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## FEATURE ARTICLE

# The role of ceramic and glass science research in meeting societal challenges: Report from an NSF-sponsored workshop

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#### 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; Ceramics in the extreme: Behavior of multimaterial 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 basic understanding and ultimately enable advancements within multiple sectors, including energy, environment, manufacturing, security, and health care.

#### KEYWORDS

defects, glass, layered ceramics, processing, ultrahigh-temperature ceramics

## 1 | 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 United States 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, nonoxides, 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.<sup>1</sup>

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.<sup>2</sup> 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.”<sup>3</sup> Although less than 5 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*,<sup>4</sup> 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.<sup>5</sup> 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 basic understanding of ceramics and glasses and enable advances in, among others, energy, environment, manufacturing, security, and health care:

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 multimaterial 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)<sup>6</sup> for the design of new ceramic materials and prediction of properties. Examples of the design of complex oxides for electronic devices<sup>7</sup> and superionic conductors<sup>8</sup> provide evidence of advancements in the field. However, the use of these techniques for highly defective structures, ultrahigh-temperature materials, or complex, multicomponent amorphous materials is sparse. A second overarching need is the advancement of probes necessary to characterize and visualize materials at smaller length scales, for example, a single atomic defect, and at higher temperatures and pressures, for example, at  $T > 2000^\circ\text{C}$ . Each challenge is described in detail below following the reports of the five subgroups.

## 2 | 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 assembly<sup>9-18</sup> and 3D printing methods.<sup>19-37</sup> 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 multiscale modeling with computer-aided design and assembly is needed to fully exploit the broadening palette of materials, architectures, and fabrication strategies.

### 2.1 | 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. Multiscale 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 toward understanding the transformation of initial building blocks, both colloidal particles and other constituents, into sintered bodies that give rise to the properties of interest.

Multiscale 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.<sup>38,39</sup> DFT can be used to generate quantum-

accurate potentials for atomic scale simulations,<sup>40,41</sup> 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 materials.<sup>42–44</sup> They can also provide mechanistic understanding of materials processes such as diffusion, interface mobilities, and phase transitions. Mesoscale modeling, predominantly phase field<sup>45</sup> and Potts kinetic Monte Carlo models,<sup>46</sup> can treat microstructure and its evolution at processing temperatures of interest under different energy fields when applicable. However, models to assess engineering properties from ceramic 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.<sup>47,48</sup> 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.*

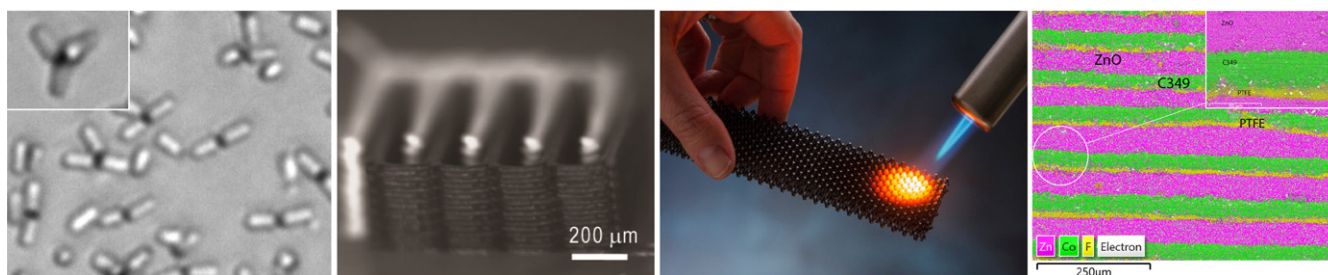
By harnessing forces ranging from weak van der Waals to external electromagnetic fields, one can guide colloidal self-assembly in two and three dimensions to create novel architectures with as yet unexplored properties. Two-dimensional assembly of nanosheets into superlattice structures guided by van der Waals forces yield completely new architectures and material combinations.<sup>9,10</sup> DNA-coated particles<sup>11,12</sup> and Janus rods coated with hydrophobic patches form “atom-like” building blocks<sup>13</sup> 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.<sup>14</sup> 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.<sup>15,16</sup> Magnetic fields can be used to orient ferroelectric particles for templated grain growth.<sup>17</sup> Importantly, even diamagnetic colloidal particles can be oriented under very high magnetic fields to produce textured ceramics.<sup>18</sup> However, to harness external fields to locally “write microstructure” in a predictive manner, 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 robocasting<sup>19–21</sup> or stereolithography,<sup>22–27</sup> 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 electrodes<sup>28</sup> (Figure 1), as well as 3D periodic lattices.<sup>21</sup> New advances in colloidal suspension design, such as biphasic mixtures composed of attractive and repulsive colloidal particles,<sup>29</sup> coupled with the implementation of active mixing and switching microfluidic print-heads,<sup>30,31</sup> would further accelerate the compositional and architectural complexity realizable by this technique.

