

Author Manuscript

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1111/jace.14881](https://doi.org/10.1111/jace.14881)

This article is protected by copyright. All rights reserved

PROF. KATHERINE T FABER (Orcid ID : 0000-0001-6585-2536)
DR. BILL FAHRENHOLTZ (Orcid ID : 0000-0002-8497-0092)
PROF. NITIN P PADTURE (Orcid ID : 0000-0001-6622-8559)
DR. CLIVE ALAN RANDALL (Orcid ID : 0000-0002-5478-2699)
PROF. HONG WANG (Orcid ID : 0000-0003-3991-6203)

Received Date : 01-Feb-2017
Revised Date : 27-Feb-2017
Accepted Date : 28-Feb-2017
Article type : Feature Article

The Role of Ceramic and Glass Science Research in Meeting Societal Challenges: Report from an NSF-Sponsored Workshop

Katherine T. Faber,^{a,#} Tewodros Asefa,^b Monika Backhaus-Ricoult,^c Richard Brow,^d Julia Y. Chan,^e Shen Dillon,^f William G. Fahrenholtz,^d Michael W. Finnis,^g Javier E. Garay,^h R. Edwin García,ⁱ Yury Gogotsi,^j Sossina M. Haile,^k John Halloran,^l Juejun Hu,^m Liping Huang,ⁿ Steven D. Jacobsen,^o Edgar Lara-Curzio,^p James LeBeau,^q William E. Lee,^g Carlos G. Levi,^r Igor Levin,^s Jennifer A. Lewis,^t Don M. Lipkin,^u Kathy Lu,^v Jian Luo,^w Jon-Paul Maria,^q Lane W. Martin,^x Steve Martin,^y Gary Messing,^z Alexandra Navrotsky,^{aa} Nitin P. Padture,^{bb} Clive Randall,^z Gregory S. Rohrer,^{cc} Anatoly Rosenflanz,^{dd} Tobias A. Schaedler,^{ee} Darrell G. Schlom,^{ff} Alp Sehriroglu,^{gg} Adam J. Stevenson,^{hh} Toshihiko Tani,ⁱⁱ Veena Tikare,^{jj} Susan Trolier-McKinstry,^z Hong Wang,^{kk} and Bilge Yildiz^{m,ll}

^a Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125; Email: ktfaber@caltech.edu

^b Department of Chemistry and Chemical Biology & Department of Chemistry and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854

^c Corning Incorporated, Crystalline Materials Research, Corning, NY 14835

^d Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65409

^e Department of Chemistry, University of Texas, Dallas, TX 75080

^f Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801

^g Department of Materials, Imperial College, London, SW7 2AZ, United Kingdom

^h Department of Mechanical and Aerospace Engineering, University of California San Diego, San Diego, CA 92093

ⁱ School of Materials Engineering, Purdue University, West Lafayette, IN 47907

^j Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104

^k Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208

¹ Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109

^m Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

ⁿ Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180

^o Department of Earth and Planetary Sciences, Northwestern University, Evanston, IL 60208

^p High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge, TN 37830

^q Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695

^r Materials Department, University of California, Santa Barbara, Santa Barbara, CA 93106

^s Materials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

^t John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138

^u GE Global Research, General Electric, Niskayuna, NY 12309

^v Department of Materials Science and Engineering, VirginiaTech, Blacksburg, VA 24061

^w Department of NanoEngineering, University of California San Diego, San Diego, CA 92093

^x Department of Materials Science and Engineering, University of California Berkeley, Berkeley, CA 94720

^y Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011

^z Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802

^{aa} Department of Chemical Engineering and Materials Science, University of California Davis, Davis, CA 95616

^{bb} School of Engineering, Brown University, Providence, RI 02912

^{cc} Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213

^{dd} Corporate Research Materials Laboratory, 3M Company, St. Paul, MN 55144

^{ee} HRL Laboratories, Malibu, CA 90265

^{ff} Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853

^{gg} Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH 44106

^{hh} Laboratoire de Synthèse et Fonctionnalisation des Céramiques, UMR3080 CNRS/Saint-Gobain, Saint-Gobain CREE, Cavaillon 84306 France

ⁱⁱ Toyota Central R&D Labs, Inc., Aichi, 480-1192, Japan

^{jj} Sandia National Laboratories, Albuquerque, NM 87185

^{kk} State Key Laboratory for Mechanical Behavior of Materials & School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, China

^{ll} Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

Abstract

Under the sponsorship of the U.S. National Science Foundation, a workshop on emerging research opportunities in ceramic and glass science was held in September 2016. Reported here are proceedings of the workshop. The report details eight challenges identified through workshop discussions: Ceramic Processing: Programmable Design and Assembly; The Defect Genome: Understanding, Characterizing and Predicting Defects across Time and Length Scales; Functionalizing Defects for Unprecedented Properties; Ceramic Flatlands: Defining Structure-Property Relations in Free-standing, Supported, and Confined Two-dimensional Ceramics; Ceramics in the Extreme: Discovery and Design Strategies and Behavior of Multi-material Systems; Understanding and Exploiting Glasses and Melts under Extreme Conditions; and Rational Design of Functional Glasses Guided by Predictive Modeling. It is anticipated that these challenges, once met, will promote ~~our~~ basic understanding and ultimately enable advancements within multiple sectors, including energy, environment, manufacturing, security and healthcare.

I. Introduction

Given the ever-increasing pace of innovation in the 21st century, the U.S. National Science Foundation (NSF) sponsored a workshop, held in September 2016, to identify emerging research areas in ceramic and glass science. The meeting brought together 42 researchers in glass and ceramic materials from the U.S. and abroad to share both their expertise and vision in defining outstanding materials challenges. Participants from academia, industry, and national laboratories were chosen to represent four material classes: amorphous materials, oxides, non-oxides, and composites. In preparation for the meeting, participants suggested topics for consideration. From these ideas the workshop co-organizers, Katherine Faber, Jennifer Lewis, Clive Randall and Gregory Rohrer, defined five themes for discussion: Ceramic Processing Science, Defect-

Enabled Phenomena, Low-Dimensional Phenomena, Ceramics for Extreme Environments, and Glasses and High Entropy Materials. These topics formed the basis of workshop presentations and breakout discussions in which challenges were formulated and shared with the entire workshop attendance. In addition, strategies of data mining were explored as a tool for identifying new areas of study and opportunities for crosscutting research.¹

NSF had sponsored two prior workshops to identify and accelerate emerging research strategies in ceramics. The first assembly, “Future Research Needs in Ceramics,” co-organized by Yet-Ming Chiang and Karl Jakus, was held at NSF headquarters in June 1997.² More recently, a workshop chaired by Gregory Rohrer and held in March 2012, highlighted eight challenges for the ceramic and glass communities in its report, “Challenges in Ceramic Science: A Report from the Workshop on Emerging Research Areas in Ceramic Science”³. Although less than five years elapsed since the previous meeting, it is well established that materials development cycles are shortening. This is frequently described in graphs of accelerating waves of innovation, first noted by economist Joseph Schumpeter. This notion gained popularity in publications like *The Economist*⁴, where the six waves of innovation since the Industrial Revolution are depicted, each with decreasing period, but with increasing amplitude meant to imply greater complexity of innovation.⁵ The sixth and current wave includes sustainability, biomimicry, renewable energy and green nanotechnology, all of which rely on materials innovation.

Reported here are eight challenges reached by consensus during workshop discussions, each describing the fundamental science required to forward ~~our~~ basic understanding of ceramics and glasses and enable advances in, among others, energy, environment, manufacturing, security and healthcare:

1. Ceramic Processing: Programmable Design and Assembly
2. The Defect Genome: Understanding, Characterizing and Predicting Defects across Time and Length Scales
3. Functionalizing Defects for Unprecedented Properties
4. Ceramic Flatlands: Defining Structure-Property Relations in Free-standing, Supported, and Confined Two-dimensional Ceramics
5. Ceramics in the Extreme: Discovery and Design Strategies
6. Ceramics in the Extreme: Behavior of Multi-material Systems
7. Understanding and Exploiting Glasses and Melts under Extreme Conditions
8. Rational Design of Functional Glasses Guided by Predictive Modeling

A common thread through these challenges is the importance of computational materials science through efforts such as integrated computational materials engineering (ICME)⁶ for the design of new ceramic materials and prediction of properties. Examples in the design of complex oxides for electronic devices⁷ and superionic conductors⁸ provide evidence of advancements in the field. However, the use of these techniques for highly defective structures, ultra-high temperature materials, or complex, multi-component amorphous materials is sparse. A second overarching need is the advancement of probes necessary to characterize and visualize materials at smaller length scales, e.g., a single atomic defect, and at higher temperatures and pressures, e.g., at $T > 2000^\circ\text{C}$. Each challenge is described in detail below following the reports of the five sub-groups.

II. Ceramics Processing Science

The ability to programmably design and assemble ceramics would enable unprecedented mechanical, electrical, thermal and other properties. Several novel routes have emerged for precisely controlling the composition and structure of ceramics over multiple length scales, including guided colloidal assembly⁹⁻¹⁸ and 3D printing methods¹⁹⁻³⁷. When those are combined with techniques, such as atomic layer deposition and “cold sintering”, ceramics can be seamlessly integrated with polymers (or metals) that melt at low temperatures. A new ceramics processing paradigm that links multi-scale modeling with computer aided design and assembly is needed to fully exploit the broadening palette of materials, architectures, and fabrication strategies.

Challenge #1: Ceramic Processing: Programmable Design and Assembly

Ceramics processing methods uniquely involve several states of matter: dry powders, colloidal suspensions and gels, green and sintered bodies. Unfortunately, the constitutive behavior of each of these states is imperfectly known. Multi-scale modeling to optimize material composition, microstructure, and topology coupled with the ability to realize those designs, offer the potential to create ceramic-based constructs with extraordinary performance. Modeling and simulation research must be directed towards understanding the transformation of initial building blocks, both colloidal particles and other constituents, into sintered bodies that give rise to the properties of interest.

Multi-scale modeling spans length scales ranging from atomistic to the mesoscale. Density functional theory (DFT) electronic structure calculations have received considerable attention as part of the Materials Genome Initiative with the aim of discovering new ceramics and their properties^{38,39}. DFT can be used to generate quantum-accurate potentials for atomic scale simulations^{40,41}, to model interfacial structure, energies and the stability of nanoscale features.

New automated techniques can generate accurate potentials when combined with DFT methods, and inform the design of the complex interfaces that are anticipated with the advanced architectures of heterogeneous materials⁴²⁻⁴⁴. They can also provide mechanistic understanding of materials processes such as diffusion, interface mobilities and phase transitions. Mesoscale modeling, predominantly phase-field⁴⁵ and Potts kinetic Monte Carlo models⁴⁶, can treat microstructure and its evolution at processing temperatures of interest under different energy fields when applicable. However, models to assess engineering properties from ceramics microstructures are immature, as they typically have to incorporate the variation in microstructural features, making for very large simulations, or need to combine simulations spanning multiple scales, requiring new methods to couple models at different length scales^{47,48}. To programmably generate ceramic-based architectures with optimized composition and structure across multiple length scales, one must know what features are desirable and then use this input to deterministically guide the assembly process.

By harnessing forces ranging from weak van der Waals to external electromagnetic fields, one can guide colloidal self-assembly in two- and three-dimensions to create novel architectures with as yet unexplored properties. Two-dimensional assembly of nanosheets into superlattice structures guided by weak van der Waals forces yield completely new architectures and material combinations^{9,10}. DNA-coated particles^{11,12} and Janus rods coated with hydrophobic patches form “atom-like” building blocks¹³ that can be assembled into 3D architectures (**Figure 1**). Photoresponsive dispersants enable creation of colloidal suspensions that can be switched on demand from a fluid to gel state upon exposure to UV light.¹⁴ With further synthetic advances, new classes of shape and chemically anisotropic particles with engineered interactions that guide self-assembly can be realized.

Beyond those strategies, external fields are also being exploited to guide colloidal assembly. For example, electric fields applied to colloid dispersions can structure particles by electrophoresis and dielectrophoresis^{15,16}. Magnetic fields can be used to orient ferroelectric particles for templated grain growth.¹⁷ Importantly, even diamagnetic colloidal particles can be oriented under very high magnetic fields to produce textured ceramics.¹⁸ However, to harness external fields to locally “write microstructure” in a predictive manner, ~~we must develop~~ a deeper understanding ~~must be developed~~ of how particle dynamics, structure, and assembly are influenced by applied external fields both in the absence and within complex molds that define their final shape. With these capabilities in hand, new classes of crystallographically tailored, polycrystalline ceramics that exhibit single crystal-like properties could be realized in a highly scalable manner.

Additive manufacturing methods, such as robocasting¹⁹⁻²¹ or stereolithography²²⁻²⁷, enable patterning of concentrated colloidal suspensions and photopolymerizable resins. For example, robocasting, also known as direct ink writing, has been used to produce lithium ion microbatteries composed of high aspect ratio, interdigitated electrodes²⁸ (**Figure 1**) as well as 3D periodic lattices²¹. New advances in colloidal suspension design, such as biphasic mixtures composed of attractive and repulsive colloidal particles²⁹, coupled with the implementation of active mixing and switching microfluidic printheads^{30,31}, would further accelerate the compositional and architectural complexity realizable by this technique.

New cellular ceramics can be fabricated by light-based 3D printing of pre-ceramic monomers, nanoparticle-filled or pure resins²²⁻²⁷. For example, non-oxide cellular ceramics that are virtually pore-free are produced by patterning a preceramic monomer resin using stereolithography followed by high temperature pyrolysis (**Figure 1**)²². However, fundamental challenges remain

to both understand and optimize the pyrolysis process to enable incorporation of fibers or active fillers within these printed architectures. Nanoparticle-filled and pure polymer structures in the form of octet trusses and other novel geometries have recently been constructed by these methods^{25,27}. In the latter case, the structures serve as sacrificial templates, which are coated with a thin layer of Al₂O₃, SiO₂ or other materials via processes such as atomic layer deposition (ALD) or chemical vapor deposition (CVD) prior to template removal to achieve cellular ceramics with exceptional strength and stiffness at ultra-low densities^{24-27,32}. This approach essentially allows one to transform 2D thin “films” into 3D cellular materials. While considerable research has been carried out to understand the structure-property relations of thin film ceramics, the mechanical properties of freestanding 3D “film-based” architectures require rigorous study.

The densification of ceramics by high temperature sintering has been the status quo for millennia. Recently, a new paradigm for sintering has been introduced, known as cold sintering³⁴⁻³⁶. It is now possible to densify ceramic green bodies at temperatures as low as 25°C to 300°C via a transient liquid phase (e.g., water). This nascent method offers the potential to heterogeneously integrate ceramics with disparate materials that would otherwise melt, decompose, or react, including ceramic-polymer (**Figure 1**) and ceramic-metal composites. To date, new dielectric materials, ionic electrolytes, and semiconducting composites and multilayers have been densified by cold sintering³⁴⁻³⁶. However, despite its significant promise, little is known about the fundamental mechanisms and limitations of this new approach.

The major progress in colloidal science, guided self-assembly, coating methods, and 3D printing, coupled with cold sintering, offers new opportunities to design and integrate dissimilar materials that were previously unimaginable. By establishing a new ceramics processing

paradigm, new materials will be created with unique combinations of matter, architecture, and properties that require fewer trade-offs. For example, it is well known that important functional and structural properties of porous materials are inversely related³⁷, i.e., their permeability, specific surface area, and corrosion rates tend to increase with increasing porosity, while their strength, creep resistance, and thermal conductivity decrease. The ability to optimize the topology and programmably fabricate multifunctional porous ceramics that combine both high strength and permeability would impact a myriad of applications, including anode-supported fuel cells and asymmetric oxygen-separation membranes. Limiting barriers imposed by similar properties trade-offs that exist across the spectrum of ceramic applications may also be overcome by this approach with appropriate transition and linkage to manufacturing engineering.

[Insert Figure 1]

Figure 1. Recent advances in ceramics processing science. From left to right: Optical image of the guided self-assembly of colloidal SiO₂ rods (~2.2 μm in length and 1.1 μm in diameter) coated on one end with a hydrophobic metallized tip (black) [Inset: Tetrahedral “atom-like” cluster composed of four rods.]¹³ (Reprinted with permission, American Chemical Society); Optical image of a lithium ion microbattery composed of 3D printed, interdigitated cathode (LFP, dark) and anode (LTO, white) high aspect ratio features²⁸ (Reprinted with permission, Wiley); SiOC microlattice fabricated by stereolithography of a preceramic monomer solution; and Multilayer thermoelectric device obtained by cold sintering at 250°C that integrates n-type ZnO, p-type Ca₃Co₄O₉, and polytetrafluoroethylene, a thermoplastic insulating material.

III. Defect-Enabled Phenomena

A defect in a material is most commonly defined as a disruption to the periodicity of its crystalline organization, i.e., a structural anomaly, or its composition, i.e., chemical irregularity. As compared to metals and semiconductors, defects in ceramics are distinguished by the additional constraints and levers of electrostatics: global charge neutrality must be preserved in the bulk^{49,50}. Structural anomalies have long played defining roles in the properties of ceramics and, in many cases, have been enabled through electrostatic considerations. In the most generalized view, point defects (e.g, vacancies, interstitials) determine transport characteristics; linear defects (dislocations) establish strain relaxation behavior; planar defects (e.g., domain and grain boundaries) govern ferroelastic, piezo- and ferroelectric response; and volume defects (e.g., secondary phases) regulate mechanical properties. Moreover, not only is the physical dimensionality of the defect relevant to its function, but also factors such as defect concentration, association configurations and dissociation interactions, length scale, and even time scale of interaction are critically important to the macroscopic material behavior. Thus, structural anomalies in ceramics exist over a complex, multi-dimensional space, **Figure 2**, and from these, opportunities emerge for precise control of material properties in both highly studied and largely overlooked regions of this space.

In this context, two challenges emerge. The first is to understand, characterize, and predict defect populations and distributions in ceramics as they exist within the phase-space of **Figure 2**. Given the fact that defects can perturb properties over orders of magnitude, success here will lead to the emergence of a “defect genome”, which will complement the materials genome for comprehensive materials design. A second challenge is to go beyond the passive characterization of defects and move to their controlled creation and towards the functionalization of these

defects. This may be achieved in particular through the control of defect-defect interactions. Such defect functionalization is expected to yield materials with unprecedented response to applied stimuli, including electrical, magnetic or optical drivers. To address both challenges, advances in defect visualization and direct characterization arise as a pressing need.

Challenge #2: The Defect Genome: Understanding, Characterizing and Predicting Defects

Across Time and Length Scales

Many of the desirable functional properties of ceramics depend on defect populations and their character. New classes of ceramic materials are envisioned, from those containing very few, precisely located, isolated anomalies to others containing extremely large defect densities that, for example, drive formation of unexpected, entropy-stabilized phases and associated emergent phenomena. Application of “stressors”, either during or after synthesis, will generate dynamic defect response that can be further manipulated for material design and property control.

In the following, a few examples illustrate critical needs to fully exploit the capabilities of current ceramics and point to new challenges in recently discovered ceramics:

Existing, simple point defect chemistry models (see textbooks^{49,50}) rapidly reach their limits when confronted with high defect concentrations, strong defect interactions⁵¹, dislocations^{52,53} or interfaces⁵⁴. Similarly, difficulties are encountered when trying to discern defect behavior far from thermodynamic equilibrium or under complex configurations of thermal gradient, stress, electrical field, or magnetic field. In most cases, point defect thermodynamic models have not yet been sufficiently developed. In the past, the required system size has exceeded in size and/or complexity the computational possibilities. Preliminary efforts have attempted to capture the interplay between anti-site defects and phase formation⁵⁵, and between electrical field, stress and

defect distribution⁵⁶. Further efforts in this direction are needed, especially those targeting dynamic system response⁵⁷.

Interaction and motion of higher dimensionality defects remain a challenge for predictive modeling and for phenomenological description. Even though motion of domain walls in ferroelectrics has been known for many years, the relevant processes are poorly understood. Several key needs emerge: (i) developing a formalism that describes long range electromechanical coupling in polycrystalline ceramics⁵⁸, including grain – to – grain and domain – to – domain coupling, (ii) enabling the theoretical framework for experimental data sets that describes the interaction of dynamic domain walls with pinning sites and various types of grain boundaries⁵⁹ and explains cascaded motion of domain walls⁶⁰, (iii) establishing processes to reliably turn domain wall motion on and off in ferroelectric materials to optimize figures of merit for particular applications, (iv) making progress towards controlled processing/generation of defect concentrations in films⁶¹, (v) characterizing the role of defects on properties across multiple length scales.

