oak Ridge National Laboratory, Tenn.), Maxime Bourdon (Setaram, France), David Lipke (Missouri Science and Technology), Elizabeth Sobalvarro Converse (Lawrence Livermore National Laboratory, Calif.), Gustavo Costa (NASA Glenn, Ohio), Sergey Ushakov (Arizona State University), Shmulik Hayun (Ben-Gurion University of the Negev, Israel), Zi-Kui Liu (The Pennsylvania State University), Philip Spencer (Spencer Group Inc., N.Y.), Jean-Philippe Harvey (Ecole Polytechnique de Montreal, Canada), Heng Wang (Netzsch, Mass.), Qi-Jun Hong (Arizona State University), Wenhao Sun (University of Michigan), Mark Asta (University of California, Berkeley), Elizabeth Opila (University of Virginia), Erica Corral (University of Arizona), Randall Hay (Air Force Research Laboratory, Ohio), Jian Luo (University of California, San Diego), Xiaofeng Guo (Washington State University), Masatomo Yashima (Tokyo Insitute of Technology, Japan), and Hiroyuki Fukuyama (Tohoku University, Japan).

The poster presenters include Stephen Wilke (Materials Development Inc., Ill.), Jakob Trammel (University of Arizona), Dwight Myers (East Central University, Okla.), Manuel Loffler (Institut fur Werkstoffwissenschaft, Germany), Benjamin Brugman (Arizona State University), Manuel Scharrer (Arizona State University), Miguel Bustamante (Arizona State University), Megan Householder (Arizona State University), Shivani Srivastava (University of California, Berkeley), Stuart Ness (University of California, Davis), William Rosenberg (University of California, Davis), Randi Swanson (University of California, Davis), Fox Thorpe (University of California, Davis), Kyle Kondrat (University of California, Davis).

The sponsors include Air Force Office of Scientific Research under contract number FA9550-22-1-0258, Netzsch, FactSage, Spencer Group Inc., Setaram, and Materials Development Inc. Arizona State University provided both staff and financial support through MotU, the Navrotsky Eyring Center for Materials of the Universe.

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References

[1]Costa, G. et al. "Energetics of reactions between ceramic coating materials and their binary oxide components with silicate melts," *Journal of the American Ceramic Society* **105**, 7795–7805 (2022).

[2]Hayun, S., Lilova, K., Salhov, S. & Navrotsky, A. "Enthalpies of formation of high entropy and multicomponent alloys using oxide melt solution calorimetry," *Intermetallics (Barking)* **125**, 106897 (2020).

[3]Goncharov, V. G. et al. "Energetics of oxidation and formation of uranium mononitride," *Journal of Nuclear Materials* **569**, 153904 (2022).

[4]Seidel, A., Soellner, W. & Stenzel, C. "EML—an electromagnetic levitator for the International Space Station," *J Phys Conf Ser* **327**, 012057 (2011).

[5]Paradis, P.-F. & Ishikawa, T. "Surface tension and viscosity measurements of liquid and undercooled alumina by containerless techniques," *Jpn J Appl Phys* **44**, 5082–5085 (2005).

[6]Paradis, P.-F. et al. "Materials properties measurements and particle beam interactions studies using electrostatic levitation," *Materials Science and Engineering: R: Reports* **76**, 1–53 (2014).

[7]Benmore, C. J. & Weber, J. K. R. "Aerodynamic levitation, supercooled liquids, and glass formation," *Adv Phys X* **2**, 717–736 (2017).

[8]Weber, J. K. R. et al. "Aero-acoustic levitation: A method for containerless liquid-phase processing at high temperatures," *Review of Scientific Instruments* **65**, 456–465 (1994).

[9]McCormack, S. J., Tamalonis, A., Weber, R. J. K. & Kriven, W. M. "Temperature gradients for thermophysical and thermochemical property measurements to 3000°C for an aerodynamically levitated spheroid," *Review of Scientific Instruments* **90**, (2019).

[10]Knights, C. F. & Perkins, R. "Levitation melting of uranium monocarbide," *Journal of Nuclear Materials* **39**, 224–225 (1971).

[11]Fukuyama, H., Watanaba, M. & Adachi, M. "Recent studies on thermophysical properties of metallic alloys with PROSPECT: Excess properties to construct a solution model," *High Temperatures-High Pressures* **49**, 197–210 (2020).

[12]Ushakov, S. v., Shvarev, A., Alexeev, T., Kapush, D. & Navrotsky, A. "Drop-and-catch (DnC) calorimetry using aerodynamic levitation and laser heating," *Journal of the American Ceramic Society* **100**, 754–760 (2017).

[13]Haberl, B. et al. "Multi-extreme conditions at the second target station," *Review of Scientific Instruments* **93**, 083907 (2022).

[14]Hong, Q.-J. et al. "Combined computational and experimental investigation of high temperature thermodynamics and structure of cubic ZrO_2 and HfO_2," *Sci Rep* **8**, 14962 (2018).

[15]McCormack, S. J. et al. "In-situ determination of the HfO_2–Ta_2O_5 temperature phase diagram up to 3000°C," *Journal of the American Ceramic Society* **102**, (2019).

[16]Yoshiasa, A. et al. "High-temperature diffraction experiments and phase diagram of ZrO_2 and $ZrSiO_4$," *Zeitschrift für Naturforschung B* **76**, 591–597 (2021).

[17]Ushakov, S. v., Saradhi, P. M., Navrotsky, A., Weber, R. J. & Benmore, C. J. "Study of $La_2Zr_2O_7$ and $La_2Hf_2O_7$ melting by thermal analysis and X-ray diffraction," *ECS Meeting Abstracts* **MA2012-02**, 2329 (2012).