New cellular ceramics can be fabricated by light-based 3D printing of preceramic monomers, nanoparticle-filled or pure resins.<sup>22–27</sup> For example, nonoxide cellular ceramics that are virtually pore free are produced by patterning a preceramic monomer resin using stereolithography followed by high-temperature pyrolysis (Figure 1).<sup>22</sup> However,



**FIGURE 1** Recent advances in ceramics processing science. From left to right: Optical image of the guided self-assembly of colloidal SiO<sub>2</sub> 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.]<sup>13</sup> (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 features<sup>28</sup> (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 Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>, and polytetrafluoroethylene, a thermoplastic insulating material



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.<sup>25,27</sup> In the latter case, the structures serve as sacrificial templates, which are coated with a thin layer of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, 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 ultralow densities.<sup>24-27,32</sup> 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 sintering*.<sup>34-36</sup> It is now possible to densify ceramic green bodies at temperatures as low as 25°C to 300°C via a transient liquid phase (eg, 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 sintering.<sup>34-36</sup> 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 related,<sup>37</sup> that is, 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 property 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.

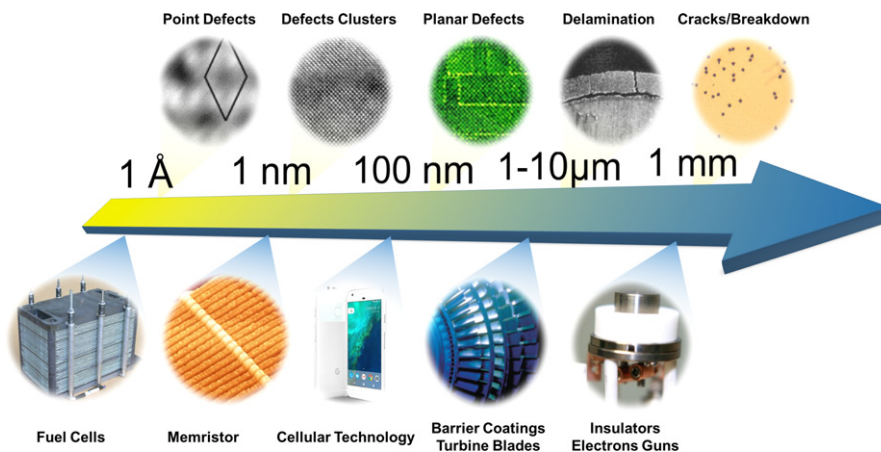
### 3 | DEFECT-ENABLED PHENOMENA

A defect in a material is most commonly defined as a disruption to the periodicity of its crystalline organization, that is, a structural anomaly, or to its composition, that is, 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.<sup>49,50</sup> 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 (eg, vacancies, interstitials) determine transport characteristics; linear defects (dislocations) establish strain relaxation behavior; planar defects (eg, domain and grain boundaries) govern ferroelastic, piezoelectric, and ferroelectric response; and volume defects (eg, 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, multidimensional 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 toward 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.

#### 3.1 | 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,



**FIGURE 2** Defects are critical for ceramic applications. From point<sup>98,99</sup> to planar<sup>100,101</sup> to bulk<sup>102</sup> defects, modern ceramic systems rely upon exacting and careful control of these features to ensure operation and performance in applications.<sup>103–107</sup> Looking toward the future, deterministic control of these defects and even formation of designed mesostructures 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  $\text{SrTiO}_3$ <sup>98</sup> (reprinted with permission, Elsevier); an HRTEM image of dislocation loops in a high-temperature irradiated  $\text{SrTiO}_3$  crystal<sup>99</sup> (reprinted with permission, Elsevier); bright-field STEM image of a  $\text{Sr}_7\text{Ti}_6\text{O}_{19}$  epitaxial film grown on (110)  $\text{DyScO}_3$ <sup>100</sup> (reprinted with permission, Nature Publishing Group); SEM micrograph of an interface delamination crack for 8%  $\text{Y}_2\text{O}_3$  partially stabilized  $\text{ZrO}_2$  thermal barrier ceramic coating on  $\text{NiCrAlY}$  subjected to six thermal fatigue cycles<sup>101</sup> (reprinted with permission, ASME); local thermal dielectric breakdown events (dark spots) linked to mechanical breakdown events in a piezoelectric film. From bottom left to right: Fuel cells<sup>103</sup> (reprinted with permission from Forschungszentrum Jülich); Memristor<sup>104</sup> (reprinted with permission from HP); Cellular Technology;<sup>105</sup> Barrier Coatings;<sup>106</sup> Electron Gun<sup>107</sup> (reprinted with permission from RBD Instruments, Inc.)

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<sup>49,50</sup>) rapidly reach their limits when confronted with high defect concentrations, strong defect interactions,<sup>51</sup> dislocations,<sup>52,53</sup> or interfaces.<sup>54</sup> 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 of the computational possibilities. Preliminary efforts have attempted to capture the interplay between antisite defects and phase formation,<sup>55</sup> and between electrical field, stress, and defect distribution.<sup>56</sup> Further efforts in this direction are needed, especially those targeting dynamic system response.<sup>57</sup>

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 ceramics,<sup>58</sup> 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 boundaries<sup>59</sup> and explains cascaded motion of domain walls,<sup>60</sup> (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 toward controlled processing/generation of defect concentrations in films,<sup>61</sup> (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 stability.<sup>62</sup> 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 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 conduction,<sup>63-65</sup> memristive switches that gain their functionality from localized reversible, reproducible redox reactions,<sup>66,67</sup> and emergent devices with 2D interfacial properties in layered structures.<sup>68-71</sup> 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 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 manner.<sup>72</sup> Key challenges and opportunities go beyond traditional chemical synthesis and focus either on establishing the desired defects in situ during the synthesis<sup>73</sup> or controlling ex situ the production of specific defect types and densities at selected sites.<sup>74,75</sup> 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 in the associated local properties.<sup>76,77</sup>