Mixed-oxide materials with configurational disorder made by populating a single sublattice with a variety of different cations have been found to exhibit unexpected crystal symmetry and high material stability⁶². This structural and chemical complexity, in which multiple types of metal cations are ‘stuffed’ into a structure, creates a highly defective, engineered material and a potential route to exceptional properties. In some cases, the resulting oxides display extremely delayed phase transitions and melting. Existing frameworks for understanding the stability of such ceramics are largely based on ionic size and charge approaches; first-principles calculations would build fundamental understanding and enable the synthesis of designed materials.

Progress in modern thin-film growth and control of growth processes has ushered in an era in which ~~we can synthesize~~ materials ~~can be synthesized~~ from the bottom up, using various designed building blocks, for example atomic layers, bilayers or block units. It is generally assumed that the individual building block chemistry and the global architecture determine the final material properties; and, in many cases, little attention is paid to defects and their interactions. Several efforts have leveraged synthesis by design in recent years, for example 3D thermoelectric materials that use building blocks to decouple electric and phonon conduction⁶³⁻⁶⁵, memristive switches that gain their functionality from localized reversible, reproducible redox reactions^{66,67}, emergent devices with 2D interfacial properties in layered structures⁶⁸⁻⁷¹. For each of these examples, an implicit control of defect structure is supporting or even driving the desired effects. Embracing these considerations for assembled structures, including defect engineering as an additional design parameter, processing ~~dial-able~~²² ~~tunable~~ defect structures will open access to a new range of materials and phenomena. So far, these approaches remain relatively underdeveloped; however, there is potential for considerable progress, if defects can be harnessed in this manner⁷². Key challenges and opportunities go beyond traditional chemical synthesis and focus either on establishing the desired defects in situ during the synthesis⁷³ or controlling ex situ the production of specific defect types and densities at selected sites^{74,75}. For controlled thin film synthesis, questions arise about the possibility of using the Vegard strains that result from defect production during film growth to induce changes locally in the lattice and the associated local properties^{76,77}.

Interface defect chemistry changes in response to “stressors” from the environment, including elevated temperatures, gas pressure, electrochemical potential, electric field and mechanical stress. Experimental and modeling efforts have started to develop formalisms for the

defect structure and chemistry of (2D) grain boundaries, surfaces and interfaces, and captured surface and grain boundary reconstruction in thermodynamic equilibrium situations⁷⁸. Improved understanding of dynamic interfaces, such as oxygen exchanging electrodes^{79,80} or oxide catalysts supporting chemical synthesis, has been gained by operando imaging and spectroscopy⁸¹ and supported by simple models⁸². However, to date it has not been possible to fully model these highly driven systems due to their size, complexity and intricate boundary conditions. More extended predictive simulation of oxide interfaces under complex drivers and at extended spatial and time scales requires further progress in computing, including both, higher performance supercomputers and novel computational methods to extend time scales⁸³ and spatial scales⁸⁴ to the ranges that address interface behavior and its evolution. Progress in computational tools is expected to enable better prediction and help to build fundamental understanding of dynamic interfaces under various stressors and for various technologies.

Li- or Na-ion conducting solid electrolytes for battery applications have significant advantages over liquid electrolytes, such as higher stability, higher transference numbers, and lack of dendrite formation⁸⁵. While a framework for tuning and optimizing the defect chemistry is available for crystalline electrolytes, it is not the case for ionic conducting glasses, where understanding of order and its evolution are missing. On the other hand, non-crystalline electrolytes generally display higher conductivity than their crystalline counterparts. This contradictory situation suggests that extending ~~our~~the understanding of glassy electrolytes, likely through atomistic level simulations, may provide tremendous pay-off in both classes of conductors. Such understanding may even encourage the consideration of new classes of materials, such as composite systems or partially crystalline glasses.

Low temperature ceramics synthesis approaches, as highlighted in Challenge #1, have been reported that use “fluxes” and drive dissolution/recrystallization-based densification at very low temperatures³⁴⁻³⁶. It is not clear, if the resulting ceramics have similar properties as those processed by high temperature sintering; and it may be necessary to study in detail the nature of the defects introduced by “flux”-supported synthesis, understand the mechanisms and extract possible levers.

Along with appropriate theoretical and computational techniques, the defect genome will complement the materials genome for comprehensive materials design. Computational capacity and speed have grown steadily over the past years; in addition, more and more multi-scale approaches and parallel networking tools have been developed, which will soon allow treatment of larger and more complex systems and address the above questions.

Challenge #3: Functionalizing Defects for Unprecedented Properties

Although functionality of defects is exploited in materials, the idea of engineered functionalization with spatial and time resolution to drive homogeneous properties, as well as device capabilities, has received far less attention. Accordingly, fewer specific examples are available of how this approach can enhance materials performance. Nevertheless, some intriguing possibilities can be envisaged. For example, deep trap states in wide band gap dielectrics have been shown to reduce electrical losses under applied field excitation⁸⁶. Can this approach be generalized such that defects become a source of material stability and functionality? Can benign defects be used to trap deleterious ones? This would be a source of ‘engineered reliability.’ Functionality may also arise via defect-defect interactions. For example, the motion of one defect could trigger the motion of many others, giving rise to cascaded motion.

In another example, in this case already demonstrated, extended defects, such as hetero-interfaces or dislocations, can influence the distribution of point defects that can, in turn, alter local properties⁸⁷. This type of emergent behavior would result in materials with exceptionally high response to the application of a given stimuli.

Defect-defect interactions further hold the potential for emergence of neuromorphic properties, resulting from the existence of multiple, reconfigurable interacting states. What kind of defect structures, if any, would lead to such properties, how would ~~we create them~~ they be created, and how would ~~we ensure~~ the appropriate time and length scales for interaction be ensured? These are intriguing questions that arise when one recognizes defects as features that can be leveraged for accessing material behavior not possible via a static, periodic arrangement of atoms.

To achieve the goals outlined above – the development of a defect genome and the functionalization of defects as toolkits for materials design – will require comprehensive understanding of relevant defect interactions, defect dynamics, and defect-property relations. Imaging and spectroscopy techniques essential for gaining this understanding have been tremendously improved over the past few years. In particular, in situ and operando direct defect analysis in realistic environments has been achieved in many settings. For example, aberration corrected (scanning) transmission electron microscopy (STEM) now provides accurate and precise quantification of atom positions directly in real-space^{88,89}, the capability to count atoms by comparing experiment and theory⁹⁰ and the ability to map chemistry at the atomic scale with electron energy loss and X-ray spectroscopies⁹¹. This progress allows direct identification and quantification of defects in terms of both their atomic and electronic structures⁹². Furthermore, recent in situ (scanning) transmission electron microscopy and scanning tunneling microscopy

techniques (STM) advances have enabled the direct tracking the material evolution as a function of time and environmental variables⁹³. For example, surface reconstructions can be directly observed in cross-section by transmission electron microscopy (TEM) and atop surface by STM during heating or catalytic/electrochemical reactions⁹⁴. At the same time, other techniques, such as high resolution phase-resolved tomography, neutron scattering, nuclear magnetic resonance (NMR), electron spin resonance (ESR), Raman, infrared (IR), Positron lifetime annihilation spectroscopy, and surface spectroscopies have also made tremendous strides in the past decade, some techniques even allowing operando observation⁹⁵⁻⁹⁷. In combination, these new tools offer opportunities to connect the behavior of defects in ceramics and their impact on properties across length and time scales.

[Insert Figure 2]

Figure 2: Defects are critical for ceramic applications. From point^{98,99} to planar^{100,101} to bulk¹⁰² defects, modern ceramic systems rely upon exacting and careful control of these features to ensure operation and performance in applications¹⁰³⁻¹⁰⁷. Looking towards the future, deterministic control of these defects and even formation of designed meso-structures based on defects are expected to enable new phenomena and better performance. From top left to right: STM images of the $c(4\times 2)$ reconstructed surface of SrTiO_3 ⁹⁸ (Reprinted with permission, Elsevier); An HRTEM image of dislocation loops in a high-temperature irradiated SrTiO_3 crystal⁹⁹ (Reprinted with permission, Elsevier); Bright-field STEM image of a $\text{Sr}_7\text{Ti}_6\text{O}_{19}$ epitaxial film grown on (110) DyScO_3 ¹⁰⁰ (Reprinted with permission, Nature Publishing Group); SEM micrograph of an interface delamination crack for 8% Y_2O_3 partially stabilized ZrO_2 thermal barrier ceramic coating on NiCrAlY subjected to six thermal fatigue cycles¹⁰¹ (Reprinted with

permission, ASME); local thermal dielectric breakdown events (dark spots) linked to mechanical breakdown events in a piezoelectric film.

IV. Low-Dimensional Phenomena

Two-dimensional structures create opportunities – and challenges – that are distinct from one-dimensional or three-dimensional materials. In particular, their high anisotropy in mechanical, electrical and transport properties lead to both novel scientific phenomena and unique functional and structural capabilities. The current scientific excitement about phenomena in exotic two-dimensional materials is exemplified by the 2016 Nobel Prize in physics (Thouless, Haldane, and Kosterlitz) that recognizes the use of concepts in topology to explain, among other things, phase and property transitions in two-dimensional materials. The materials that embody the current challenge span free-standing materials, surfaces and supported layers, and materials confined at interfaces and grain boundaries, as illustrated in Figure 3. ~~Our~~The challenge is to define structure-property relations for these materials.

[Insert Figure 3]

Figure 3. Schematic representations and micrographs of real two-dimensional ceramics. (a) Free-standing layer; (b) plan view TEM of single layer h-BN¹⁰⁸ (Reprinted with permission, AAAS); (c) supported layer; (d) transverse TEM image of a vanadia layer on TiO₂¹⁰⁹ (Reprinted with permission, AIP); (e) confined layer; and (f) TEM of grain boundary complexion (Nd bilayer between alumina grains)¹¹⁰ (Reprinted with permission, Elsevier).

Challenge 4: Ceramic Flatlands: Defining Structure-Property Relations in Free-standing, Supported, and Confined Two-dimensional Ceramics

It has been known for decades that it is possible to delaminate or exfoliate layered crystals into two-dimensional sheets a few atoms thick.¹¹¹ However, there has been a recent growth of research in this area and the range of materials available has grown enormously.¹¹² Among the ceramics that can be produced in single layer form are clays¹¹³, hydroxides¹¹⁴, oxides¹¹⁵, h-BN¹¹⁶, and transition metal carbides.¹¹⁷ Most of these materials have a van der Waals gap between the separable layers. In some cases, the materials can be exfoliated in solution simply by sonication. In other cases, ions may be intercalated into the gap, increasing the separation of layers, and thereby reducing the strength of the bonding between layers, making exfoliation possible in appropriate solutions. When the bonding between the layers is stronger, it has also been shown that the layers can be separated by etching or protonation in strong acid.

The free-standing layers described above are produced at low temperature and are kinetically stable in this form. In addition, there are also spontaneously forming two-dimensional ceramic interfacial phases, which are called “complexions” to differentiate them from the three-dimensional bulk phases rigorously defined by Gibbs.¹¹⁸ These complexions can form on free surfaces¹¹⁹, at grain boundaries¹¹⁸, and hetero-phase boundaries.¹²⁰ Among supported surface complexions, ~~we consider~~ adsorbate-based surficial films¹¹⁹, reconstructions¹²¹, and controlled surface terminations ~~are considered~~.¹²² These two-dimensional materials can be thought of as thermodynamically stable nanoscale coatings or atomic level surface modifications that can be controlled by changing the temperature or chemical potential of the constituents to alter the transport and catalytic properties.

The formation and control of grain boundary complexions can be used to influence microstructure evolution during processing. Specifically, the recent discovery of grain boundary phase-like behaviors has already provided new insights on several long-standing scientific

mysteries that puzzled the ceramic community for decades, e.g., the origins and atomistic mechanisms of solid-state activated sintering¹²³ and abnormal grain growth.¹²⁴ Beyond the interfacial diffusivity and mobility that govern the microstructural development, grain boundary complexions often control properties of structural and functional ceramics, including – but not limited to – strength, toughness, creep resistance, electrical, thermal and ionic conductivities, the non-linear I-V character of varistors, and the critical current of superconductors.¹²⁵

Two-dimensional ceramics possess characteristics that make them scientifically interesting and potentially useful. For example, enhanced transport properties in two-dimensional ceramics can enable energy storage devices^{126,127} and may play a role in cold sintering.¹²⁸ The rich catalytic properties of two-dimensional ceramics enable reactions that are important for the production and utilization of solar fuels.¹²⁹ Interface complexions, which have been shown to be thermodynamically stable, undergo transformations that control the evolution and properties of the microstructure. The properties are tunable by temperature, pressure, and chemistry and may even be switchable by external fields. The recent demonstration that complexion transformation kinetics could be represented on conventional time-temperature-transformation diagrams opens up the possibility of establishing predictable control over the microstructural evolution of ceramics.¹³⁰ The next obvious step in both advancing the science of two-dimensional ceramics is understanding structure-property relations. To date, ~~we are unable~~ it is not possible to predict how the properties of oxides only known to exist in the bulk state change when those oxides are made into nanometer thin sheets.¹³¹ Similarly, ~~we are unable to~~ predicting the properties of (both free-standing and confined) two-dimensional materials that have stoichiometries and structures that do not appear in the bulk is not feasible.^{117,118}

Two-dimensional ceramic materials are ripe for investigation and discovery. For the past decade, there has been an intense focus on modeling two-dimensional systems, including the two-dimensional electron gas at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface¹³² and graphene.¹³³ This foundation has provided a wealth of experimental techniques for the synthesis and characterization of two-dimensional materials. At the same time, there has been a rapid growth in the discovery of new two-dimensional ceramics^{112,117} that have not been subjected to the same detailed studies as the model systems. Therefore, there is an opportunity to adapt the techniques used to study the model materials to a wide range of new materials. Since this is a synthesis, processing, and characterization problem, it fits more naturally in the ceramics domain than any other. As a result of developing structure-property relationships for these materials, it will be possible to identify new targets for synthesis.

The study of two-dimensional systems also presents challenges and opportunities for modeling. Specifically, the analysis of the atomistic stability of two-dimensional ceramic structures, including the calculation of the structure, while incorporating intrinsic and extrinsic defects into the formulation remains a challenge.¹³⁴ For example, the calculation of energies of formation for charged point defects (while conserving the charge neutrality condition), energy barriers for ionic diffusion, the impact of phonon-defect, defect-defect, and photon-defect interactions, surface-atmosphere or solution interactions, and their impact on the stability of two-dimensional ceramic structures is still done on a case-by-case basis.^{135,136} In many instances, these calculations are not yet possible, particularly for cases where the interface provides technologically relevant functionalities such as ferroelectrics, thermoelectrics, rechargeable batteries, and fuel cells. The rational integration of atomistic results into meso- and continuum descriptions is not yet possible and the formulation of descriptions to define their two-

dimensional equilibrium as a result of the abutting three-dimensional phases is limited to only a few cases.¹³⁷ The formulation of automated theoretical and numerical formalisms that guide the synthesis of tailored properties for two-dimensional systems that parallel the development of existing three-dimensional systems such as the Alloy Theoretic Automated Toolkit¹³⁸ and the Atomic Simulation Environment¹³⁹ at the atomic level, or OOF¹⁴⁰ and MOOSE¹⁴¹ at the meso- or continuum scale are not available and, therefore, there is a unique opportunity for the ceramics community to develop multi-scale two-dimensional tools and platforms that will enable the rational and systematic exploration of these systems. Further, uncertainty quantification of two-dimensional systems that are able to assess the impact of average and extremal events is nonexistent, even though numerical tools such as Dakota¹⁴² are emerging and can provide the context to understand their impact.

Energy storage is already an important part of ceramics research and is likely to increase in activity considering that the industry forecasts that by 2019, the market will be as large as US \$120B. Ceramic materials are key performance-determining constituents of Li-ion batteries,¹⁴³ pseudocapacitors¹²⁷ and hybrid devices for energy storage¹⁴⁴. The two-dimensional materials already mentioned have the potential to enable the next-generation of thin and flexible rechargeable batteries with improved storage capability, faster charging rates, safer operation and a longer lifetime. While graphene has been extensively studied, much less is known about structure-property relations in two-dimensional ceramics.¹⁴⁵ Fast intercalation of not only lithium, but also sodium, potassium and multivalent ions (aluminum or magnesium) into electrodes built of free-standing two-dimensional ceramic nanosheets may lead to improved batteries. Additionally, two-dimensional ceramics may dramatically expand the range of solutions for automotive power systems and the large-scale stationary storage of renewable

energy, as soon as they can be produced in large quantities. Also, emerging energy storage devices entirely based on solid-state (ceramic) technology are currently limited by the interfacial structure and properties of the two-dimensional hetero-interfaces through which they are spatially coupled. Thus, a fundamental understanding of their stability and transport properties is the first step to remove existing performance bottlenecks.

Two-dimensional ceramic materials will also impact challenging yet important problems related to catalysis. These materials have the right structural features to serve as catalysts for the most important reactions in energy conversion systems. They are also among the most promising contenders for fundamental studies of the electrochemical and photochemical properties in materials. Their unique properties provide catalytically rich surfaces for reactions pertinent to renewable energy applications, such as the hydrogen evolution reaction and the oxygen evolution reaction.^{129,146} Many of them have also been shown to catalyze the oxygen reduction reaction in fuel cells, assisting in the generation of energy from green energy carriers such as hydrogen. These unique attributes, coupled with the many strategies available to produce them with numerous structures and compositions, as well as their tunable electronic, surface and defect properties, make two-dimensional ceramics valuable in the search for sustainable energy resources.

In summary, the recent discovery of many two-dimensional structures has outpaced the our understanding of their properties. Establishing an understanding of structure-property-processing relations for two-dimensional structures is expected to lead to easily tunable properties through small changes in chemistry, processing, or external fields. These two-dimensional structures may have impact on energy applications (batteries, supercapacitors,

catalytic materials), miniaturization of switching devices, low energy computing, and novel functional and mechanical properties.

V. Ceramics for Extreme Environments

Attributes that make ceramics attractive for society's imperatives in energy, transportation, and national security include their refractoriness, stability in chemically aggressive and radiation environments, as well as a diverse range of unique functional and mechanical properties, notwithstanding their limited toughness. Nevertheless, societal demands for continuing technological progress translate into a relentless drive to further extend the capabilities of ceramics into regimes of unprecedented severity. These demands pose new challenges to the scientific understanding of ceramic materials and specifically, to the elucidation of mechanisms that control their response in extreme environments. Concomitantly, these demands motivate the discovery and synthesis of new ceramics.

The performance limits of materials may be defined in terms of (i) loss of functionality, such as resulting from a phase transition with increasing temperature; (ii) loss of shape or physical integrity under thermo-mechanical stresses or applied fields, such as deformation or fracture; or (iii) degradation of structure and properties over time, such as creep rupture or radiation damage. Any situation that drives known materials past their performance limits may be defined as "extreme," providing at once a series of technological challenges and an opportunity for fundamental materials development. For the purposes of this discussion, extreme environments are defined as those for which there are no known materials solutions, wherein the motivation for discovery is greatest, and where the theoretical and experimental infrastructure to study and

understand their behavior is still inadequate. Extreme environments are further exacerbated when more than one excessively harsh condition is simultaneously involved.

Notable examples of technologically extreme environments driving scientific research in ceramics are illustrated in **Figure 4**. These include:

[Insert Figure 4]

Figure 4. Challenges for ceramics in extreme environments arise across broad applications in energy, security, and transportation. Sources for images: High- T_c superconductors (HTSC) for plasma confinement¹⁴⁷ (Reprinted with permission, Nature Publishing Group); armor¹⁴⁸; ceramic-matrix composite¹⁴⁹; reaction zone between environmental barrier coating with calcium-magnesium-aluminosilicate¹⁵⁰; and ultra-high temperature ceramic leading edges¹⁵¹.

(i) Hypersonic flight, where sharp leading edges are required in aircraft for reduced draft and improved maneuverability¹⁵². Required temperatures are in excess of 2000°C ¹⁵³, with heat fluxes of multiple MW/m^2 ¹⁵⁴ which can translate into extreme thermal gradients and stresses. Ionization of the impinging air¹⁵⁵ enhances oxidation potential¹⁵⁶, followed by catalytic recombination at the surface, leading to still further heating¹⁵⁷. Ultra-high temperature ceramics (UHTCs)¹⁵⁸ and C/SiC composites¹⁵⁹, current candidate materials for these applications, are hindered by severe oxidation at the target temperatures¹⁶⁰⁻¹⁶³.