[18]Converse, E. et al. "In-situ high temperature spatially resolved X-ray diffraction of TiB_2 up to ~3050°C," *J Eur Ceram Soc* (2023).

[19]Benmore, C. J. & Weber, J. K. R. "Aerodynamic levitation, supercooled liquids and glass formation," *Adv Phys X* **2**, 717–736 (2017).

[20]Weber, J. K. R., Benmore, C. J., Jennings, G., Wilding, M. C. & Parise, J. B. "Instrumentation for fast in-situ X-ray structure measurements on non-equilibrium liquids," *Nucl Instrum Methods Phys Res A* **624**, 728–730 (2010).

[21]Kohara, S. et al. "Atomic and electronic structures of an extremely fragile liquid," *Nat Commun* **5**, 5892 (2014).

[22]Gallington, L. et al. "The structure of liquid and amorphous hafnia," *Materials* **10**, 1290 (2017).

[23]Yashima, M., Kobayashi, S. & Yasui, T. "Positional disorder and diffusion path of oxide ions in the yttria-doped ceria $Ce_{0.93}Y_{0.07}O_{1.96}$," *Faraday Discuss* **134**, 369–76; discussion 399-419 (2007).

[24]Golden, R. A. & Opila, E. J. "A method for assessing the volatility of oxides in high-temperature high-velocity water vapor," *J Eur Ceram Soc* **36**, 1135–1147 (2016).

[25]Miller-Oana, M. et al. "Oxidation behavior of aerospace materials in high enthalpy flows using an oxyacetylene torch facility," *Journal of the American Ceramic Society* **98**, 1300–1307 (2015).

[26]Wang, C. et al. "A general method to synthesize and sinter bulk ceramics in seconds," *Science (1979)* **368**, 521–526 (2020).

[27]Nie, J., Hu, C., Yan, Q. & Luo, J. "Discovery of electrochemically induced grain boundary transitions," *Nat Commun* **12**, 2374 (2021).

[28]Luo, J. "Developing interfacial phase diagrams for applications in activated sintering and beyond: Current status and future directions," *Journal of the American Ceramic Society* **95**, 2358–2371 (2012).

[29]Ushakov, S. v. & Navrotsky, A. "Experimental approaches to the thermodynamics of ceramics above 1500°C," *Journal of the American Ceramic Society* **95**, 1463–1482 (2012).

[30]Winner, N., Williams, H., Scarlat, R. O. & Asta, M. "Ab-initio simulation studies of chromium solvation in molten fluoride salts," *J Mol Liq* **335**, 116351 (2021).

[31]Spencer, P. "Development of a thermodynamic database for refractory boride, carbide, nitride, and silicide systems," in *Contributed Papers from MS&T17* 1230–1238 (MS&T17, 2017). doi:10.7449/2017/mst_2017_1230_1238.

[32]Pham, D. et al. "Thermodynamic assessment within the Zr-B-C-O quaternary system," *Journal of the American Ceramic Society* (2022) doi:10.1111/jace.18958.

[33]Harvey, J.-P., Gheribi, Ä. E., Rincent, A., Jofré, J. & Lafaye, P. "On the elaboration of the next generation of thermodynamic models of solid solutions," *Physical Chemistry Chemical Physics* **22**, 19999–20013 (2020).

[34]Liu, Z.-K., Wang, Y. & Shang, S.-L. "Zentropy theory for positive and negative thermal expansion," *J Phase Equilibria Diffus* **1–8** (2022) doi:10.1007/s11669-022-00942-z.

[35]Liu, Z.-K. "Theory of cross phenomena and their coefficients beyond Onsager theorem," *Mater Res Lett* **10**, 393–439 (2022).

[36]Hong, Q.-J., Ushakov, S. v., van de Walle, A. & Navrotsky, A. "Melting temperature prediction using a graph neural network model: From ancient minerals to new materials," *Proceedings of the National Academy of Sciences* **119**, e2209630119 (2022).

[37]Bocklund, B. et al. "ESPEI for efficient thermodynamic database development, modification, and uncertainty quantification: application to Cu–Mg," *MRS Commun* **9**, 618–627 (2019).

[38]Otis, R. & Liu, Z.-K. "PyCalphad: CALPHAD-based Computational Thermodynamics in Python," *J Open Res Softw* **5**, 1 (2017).

[39]Adachi, M. et al. "Temperature dependence of crystal growth behavior of AlN on Ni–Al using electromagnetic levitation and computer vision technique," *Mater Sci Semicond Process* **153**, 107167 (2023).

[40]Lu, H. et al. "Particle surface temperature measurements with multicolor band pyrometry," *AIChE Journal* **55**, 243–255 (2009).

[41]Hong, Q.-J. & van de Walle, A. "A user guide for SLUSCHI: Solid and Liquid in Ultra Small Coexistence with Hovering Interfaces," *Calphad* **52**, 88–97 (2016).

[42]Hong, Q.-J., van de Walle, A., Ushakov, S. v. & Navrotsky, A. "Integrating computational and experimental thermodynamics of refractory materials at high temperature," *Calphad* **79**, 102500 (2022).

[43]Miura, A. et al. "Observing and modeling the sequential pairwise reactions that drive solid-state ceramic synthesis," *Advanced Materials* **33**, 2100312 (2021).

[44]Hong, Q.-J. & van de Walle, A. "Prediction of the material with highest known melting point from ab initio molecular dynamics calculations," *Phys Rev B* **92**, 020104 (2015). ■