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 have captured surface and grain-boundary reconstruction in thermodynamic equilibrium situations.<sup>78</sup> Improved understanding of dynamic interfaces, such as oxygen exchanging electrodes<sup>79,80</sup> or oxide catalysts supporting chemical synthesis, has been gained by operando imaging and spectroscopy<sup>81</sup> and supported by simple models.<sup>82</sup> 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 scales<sup>83</sup> and spatial scales<sup>84</sup> 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 formation.<sup>85</sup> 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, noncrystalline electrolytes generally display higher conductivity than their crystalline counterparts. This contradictory situation suggests that extending the understanding of glassy electrolytes, likely through atomistic level simulations, may provide tremendous payoff 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 temperatures.<sup>34-36</sup> It is not clear if the resulting ceramics have similar properties as those processed by high-temperature sintering; 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 multiscale approaches and parallel networking tools have been developed, which will soon allow treatment of larger and more complex systems and address the above opportunities.

### 3.2 | 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 excitation.<sup>86</sup> 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 properties.<sup>87</sup> 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 they be created, and how would 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,<sup>88,89</sup> the capability to count atoms by comparing experiment and theory<sup>90</sup> and the ability to map chemistry at the atomic scale with electron energy loss and X-ray spectroscopies.<sup>91</sup> This progress allows direct identification and quantification of defects in terms of both their atomic and electronic structures.<sup>92</sup> Furthermore, recent in situ (scanning) transmission electron microscopy and scanning tunneling microscopy (STM) techniques advances have enabled the direct tracking the material evolution as a function of time and environmental variables.<sup>93</sup> 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 reactions.<sup>94</sup> 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, and surface spectroscopies have also made tremendous strides in the past decade, some techniques even allowing operando observation.<sup>95-97</sup> 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.

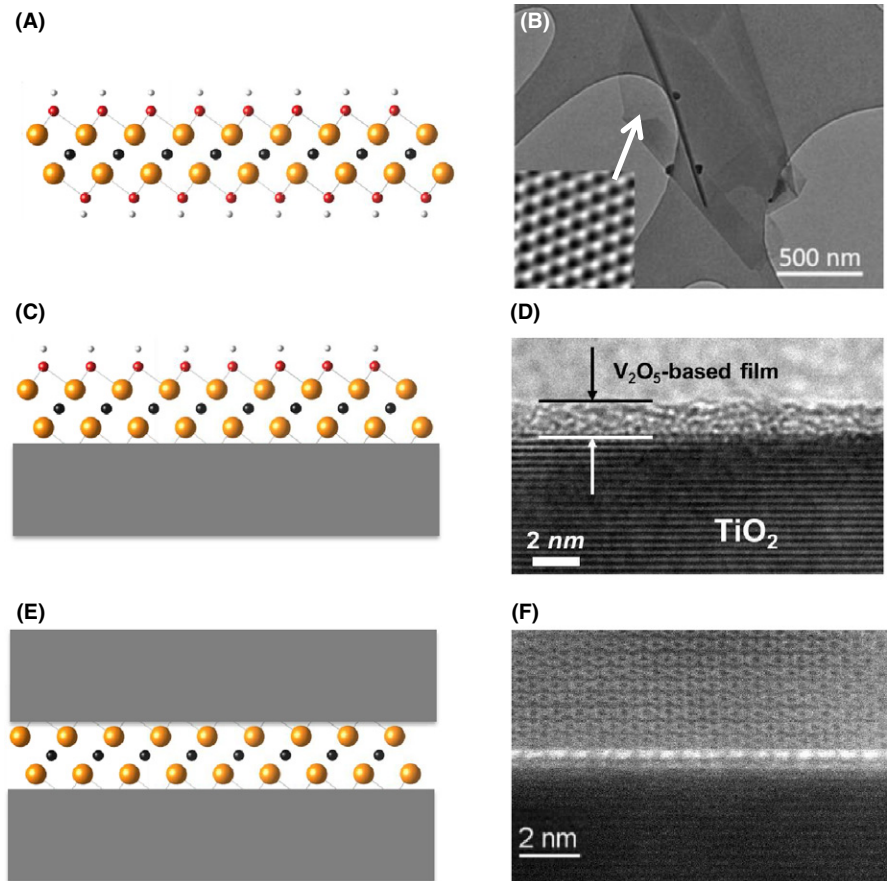
## 4 | LOW-DIMENSIONAL PHENOMENA

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, as well as materials confined at interfaces and grain boundaries, as illustrated in Figure 3. The challenge is to define structure-property relations for these materials.