(ii) Aerospace propulsion, encompassing gas turbines, scramjets and rocket engines, with prospective gas temperatures in excess of $\sim 1700^\circ\text{C}$ ¹⁶⁴, $\sim 2000^\circ\text{C}$ ¹⁵² and $\sim 3000^\circ\text{C}$ ¹⁵⁷, respectively. Gas turbines for aircraft propulsion and power generation share common goals, namely increased efficiency and reduced emissions, although aircraft engines presently lack renewable or carbon-neutral alternatives. Target material temperatures exceed 1500°C in near-sonic flows of

combustion gases at pressures of order 5 MPa (~50 atmospheres), containing well over 6 vol% of water vapor as a combustion product. Erosive/corrosive entrained debris that may impact or deposit on component surfaces further exacerbates the operating environment. All known turbine hot-section materials, whether metallic^{165 - 167} or the recently introduced ceramic composites (CMCs)^{164,168}, rely on ceramic coatings. However, both the thermal barrier coatings (TBCs) used to protect metallic components^{164,169} and the environmental barrier coatings (EBCs) used to protect CMCs^{164,170} are temperature-limited when exposed to molten dusts, which are comprised of highly corrosive calcium-magnesium aluminosilicates (CMAS)^{164,171-175}. A second major barrier is associated with coating toughness limitations¹⁷¹, as the consequences of coating loss become more critical with increasing reliance on their continued protection. No present material meets both the toughness and CMAS resistance requirements over the relevant range of temperatures. Ceramics in hypersonic and rocket propulsion operate in arguably mechanically simpler environments, where the problems introduced by the rotation of gas turbine components are largely absent, but heat fluxes can be much more severe owing in part to the concepts involving fuel cooling of the hot walls. Materials of the same families considered for leading edges are of interest, but subject to similar durability concerns due to the extreme environments.

(iii) Advanced Nuclear Energy, where materials must withstand high fluxes of energetic particles¹⁷⁶. While current and prospective next generation fission reactors pose substantial challenges to ceramics, e.g. as advanced fuels and wastefoms¹⁷⁶, fusion reactors arguably represent one of the most ambitious challenges to the spectrum of extreme materials technology¹⁷⁷. Temperature extremes in fusion reactors range from cryogenic in the superconducting magnets that contain the plasma to well over 1000°C for the plasma facing first wall and diverter, which are subject to radiation by 14 MeV neutrons and thermal fluxes

exceeding 20 MW/m². The neutrons interact primarily with the first wall and the breeder blanket, but affect all other components in the system¹⁷⁸, with local temperatures influencing the extent of recovery from the radiation damage. Low-activation materials are essential to minimize radioactive waste. High temperature superconductors for the containment magnets, Li-based oxides for the tritium breeder blanket, WC cermets for diverter shielding, SiC-based CMCs and possibly UHTCs for plasma facing components all lack the required durability and/or functionality. The fundamental understanding of how to tailor materials for such extreme environments must be developed before implementation of fusion systems becomes a reality.

(iv) Tribological, Superabrasive and Armor Materials that serve under extreme static and dynamic mechanical loads, often combined with temperature extremes. These include operation at ultra-high pressures or contact loads (10 GPa – 1 TPa), such as those generated within diamond anvil cells (DACs)¹⁷⁹, machining tools (e.g., cutting, drilling, grinding) which benefit from super and ultra-hard materials¹⁸⁰, and operation under highly dynamic loads found, for example, in armor applications, where impact pressures can exceed 10 GPa¹⁸¹. While phase transformations under pressure can lead to the discovery of new structures with novel properties, they may also be deleterious to the expected performance, as in the solid-state amorphization of B₄C under high velocity impacts¹⁸². As is the case with ballistic armor, the discovery and fundamental understanding of superhard materials is still in its early stages of identifying and leveraging advanced simulation, synthesis, and characterization tools.

Severe environments of one sort or another are also encountered in a broad spectrum of functional applications, such as high temperature thermoelectrics¹⁸³, electrochemical systems in batteries¹⁸⁴ and solid oxide fuel cells (SOFCs)¹⁸⁵, high-voltage insulators¹⁸⁶, magnets¹⁸⁷, superconductors¹⁸⁸ and, optical/optoelectronic devices subject to high photon fluxes¹⁸⁹. A

common issue is the evolution of defects as the field or flux interacts with the ceramic, which limits the subsequent system performance¹⁸⁹. Despite differences in the details of the mechanisms and associated dynamics, these issues have analogues with the categories discussed above, namely degradation by energetic particles and high-flux thermal fields, thermochemical reactions with aggressive species, and extreme transient loads.

A fundamentally rigorous, computationally backed experimental strategy is required to elucidate the phenomena that govern extreme-environment ceramics at multiple length and time scales. Most extreme environments will likely require multi-material systems, wherein performance is not dependent solely on the properties of each individual constituent, but rather on the interplay among them^{164,190}. From that perspective, two challenges are identified in ceramics for extreme environments, one related to the discovery and design strategies for new materials and the other to advance the understanding of complex systems (including interactions across interfaces) under extreme thermal, chemical and mechanical environments. Both challenges share limitations on the theoretical and modeling infrastructure to predict behavior (even under a single extreme condition), as well as on the experimental capabilities to measure properties and assess performance in the more complex situations that combine extremes.

Challenge #5: Ceramics in the Extreme: Discovery and Design Strategies

As noted above, the extreme environments of interest are those for which no satisfactory materials solution yet exists, even if some materials meet a subset of the required properties. For example, UHTCs based on refractory metal borides, carbides or nitrides exhibit some of the highest melting temperatures available and form highly refractory, stable oxides^{158,163}. However, these oxides are porous and tend to crack due to thermal expansion mismatch with their parent material, rendering them non-protective¹⁹¹. Use of UHTC composites with SiC additions leads

to a passivating liquid silicate coating which is susceptible to ablation by turbulent flows and experiences volatilization above $\sim 1600^\circ\text{C}$ ^{160,163}. Efforts to form solid protective coatings using rare-earth additives lead to formation of refractory oxide scales, e.g., LaZr_2O_7 ¹⁹², but these too are unlikely to survive above $\sim 1800^\circ\text{C}$ due to thermal expansion mismatch. Conversely, environmental barrier coatings for CMCs based on rare-earth disilicates are sufficiently refractory and better matched to the substrate than their rare-earth monosilicate counterparts but have inferior resistance to volatilization in water vapor¹⁶⁹. Moreover, neither ceramic has adequate resistance to attack by molten silicates^{173,174,193}. In these, as in many other cases, the known menu of candidate materials is sparse and highlights the critical need for the discovery/design of new materials and architectural concepts.

Theory and computational modeling are essential tools to guide the discovery process. The value of theory is illustrated by recent work that provided a fundamental explanation for the reported maximum in melting point for rock-salt solutions of TaC-HfC at $\sim(\text{Ta}_{0.8}\text{Hf}_{0.2})\text{C}_{0.875}$.¹⁹⁴⁻
¹⁹⁷ The authors further predicted that compounds in the Hf-C-N system could exhibit melting points at least 200°C higher than in Ta-Hf-C, although this prediction is yet to be validated experimentally. Methods based on DFT are now able to calculate mechanical, electronic and thermophysical properties of ceramics at low temperatures¹⁹⁸. High-temperature properties of ceramics require calculation of the Gibbs free energy, which may involve electronic excitations and defects. Such calculations are much more demanding and not yet generally available, although an early approach for elemental metals was demonstrated in the 1990s by DFT calculations of the melting curve of Fe up to 6000K in the earth's core, at pressures up to 350 GPa¹⁹⁹. Progress has since enabled DFT calculations of thermal expansion and heat capacity of

pure ZrC up to 3500K²⁰⁰. Though not yet possible, extension of these ideas to the prediction of new materials is encouraging.

Understanding phase stability and structural transformations in chemically complex systems is paramount to all discovery and design strategies and arguably requires continuum level approaches based on CALPHAD, phase field and other computational methods. CALPHAD has been invaluable in providing a methodology to assess phase equilibria in multicomponent systems, but is largely based on fitting of free energy models to reproduce experimental data. This presents two obstacles. First, determination of thermodynamic properties is hindered for materials that are not readily synthesized. Here, exploration and property predictions based on DFT may prove invaluable²⁰¹; in fact, on-going activities are focusing on exploring avenues to bypass the CALPHAD approach altogether by using DFT and applying advanced sampling techniques²⁰¹. The second obstacle is related to the measurement of thermodynamic properties at extreme temperatures, notably enthalpies of transformations and heat capacities^{202, 203}. Containment of materials at these temperatures without introducing contamination or measurement artifacts is a major practical issue. This challenge can be addressed by novel calorimetric techniques combining, for example, aerodynamic levitation with laser melting²⁰³. Examples of techniques applicable to extreme environments are illustrated in **Figure 5**; however, many are still emerging and much development remains. Phase transformation temperatures in the solid state can also be addressed with X-rays²⁰⁴ coupled with non-contact methods of heating, such as quadrupole lamp furnaces²⁰⁵, though the latter are still limited to temperatures below about 2000°C. Resistive heating of UHTCs has been employed in oxidation studies to 2000°C^{206,207}, taking advantage of the metallic conductivity of refractory borides and suitable

specimen design, though these approaches are limited to conductive materials and may also be prone to artifacts²⁰⁷.

[Insert Figure 5]

Figure 5. High temperature and pressure techniques applicable to extreme environmental research; clockwise from upper left: high-resolution micro-computed tomography (μ -CT) of SiC-SiC composites²¹⁹ (Reprinted with permission, Nature Publishing Group); arc jet test¹⁵¹; diamond anvil cell for extreme pressures; ultra high-temperature (UHT) calorimetry²⁰⁸; and a time sequence of surface melting of silicate deposits from a high heat flux laser gradient test²⁰⁹.

While characterization of materials under combined extremes is still challenging, progress has been made in measuring behaviors in simplified environments typically dominated by a single extreme condition. For example, one can measure melting temperatures well over 3000°C using new laser techniques²¹⁰, as demonstrated recently on $\text{HfC}_{0.98}$, ($3959 \pm 84^\circ\text{C}$)¹⁹⁵. It is also possible to measure strength²¹¹, thermal diffusivity²¹², heat capacity²⁰³, coefficient of thermal expansion^{204,213} and electrical conductivity²¹⁴ at very high temperatures, as well as material responses in extreme heat fluxes^{215,216}. A limiting factor often becomes the stability and inertness of the sensors needed to measure the quantities of interest, both in the environment as well as in contact with the specimen.

Elucidating mechanical behavior at extreme temperatures still presents major barriers. Among these is the characterization of the constitutive behavior. Micromechanical models that combine the effect of composition, phase constitution and defects, all of which can evolve over time²¹⁷, and finite element models that can be informed by the emerging micromechanical understanding must be developed. Advances in high-resolution X-ray computed tomography

(CT) provide new insights into the evolution of defects and damage with increasing strain^{218,219}, which can then illuminate the development of virtual test methods and predictive models for failure. Toughness is a particularly critical property, often limiting the applicability of ceramics, but capabilities to develop fundamental understanding of this property at extreme temperatures are lacking. Novel tests have been developed, especially for porous materials²²⁰⁻²²², but their applicability above ambient temperature is limited by the lack of appropriate tooling and sensors, as well as the lack of models for the interpretation of results. The increasing availability of synchrotron-compatible diamond anvil cells and environmental systems with heating sources allows a wide range of high temperatures/high pressures, and controlled-environment physical properties to be monitored in situ, including structure, compressibility, elasticity, thermal expansion, transport properties, rheology and chemical reactions^{223,224}. However, constitutive behavior under non-hydrostatic stresses at extreme temperatures is still a challenge.

Challenge #6: Ceramics in the Extreme: Behavior of Multi-material Systems

The complexity of extreme environments favors reliance on multi-phase/multi-element materials having tailored microstructures and architectures. A scientific approach that captures the complexity of the salient thermochemical and thermomechanical material interactions is essential. This includes modeling of the interactions of the constituents in different atomic-scale configurations, requiring input from thermodynamic measurements to inform phase stability and kinetic models in multicomponent systems; processing approaches to develop the desired architectures; and experimental assessment of the multi-phase/microstructurally designed material systems in extreme environments. In situ and operando measurements are becoming increasingly critical, requiring development of testing systems and sensors for extreme conditions.

Modeling challenges include the integration of the relevant physical phenomena within the constituents of the system, their interfaces and the dynamics of the multi-material assemblage to identify the performance-limiting factors in the extreme environment^{225, 226}. The overall infrastructure, integrated along the guidelines of the materials genome initiative, requires further developments in continuum and microstructure-level models, such as those emerging from multi-scale finite and discrete element methods²²⁷. Micromechanical, thermodynamic, and kinetic models are also essential. Of particular interest are models describing the oxidation of multi-phase materials, especially when one or more of the oxidation products is subject to volatilization^{156,161,163,228}, all of which are limited by insufficient thermodynamic and kinetic information. Concepts involving the development of a protective scale during extreme oxidation environments are of particular interest, especially for non-oxide ceramics¹⁹².

Extensive experimental infrastructure, both user facilities as well as laboratory-scale academic capability, is needed to meet this grand challenge for both scientific and technological progress as well as training ~~Such infrastructure will support scientific academic progress, train a generation of new researchers, and solve real world materials problems whose solutions have been elusive so far.~~ Examples of critical facilities include plasma and wind tunnels for testing under hypersonic conditions^{154,157,162,229,230}, facilities for studying nuclear radiation effects on fusion materials, and also for the study of materials under high heat fluxes^{231,232}.

While some facilities capable of simulating complex in-service environments are in place (e.g., for simulation of environments relevant to turbine engines^{216,232,233}), their capabilities are still limited, e.g., to quantitatively assess the effects of ionic dissociation in hypersonics, or the role of water vapor at high pressures and high velocities. In situ measurements of material characteristics and operando monitoring of materials evolution are critically needed to enable a

quantitative understanding of the composition-structure-property relations in a complex environment. Using X-rays as probes, especially in combination with μ -CT, one should be able to assess the synergistic effects of temperature, environment and stress on the mechanical properties and the mechanisms of failure^{218,219,234}, phase stability, oxidation, oxidation-induced stresses²³⁵, and effects of high-temperature corrosion by CMAS^{236,237} and gradients in internal strain²³⁸.

VI. Glasses

The current status of glass science and engineering and future outlook was recently discussed in two splendid reviews^{239,240}. The challenges in glass science and engineering identified here build on these and other recent advances and emerging opportunities.

Challenge #7: Understanding and Exploiting Glasses and Melts under Extreme Conditions

By studying the responses of glasses and melts to extremes in temperature, pressure, deep super-cooling, or steep chemical, electrochemical and magnetic gradients using in situ or operando characterization tools and methods, ~~our~~ knowledge of the glassy state can be substantially extended. Analogous to challenges posed for crystalline ceramics in Challenge #5, some extreme conditions can be used to synthesize novel glasses with new and unexpected properties and functionalities that are otherwise not possible with conventional processing techniques. Further, designing new and novel glasses that function under such extreme conditions is likewise important for a variety of applications, including electrochemical, aerospace, and biomedical.

Among the extremes, pressure and temperature are important basic thermodynamic variables that determine the structure, dynamics, and macroscopic properties of glasses and glass-forming

liquids²⁴¹. ~~From the beginning,~~ Artisans, technologists and scientists ~~have tailored~~ tailor glass properties (and structures) by controlling thermal history. Because of experimental difficulties, the pressure variable has been used sparingly to modify glass properties, even though available literature shows that pressure could be very effective in synthesizing novel glasses with desirable properties²⁴² and could provide a better understanding of the glass transition^{243,244} as well as phenomena like polyamorphism²⁴⁵⁻²⁵⁰. The pressure variable can be employed to help advance glass science and technology in at least two different ways: 1) to gain insights into glass structure and properties by, for example, characterizing how pressure affects the mechanical response of glass (crack resistance, elasticity/plasticity, and equation of state, etc.); and 2) using pressure as a synthesis parameter to tailor the structure and properties of glass beyond what can be achieved just through composition and/or thermal control alone.

Most of the high-pressure studies on glasses have been done by the geoscience community on geologically relevant systems using multi-anvil apparatuses (MAA) or diamond anvil cells (DAC) to provide a better understanding of volcanology and/or magmatic processes. High pressure apparatuses with and without resistive or laser heating have been integrated with synchrotron X-ray and neutron diffraction, inelastic X-ray scattering, Raman and Brillouin light scattering, X-ray absorption spectroscopy (XAS) (including both X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)) to study the physical and chemical properties of glasses and melts under high pressure/temperature conditions²⁵¹⁻²⁵⁵. Fairly recently, in situ high pressure nuclear magnetic resonance (NMR) probes that can operate at pressures up to 2.5 GPa have been developed to study the structure of glass under pressure²⁵⁶. In situ high pressure/temperature studies have been done on prototypical network-forming oxide glasses, such as SiO₂, GeO₂, B₂O₃, etc.²⁴⁵⁻²⁵⁰; however, much less is known about the structure

and properties of multi-component glasses and melts under pressure. A close collaboration between researchers in the glass science and geoscience communities is needed to adapt these in-situ high pressure/temperature characterization techniques to study multi-component glasses²⁵⁷⁻²⁵⁹ and melts, particularly those which are of industrial relevance and technological importance, such as those to develop new kinds of solid electrolytes for safer and higher energy density batteries.

Pressure effects on structure and properties are generally studied on quenched glasses after application of pressure. Pressurization is either carried out at room temperature or at elevated temperatures, near the glass transition temperature (T_g)²⁶⁰. Studies have shown that pressure quenching is an effective way to change the atomic packing and bonding of glasses²⁶¹. Pressure quenching can be used to prepare glasses with different structures and properties, and this approach is easier than the hyper-quenching technique²⁶²⁻²⁶⁴, especially for the synthesis of bulk samples. For example, while pristine silica glass deforms predominantly via densification under indentation, densified silica glass is capable of shear flow under indentation²⁶⁵, which was confirmed in classical molecular dynamics (MD) simulations²⁶⁶ (**Figure 6**). Pressure-quenched glasses with high elastic moduli and high thermo-mechanical stability may find potential applications in many fields of technological importance such as the aerospace industries²⁶⁵. Recent studies have shown that the same degree of densification induced by cold compression at room temperature or hot compression near T_g , or by annealing at ambient pressure can lead to different structure and properties^{260,267}. These findings indicate new possibilities for the rational design of glasses with fine-tuned properties otherwise not possible through conventional composition and/or thermal control. Furthermore, hot-compression of glass in the non-rigid state in the glass transition range may also provide a means to study the structure and properties of

glass-forming liquids under pressure, which is of critical importance to understand geological processes in the Earth's interior.

[Insert Figure 6]

Figure 6. Atomic configuration (first row), local shear strain (second row), local density (third row) and local density change mapping under indenter (fourth row) after nanoindentation test for silica glass quenched under 0 GPa and 15 GPa²⁶⁶.

Among the high-temperature and high-pressure apparatuses, DAC can achieve very high pressures (>100 GPa) and very high temperatures (>3000K with laser heating), but the sample size is very small, typically on the order of tens of μm^3 . Similar pressures and temperatures have been achieved by MAA techniques, but with significantly larger (mm^3) samples²⁶⁸. Larger samples (cm^3) cooled from high temperatures and modest pressures (up to 1 GPa) are possible using a recently opened gas-medium high-temperature and high-pressure facility in Poland²⁶⁹, making it now possible to study the effects of pressure on macroscopic properties and to use conventional structural characterization techniques. Further development of large volume high-temperature and high-pressure techniques is needed to enable in-depth studies of glasses and melts under pressure, especially those of technological importance.

Another way of exploring the properties of melts under unusual conditions, particularly those that do not readily form glasses on quenching, is to subject them to deep undercooling in ways that minimize heterogeneous nucleation initiated at container walls, or that avoid homogeneous nucleation by rapid undercooling. For instance, ~~Duwez et al. employed~~ splat quenching techniques, with cooling rates reaching 10^6 - 10^7 °C/s, ~~were employed~~ to synthesize

amorphous metallic alloys²⁷⁰. That original work has led to extensive investigation of “metallic glasses” as they later became known, ultimately succeeding in establishing composition-driven predictive capabilities for bulk glass formation, glass stability and nano-crystallization in such systems²⁷¹. In many respects, the original research in systems requiring extraordinarily high cooling rates built a foundation for the synthesis of novel bulk metallic glasses that can now be prepared under more normal processing conditions, with some of the best glass-forming alloys now being prepared at cooling rates as low as 0.5 °C/min²⁷². Rapid quenching techniques have been used by many in the inorganic glass community, most actively in the 1970s and 80s ~~through research of Sarjeant and Roy~~²⁷³⁻²⁷⁵, although most of these studies were done to catalogue unusual glass-forming systems. In some cases, unusual properties were measured for these rapidly quenched systems, including high ionic conductivity²⁷⁶ and magnetic properties²⁷⁴. Additional examples of glass formation in technologically important Al₂O₃-based systems have been reported more recently^{277, 278}. Yet, overall this research has not yielded predictive capabilities beyond fairly trivial “eutectic” and “mixed metal-oxide, kitchen sink” rules, let alone formation of novel glasses utilizing conventional glass synthesis approaches.

Containerless melting techniques such as laser melting combined with levitation, are uniquely suited for studies of deeply supercooled melts. These techniques emerged relatively recently and have been used for studies of interesting phenomena such as polyamorphic glass transitions in Al₂O₃-Y₂O₃ system²⁷⁷. They also provide a viable way to form novel glasses with unique properties otherwise not possible with conventional glass forming techniques, such as TiO₂-, Ta₂O₅-, WO₃- and Al₂O₃-based glasses without any classical network formers²⁷⁹⁻²⁸⁴. It was recently shown that Al₂O₃-SiO₂ binary glasses with up to 60 mol% Al₂O₃ could be

synthesized by using the containerless technique and that these glasses possess high elastic moduli, high hardness and high crack-resistance²⁸⁵ (see **Figure 7**).

Combining containerless melting with in situ characterization capabilities is a powerful tool to study the structure and dynamics of deeply supercooled liquids without contamination or crystallization. First principles theoretical calculations of structures present in deeply supercooled melts should further shed light on such important aspects as network connectivity and viscosity-temperature profiles. A combination of experimental and theoretical studies should further advance ~~our~~ the understanding of whether the designation “glass” can be used for such “frozen melts”. A solid that is X-ray amorphous could be designated as a non-crystalline solid (NCS) or a short-range order solid (SROS), but without evidence of a glass transition, a more restrictive “glass” designation is unwarranted.

Levitation systems have been combined with synchrotron X-ray and neutron diffraction at Argonne and Oak Ridge National Laboratories to study glasses and super-cooled liquids^{286,287}, although few such systems are available at universities. Combining levitation systems with high speed cameras and various diffraction and scattering techniques will enable us to study a range of structural, thermodynamic, viscoelastic properties of glasses and melts.

[Insert Figure 7]

Figure 7. Composition dependence of elastic moduli (left) and Vickers hardness (right) for the $x\text{Al}_2\text{O}_3-(100-x)\text{SiO}_2$ glasses. Vickers indentation imprints for the $x\text{Al}_2\text{O}_3-(100-x)\text{SiO}_2$ glasses. Blue-shaded photographs show the cracked samples. Gray-shaded photographs show the non-cracked samples²⁸⁵.

Challenge #8: Rational Design of Functional Glasses Guided by Predictive Modeling

The traditional approach for glass research is largely empirical. A rational design approach to develop new glasses with desired properties and functionalities is usually hampered by the lack of understanding of the impact of composition and processing conditions (e.g., thermal or pressure history) on the resulting glass structures and macroscopic properties. Although multi-scale computer simulation and modeling techniques have been widely applied to study the structure and properties of glass²⁸⁸ (see **Figure 8**), they have only achieved limited success to date. This is due in part to the limited time ($\sim\mu\text{s}$) and length ($\sim\mu\text{m}$) scales accessible by even the most powerful parallel computers and to the deficiencies in existing techniques, such as the lack of reliable structural models for first-principles calculations and potential models for classical MD simulations. More importantly, to design multi-functional glasses, models at different scales are needed to predict manufacturing-related attributes, e.g., temperature-dependent viscosity, liquidus temperatures, and refractory compatibility, as well as the relevant end-use properties, e.g., elastic moduli, hardness, and damage resistance for cover glass in personal electronics. It remains a challenge to have all models validated by experiments, often information from a smaller scale model is used to fit and validate models at larger scales. For example, force fields used in classical MD simulations are often developed by using first-principles data to fit the potential parameters, while outputs from MD simulations, such as atomic structure, elastic moduli and diffusion coefficients are used as inputs in topological constraint modeling, in finite element analysis, and analytical modeling. Thus it is of critical importance to ensure that the fundamental chemistry and physics of glass are built into the models used in first-principles calculations and in classical MD and Monte Carlo simulations.

[Insert Figure 8]

Figure 8. Overview of modeling techniques for glasses, from purely empirical models to those firmly grounded in fundamental physics²⁸⁸ (Reprinted with permission, American Chemical Society).

Predictive modeling of the mechanical, electronic, electrochemical, thermal and optical properties of glass and amorphous solids using first-principle techniques (e.g., DFT) mandates the construction of structural models that properly reflect experimentally relevant glassy states. Such structural models are relatively well established for simple glasses such as vitreous silica²⁸⁹⁻²⁹¹, but more often than not are inaccessible for complex multi-component glass systems. The challenge of building realistic structural models for laboratory glass is two-fold. From the modeling side, all structural models must be completely relaxed to a desired level of accuracy for first-principles simulations such that they can be used in electronic structure calculation and for subsequent quantum mechanical modeling of physical properties. For complex glass systems, in particular non-oxide glasses where reliable interatomic potentials are often not available, ab initio molecular dynamics (AIMD) in principle offers a viable alternative to classical MD. However, due to its excessive computational needs, AIMD is severely limited in size and time scales and therefore cannot represent realistic glass forming processes. Building structural models for solids under external stimuli (e.g., photosensitive glass under light exposure) presents an additional challenge. On the experimental end, quantitative glass structure characterization typically relies on diffraction techniques or advanced imaging tools. For multi-component glasses consisting of atoms of similar sizes, accurate structure identification remains a challenging task. Furthermore, structure factors and pair distribution functions obtained from

diffraction measurements are one-dimensional functions that are inherently unable to fully capture the three-dimensional glass structure. Classical reverse Monte Carlo (RMC) simulations²⁹² as well as emerging, further refined computational methods²⁹³ allow inversion of diffraction data to extract glass structures, although still with some ambiguity. Advanced atomic-scale imaging based on electron microscopy complements diffraction techniques by providing direct visualization of glass structures in real space. For instance, electron tomography is now applied to the reconstruction of three-dimensional amorphous structures with nanometer spatial resolution²⁹⁴. The direct imaging of two-dimensional silica glass comprising bi-layers of SiO₄ tetrahedra using STEM is another salient example²⁹⁵. Nevertheless, the imaging approach requires complicated sample preparation and also poses constraints on sample dimensions, and are only suited for model validation rather than predictive material design. Overall, construction of realistic glass structural models for first-principles predictive modeling of mechanical, electronic, electrochemical, and optical properties in glasses remains a standing challenge. Resolving this challenge will entail the development of new efficient modeling techniques as well as reliable, large-scale structure characterization methods. It is worth mentioning that high-throughput synthesis and measurement methods, coupled with data-based materials informatics, will likely complement first-principles approaches to enable predictive modeling capabilities for glass materials.

Because of the semi-empirical nature of interaction potential models used in atomistic simulations, they must be validated against experimental or first-principles data. This is done by optimizing potential parameters to reproduce the physical properties of known structures, e.g., static properties, such as bonding energy, density, bond lengths, bond angles, structure factors and elastic moduli, and dynamic properties, such as the vibrational density of states (VDOS), IR

and Raman spectra, as well as transport properties, such as diffusion coefficients. The position and depth of the potential well largely determines bond length, density and defect formation energy, while the shape of the minimum affects atomic vibrations and elastic moduli. It is the shape of the tail that mainly tells how easily atoms can migrate out of the potential well. Most of the force fields were developed by mainly using structural information and properties near the potential minimum (dominated by the harmonic part) from experiments or first-principles calculations at ambient conditions. High-temperature in situ characterization of well-designed model systems is needed to provide structure and properties determined by the anharmonic part of the potential to fit and validate computer models, such as thermal expansion coefficient or viscosity/diffusion coefficient. Levitation combined with laser heating and in situ characterizations can be a viable and “clean” way to obtain such structure and properties of glasses at high temperatures, especially for compositions that may not be stable using conventional routes. Studies of the structure and properties of glass under high pressure, similar to those suggested for polycrystalline ceramics in Challenge #5, can provide inputs for fitting or validating the repulsive part of the interaction potential. Reasonably accurate potential models are available for simple silicate glasses, but for borate glasses, phosphate glasses or multicomponent glasses with mixed network formers, such force fields are currently lacking. Therefore, there is a pressing need to develop potential models for such systems to enable predictive design of their structure and properties.

Human-produced glasses have been available for 5000+ years, but many puzzles related to their structural and dynamic nature remain, in situ or operando characterization and modeling of glasses and melts are needed to develop predictive computer models. With reliable and predictive computer models, ~~we will be able to design~~ glass compositions and/or processing

conditions for various applications starting from atomic structure models from simulations **can be designed**. This can dramatically change the nature of glass research and, just like designing new drugs in the pharmaceutical industry, will allow for the design of new functional glasses based on computations, including those with high strength, high fracture toughness, or high ionic conductivity.

VII. Summary

Eight grand challenges for fundamental ceramic and glass science research form the basis for progress in creating knowledge with transformational technological impact potential. These challenges focus on strategies for the design of new materials and understanding of their structure and properties. Ultimately, these are expected to afford new capabilities in function and performance. The challenges demand innovation in both experiments and models; in the former, for example, at extreme conditions of temperature, pressure, or radiation flux, while in the latter, for instance, models for defect-defect interaction, particularly for cases with large defect concentrations, and defects confined in 2D arrays, are particularly vexing. It is anticipated that these challenges will provide inspiration for research in the ceramic and glass communities with societal and industrial import.

Acknowledgments

This workshop and the resulting report were supported by NSF DMR-1619666. The assistance of Thorston Bayer (The Pennsylvania State University), Joseph Muth (Harvard University), and Xiaoting Zhong (Carnegie Mellon University) as scribes during the workshop is

greatly appreciated. Joshua C. Agar (University of California, Berkeley) assembled Figure 3. The co-organizers thank Dr. Lynnette Madsen for her counsel during the planning and conduct of the workshop.

Author Manuscript

References

- ¹ S. Deville and A. J. Stevenson, "Mapping Ceramics Research and its Evolution," *Journal of the American Ceramic Society*, **98** [8] 2324-32 (2015).
- ² <http://www-unix.ecs.umass.edu/~jakus/nsf/nsf.ceramics.report6.pdf>
- ³ G. S. Rohrer, M. Affatigato, M. Backhaus, R. K. Bordia, H. M. Chan, et al., "Challenges in Ceramic Science: A Report from the Workshop on Emerging Research Areas in Ceramic Science," *Journal of the American Ceramic Society*, **95** [12] 3699-712 (2012)
- ⁴ "Catch the wave: The long cycles of industrial innovation are becoming shorter," *The Economist*, print edition, February 18, 1999.
- ⁵ <http://www.naturaledgeproject.net/Keynote.aspx>, accessed 10/20/15.
- ⁶ T. M. Pollock, J. E. Allison, D. G. Backman, M. C. Boyer, M. Gersh, et al., *Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security*. National Academy of Sciences, Washington, DC, 2008.
- ⁷ J. M. Rondinelli, K. R. Poeppelmeier, and A. Zunger, "Research Update: Towards Designed Functionalities in Oxide-based Electronic Materials," *APL Materials*, **3** 080702 (2015).
- ⁸ Y. Wang, W. D. Richards, S. P. Ong, K.J. Miara, J. C. Kim, et al., "Design principles for solid-state lithium superionic conductors," *Nature Materials*, **14** [10] 1026- (2015).
- ⁹ B. Li, M. Osada, T. C. Ozawa, Y Ebina, K. Akatsuka, et al., "Engineered Interfaces of Artificial Perovskite Oxide Superlattices via Nanosheet Deposition Process," *ACS Nano*, **4** [11] 6673–6680 (2010).

- ¹⁰ B.Li, M. Osada, Y. Ebina, S. Ueda, and T. Sasaki, “Coexistence of Magnetic Order and Ferroelectricity at 2D Nanosheet Interfaces,” *Journal of the American Chemical Society*, **138** (24) 7621-7625 (2016).
- ¹¹ Y. Wang, Y. Wang, D. R. Breed, V. N. Manoharan, L. Feng, et al., “Colloids with valence and specific directional bonding,” *Nature*, **491** [7422] 51-55 (2012).
- ¹² E. Auyeung, T. Li, A. J. Senesi, A. L. Schmucker, B. C. Pals, et al., “DNA-mediated nanoparticle crystallization into Wulff polyhedral” *Nature*, **505**, 73 (2014).
- ¹³ K. Chaudhary, Q. Chen, J. J. Juarez, S. Granick, and J.A. Lewis, “Janus Colloidal Matchsticks,” *Journal of the American Chemical Society*, **134** [31] 12901-12903 (2012).
- ¹⁴ K. Plunkett, A. Mohraz, J. A. Lewis, and J.S. Moore, “Light-Regulated Electrostatic Interactions in Colloidal Suspensions,” *Journal of the American Chemical Society*, **127**, 14574-75 (2005).
- ¹⁵ K. Chaudhary, J. Juarez, Q. Chen, S. Granick, and J. A. Lewis, “Reconfigurable Assemblies of Janus Rods in AC Electric Fields,” *Soft Matter* **10**, 1320-1324 (2014).
- ¹⁶ S. Gangwal, O.J. Cayre, O.D. Velev, “Dielectrophoretic assembly of metallodielectric Janus particles in AC fields,” *Langmuir* **24** [23] 13312-20 (2008).
- ¹⁷ S.F. Poterala, R. J. Meyer and G.L. Messing, “Low-field dynamic magnetic alignment and templated grain growth of diamagnetic PMN–PT ceramics,” *Journal of Materials Research*, **28** 2960-2969 (2013).
- ¹⁸ Y. Sakka, T. S. Suzuki, and T. Uchikoshi, “Fabrication and some properties of textured alumina-related compounds by colloidal processing in high-magnetic field and sintering,” *Journal of the European Ceramic Society*, **28** 935–942 (2008).

- ¹⁹ J. Cesarano III and P. Calvert, “Freeforming Objects with Low-Binder Slurry,” U.S. Patent 6,027,326 (2000).
- ²⁰ J. Cesarano III, R. Segalman, and P. Calvert, “Robocasting Provides Moldless Fabrication from Slurry Deposition,” *Ceramic Industry*, **148**, 94 (1998).
- ²¹ J. E. Smay, J. Cesarano, and J. A. Lewis, “Colloidal Inks for Directed Assembly of 3-D Periodic Structures,” *Langmuir*, **18** [14]5429–5437 (2002).
- ²² Z. C. Eckel, C. Zhou, J. H. Martin, A. J. Jacobsen, W. B. Carter, T.A. Schaedler, “Additive manufacturing of polymer-derived ceramics,” *Science*, **351** [6268] 58-62 (2016).
- ²³ J. W. Halloran “Ceramic Stereolithography: Additive Manufacturing for Ceramics by Photopolymerization” *Annual Review of Materials Research*, **46**, 19-40 (2016).
- ²⁴ K. J. Maloney, C. S. Roper, A. J. Jacobsen, W. B. Carter, L. Valdevit, T. A. Schaedler “Microlattices as architected thin films: Analysis of mechanical properties and high strain elastic recovery,” *APL Materials*, **1**, 022106 (2013).
- ²⁵ L. R. Meza, S. Das, J. R. Greer “Strong, lightweight, and recoverable three-dimensional ceramic nanolattices,” *Science*, **345**, 1322-1326 (2014).
- ²⁶ E. Zanchetta, M. Cattaldo, G. Franchin, M. Schwentenwein, J. Homa, et al., “Stereolithography of SiOC Ceramic Microcomponents,” *Advanced Materials*, **28**, 370–376 (2016).
- ²⁷ X. Zheng, H. Lee, T. H. Weisgraber, M. Shusteff, J. DeOtte, et al., “Ultralight, Ultrastiff Mechanical Metamaterials,” *Science*, **344**, 1373 (2014).
- ²⁸ K. Sun, T.-S. Wei, B. Y. Ahn, J. Y. Seo, S. J. Dillon, J. A. Lewis, “3D Printing of Interdigitated Li-Ion Microbattery Architectures,” *Advanced Materials*, **25**, 4539 (2013).

- ²⁹ A. Mohraz, E.R. Weeks, and J.A. Lewis, “Structure and Dynamics of Biphasic Colloidal Mixtures,” *Physical Review E – Rapid Communication*, **77** [6] 060403 (2008).
- ³⁰ T.J. Ober, D. Foresti, and J.A. Lewis, “Active Mixing of complex fluids at the microscale,” *Proceedings of the National Academy of Sciences*, **12** [40] 12293-12298 (2015).
- ³¹ J. O. Hardin, T. J. Ober, A. D. Valentine, and J. A. Lewis, “Microfluidic Printheads for Multi-Material 3D Printing of Viscoelastic Inks,” *Advanced Materials*, **27** [21] 3279-3284 (2015).
- ³² J. Bauer, S. Hengsbach, I. Tesari, R. Schwaiger, O. Kraft, “High-strength cellular ceramic composites with 3D microarchitecture,” *Proceedings of the National Academy of Sciences*, **111** [7] 2453-8 (2014).
- ³³ A. Zocca, P. Colombo, C. M. Gomes, J. Günster, “Additive Manufacturing of Ceramics: Issues, Potentialities, and Opportunities,” *Journal of the American Ceramic Society*, **98**, 1983–2001 (2015).
- ³⁴ H. Kähäri, M. Teirikangas, J. Juuti, and H. Jantunen, “Dielectric Properties of Lithium Molybdate Ceramic Fabricated at Room Temperature,” *Journal of the American Ceramic Society*, **97** [11] 3378–3379 (2014).
- ³⁵ J. Guo, H. Guo, A. Baker, M. T. Lanagan, E.R. Kupp, et al., “Cold Sintering: A Paradigm Shift for Processing and Integration of Ceramics,” *Angewandte Chemie International Edition*, **55** [38] 11457-61 (2016).
- ³⁶ J. Guo, S. S. Berbano, H. Guo, A. L. Baker, M. T. Lanagan, and C. A. Randall, “Cold Sintering Process of Composites: Bridging the Processing Gap of Ceramics and Polymers,” *Advanced Functional Materials*, **26** [39] 7115-21 (2016).
- ³⁷ P. Colombo, “In Praise of Pores” *Science*, **322**, 5900 381–383 (2008).

- ³⁸ K. Burke, "Perspective on density functional theory," *The Journal of Chemical Physics*, **136** [15] 1590901 (2012).
- ³⁹ C. E. Calderon, J. J. Plata, C. Toher, C. Oses, O. Levy, et al., "The AFLOW standard for high-throughput materials science calculations," *Computational Materials Science*, **108** Part A 233-38 (2015).
- ⁴⁰ A.C.T. van Duin, S. Dasgupta, F. Lorant and W.A. Goddard III, "ReaxFF: A Reactive Force Field for Hydrocarbons," *Journal of Physical Chemistry A*, **105** 9396-9409 (2001).
- ⁴¹ Focus section on semi-empirical interatomic potentials, *Modelling and Simulation in Materials Science and Engineering*, edited by Martin H Muser, **23** [7] (2015)
- ⁴² C. R. Trott, S. D. Hammond, A. P. Thompson, "SNAP: Strong scaling high fidelity molecular dynamics simulations on leadership-class computing platforms," *International Supercomputing Conference*, 19-34 (2014).
- ⁴³ P. Brommer, A. Kiselev, D. Schopf, P. Beck, J. Roth, H.-R Trebin, "Classical interaction potentials for diverse materials from ab initio data: a review of potfit," *Modelling and Simulation in Materials Science and Engineering*, **23** [7] 074002 (2015).
- ⁴⁴ A. P. Thompson, L. P. Swiler, C. R. Trott, S. M. Foiles and G. J. Tucker, "Spectral neighbor analysis method for automated generation of quantum-accurate interatomic potentials," *Journal of Computational Physics*, **285** 316 (2015).
- ⁴⁵ Ingo Steinbach, "Phase-Field Model for Microstructure Evolution at the Mesoscopic Scale," *Annual Review of Materials Research*, **43**, 89-107 (2013).
- ⁴⁶ E. A. Holm and C. C. Battaile, "The Computer Simulation of Microstructural Evolution," *Journal of Metals*, **53** [9] 20-23 (2001).