### 4.1 | 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.<sup>111</sup> However, there has been a recent growth of research in this area and the range of materials available has grown enormously.<sup>112</sup> Among the ceramics that can be produced in single layer form are clays,<sup>113</sup> hydroxides,<sup>114</sup> oxides,<sup>115</sup> h-BN,<sup>116</sup> and transition-metal carbides.<sup>117</sup> 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.<sup>118</sup> These



**FIGURE 3** Schematic representations and micrographs of real two-dimensional ceramics. (A) Free-standing layer; (B) plan view TEM of single layer h-BN<sup>108</sup> (reprinted with permission, AAAS); (C) supported layer; (D) transverse TEM image of a vanadia layer on TiO<sub>2</sub><sup>109</sup> (reprinted with permission, AIP); (E) confined layer; and (F) TEM of grain-boundary complexions (Nd bilayer between alumina grains)<sup>110</sup> (reprinted with permission, Elsevier)

complexions can form on free surfaces,<sup>119</sup> at grain boundaries,<sup>118</sup> and heterophase boundaries.<sup>120</sup> Among supported surface complexions, adsorbate-based surficial films,<sup>119</sup> reconstructions,<sup>121</sup> and controlled surface terminations are considered.<sup>122</sup> 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 into several long-standing scientific mysteries that puzzled the ceramic community for decades, for example, the origins and atomistic mechanisms of solid-state activated sintering<sup>123</sup> and abnormal grain growth.<sup>124</sup> 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 nonlinear I-V character of varistors, and the critical current of superconductors.<sup>125</sup>

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<sup>126,127</sup> and may play a role in cold sintering.<sup>128</sup> The rich catalytic properties of two-dimensional ceramics enable reactions that are important for the production and utilization of solar fuels.<sup>129</sup> 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.<sup>130</sup> The next obvious step in advancing the science of two-dimensional ceramics is understanding structure-property relations. To date, 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.<sup>131</sup> Similarly, 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.<sup>117,118</sup>

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  $\text{LaAlO}_3/\text{SrTiO}_3$  interface<sup>132</sup> and graphene.<sup>133</sup> 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<sup>112,117</sup> 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.<sup>134</sup> 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.<sup>135,136</sup> 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.<sup>137</sup> 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 toolkit<sup>138</sup> and the atomic simulation environment<sup>139</sup> at the atomic level, or OOF<sup>140</sup> and MOOSE<sup>141</sup> at the meso- or continuum scale, are not available. Therefore, there is a unique opportunity for the ceramics community to develop multiscale two-dimensional tools and platforms that will enable the rational and systematic exploration of these systems. Furthermore, 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 Dakota<sup>142</sup> 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,<sup>143</sup> pseudocapacitors,<sup>127</sup> and hybrid devices for energy storage.<sup>144</sup> 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.<sup>145</sup> 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, once they can be produced in large quantities. Also, emerging energy storage devices entirely based on solid-state (ceramic) technology are currently limited by the structure and properties of the two-dimensional heterointerfaces through which they are spatially coupled. Thus, a fundamental understanding of interface 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 of 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.<sup>129,146</sup> 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 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.

## 5 | 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 thermomechanical 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:

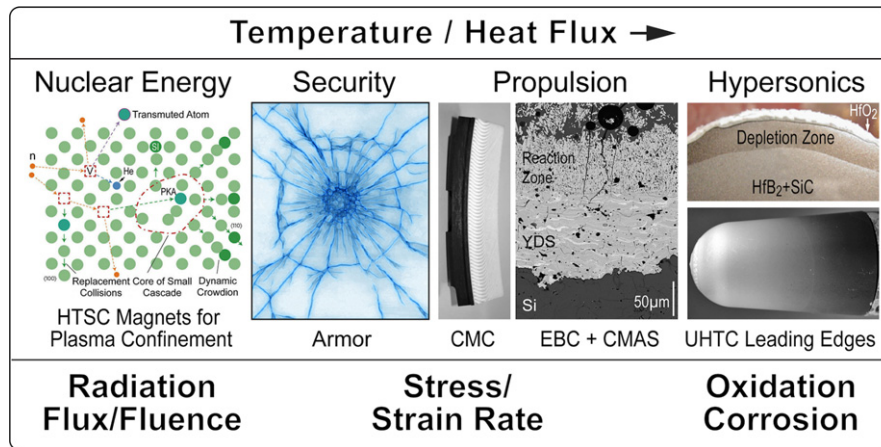
(i) *Hypersonic flight*, where sharp leading edges are required in aircraft for reduced draft and improved maneuverability.<sup>152</sup> Required temperatures are in excess of 2000°C,<sup>153</sup> with heat fluxes of multiple MW/m<sup>2</sup>,<sup>154</sup> which can translate into extreme thermal gradients and stresses. Ionization of the impinging air<sup>155</sup> enhances oxidation potential,<sup>156</sup> followed by catalytic recombination at the surface, leading to still further heating.<sup>157</sup> Ultrahigh-temperature ceramics (UHTCs)<sup>158</sup> and C<sub>f</sub>/SiC composites,<sup>159</sup> current candidate materials for these applications, are hindered by severe oxidation at the target temperatures.<sup>160-163</sup>

(ii) *Aerospace propulsion*, encompassing gas turbines, scramjets, and rocket engines, with prospective gas temperatures in excess of ~1700°C,<sup>164</sup> ~2000°C,<sup>152</sup> and ~3000°C,<sup>157</sup> 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<sup>165-167</sup> or the recently introduced ceramic composites (CMCs),<sup>164,168</sup> rely on ceramic coatings. However, both the thermal barrier coatings (TBCs) used to protect metallic components<sup>164,169</sup> and the environmental barrier coatings (EBCs) used to protect CMCs<sup>164,170</sup> are temperature limited when exposed to molten dusts, which comprise highly corrosive calcium-magnesium aluminosilicates (CMAS).<sup>164,171-175</sup> A second major barrier is associated with coating toughness limitations,<sup>171</sup> 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 particles.<sup>176</sup> While current and prospective next-generation fission reactors pose substantial challenges to ceramics, for example, as advanced fuels and wasteforms,<sup>176</sup> fusion reactors arguably represent one of the most ambitious challenges to the spectrum of extreme materials technology.<sup>177</sup> 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/m<sup>2</sup>. The neutrons interact primarily with the first wall and the breeder blanket, but affect all other components in the system,<sup>178</sup> 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