- ⁴⁷ D. M. Dimiduk, "Microstructure-Property-Design Relationships in the Simulation Era: An Introduction", in Computational Methods for Microstructure-Property Relationships, Edited by D. Dimiduk, and S. Ghosh, Springer US, 2010.
- ⁴⁸ Modeling Across Scales: A Roadmapping Study for Connecting Materials Models and Simulations Across Length and Time Scales, www.tms.org/multiscalestudy, The Minerals, Metals and Materials Society, Warrendale, PA
- ⁴⁹ H. Schmalzried, Chemical Kinetics of Solids, Weinheim: VCH, 1995.
- ⁵⁰ J. Maier, Physical Chemistry of Ionic Materials: Ions and Electrons in Solids, Weinheim: Wiley Verlag, 2004.
- ⁵¹ D. S. Mebane, R. A. De Souza, "A generalized space-charge theory for extended defects in oxygen-ion conducting electrolytes: from dilute to concentrated solid solutions," Energy and Environmental Science, **8** 2935-2940 (2015)
- ⁵² K. Mo, Z. Zhou, Y. Miao, D. Yun, H.-M. Tung et al., "Synchrotron study on load partitioning between ferrite/martensite and nanoparticles of a 9Cr ODS steel," Journal of Nuclear Materials, **445**, 209-217 (2014).
- ⁵³ L. Sun, D. Marrocchelli, and B. Yildiz, "Edge dislocation slows down oxide ion diffusion in doped CeO₂ by segregation of charged defects," Nature Communications, **6**, 6294 (2015)
- ⁵⁴ J. Maier, "Crystalline solid electrolytes and defect chemistry: Some novel thermodynamic and kinetic results," Solid State Ionics, **86-88**, 55-57 (1996).
- ⁵⁵ J. L. Alonso, "Phase diagram and influence of defects in the double perovskites," Physical Review B, **76**, 214423 (2003).
- ⁵⁶ R. Korobko, A. Patlolla, A. Kosoy, E. Wachtel, H. Tuller et al., "Giant Electrostriction in Gd-Doped Ceria," Advanced Materials, **24** 5857-5861 (2012).

- ⁵⁷ R. A. De Souza, "Introduction to the special issue on defects and transport in complex oxides," *Computational Materials Science*, **103**, 205 (2015).
- ⁵⁸ D. Pramanick, D. Damjanovic, J. E. Daniels, J. C. Nino, J. L. Jones, "Origins of electro-mechanical coupling in polycrystalline ferroelectrics during subcoercive electrical loading," *Journal of the American Ceramic Society*, **94** [2] 293-309 (2011).
- ⁵⁹ D. M. Marincel, K. Zhang, S. Jesse, S. V. Kalinin, W. M. Rainforth, et al., "Influence of a single grain boundary on domain wall motion in ferroelectrics," *Advanced Functional Materials* **24** [10] 1409-1417 (2014).
- ⁶⁰ P. Bintachitt, S. Jesse, D. Damjanovic, Y. Han, I. M. Reaney, et al., "Collective Dynamics Underpins Rayleigh Behavior in Disordered Polycrystalline Ferroelectrics," *Proceedings of the National Academy of Sciences*, **107** [16] 7219-7224 (2010).
- ⁶¹ L. R. Dedon, S. Saremi, Z. H. Chen, A. R. Damodaran, B. A. Apgar, et al., "Nonstoichiometry, Structure, and Properties of BiFeO₃ Films," *Chemistry of Materials*, **28** [16] 5952-5961 (2016).
- ⁶² C. M. Rost, E. Sachet, T. Borman, A. Moballegh, E. C. Dickey, et al., "Entropy-stabilized oxides," *Nature Communications*, **6**, 8485 (2015).
- ⁶³ K. Koumoto, R. Funahashi, E. Guilmeau, Y. Miyazaki, A. Weidenkaff, et al., "Thermoelectric ceramics for energy harvesting," *Journal of the American Ceramic Society*, **96** [1] 1-23 (2012).
- ⁶⁴ M. Backhaus-Ricoult, J. Rustad, L. Moore, C. Smith, J. Brown, "Semiconducting large bandgap oxides as potential thermoelectric materials for high-temperature power generation?," *Applied Physics A*, **116** [2] 433-70 (2014).

- ⁶⁵ N. Biškup, J. Salafranca, V. Mehta, M. P. Oxley, Y. Suzuki, et al., “Insulating Ferromagnetic LaCoO_{3-δ} Films: A Phase Induced by Ordering of Oxygen Vacancies,” *Physical Review Letters*, **112**, 087202-087205 (2014).
- ⁶⁶ J. J. Yang, D. B. Strukov, D. R. Stewart, “Memristive devices for computing,” *Nature Nanotechnology*, **8**, 13-24 (2013).
- ⁶⁷ F. Messerschmitt, M. Kubicek, S. Schweiger, and J. L. Rupp, “Memristor Kinetics and Diffusion Characteristics for Mixed Anionic-Electronic SrTiO_{3-δ} Bits: The Memristor-Based Cottrell Analysis Connecting Material to Device Performance,” *Advanced Functional Materials*, **24** [47] 7448-7460 (2014).
- ⁶⁸ E. Breckenfeld, N. Bronn, J. Karthik, A. R. Damndaran, S. Lee, et al., “Effect of Growth Induced (Non)Stoichiometry on Interfacial Conductance in LaAlO₃/SrTiO₃,” *Physical Review Letters*, **110**, 196804 (2013).
- ⁶⁹ M. P. Warusawithana, C. Richter, J. A. Mundy, P. Roy, J. Ludwig, et al., “LaAlO₃ stoichiometry is key to electron liquid formation at LaAlO₃/SrTiO₃ interfaces,” *Nature Communications*, **4**, 2351 (2013).
- ⁷⁰ H.K. Sato, C. Bell, Y. Hikita, H.Y. Hwang, et al., “Stoichiometry control of the electronic properties of the LaAlO₃/SrTiO₃ heterointerface,” *Applied Physics Letters*, **102**, 251602 (2013).
- ⁷¹ E. Breckenfeld, N. Bronn, N. Mason, and L. W. Martin, “Tunability of conduction at the LaAlO₃/SrTiO₃ heterointerface: Thickness and compositional studies,” *Applied Physics Letters*, **105**, 121610 (2014).

- ⁷² S.V. Kalinin, A. Borisevich, and D. Fong, “Beyond Condensed Matter Physics on the Nanoscale: The Role of Ionic and Electrochemical Phenomena in the Physical Functionalities of Oxide Materials,” *ACS Nano* **6**, 10423-10437 (2012).
- ⁷³ E. Breckenfeld, A. B. Shah, and L. W. Martin, “Strain evolution in non-stoichiometric heteroepitaxial thin-film perovskites,” *Journal of Materials Chemistry C*, **1**, 8052-8059 (2013).
- ⁷⁴ T. Minato, M. Kawai, and Y. Kim, “Creation of single oxygen vacancy on titanium dioxide surface,” *Journal of Materials Research*, **27**, 2237-2240 (2012).
- ⁷⁵ K. K. Adepilli, M. Kelsch, R. Merkle, and J. Maier, “Influence of line defects on the electrical properties of single crystal TiO₂,” *Advanced Functional Materials*, **23**, 1798-1806 (2013).
- ⁷⁶ A. N. Morozovska, E. A. Eliseev, A. K. Tagantsev, S. L. Bravina, L.-Q. Chen, and S. V. Kalinin, “Thermodynamics of electromechanically coupled mixed ionic-electronic conductors: Deformation potential, Vegard strains, and flexoelectric effect,” *Physical Review B*, **83**, 195313 (2011).
- ⁷⁷ A. R. Damodaran, E. Breckenfeld, Z. Chen, S. Lee, and L. W. Martin, “Enhancement of Ferroelectric Curie Temperature in BaTiO₃ Films via Strain- Induced Defect Dipole Alignment,” *Advanced Materials*, **26**, 6341-6347 (2014).
- ⁷⁸ Z. Wang, A. Loon, A. Subramanian, S. Gerhold, E. McDermott, et al., “Transition from Reconstruction toward Thin Film on the (110) Surface of Strontium Titanate,” *Nano Letters*, **16**, 2407-2412 (2016).
- ⁷⁹ W. Lee, J. W. Han, Y. Chen, Z. Cai and B. Yildiz, “Cation Size Mismatch and Charge Interactions Drive Dopant Segregation at the Surfaces of Manganite Perovskites,” *Journal of the American Chemical Society* **135** [21] 7909–7925 (2013).

- ⁸⁰ M. Backhaus-Ricoult, “Interface chemistry in LSM–YSZ composite SOFC cathodes,” *Solid State Ionics*, **177**, 2195–2200 (2006).
- ⁸¹ N. Tsvetkov, Q. Lu, L. Sun, E. Crumlin and B. Yildiz, “Improved chemical and electrochemical stability of perovskite oxides with less reducible cations at the surface,” *Nature Materials*, **15**, 1010–1016 (2016).
- ⁸² R. Jacobs, J. Booske, and D. Morgan, “Understanding and Controlling the Work Function of Perovskite Oxides Using Density Functional Theory,” *Advanced Functional Materials*, **10**, 1002 (2016).
- ⁸³ Y. Fan, Y. N. Osetskly, S. Yip, and B. Yildiz, “Mapping strain rate dependence of dislocation-defect interactions by atomistic simulations,” *Proceedings of the National Academy of Sciences*, **110** [44] 17756-17761 (2013).
- ⁸⁴ E. A. Carter, “Challenges in Modeling Materials Properties Without Experimental Input,” *Science*, **321**, 800 (2008).
- ⁸⁵ P. Knauth, “Inorganic solid Li ion conductors: An overview,” *Solid State Ionics*, **180** 911-916 (2009).
- ⁸⁶ S. Saremi, R. Xu, L. R. Dedon, J. A. Mundy, S. L. Hsu, et al., “Enhanced Electrical Resistivity and Properties via Ion Bombardment of Ferroelectric Thin Films,” *Advanced Materials*, **10**, 1002 (2016).
- ⁸⁷ N. Sata, K. Eberman, K. Eberl, and J. Maier, “Mesoscopic fast ion conduction in nanometre-scale planar heterostructures,” *Nature*, **408** [6815] 946-9 (2000).
- ⁸⁸ X. Sang and J. M. LeBeau, “Revolving scanning transmission electron microscopy: Correcting sample drift distortions without prior knowledge,” *Ultramicroscopy* **138**, 28-35 (2014)

- ⁸⁹ A. B. Yankovich, B. Berkels, W. Dahmen, P. Binev, S. I. Sanchez, et al., “Picometre-precision analysis of scanning transmission electron microscopy images of platinum catalysis,” *Nature Communications*, **5**, 4155 (2014).
- ⁹⁰ J. M. LeBeau, S. D. Findlay, L. J. Allen, and S. Stemmer, “Standardless Atom Counting in Scanning Transmission Electron Microscopy,” *Nano Letters*, **10** [11] 4405-08 (2010).
- ⁹¹ D. A. Muller, L. F. Kourkoutis, M. Murfitt, J. H. Song, H. Y. Hwang, et al., “Atomic-scale chemical imaging of composition and bonding by aberration-corrected microscopy,” *Science*, **319** 1073-76 (2008)
- ⁹² M. Varela, S. D. Findlay, A. R. Lupini, H. M. Christen, A. Y. Borisevich, et al., “Spectroscopic imaging of single atoms within a bulk solid,” *Physical Review Letters*, **92** [9] 95502 (2004).
- ⁹³ L. F. Allard, W. C. Bigelow, M. Jose-Yacamán, D. P. Nackashi, J. Damiano, and S. E. Mick, “A New MEMS-Based System for Ultra-High-Resolution Imaging at Elevated Temperatures,” *Microsc. Res. Tech.*, **72** [3] 208-15 (2009)
- ⁹⁴ S. Baier, A. Wittstock, C. D. Damsgaard, A. Diaz, J. Reinhardt, et al., “Influence of gas atmospheres and ceria on the stability of nanoporous gold studied by **environmental** electron microscopy and in situ ptychography,” *RSC Advances*, **6** [86] 83031-43 (2016).
- ⁹⁵ M. Backhaus-Ricoult, K. Adib, T. St.Clair, B. Luerssen, L. Gregoratti, A. Barinov, “In-situ study of operating SOFC LSM/YSZ cathodes under polarization by photoelectron microscopy,” *Solid State Ionics*, **179** [21–26] 891–895 (2008).
- ⁹⁶ M. Backhaus-Ricoult, K. Work, K. Adib, L. Gregoratti, and M. Amati, “Impact of Surface Chemistry on the Electrochemical Performance of Perovskite Cathodes,” *ECS Transactions*, **61**, 3-21 (2014).

- ⁹⁷ M. Backhaus-Ricoult, K. Adib, K. Work, M. Badding, T. Ketcham, M. Amati, L. Gregoratti, “In-situ scanning photoelectron microscopy study of operating (La,Sr)FeO₃-based NO_x-sensing surfaces,” *Solid State Ionics*, **225**, 716–726 (2012).
- ⁹⁸ M. R. Castell, “Scanning tunneling microscopy of reconstructions of the SrTiO₃(001) surface,” *Surface Science*, **505**, 1-13 (2002).
- ⁹⁹ M. J. Zhou, L. Yan, E. G. Fu, Y. Q. Wang, A. Misra, et al., “Phase transformations and defect clusters in single crystal SrTiO₂ irradiated at different temperatures,” *Journal of Nuclear Materials*, **442** [1-3] 143-47 (2013).
- ¹⁰⁰ C.-H. Lee, N. D. Orloff, T. Birol, Y. Zhu, V. Goian, et al., “Exploiting dimensionality and defect mitigation to create tunable microwave dielectrics,” *Nature*, **502**, 532-536 (2013).
- ¹⁰¹ Y. C. Zhou and T. Hashida, “Delamination **Cracking** in Thermal Barrier Coating System,” *Journal of Engineering for Gas Turbines and Power*, **124** [4] 922-930 (2002).
- ¹⁰² S. Lee, H. Seo, G. Lucovsky, L. B. Fleming, M. D. Ulrich, et al., “Bulk defects in nano-crystalline and in non-crystalline HfO₂-based thin film dielectrics,” *Thin Solid Films*, **517** [1] 437-40 (2008).
- ¹⁰³ <https://fuelcellsworks.com/archives/2012/03/30/world-record-julich-fuel-cell-passes-40000-hour-mark/>
- ¹⁰⁴ Memristor – Wikipedia - <https://en.wikipedia.org/wiki/Memristor>
- ¹⁰⁵ <https://madeby.google.com/phone/>
- ¹⁰⁶ Turbine blades – <http://www.supergenple.net/themes/theme2/turbines.png>
- ¹⁰⁷ <http://www.rbdinstruments.com/blog/tag/filament/> (Used with permission.)

- ¹⁰⁸ J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, et al., "Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials," *Science*, **331** [6017] 568-71 (2011). 10.1126/science.1194975
- ¹⁰⁹ H. Qian and J. Luo, "Vanadia-based equilibrium-thickness amorphous films on anatase (101) surfaces," *Applied Physics Letters*, **91** [6] (2007). 10.1063/1.2768315
- ¹¹⁰ S. J. Dillon, M. Tang, W. C. Carter, and M. P. Harmer, "Complexion: A new concept for kinetic engineering in materials science," *Acta Materialia*, **55** [18] 6208-18 (2007). 10.1016/j.actamat.2007.07.029
- ¹¹¹ M. M. J. Treacy, S. B. Rice, A. J. Jacobson, and J. T. Lewandowski, "Electron-Microscopy study of delimitation in dispersions of the perovskite-related layered phases of $\text{KCa}_2\text{NaN}_3\text{Nb}_3\text{O}_{3N+1}$ - evidence for single-layer formation," *Chemistry of Materials*, **2** [3] 279-86 (1990). 10.1021/cm00009a018
- ¹¹² V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, and J. N. Coleman, "Liquid Exfoliation of Layered Materials," *Science*, **340** [6139] 1420-+ (2013). 10.1126/science.1226419
- ¹¹³ P. F. Luckham and S. Rossi, "The colloidal and rheological properties of bentonite suspensions," *Advances in Colloid and Interface Science*, **82** [1-3] 43-92 (1999). 10.1016/s0001-8686(99)00005-6
- ¹¹⁴ R. Ma and T. Sasaki, "Nanosheets of Oxides and Hydroxides: Ultimate 2D Charge-Bearing Functional Crystallites," *Advanced Materials*, **22** [45] 5082-104 (2010). 10.1002/adma.201001722

- ¹¹⁵ M. Osada and T. Sasaki, "Two-Dimensional Dielectric Nanosheets: Novel Nanoelectronics From Nanocrystal Building Blocks," *Advanced Materials*, **24** [2] 210-28 (2012).
10.1002/adma.201103241
- ¹¹⁶ D. Golberg, Y. Bando, Y. Huang, T. Terao, M. Mitome, et al., "Boron Nitride Nanotubes and Nanosheets," *ACS Nano*, **4** [6] 2979-93 (2010). 10.1021/nn1006495
- ¹¹⁷ M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, et al., "Two-Dimensional Transition Metal Carbides," *ACS Nano*, **6** [2] 1322-31 (2012). 10.1021/nn204153h
- ¹¹⁸ P. R. Cantwell, M. Tang, S. J. Dillon, J. Luo, G. S. Rohrer, and M. P. Harmer, "Grain boundary complexions," *Acta Materialia*, **62**, 1-48 (2014). 10.1016/j.actamat.2013.07.037
- ¹¹⁹ J. Luo and Y.-M. Chiang, "Wetting and prewetting on ceramic surfaces," *Annual Review of Materials Research*, **38**, 227-49 (2008). 10.1146/annurev.matsci.38.060407.132431
- ¹²⁰ M. Baram, D. Chatain, and W. D. Kaplan, "Nanometer-Thick Equilibrium Films: The Interface Between Thermodynamics and Atomistics," *Science*, **332** [6026] 206-09 (2011).
10.1126/science.1201596
- ¹²¹ S. Kim, O. Sinai, C.-W. Lee, and A. M. Rappe, "Controlling oxide surface dipole and reactivity with intrinsic nonstoichiometric epitaxial reconstructions," *Physical Review B*, **92** [23] (2015). 10.1103/PhysRevB.92.235431
- ¹²² Y. Zhu, P. A. Salvador, and G. S. Rohrer, "Controlling the Relative Areas of Photocathodic and Photoanodic Terraces on the SrTiO₃(111) Surface," *Chemistry of Materials*, **28** [14] 5155-62 (2016). 10.1021/acs.chemmater.6b02205
- ¹²³ J. Luo, "Developing Interfacial Phase Diagrams for Applications in Activated Sintering and Beyond: Current Status and Future Directions," *Journal of the American Ceramic Society*, **95** [8] 2358-71 (2012). 10.1111/j.1551-2916.2011.05059.x

- ¹²⁴ M. P. Harmer, "Interfacial Kinetic Engineering: How Far Have We Come Since Kingery's Inaugural Sosman Address?," *Journal of the American Ceramic Society*, **93** [2] 301-17 (2010). 10.1111/j.1551-2916.2009.03545.x
- ¹²⁵ J. Luo, "Stabilization of nanoscale quasi-liquid interfacial films in inorganic materials: A review and critical assessment," *Critical Reviews in Solid State and Materials Sciences*, **32** [1-2] 67-109 (2007). 10.1080/10408430701364388
- ¹²⁶ A. Orum, M. M. Yildizhan, M. Sezen, M. A. Gulgun, K. Takatori, et al., "Transmission electron microscopy of topochemical conversion interface between $\text{La}_2\text{Ti}_2\text{O}_7$ reactive template and perovskite product $\text{Li}_{0.16}\text{La}_{0.62}\text{TiO}_3$ electrolyte," *Solid State Ionics*, **296**, 78-84 (2016).
- ¹²⁷ P. Simon, Y. Gogotsi, and B. Dunn, "Where Do Batteries End and Supercapacitors Begin?," *Science*, **343** [6176] 1210-11 (2014). 10.1126/science.1249625
- ¹²⁸ H. Z. Guo, A. L. Baker, J. Guo, C.A. Randall, "Cold Sintering Process: A Novel Technique for Low-Temperature Ceramic Processing of Ferroelectrics," *Journal of the American Ceramic Society*, **99** [11] 3489-507 (2016).
- ¹²⁹ X. Zou, A. Goswami, and T. Asefa, "Efficient Noble Metal-Free (Electro)Catalysis of Water and Alcohol Oxidations by Zinc-Cobalt Layered Double Hydroxide," *Journal of the American Chemical Society*, **135** [46] 17242-45 (2013). 10.1021/ja407174u
- ¹³⁰ P. R. Cantwell, S. Ma, S. A. Bojarski, G. S. Rohrer, and M. P. Harmer, "Expanding time-temperature-transformation (TTT) diagrams to interfaces: A new approach for grain boundary engineering," *Acta Materialia*, **106** 78-86 (2016). 10.1016/j.actamat.2016.01.010

- ¹³¹ X. Xiao, H. Song, S. Lin, Y. Zhou, X. Zhan, et al., "Scalable salt-templated synthesis of two-dimensional transition metal oxides," *Nature Communications*, **7** (2016).
10.1038/ncomms11296
- ¹³² A. Ohtomo and H. Y. Hwang, "A high-mobility electron gas at the $\text{LaAlO}_3/\text{SrTiO}_3$ heterointerface," *Nature*, **427** [6973] 423-26 (2004). 10.1038/nature02308
- ¹³³ A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nature Materials*, **6** [3] 183-91 (2007). 10.1038/nmat1849
- ¹³⁴ S. Bajaj, H. Wang, J. W. Doak, C. Wolverton, and G. J. Snyder, "Calculation of dopant solubilities and phase diagrams of X-Pb-Se (X = Br, Na) limited to defects with localized charge," *Journal of Materials Chemistry C*, **4** [9] 1769-75 (2016). 10.1039/c5tc03970c
- ¹³⁵ R. Armiento, B. Kozinsky, M. Fornari, and G. Ceder, "Screening for high-performance piezoelectrics using high-throughput density functional theory," *Physical Review B*, **84** [1] (2011). 10.1103/PhysRevB.84.014103
- ¹³⁶ A. Jain, O. Shyue Ping, G. Hautier, W. Chen, W. D. Richards, et al., "Commentary: The Materials Project: A materials genome approach to accelerating materials innovation," *APL Materials*, **1** [1] (2013). 10.1063/1.4812323
- ¹³⁷ M. Tang, W. C. Carter, and R. M. Cannon, "Diffuse interface model for structural transitions of grain boundaries," *Physical Review B*, **73** [2] 14 (2006). 10.1103/PhysRevB.73.024102
- ¹³⁸ Alloy Theoretic Automated Toolkit (ATAT) Home Page,
<https://www.brown.edu/Departments/Engineering/Labs/avdw/atat/>.
- ¹³⁹ Atomic Simulation Environment, <https://wiki.fysik.dtu.dk/ase>, 2016.
- ¹⁴⁰ Object Oriented Finite Element Analysis for material microstructures,
<http://www.ctcms.nist.gov/oof/oof3d/>.