**FIGURE 4** Challenges for ceramics in extreme environments arise across broad applications in energy, security, and transportation. Sources for images, from left to right: high- $T_c$  superconductors (HTSC) for plasma confinement<sup>147</sup> (reprinted with permission, Nature Publishing Group); armor<sup>148</sup>; ceramic-matrix composite<sup>149</sup> (reprinted with permission, General Electric Company); reaction zone between environmental barrier coating with calcium-magnesium-aluminosilicate<sup>150</sup>; and ultrahigh-temperature ceramic leading edges<sup>151</sup> (Source: NASA Ames Research Center)

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 ultrahigh pressures or contact loads (10 GPa–1 TPa), such as those generated within diamond anvil cells (DACs),<sup>179</sup> machining tools (eg, cutting, drilling, grinding) which benefit from super- and ultrahard materials,<sup>180</sup> and operation under highly dynamic loads found, for example, in armor applications, where impact pressures can exceed 10 GPa.<sup>181</sup> 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  $B_4C$  under high-velocity impacts.<sup>182</sup> 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 thermoelectrics,<sup>183</sup> electrochemical systems in batteries,<sup>184</sup> solid oxide fuel cells (SOFCs),<sup>185</sup> high-voltage insulators,<sup>186</sup> magnets,<sup>187</sup> superconductors,<sup>188</sup> and optical/optoelectronic devices subject to high photon fluxes.<sup>189</sup> A common issue is the evolution of defects as the field or flux interacts with the ceramic, which limits the subsequent system performance.<sup>189</sup> Despite differences in the details of the mechanisms and associated dynamics, these issues have analogs 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 multimaterial systems, wherein performance is not dependent solely on the properties of each individual constituent, but rather on the interplay among them.<sup>164,190</sup> From that perspective, two challenges are identified in ceramics for extreme environments, one related to discovery and design strategies for new materials and the other to improved understanding of complex systems (including interactions across interfaces) under extreme thermal, chemical, and mechanical environments. Both challenges share limitations of the theoretical and modeling infrastructure to predict behavior (even under a single extreme condition), as well as of the experimental capabilities to measure properties and assess performance in the more complex situations that combine extremes.

## 5.1 | Challenge #5: Ceramics in the extreme: Discovery and design strategies

As noted earlier, 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.<sup>158,163</sup> However, these oxides are porous and tend to crack due to thermal expansion mismatch with their parent material, rendering them nonprotective.<sup>191</sup> Use of



UHTC composites with SiC additions leads to a passivating liquid silicate coating that is susceptible to ablation by turbulent flows and experiences volatilization above  $\sim 1600^\circ\text{C}$ .<sup>160,163</sup> Efforts to form solid protective coatings using rare-earth additives lead to formation of refractory oxide scales, for example,  $\text{LaZr}_2\text{O}_7$ ,<sup>192</sup> 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 vapor.<sup>169</sup> Moreover, neither ceramic has adequate resistance to attack by molten silicates.<sup>173,174,193</sup> 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.

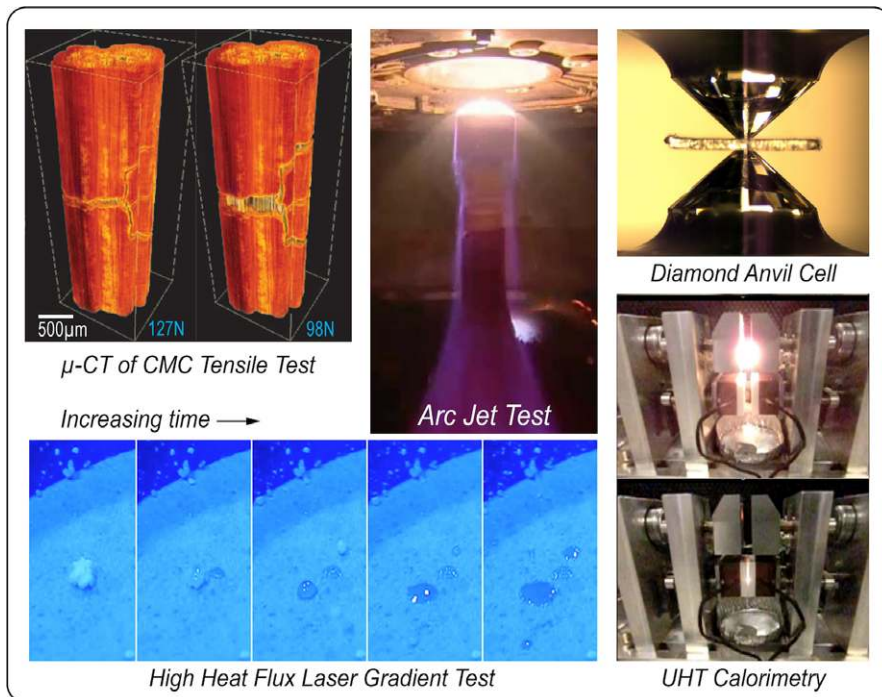
Theory and computational modeling are essential tools to guide the discovery process. The value of theory is illustrated by recent work that provided a fundamental explanation for the reported maximum in melting point for rock-salt solutions of TaC–HfC at  $\sim(\text{Ta}_{0.8}\text{Hf}_{0.2})\text{C}_{0.875}$ .<sup>194–197</sup> The authors further predicted that compounds in the Hf–C–N system could exhibit melting points at least  $200^\circ\text{C}$  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 temperatures.<sup>198</sup> 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 6000 K in the earth's core, at pressures up to 350 GPa.<sup>199</sup> Progress has since enabled DFT calculations of thermal expansion and heat capacity of pure ZrC up to 3500 K.<sup>200</sup> Although 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 invaluable;<sup>201</sup> in fact, ongoing activities are focusing on exploring avenues to bypass the CALPHAD approach altogether by using DFT

and applying advanced sampling techniques.<sup>201</sup> The second obstacle is related to the measurement of thermodynamic properties at extreme temperatures, notably enthalpies of transformations and heat capacities.<sup>202,203</sup> 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 melting.<sup>203</sup> 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-rays<sup>204</sup> coupled with noncontact methods of heating, such as quadrupole lamp furnaces,<sup>205</sup> though the latter are still limited to temperatures below  $\sim 2000^\circ\text{C}$ . Resistive heating of UHTCs has been employed in oxidation studies to  $2000^\circ\text{C}$ ,<sup>206,207</sup> 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 artifacts.<sup>207</sup>

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  $3000^\circ\text{C}$  using new laser techniques,<sup>210</sup> as demonstrated recently on  $\text{HfC}_{0.98}$ , ( $3959^\circ\text{C} \pm 84^\circ\text{C}$ ).<sup>195</sup> It is also possible to measure strength,<sup>211</sup> thermal diffusivity,<sup>212</sup> heat capacity,<sup>203</sup> coefficient of thermal expansion,<sup>204,213</sup> and electrical conductivity<sup>214</sup> at very high temperatures, as well as material responses in extreme heat fluxes.<sup>215,216</sup> 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 effects of composition, phase constitution, and defects, all of which can evolve over time,<sup>217</sup> and finite element models that can be informed by the emerging micromechanical understanding must be developed. Advances in high-resolution X-ray computed tomography provide new insights into the evolution of defects and damage with increasing strain,<sup>218,219</sup> 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 materials,<sup>220–222</sup> 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



**FIGURE 5** High-temperature and high-pressure techniques applicable to extreme environmental research; clockwise from upper left: high-resolution microcomputed tomography ( $\mu$ -CT) of SiC-SiC composites<sup>219</sup> (reprinted with permission, Nature Publishing Group); arc jet test<sup>151</sup> (Source: NASA Ames Research Center); diamond anvil cell for extreme pressures; ultra high-temperature (UHT) calorimetry<sup>208</sup>; and a time sequence of surface melting of silicate deposits from a high heat flux laser gradient test<sup>209</sup>

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.<sup>223,224</sup> However, constitutive behavior under nonhydrostatic stresses at extreme temperatures is still a challenge.

## 5.2 | Challenge #6: Ceramics in the extreme: Behavior of multimaterial systems

The complexity of extreme environments favors reliance on multiphase/multielement 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 multiphase/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 multimaterial assemblage to identify the performance-limiting factors in the extreme environment.<sup>225,226</sup> 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 multiscale finite and discrete element methods.<sup>227</sup> Micromechanical, thermodynamic, and kinetic models are also essential. Of particular interest are models describing the oxidation of multiphase materials, especially when one or more of the oxidation products is subject to volatilization,<sup>156,161,163,228</sup> 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 nonoxide ceramics.<sup>192</sup>

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 a generation of new researchers. Examples of critical facilities include plasma and wind tunnels for testing under hypersonic conditions,<sup>154,157,162,229,230</sup> facilities for studying nuclear radiation effects on fusion materials, and also for the study of materials under high heat fluxes.<sup>231,232</sup>

While some facilities capable of simulating complex in-service environments are in place (eg, for simulation of environments relevant to turbine engines<sup>217,232,233</sup>), their capabilities are still limited, for example, 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  $\mu$ -CT, one should be able to assess the synergistic effects of temperature, environment, and stress on the mechanical properties and the mechanisms of failure,<sup>219,220,234</sup> phase stability, oxidation, oxidation-induced stresses,<sup>235</sup> and effects of high-temperature corrosion by CMAS<sup>236,237</sup> and gradients in internal strain.<sup>238</sup>

## 6 | GLASSES

The current status and future outlook of glass science and engineering were recently discussed in two splendid reviews.<sup>239,240</sup> The challenges in glass science and engineering identified here build on these and other recent advances and emerging opportunities.

### 6.1 | 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, 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. Furthermore, designing new and novel glasses that function under such extreme conditions is likewise important for a variety of applications, including electrochemical, aerospace, and biomedical.