- ¹⁴¹ MOOSE Framework Open Source Multiphysics, <http://mooseframework.org>, 2016.
- ¹⁴² Dakota: Algorithms for design exploration and simulation credibility, <https://dakota.sandia.gov/content/packages>, 2016.
- ¹⁴³ M. Armand and J. M. Tarascon, "Building better batteries," *Nature*, **451** [7179] 652-57 (2008).
10.1038/451652a
- ¹⁴⁴ M. R. Lukatskaya, B. Dunn, and Y. Gogotsi, "Multidimensional materials and device architectures for future hybrid energy storage," *Nature Communications*, **7**, 12647-47 (2016).
10.1038/ncomms12647
- ¹⁴⁵ W. Lei, V. N. Mochalin, D. Liu, S. Qin, Y. Gogotsi, and Y. Chen, "Boron nitride colloidal solutions, ultralight aerogels and freestanding membranes through one-step exfoliation and functionalization," *Nature Communications*, **6**, 8849 (2015). 10.1038/ncomms9849
- ¹⁴⁶ B. R. Sathe, X. Zou, and T. Asefa, "Metal-free B-doped graphene with efficient electrocatalytic activity for hydrogen evolution reaction," *Catalysis Science & Technology*, **4** [7] 2023-30 (2014). 10.1039/c4cy00075g
- ¹⁴⁷ J. Knaster, A. Moeslang and T. Muroga: "Materials research for fusion," *Nature Physics* **12** 424-434 (2016).
- ¹⁴⁸ Unpublished image, courtesy of Frank W. Zok
- ¹⁴⁹ <http://www.gereports.com/post/119035992715/these-space-age-ceramics-will-be-your-jet-engines/>
- ¹⁵⁰ Unpublished image, courtesy of John Shaw

- ¹⁵¹ D. Ellerby, S. Beckman, E. Irby, S. M. Johnson, M. Gasch and M. Gusman, "Materials Development and Characterization of HfB₂/SiC Ceramics For Use In Sharp Leading Edge Applications", Proceedings of the 2004 Joint Army Navy NASA Air Force Conference.
- ¹⁵² D. M. Van Wie, D. G. Drewry, D. E. King, and C. M. Hudson, "The hypersonic environment: Required operating conditions and design challenges," *Journal of Materials Science*, **39** [19] 5915-5924, (2004).
- ¹⁵³ A. Paul, D. D. Jayaseelan, S. Venugopal, E. Zapata-Solvas, J. Binner, et al., "UHTC composites for hypersonic applications," *American Ceramic Society Bulletin*, **91** [1] 22-29 (2012).
- ¹⁵⁴ F. Monteverde, R. Savino, M. S. Fumo, and A. Di Maso, "Plasma wind tunnel testing of ultra-high temperature ZrB₂-SiC composites under hypersonic re-entry conditions," *Journal of the European Ceramic Society*, **30** 2313-2321 (2010).
- ¹⁵⁵ T. H. Squire and J. Marschall, "Material property requirements for analysis and design of UHTC components in hypersonic applications," *Journal of the European Ceramic Society*, **30**, 2239-2251 (2010).
- ¹⁵⁶ A. Bongiorno, C. J. Fröst, R. K. Kalia, J. Li, J. Marschall, et al., "A Perspective on Modeling Materials in Extreme Environments: Oxidation of Ultrahigh-Temperature Ceramics," *MRS Bulletin*, **31** 410-418 (2006).
- ¹⁵⁷ J. Marschall, A. Chamberlain, D. Crunkleton, and B. Rogers, "Catalytic Atom Recombination on ZrB₂/SiC and HfB₂/SiC Ultrahigh-Temperature Ceramic Composites," *Journal of Spacecraft and Rockets*, **41** [4] (2004)

- ¹⁵⁸ W. G. Fahrenholtz and G. E. Hilmas, "Refractory Diborides of Zirconium and Hafnium," *Journal of the American Ceramic Society*, **90** [5] 1347-1364 (2007).
- ¹⁵⁹ D. B. Marshall and B. N. Cox, "Integral Textile Ceramic Structures," *Annual Reviews of Materials Research*, **38**, 425-443 (2008).
- ¹⁶⁰ S. R. Levine, E. J. Opila, M. C. Halbig, J. D. Kiser, M. Singh, and J. A. Salem, "Evaluation of ultra-high temperature ceramics for aeropropulsion use," *Journal of the European Ceramic Society*, **22** [14-15] 2757-2767 (2002).
- ¹⁶¹ W. G. Fahrenholtz, "Thermodynamic Analysis of ZrB_2 -SiC Oxidation: Formation of a SiC-Depleted Region," *Journal of the American Ceramic Society*, **90** [1] 143-148 (2007).
- ¹⁶² M. Gasch and S. Johnson, "Physical characterization and arcjet oxidation of hafnium-based ultra high temperature ceramics fabricated by hot pressing and field-assisted sintering," *Journal of the European Ceramic Society*, **30** [11] 2337-2344 (2010).
- ¹⁶³ D. L. Poerschke, M. D. Novak, N. M. Abdul-Jabbar, M. D. Novak, S. Krämer, and C. G. Levi, "Selective active oxidation in hafnium boride-silicon carbide composites above 2000°C," *Journal of the European Ceramic Society*, **36** [15] 3697-3707 (2016).
- ¹⁶⁴ N. P. Padture, "Advanced structural ceramics in aerospace propulsion," *Nature Materials*, **15** 804-809 (2016).
- ¹⁶⁵ R. C. Reed, "The Superalloys: Fundamentals and Applications," pp. 372. New York: Cambridge University Press. (2006).
- ¹⁶⁶ J. H. Perepezko, "The Hotter the Engine, the Better," *Science*, **326** [5956] 1068-1069 (2009).
- ¹⁶⁷ T. M. Pollock, J. Dibbern, M. Tsunekane, J. Zhu, and A. Suzuki, "New Co-based γ - γ' High-temperature Alloys," *Journal of Metals*, **62** [1] 58-63 (2010).

- ¹⁶⁸ F. W. Zok, "Ceramic-matrix composites enable revolutionary gains in turbine engine efficiency," *American Ceramic Society Bulletin*, **95** [5] 22-28 (2016).
- ¹⁶⁹ A. G. Evans, D. R. Clarke, and C. G. Levi, "The influence of oxides on the performance of advanced gas turbines," *Journal of the European Ceramic Society*, **28** [7] 1405-1419 (2008).
- ¹⁷⁰ K. N. Lee, D. S. Fox, and N. P. Bansal, "Rare earth silicate environmental barrier coatings for SiC/SiC composites and Si₃N₄ ceramics," *Journal of the European Ceramic Society*, **25**, 1705-1715 (2005).
- ¹⁷¹ C. G. Levi, J. W. Hutchinson, M.-H. Vidal-Setif, and C. A. Johnson, "Environmental Degradation of TBCs by Molten Deposits," *MRS Bulletin*, **37** [10] 932-941 (2012).
- ¹⁷² R. W. Jackson, E. M. Zaleski, B. T. Hazel, M. R. Begley, and C. G. Levi, "Response of Molten Silicate Infiltrated Gd₂Zr₂O₇ Thermal Barrier Coatings to Temperature Gradients," *Acta Materialia*, (**submitted**), (2016).
- ¹⁷³ D. L. Poerschke, D. D. Hass, S. Eustis, G. G. E. Seward, J. S. Van Sluytman, and C. G. Levi, "Stability and CMAS resistance of ytterbium-silicate/hafnate TBC/EBCs for SiC Composites," *Journal of the American Ceramic Society*, **98** [1] 278-286 (2015).
- ¹⁷⁴ F. Stolzenburg, M.T. Johnson, K.N. Lee, and K. T. Faber, "The interaction of calcium-magnesium-aluminosilicate with ytterbium silicate environmental barrier materials," *Surface Coatings and Technology*, **284** 44-50 (2015).
- ¹⁷⁵ H. B. Zhao, B. T. Richards, C. G. Levi, and H. N. G. Wadley, "Molten silicate reactions with plasma sprayed ytterbium silicate coatings," *Surface and Coatings Technology*, **288** 151-162 (2016).

- ¹⁷⁶ W. E. Lee, M. Gilbert, S. T. Murphy, and R. W. Grimes, "Opportunities for Advanced Ceramics and Composites in the Nuclear Sector," *Journal of the American Ceramic Society*, **96** [7] 2005-2030 (2013).
- ¹⁷⁷ B. D. Wirth, K. Nordlund, D. G. Whyte, and D. Xu, "Fusion Materials Modeling: Challenges and Opportunities," *MRS Bulletin*, **36** [3] 216-222 (2011).
- ¹⁷⁸ M. Victoria, N. Baluc, and P. Spätig, "Structural materials for fusion reactors," *Nuclear Fusion*, **41** [8] 1047-1053 (2001).
- ¹⁷⁹ N. Dubrovinskaia, L. Dubrovinsky, N. A. Solopova, A. Abakmov, S. Turner, et al., "Terapascal static pressure generation with ultrahigh yield strength nanodiamond," *Science Advances*, **2** [e1600341] 1-12 (2016).
- ¹⁸⁰ X. Liu, X. Chen, H.-A. Ma, X. Jia, J. Wu, et al., "Ultrahard stitching of nanotwinned diamond and cubic boron nitride in C₂-BN composite," *Scientific Reports*, **6** [30518] 1-9 (2016).
- ¹⁸¹ B. G. Compton, E. A. Gamble, and F. W. Zok, "Failure initiation during impact of metal spheres onto ceramic targets," *International Journal of Impact Engineering*, **55**, 11-23 (2013).
- ¹⁸² G. Subhash, A. P. Awasthi, C. Kunka, P. Jannotti, and M. DeVries, "In search of amorphization-resistant boron carbide," *Scripta Materialia*, **123**, 158-162 (2016).
- ¹⁸³ K. Koumoto, Y. Wang, R. Zhang, A. Kosuga, and R. Funahashi, "Oxide Thermoelectric Materials: A Nanostructuring Approach," *Annual Reviews of Materials Research*, **40**, 363-394 (2010).
- ¹⁸⁴ J.-M. Tarascon, "Solid oxide fuel cells for power generation," *Philosophical Transactions: Mathematical, Physical and Engineering Sciences*, **368** [1923] 3227-3241 (2010).

- ¹⁸⁵ S. C. Singhal, "Solid oxide fuel cells for power generation," *Wiley Interdisciplinary Reviews - Energy and Environment*, **3** [2] 179-194 (2014).
- ¹⁸⁶ C. Kim, G. Pilania, and R. Ramprasad, "From Organized High-Throughput Data to Phenomenological Theory using Machine Learning: The Example of Dielectric Breakdown," *Chemistry of Materials*, **28**, 1304-1311 (2016).
- ¹⁸⁷ O. Gutfleisch, M. A. Willard, E. Brück, C. H. Chen, S. G. Sankar, and J. P. Liu, "Magnetic Materials and Devices for the 21st Century: Stronger, Lighter, and More Energy Efficient " *Advanced Materials*, **23**, 821-842 (2011).
- ¹⁸⁸ M. R. Norman, "Materials design for new superconductors," *Reports of Progress in Physics*, **79** [074502] 1-9 (2016).
- ¹⁸⁹ J. Wadsworth, G. W. Crabtree, and R. J. Hemley, "Basic Research Needs for Materials under Extreme Environments," DOE Office of Basic Energy Sciences, (2008).
- ¹⁹⁰ M. R. Begley and J. W. Hutchinson, "The Mechanics and Reliability of Films, Coatings and Multilayers." New York, NY: Cambridge University Press. (2016).
- ¹⁹¹ T. A. Parthasarathy, R. A. Rapp, M. Opeka, and R. J. Kerans, "A model for the oxidation of ZrB₂, HfB₂ and TiB₂," *Acta Materialia*, **55** [17] 5999-6010, (2007).
- ¹⁹² D. D. Jayaseelan, E. Zapata-Solvas, P. Brown, and W. E. Lee, "In situ Formation of Oxidation Resistant Refractory Coatings on SiC-Reinforced ZrB₂ Ultra High Temperature Ceramics," *Journal of the American Ceramic Society*, **95** [4] 1247-1254 (2012).
- ¹⁹³ K. M. Grant, S. Krämer, J. P. A. Löfvader, and C. G. Levi, "CMAS degradation of environmental barrier coatings," *Surface and Coatings Technology*, **202**, 653-657 (2007).

- ¹⁹⁴ Q.-J. Hong and A. Van de Walle, "Prediction of the material with highest known melting point from ab initio molecular dynamics calculations," *Physical Review B*, **92** [020104] 1-6 (2015).
- ¹⁹⁵ O. Cedillos-Barraza, D. Manara, K. Boboridis, T. Wakins, et al., "Investigating the highest melting temperature materials: A laser melting study of the TaC-HfC system," *Scientific Reports*, **6** 37962/ DOI:10.1038/srep37962 (2016).
- ¹⁹⁶ E. Rudy, "Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems. Part V. Compendium of Phase Diagram Data," Technical Report AFML-TR-65-2, Part V., Air Force Materials Laboratory, (1969).
- ¹⁹⁷ Y. Pan, P. Zhou, Y. Peng, Y. Du, and F. Luo, "A thermodynamic description of the C-Hf-Ta system over the whole composition and temperature ranges," *CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry*, **53** 1-9 (2016).
- ¹⁹⁸ A. L. Ivanovskii, "Mechanical and electronic properties of diborides of transition 3d-5d metals from first principles: Toward search of novel ultra-incompressible and superhard materials," *Progress in Materials Science*, **57**, 184-228 (2012).
- ¹⁹⁹ D. Alfè, M. J. Gillian, and G. D. Price, "The melting curve of iron at the pressures of the Earth's core from ab initio calculations," *Nature*, **401**, 462-464 (1999).
- ²⁰⁰ A. I. Duff, T. Davey, D. Korbmacher, A. Glensk, B. Grabowski, et al., "Improved method of calculating ab initio high-temperature thermodynamic properties with application to ZrC," *Physical Review B*, **91** [214311] 1-8, (2015).
- ²⁰¹ R. J. N. Baldock, L. B. Pártay, A. P. Bartók, M. C. Payne, and G. Csányi, "Determining pressure-temperature phase diagrams of materials," *Physical Review B*, **93** [174108] 1-9 (2016).

- ²⁰² S. V. Ushakov and A. Navrotsky, "Experimental Approaches to the Thermodynamics of Ceramics Above 1500°C," *Journal of the American Ceramic Society*, **95** [5] 1463-1482 (2012).
- ²⁰³ A. Navrotsky, "Progress and New Directions in Calorimetry: A 2014 Perspective," *Journal of the American Ceramic Society*, **97** [11] 3349-3359 (2014).
- ²⁰⁴ J. A. Krogstad, Y. Gao, J. Bai, J. Wang, D. M. Lipkin, and C. G. Levi, "In situ Diffraction Study of the High-Temperature Decomposition of t'-Zirconia," *Journal of the American Ceramic Society*, **98** [1] 247-254 (2015).
- ²⁰⁵ P. Sarin, W. Yoon, K. Jurkschat, P. Zschack, and W. M. Kriven, "Quadrupole lamp furnace for high temperature (up to 2050 K) synchrotron powder xray diffraction studies in air in reflection geometry," *Review of Scientific Instruments*, **77** [093906] 1-9 (2006).
- ²⁰⁶ S. N. Karlsdottir and J. W. Halloran, "Rapid Oxidation Characterization of Ultra-High Temperature Ceramics," *Journal of the American Ceramic Society*, **90** [10] 3233-3238 (2007).
- ²⁰⁷ C. Carney, T. A. Parthasarathy, and M. K. Cinibulk, "Separating Test Artifacts from Material Behavior in the Oxidation studies of HfB₂-SiC at 2000°C and Above," *International Journal of Applied Ceramic Technology*, **10** [2] 293-300 (2013).
- ²⁰⁸ Unpublished image, courtesy of Sergey Ushakov.
- ²⁰⁹ Unpublished images, courtesy of R. Wesley Jackson and Elisa M. Zaleski.
- ²¹⁰ D. Manara, M. Sheindin, W. Heinz, and C. Ronchi, "New techniques for high-temperature melting measurements in volatile refractory materials via laser surface heating," *Review of Scientific Instruments*, **79** [113901] 1-7 (2008).

- ²¹¹ E. W. Neuman, G. E. Hilmas, and W. G. Fahrenholtz, "Strength of Zirconium Diboride to 2300°C," *Journal of the American Ceramic Society*, **96** [1] 47-50 (2013).
- ²¹² M. Gasch, S. Johnson, and J. Marschall, "Thermal Conductivity Characterization of Hafnium Diboride-Based Ultra-High-Temperature Ceramics," *Journal of the American Ceramic Society*, **91** [5] 1423-1432 (2008).
- ²¹³ J. Blumm and J. Opfermann, "Thermophysical Properties of Silicon Carbide Green Bodies Prior to, During and After the Sintering Process," *High Temperatures/High Pressures*, **35** [5] 513-520 (2003).
- ²¹⁴ G. J. K. Harrington, "Effect of Solid Solutions and Second Phases on the Thermal Conductivity of Zirconium Diboride Ceramics," Ph.D. Thesis in Materials Science and Engineering, Missouri University of Science and Technology (2014).
- ²¹⁵ R. Savino, M. S. Fumo, L. Silvestroni, and D. Sciti, "Arc-jet testing on HfB₂ and HfC-based ultra-high temperature ceramic materials," *Journal of the European Ceramic Society*, **28** [9] 1899-1907 (2008).
- ²¹⁶ L. Larrimbe, M. Pettinà, K. Nikbin, E. L. Jones, A. P. Katz, et al., "High Heat Flux Laser Testing of HfB₂ Cylinders," *Journal of the American Ceramic Society*, **99** (published online), (2016).
- ²¹⁷ I. Szlufarska, K. T. Ramesh, and D. H. Warner, "Simulating Mechanical Behavior of Ceramics Under Extreme Conditions," *Annual Reviews of Materials Research*, **43**, 131-156 (2013).
- ²¹⁸ A. Haboub, H. A. Bale, J. R. Nasiatka, B. N. Cox, D. B. Marshall, et al., "Tensile testing of materials at high temperatures above 1700 °C with in situ synchrotron X-ray microtomography," *Review of Scientific Instruments*, **85** [083702] 1-13 (2014).

- ²¹⁹ H. A. Bale, A. Haboub, A. A. MacDowell, J. R. Nasiatka, D. Y. Parkinson, et al., "Real-time quantitative imaging of failure events in materials under load at temperatures above 1,600°C," *Nature Materials*, **12** [1] 40-46 (2013).
- ²²⁰ A. Shyam and E. Lara-Curzio, "The double-torsion testing technique for determination of fracture toughness and slow crack growth behavior of materials: A review," *Journal of Materials Science*, **41** [13] 4093-4104 (2006).
- ²²¹ G. Dwivedi, V. Viswanathan, S. Sampath, A. Shyam, and E. Lara-Curzio, "Fracture Toughness of Plasma-Sprayed Thermal Barrier Ceramics: Influence of Processing, Microstructure, and Thermal Aging," *Journal of the American Ceramic Society*, **97** [9] 2736-2744 (2014).
- ²²² E. M. Donohue, N. R. Philips, M. R. Begley, and C. G. Levi, "Thermal barrier coating toughness: measurement and identification of a bridging mechanism enabled by segmented microstructure," *Materials Science and Engineering A*, **564**, 324-330 (2013).
- ²²³ W. A. Bassett, "Diamond anvil cell, 50th birthday," *High Pressure Research*, **29** 163-186 (2009).
- ²²⁴ A.N. Clark, C.E. Lesher, S.D. Jacobsen, and S. Sen, "Mechanisms of anomalous compressibility of vitreous silica," *Physical Review B*, **90** [17] 174110 (2014).
- ²²⁵ M. Pettinà, F. Biglari, A. Heaton, P. Brown, and K. Nikbin, "Modelling damage and creep crack growth in structural ceramics at ultra-high temperatures," *Journal of the European Ceramic Society*, **34**, 2799-2805 (2014).
- ²²⁶ M. Pettinà, R. W. Harrison, L. J. Vandeperre, F. R. Biglari, P. Brown, et al., "Diffusion-based and creep continuum damage modelling of crack formation during high temperature

- oxidation of ZrN ceramics," *Journal of the European Ceramic Society*, **36**, 2341-2349 (2016).
- ²²⁷ M. R. Begley, N. R. Philips, B. G. Compton, D. Wilbrink, R. O. Ritchie, and M. Utz, "Micromechanical models to guide the development of brick and mortar composites," *Journal of the Mechanics and Physics of Solids*, **60** [8] 1545-1560 (2012).
- ²²⁸ T. A. Parthasarathy, R. A. Rapp, M. M. Opeka, and M. K. Cinibulk, "Modeling Oxidation Kinetics of SiC-Containing Refractory Diborides," *Journal of the American Ceramic Society*, **95** [1] 338-349 (2012).
- ²²⁹ M. Gasch, D. Ellerby, E. Irby, S. Beckman, M. Gusman, and S. Johnson, "Processing, properties and arc jet oxidation of hafnium diboride/silicon carbide ultra high temperature ceramics," *Journal of Materials Science*, **39** [19] 5925-5937 (2004).
- ²³⁰ J. Marschall, D. A. Pejakovic, W. G. Fahrenholtz, G. E. Hilmas, F. Panerai, and O. Chazot, "Temperature Jump Phenomenon During Plasmatron Testing of ZrB₂-SiC Ultrahigh-Temperature Ceramics," *Journal of Thermophysics and Heat Transfer*, **26** [559-572] (2012).
- ²³¹ J. Marschall and D. G. Fletcher, "High-enthalpy test environments, flow modeling and in situ diagnostics for characterizing ultra-high temperature ceramics," *Journal of the European Ceramic Society*, **30**, 2323-2336 (2010).
- ²³² M. D. Novak and F. W. Zok, "High temperature materials testing with full-field strain measurement: Experimental design and practice," *Review of Scientific Instruments*, **82** [115101] (2012).
- ²³³ R. W. Jackson, E. M. Zaleski, D. L. Poerschke, B. T. Hazel, M. R. Begley, and C. G. Levi, "Interaction of Molten Silicates with Thermal Barrier Coatings under Temperature Gradients.," *Acta Materialia*, **89**, 396-407 (2015).

- ²³⁴ S. F. Siddiqui, K. Knipe, A. Manero, C. Meid, J. Wischek, et al., "Synchrotron X-ray measurement techniques for thermal barrier coated cylindrical samples under thermal gradients," *Review of Scientific Instruments*, **84** [083904] 1-7 (2013).
- ²³⁵ C. M. Weyant, J. Almer, and K. T. Faber, "Through-thickness determination of phase composition and residual stresses in thermal barrier coatings using high-energy X-rays," *Acta Materialia*, **58**, 943-951, (2010).
- ²³⁶ B. J. Harder, J. Ramirez-Rico, J. D. Almer, K. N. Lee, and K. T. Faber, "Chemical and Mechanical Consequences of Environmental Barrier Coating Exposure to Calcium–Magnesium–Aluminosilicate," *Journal of the American Ceramic Society*, **94** [S1] S178-S185, (2011).
- ²³⁷ F. Stolzerburg, P. Kenesei, J. Almer, K. N. Lee, M. T. Johnson, and K. T. Faber, "The influence of calcium-magnesium-aluminosilicate deposits on internal stresses in $\text{Yb}_2\text{Si}_2\text{O}_7$ multilayer environmental barrier coatings," *Acta Materialia*, **105**, 189-198 (2016).
- ²³⁸ P. Staron, T. Fischer, J. Keckes, S. Schratte, T. Hatzebichler, et al., "Depth-Resolved Residual Stress Analysis with High-Energy Synchrotron X-Rays Using a Conical Slit Cell," *Materials Science Forum*, **768-769** 72-75, (2014).
- ²³⁹ J.C. Mauro, C.S. Philip, D.J. Vaughn, and M.S. Pambianchi, "Glass Science in the United States: Current Status and Future Directions," *International Journal of Applied Glass Science*, **5** [1] 2-15 (2014).
- ²⁴⁰ J.C. Mauro and E.D. Zanotto, "Two Centuries of Glass Research: Historical Trends, Current Status, and Grand Challenges for the Future," *International Journal of Applied Glass Science*, **5** [3] 313-327 (2014).

- ²⁴¹ J.S. Schilling, "The use of high pressure in basic and materials science," *Journal of Physics and Chemistry of Solids*, **59** [4] 553-568 (1998).
- ²⁴² T. Grande, J.R. Holloway, P.F. McMillan, and C.A. Angell, "Nitride Glasses Obtained by High-Pressure Synthesis," *Nature*, **369** [6475] 43-45 (1994).
- ²⁴³ K.L. Ngai and S. Capaccioli, "Impact of the application of pressure on the fundamental understanding of glass transition," *Journal of Physics-Condensed Matter*, **20**, 244101 (2008).
- ²⁴⁴ L. Wondraczek, S. Sen, H. Behrens, and R.E. Youngman, "Structure-energy map of alkali borosilicate glasses: Effects of pressure and temperature," *Physical Review B*, **76** (1) (2007).
- ²⁴⁵ M. Grimsditch, "Polymorphism in Amorphous SiO₂," *Physical Review Letters*, **52**, 2379 (1984).
- ²⁴⁶ M. Murakami and J.D. Bass, "Spectroscopic Evidence for Ultrahigh-Pressure Polymorphism in SiO₂ Glass," *Physical Review Letters*, **104** (2) (2010).
- ²⁴⁷ J. Nicholas, S. Sinogeikin, J. Kieffer, and J. Bass, "Spectroscopic evidence of polymorphism in vitreous B₂O₃," *Physical Review Letters*, **92** (21) (2004).
- ²⁴⁸ Y. Kono, C. Kenney-Benson, D. Ikuta, Y. Shibazaki, Y.B. Wang, and G.Y. Shen, "Ultrahigh-pressure polyamorphism in GeO₂ glass with coordination number > 6," *Proceedings of the National Academy of Sciences*, **113** [13] 3436-3441 (2016).
- ²⁴⁹ O. B. Tsiok, V. V. Brazhkin, A. G. Lyapin, and L. G. Khvostantsev, "Logarithmic Kinetics of the Amorphous-Amorphous Transformations in SiO₂ and GeO₂ Glasses under High Pressure," *Physical Review Letters*, **80**, 999 (1998).
- ²⁵⁰ A. Zeidler, K. Wezka, R. F. Rowlands, D.A.J. Whittaker, P.S. Salmon, et al., "High-Pressure Transformation of SiO₂ Glass from a Tetrahedral to an Octahedral Network: A Joint

Approach Using Neutron Diffraction and Molecular Dynamics," *Physical Review Letters*, **113**, 135501 (2014).

- ²⁵¹ Y. Meng, R. Hrubiak, E. Rod, R. Boehler, and G.Y. Shen, "New developments in laser-heated diamond anvil cell with in situ synchrotron x-ray diffraction at High Pressure Collaborative Access Team," *Review of Scientific Instruments*, **86** [7] 072201 (2015).
- ²⁵² P. S. Salmon and A. Zeidler, "Networks under pressure: the development of in situ high-pressure neutron diffraction for glassy and liquid materials," *Journal of Physics-Condensed Matter*, **27**, 133201 (2015).
- ²⁵³ S. K. Lee, P. J. Eng, H. K. Mao, Y. Meng, M. Newville, et al., "Probing of bonding changes in B₂O₃ glasses at high pressure with inelastic X-ray scattering," *Nature Materials*, **4** [11] 851-854 (2005).
- ²⁵⁴ J. F. Lin, M. Santoro, V. V. Struzhkin, H. K. Mao, and R. J. Hemley, "In situ high pressure-temperature Raman spectroscopy technique with laser-heated diamond anvil cells," *Review of Scientific Instruments*, **75** [10] 3302-3306 (2004).
- ²⁵⁵ F. F. Li, Q. L. Cui, Z. He, T. Cui, C. X. Gao, Q. Zhou, and G. T. Zou, "Brillouin scattering spectroscopy for a laser heated diamond anvil cell," *Applied Physics Letters*, **88** [20] 203507 (2006).
- ²⁵⁶ T. Edwards, T. Endo, J. H. Walton, and S. Sen, "Observation of the transition state for pressure-induced BO₃ → BO₄ conversion in glass," *Science*, **345** [6200] 1027-1029 (2014).
- ²⁵⁷ M. Storek, M. Adjei-Acheamfour, R. Christensen, S. W. Martin, and R. Boehmer, "Positive and Negative Mixed Glass Former Effects in Sodium Borosilicate and Borophosphate Glasses Studied by ²³Na NMR," *Journal of Physical Chemistry B*, **120** [19] 4482-4495 (2016).

- ²⁵⁸ S. W. Martin, C. Bischoff, and K. Schuller, "Composition Dependence of the Na⁺ Ion Conductivity in 0.5Na₂S + 0.5[xGeS₂ + (1 - x)PS_{5/2}] Mixed Glass Former Glasses: A Structural Interpretation of a Negative Mixed Glass Former Effect," *Journal of Physical Chemistry B*, **119** [51] 15738-15751 (2015).
- ²⁵⁹ R. Christensen, G. Olson, and S. W. Martin, "Ionic Conductivity of Mixed Glass Former 0.35Na₂O + 0.65[xB₂O₃ + (1 - x)P₂O₅] Glasses," *Journal of Physical Chemistry B*, **117** [51] 16577-16586 (2013).
- ²⁶⁰ M. Guerette, M. R. Ackerson, J. Thomas, F. L. Yuan, E. B. Watson, et al., "Structure and Properties of Silica Glass Densified in Cold Compression and Hot Compression," *Scientific Reports*, **5**, 15343 (2015).
- ²⁶¹ L. P. Huang and J. Kieffer, "Anomalous thermomechanical properties and laser-induced densification of vitreous silica," *Applied Physics Letters*, **89** [14] 141915 (2006).
- ²⁶² C. A. Angell, "Calorimetric studies of the energy landscapes of glassformers by hyperquenching methods," *Journal of Thermal Analysis and Calorimetry*, **69** [3] 785-794 (2002).
- ²⁶³ C. A. Angell, Y. Z. Yue, L. M. Wang, J.R.D. Copley, S. Borick, and S. Mossa, "Potential energy, relaxation, vibrational dynamics and the boson peak, of hyperquenched glasses," *Journal of Physics-Condensed Matter* **15** [11] S1051-S1068 (2003).
- ²⁶⁴ T. J. Kiczanski and J. F. Stebbins, "The development of a rapid quenching device for the study of the dependence of glass structure on fictive temperature," *Review of Scientific Instruments*, **77** [1] 013901 (2006).

- ²⁶⁵ T. Rouxel, H. Ji, J.P. Guin, F. Augereau, and B. Ruffle, "Indentation deformation mechanism in glass: Densification versus shear flow," *Journal of Applied Physics*, **107**, 9 (2010).
- ²⁶⁶ F.L. Yuan and L. P. Huang, "Brittle to Ductile Transition in Densified Silica Glass," *Scientific Reports*, **4**, 5035 (2014).
- ²⁶⁷ M. M. Smedskjaer, M. Bauchy, J. C. Mauro, S. J. Rzoska, and M. Bockowski, "Unique effects of thermal and pressure histories on glass hardness: Structural and topological origin," *Journal of Chemical Physics*, **143**, 16 (2015).
- ²⁶⁸ R. C. Liebermann, "Multi-anvil, high pressure apparatus: a half-century of development and progress," *High Pressure Research*, **31** [4] 493-532 (2011).
- ²⁶⁹ M. M. Smedskjaer, S. J. Rzoska, M. Bockowski, and J. C. Mauro, "Mixed alkaline earth effect in the compressibility of aluminosilicate glasses," *Journal of Chemical Physics*, **140**, 5 (2014).
- ²⁷⁰ W. Klement, R. H. Willens, and P. Duwez, "Non-Crystalline Structure in Solidified Gold-Silicon Alloys," *Nature*, **187** [4740] 869-870 (1960).
- ²⁷¹ A. Inoue, T. Zhang, and T. Masumoto, "Glass-forming Ability of Alloys," *Journal of Non-Crystalline Solids*, **156**, 473-480 (1993).
- ²⁷² A. Inoue, "Stabilization of metallic supercooled liquid and bulk amorphous alloys," *Acta Materialia*, **48** [1] 279-306 (2000).
- ²⁷³ P. T. Sarjeant and R. Roy, *Reactivity of Solids*, ed. R.C.D. J. W. Mitchell, R. W. Roberts, P. Cannon, John Wiley & Sons, Inc., New York, 1969.
- ²⁷⁴ K. Nassau, "Rapidly Quenched Glasses," *Journal of Non-Crystalline Solids*, **42** [1-3] 423-431 (1980).

- ²⁷⁵ D. R. Ulrich and E. J. Smoke, "Devitrified Barium Titanate Dielectrics," *Journal of the American Ceramic Society*, **49** [4] 210-215 (1966).
- ²⁷⁶ K. Nassau, R. J. Cava, and A. M. Glass, "The Ionic-conductivity Variation in Rapidly Quenched Lithium-containing Glasses," *Solid State Ionics*, **2** [3] 163-170 (1981).
- ²⁷⁷ J. K. R. Weber, J. G. Abadie, A. D. Hixson, P. C. Nordine, and G. A. Jerman, "Glass formation and polyamorphism in rare-earth oxide-aluminum oxide compositions," *Journal of the American Ceramic Society*, **83** [8] 1868-1872 (2000).
- ²⁷⁸ A. Rosenflanz, M. Frey, B. Endres, T. Anderson, E. Richards, and C. Schardt, "Bulk glasses and ultrahard nanoceramics based on alumina and rare-earth oxides," *Nature*, **430** [7001] 761-764 (2004).
- ²⁷⁹ M. Kaneko, J. D. Yu, A. Masuno, H. Inoue, M. S. V. Kumar, et al., "Glass Formation in $\text{LaO}_{3/2}$ - TiO_2 Binary System by Containerless Processing," *Journal of the American Ceramic Society*, **95** [1] 79-81 (2012).
- ²⁸⁰ G. A. Rosales-Sosa, A. Masuno, Y. Higo, H. Inoue, Y. Yanaba, et al., "High Elastic Moduli of a $54\text{Al}_2\text{O}_3$ - $46\text{Ta}_2\text{O}_5$ Glass Fabricated via Containerless Processing," *Scientific Reports*, **5**, 15233 (2015).
- ²⁸¹ Y. Watanabe, A. Masuno, and H. Inoue, "Glass formation of rare earth aluminates by containerless processing," *Journal of Non-Crystalline Solids*, **358** [24] 3563-3566 (2012).
- ²⁸² R. Weber, S. Sen, R. E. Youngman, R. T. Hart, and C. J. Benmore, "Structure of High Alumina Content Al_2O_3 - SiO_2 Composition Glasses," *Journal of Physical Chemistry B* **112**(51), 16726-16733 (2008).

- ²⁸³ K. Yoshimoto, A. Masuno, H. Inoue, and Y. Watanabe, "Transparent and High Refractive Index $\text{La}_2\text{O}_3\text{-WO}_3$ Glass Prepared Using Containerless Processing," *Journal of the American Ceramic Society*, **95** [11] 3501-3504 (2012).
- ²⁸⁴ A. Masuno, H. Inoue, J. Yu, and Y. Arai, "Refractive index dispersion, optical transmittance, and Raman scattering of BaTi_2O_5 glass," *Journal of Applied Physics*, **108** (6) (2010).
- ²⁸⁵ G. A. Rosales-Sosa, A. Masuno, Y. Higo, and H. Inoue, "Crack-resistant $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses," *Scientific Reports*, **6**, 23620 (2016).
- ²⁸⁶ J. K. R. Weber, A. Tamalonis, C. J. Benmore, O. L. G. Alderman, S. Sendelbach, et al., "Aerodynamic levitator for in situ x-ray structure measurements on high temperature and molten nuclear fuel materials," *Review of Scientific Instruments* **87** (7) (2016).
- ²⁸⁷ N. A. Mauro, A. J. Vogt, K. S. Derendorf, M. L. Johnson, G. E. Rustan, et al., "Electrostatic levitation facility optimized for neutron diffraction studies of high temperature liquids at a spallation neutron source," *Review of Scientific Instruments*, **87** [1] 073902 (2016).
- ²⁸⁸ J. C. Mauro, A. Tandia, K. D. Vargheese, Y. H. Z. Mauro, and M. M. Smedskjaer, "Accelerating the Design of Functional Glasses through Modeling," *Chemistry of Materials*, **28** [12] 4267-4277 (2016).
- ²⁸⁹ N. Li and W.-Y. Ching, "Structural, electronic and optical properties of a large random network model of amorphous SiO_2 glass," *Journal of Non-Crystalline Solids*, **383**, 28-32 (2014).
- ²⁹⁰ G.S. Henderson, G. Calas, and J. F. Stebbins, "The structure of silicate glasses and melts," *Elements*, **2** [5] 269-273 (2006).

- ²⁹¹ M. Benoit, S. Ispas, P. Jund, and R. Jullien, "Model of silica glass from combined classical and ab initio molecular-dynamics simulations," *The European Physical Journal B-Condensed Matter and Complex Systems*, **13** [4] 631-636 (2000).
- ²⁹² R. McGreevy and L. Pusztai, "Reverse Monte Carlo simulation: a new technique for the determination of disordered structures," *Molecular Simulation*, **1** [6] 359-367 (1988).
- ²⁹³ A. Pandey, P. Biswas, and D. A. Drabold, "Inversion of diffraction data for amorphous materials," *Scientific Reports*, **6**, 33731 (2016).
- ²⁹⁴ C. Kübel, A. Voigt, R. Schoenmakers, M. Otten, D. Su, et al., "Recent advances in electron tomography: TEM and HAADF-STEM tomography for materials science and semiconductor applications," *Microscopy and Microanalysis*, **11** [5] 378-400 (2005).
- ²⁹⁵ P.Y. Huang, S. Kurasch, A. Srivastava, V. Skakalova, J. Kotakoski, et al., "Direct imaging of a two-dimensional silica glass on graphene," *Nano Letters*, **12** [2] 1081-1086 (2012).

Figure Captions

Figure 1. Recent advances in ceramics processing science. From left to right: Optical image of the guided self-assembly of colloidal SiO₂ rods (~2.2 μm in length and 1.1 μm in diameter) coated on one end with a hydrophobic metallized tip (black) [Inset: Tetrahedral “atom-like” cluster composed of four rods.]¹³ (Reprinted with permission, American Chemical Society); Optical image of a lithium ion microbattery composed of 3D printed, interdigitated cathode (LFP, dark) and anode (LTO, white) high aspect ratio features²⁸ (Reprinted with permission, Wiley); SiOC microlattice fabricated by stereolithography of a preceramic monomer solution; and Multilayer thermoelectric device obtained by cold sintering at 250°C that integrates n-type ZnO, p-type Ca₃Co₄O₉, and polytetrafluoroethylene, a thermoplastic insulating material.