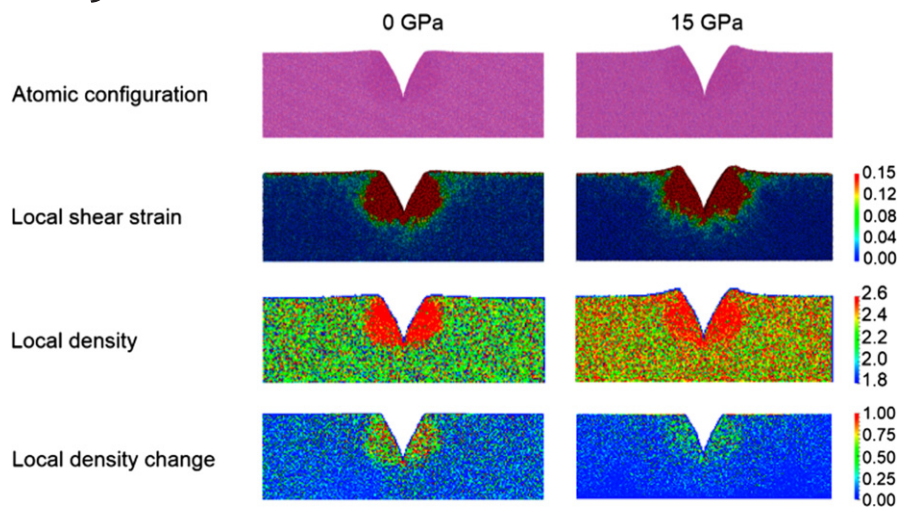
Among the extremes, pressure and temperature are important basic thermodynamic variables that determine the structure, dynamics, and macroscopic properties of glasses and glass-forming liquids.<sup>241</sup> Artisans, technologists, and scientists tailor glass properties (and structures) by controlling 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 properties<sup>242</sup> and could provide a better understanding of the glass transition<sup>243,244</sup> as well as phenomena like polyamorphism.<sup>245-250</sup> The pressure variable can be employed to help advance glass science and technology in at least two different ways: (i) 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 (ii) 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 multianvil 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/high-temperature conditions.<sup>251-255</sup> 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 pressure.<sup>256</sup> In situ high-pressure/temperature studies have been done on prototypical network-forming oxide glasses, such as SiO<sub>2</sub>, GeO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, etc.<sup>245-250</sup>; however, much less is known about the structure and properties of multicomponent 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 multicomponent glasses<sup>257-259</sup> and melts, particularly those which are of industrial relevance and technological importance, for example, 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 ( $T_g$ ).<sup>260</sup> Studies have shown that pressure quenching is an effective way to change the atomic packing and bonding of glasses.<sup>261</sup> Pressure quenching can be used to prepare glasses with different structures and properties, and this approach is easier than the hyperquenching technique,<sup>262-264</sup> 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 indentation,<sup>265</sup> which was confirmed in classical molecular dynamics (MD) simulations<sup>266</sup> (Figure 6). Pressure-quenched glasses with high elastic moduli and high thermomechanical stability may find potential applications in many fields of technological importance such as the aerospace industries.<sup>265</sup> 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





**FIGURE 6** Atomic configuration (first row), local shear strain (second row), local density (third row), and local density change mapping (fourth row) under indenter after nanoindentation test for silica glass quenched under 0 GPa and 15 GPa<sup>266</sup>

to different structure and properties.<sup>260,267</sup> 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 nonrigid 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.

Among high-temperature and high-pressure apparatuses, DAC can achieve very high pressures (>100 GPa) and very high temperatures (>3000 K with laser heating), but the sample size is very small, typically on the order of tens of  $\mu\text{m}^3$ . Similar pressures and temperatures have been achieved by MAA techniques, but with significantly larger ( $\text{mm}^3$ ) samples.<sup>268</sup> Larger samples ( $\text{cm}^3$ ) 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 Poland,<sup>269</sup> 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.

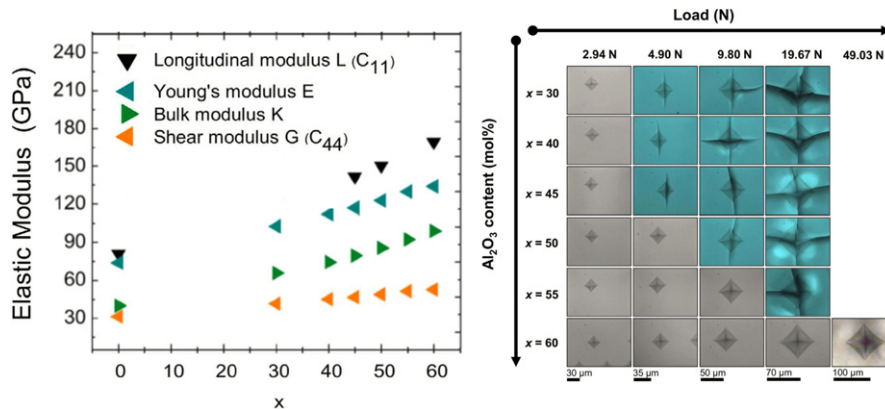
Another way of exploring the properties of melts under unusual conditions, particularly those that do not readily form glasses on quenching, is to subject them to deep undercooling in ways that minimize heterogeneous nucleation initiated at container walls, or that avoid homogeneous nucleation by rapid undercooling. For instance, splat quenching techniques, with cooling rates reaching  $10^6$ – $10^7$  °C/s, were employed to synthesize amorphous metallic alloys.<sup>270</sup> 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 nanocrystallization in such systems.<sup>271</sup> 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  $0.5^\circ\text{C}/\text{min}$ .<sup>272</sup> Rapid quenching techniques have been used by many in the inorganic glass community, most actively in the 1970s and 1980s,<sup>273–275</sup> although most of these studies were done to catalog unusual glass-forming systems. In some cases, unusual properties were measured for these rapidly quenched systems, including high ionic conductivity<sup>276</sup> and magnetic properties.<sup>274</sup> Additional examples of glass formation in technologically important  $\text{Al}_2\text{O}_3$ -based systems have been reported more recently.<sup>277,278</sup> 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  $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  system.<sup>277</sup> They also provide a viable way to form novel glasses with unique properties otherwise not possible with conventional glass-forming techniques, such as  $\text{TiO}_2$ -,  $\text{Ta}_2\text{O}_5$ -,  $\text{WO}_3$ -, and  $\text{Al}_2\text{O}_3$ -based glasses without any classical network formers.<sup>279–284</sup> It was recently shown that  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  binary glasses with up to 60 mol%  $\text{Al}_2\text{O}_3$  could be synthesized by using the containerless technique and that these glasses possess high elastic moduli, high hardness, and high crack resistance<sup>285</sup> (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