Figure 2: Defects are critical for ceramic applications. From point^{98,99} to planar^{100,101} to bulk¹⁰² defects, modern ceramic systems rely upon exacting and careful control of these features to ensure operation and performance in applications¹⁰³⁻¹⁰⁷. Looking towards the future, deterministic control of these defects and even formation of designed meso-structures based on defects are expected to enable new phenomena and better performance. From top left to right: STM images of the c(4×2) reconstructed surface of SrTiO₃⁹⁸ (Reprinted with permission, Elsevier); An HRTEM image of dislocation loops in a high-temperature irradiated SrTiO₃ crystal⁹⁹ (Reprinted with permission, Elsevier); Bright-field STEM image of a Sr₇Ti₆O₁₉ epitaxial film grown on (110) DyScO₃¹⁰⁰ (Reprinted with permission, Nature Publishing Group); SEM micrograph of an interface delamination crack for 8% Y₂O₃ partially stabilized ZrO₂ thermal barrier ceramic coating on NiCrAlY subjected to six thermal fatigue cycles¹⁰¹ (Reprinted with

permission, ASME); local thermal dielectric breakdown events (dark spots) linked to mechanical breakdown events in a piezoelectric film.

Figure 3. Schematic representations and micrographs of real two-dimensional ceramics. (a) Free-standing layer; (b) plan view TEM of single layer h-BN¹⁰⁸ (Reprinted with permission, AAAS); (c) supported layer; (d) transverse TEM image of a vanadia layer on TiO₂¹⁰⁹ (Reprinted with permission, AIP); (e) confined layer; and (f) TEM of grain boundary complexion (Nd bilayer between alumina grains)¹¹⁰ (Reprinted with permission, Elsevier).

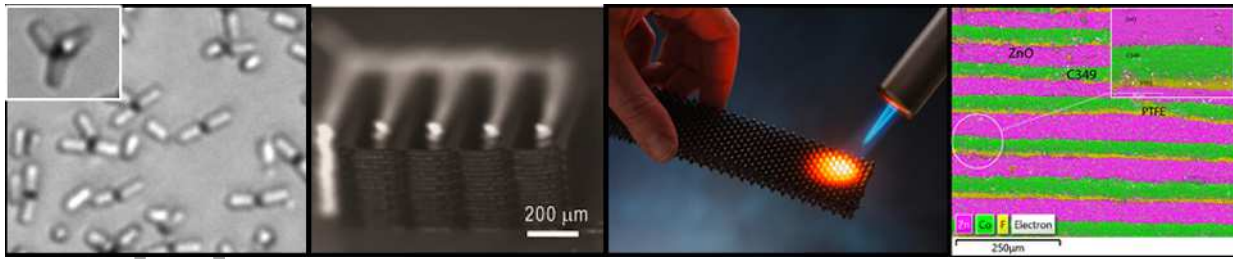
Figure 4. Challenges for ceramics in extreme environments arise across broad applications in energy, security, and transportation. Sources for images: High-T_c superconductors (HTSC) for plasma confinement¹⁴⁷ (Reprinted with permission, Nature Publishing Group); armor¹⁴⁸; ceramic-matrix composite¹⁴⁹; reaction zone between environmental barrier coating with calcium-magnesium-aluminosilicate¹⁵⁰; and ultra-high temperature ceramic leading edges¹⁵¹.

Figure 5. High temperature and pressure techniques applicable to extreme environmental research; clockwise from upper left: high-resolution micro-computed tomography (μ -CT) of SiC-SiC composites²¹⁹ (Reprinted with permission, Nature Publishing Group); arc jet test¹⁵¹; diamond anvil cell for extreme pressures; ultra high-temperature (UHT) calorimetry²⁰⁸; and a time sequence of surface melting of silicate deposits from a high heat flux laser gradient test²⁰⁹.

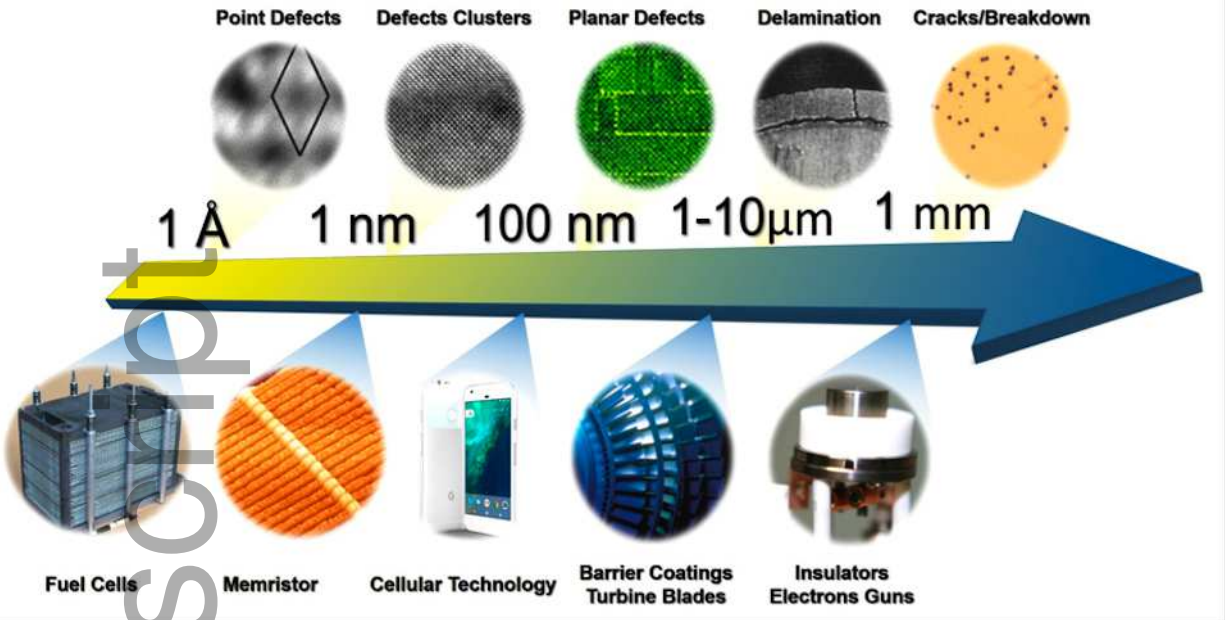
Figure 6. Atomic configuration (first row), local shear strain (second row), local density (third row) and local density change mapping under indenter (fourth row) after nanoindentation test for silica glass quenched under 0 GPa and 15 GPa²⁶⁶.

Figure 7. Composition dependence of elastic moduli (left) and Vickers hardness (right) for the $x\text{Al}_2\text{O}_3-(100-x)\text{SiO}_2$ glasses. Vickers indentation imprints for the $x\text{Al}_2\text{O}_3-(100-x)\text{SiO}_2$ glasses. Blue-shaded photographs show the cracked samples. Gray-shaded photographs show the non-cracked samples²⁸⁵.

Figure 8. Overview of modeling techniques for glasses, from purely empirical models to those firmly grounded in fundamental physics²⁸⁸ (Reprinted with permission, American Chemical Society).

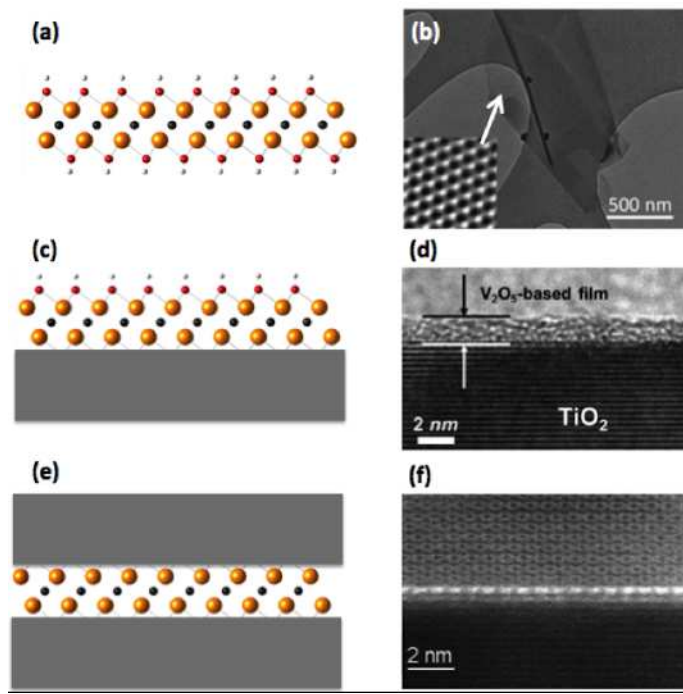


jace_14881_f1.tif

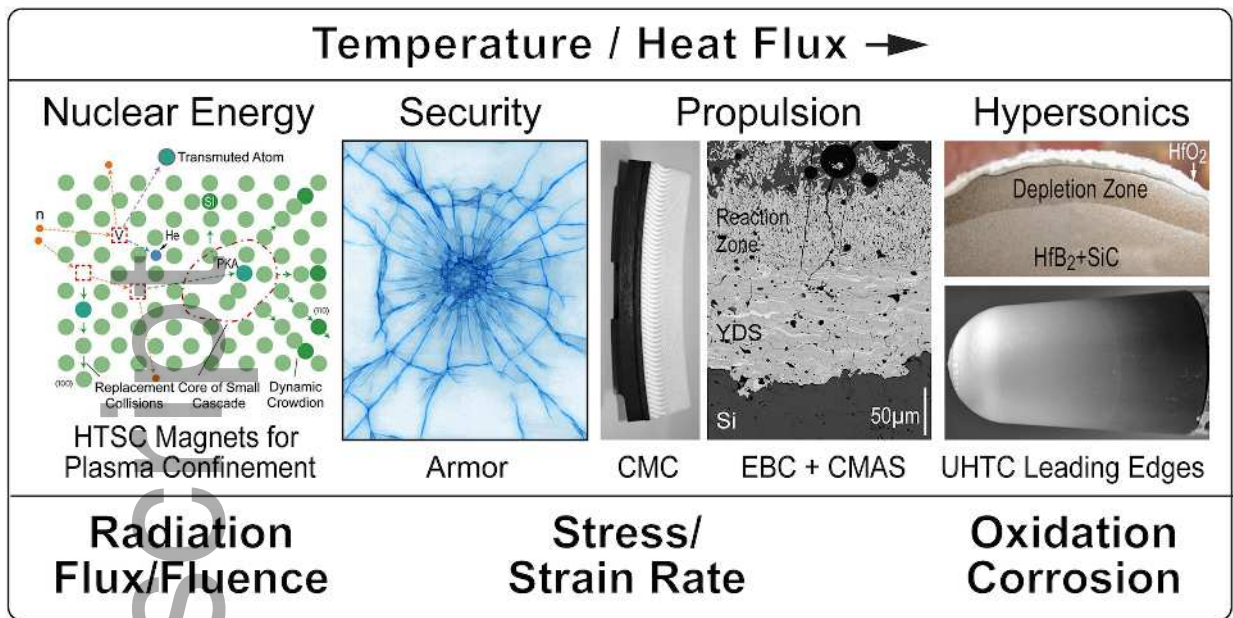


jace_14881_f2.tif

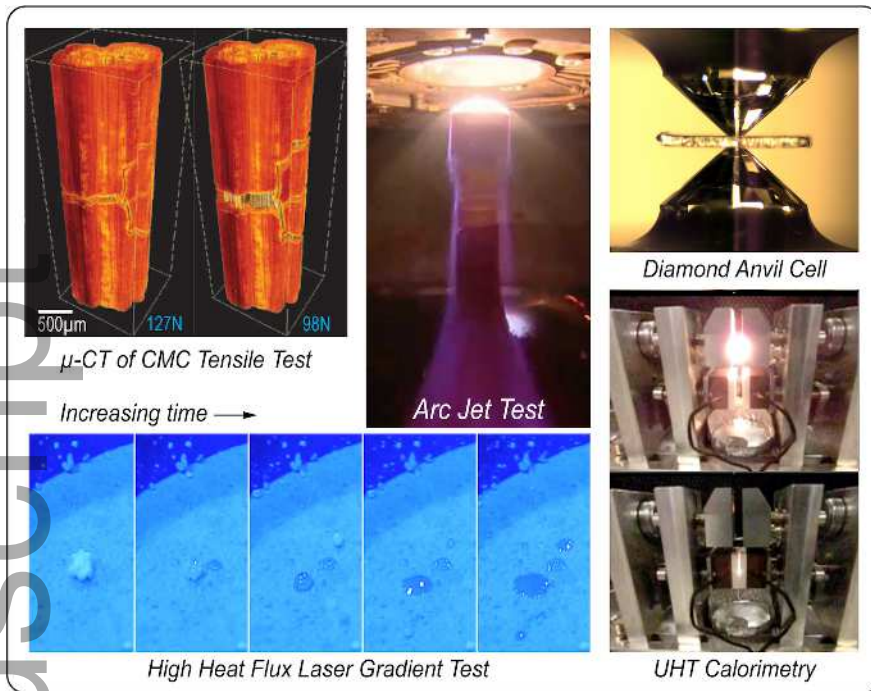
Author Manuscript



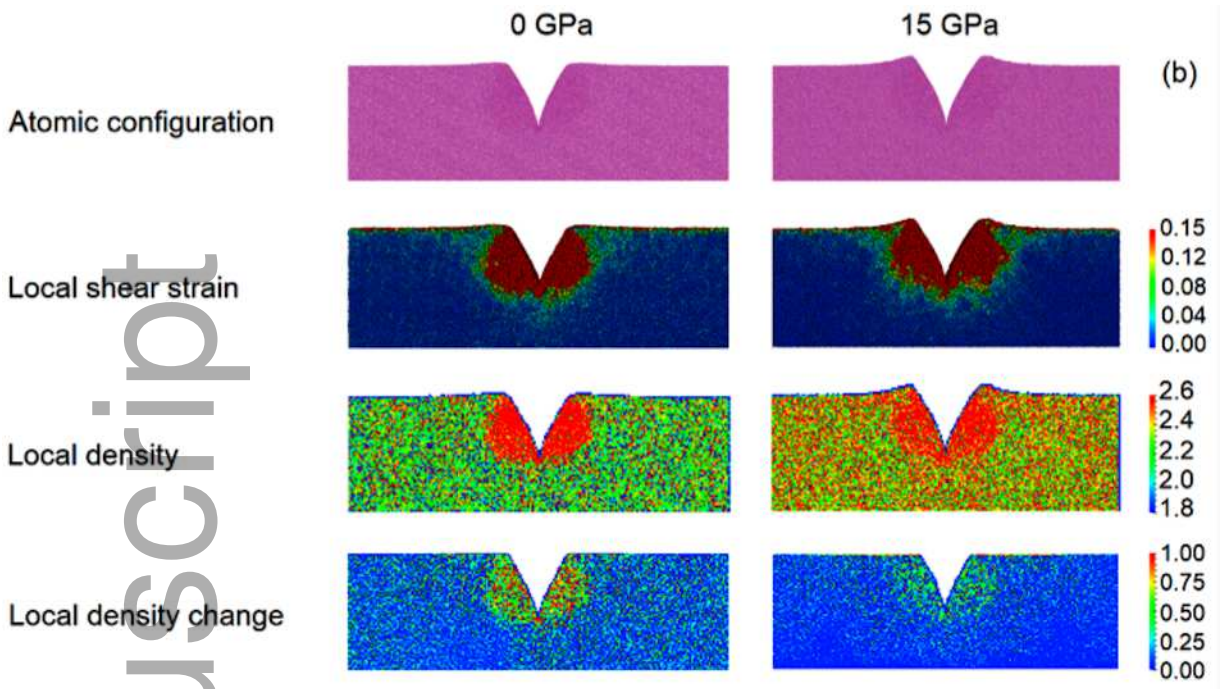
jace_14881_f3.tif



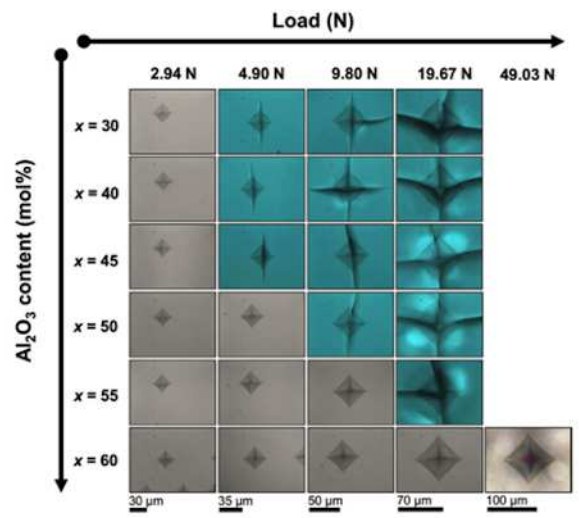
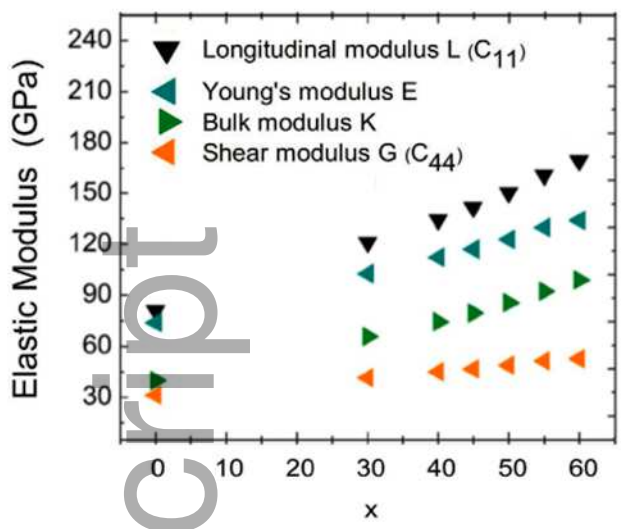
jace_14881_f4.tif



jace_14881_f5.tif

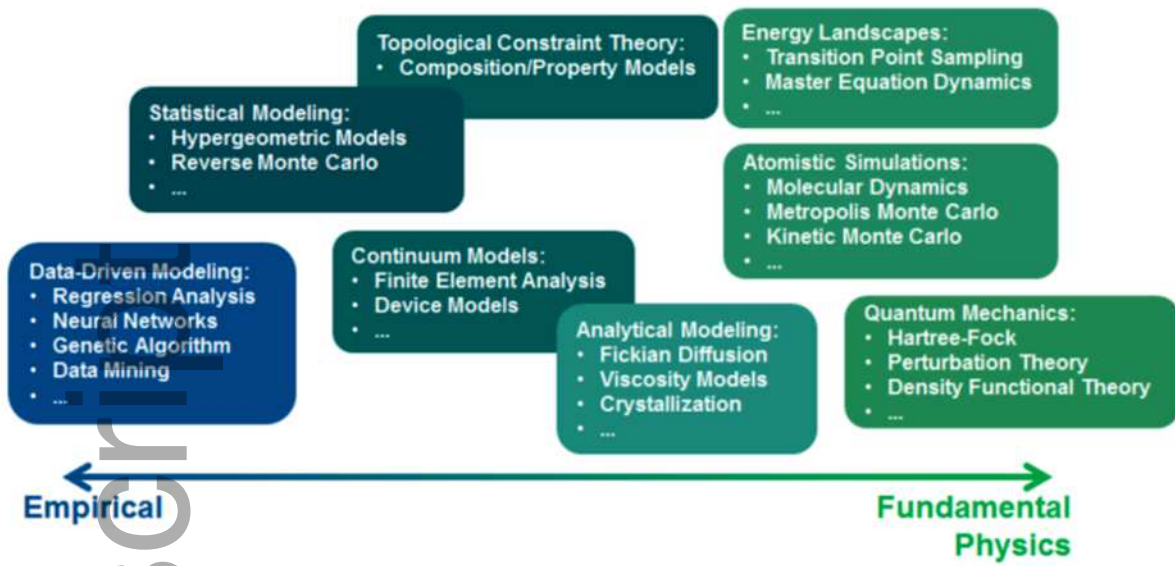


jace_14881_f6.tif



jace_14881_f7.tif

Author Manuscript



jace_14881_f8.tif

Author Manuscript