**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 noncracked samples.<sup>285</sup>



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 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 noncrystalline 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 supercooled liquids,<sup>286,287</sup> 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.

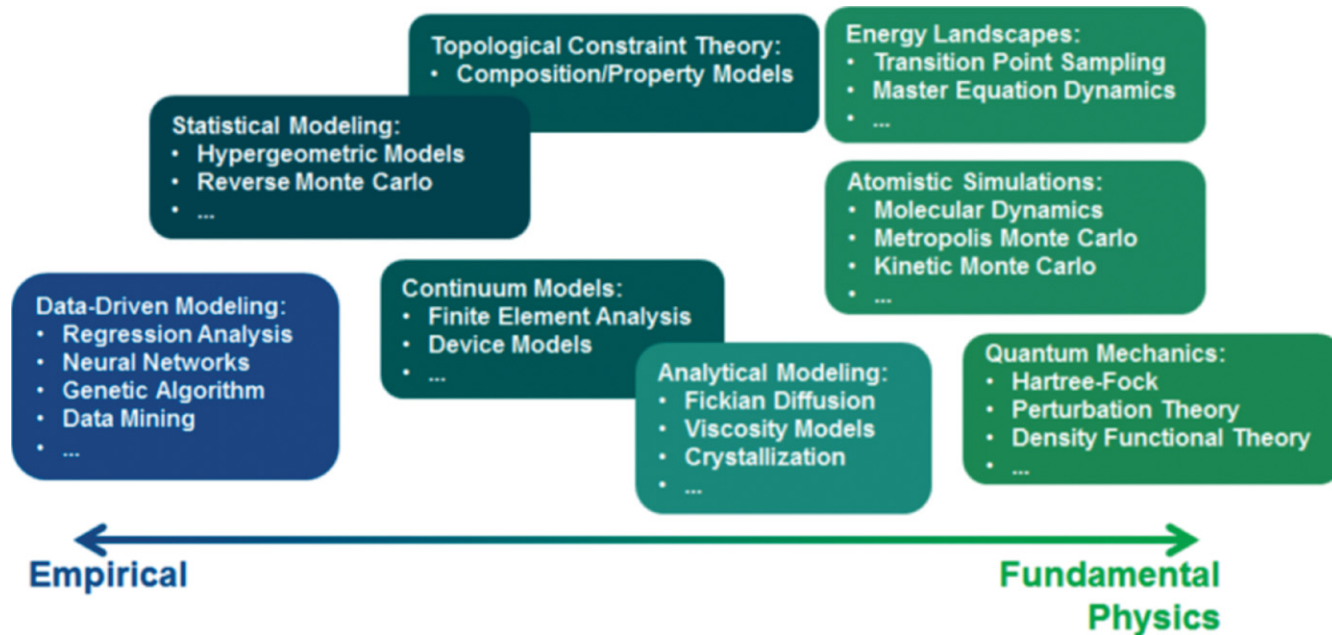
## 6.2 | Challenge #8: Rational design of functional glasses guided by predictive modeling

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 (eg, thermal or pressure history) on the resulting glass structures and macroscopic properties. Although multiscale computer simulation and modeling techniques have been widely applied to study the structure and properties of glass<sup>288</sup> (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 multifunctional

glasses, models at different scales are needed to predict manufacturing-related attributes, for example, temperature-dependent viscosity, liquidus temperatures, and refractory compatibility, as well as the relevant end-use properties, for example, 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, 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.

Predictive modeling of the mechanical, electronic, electrochemical, thermal, and optical properties of glass and amorphous solids using first-principle techniques (eg, 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 silica,<sup>289-291</sup> but more often than not are inaccessible for complex multicomponent glass systems. The challenge of building realistic structural models for laboratory glass is twofold. 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 nonoxide 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





**FIGURE 8** Overview of modeling techniques for glasses, from purely empirical models to those firmly grounded in fundamental physics<sup>288</sup> (reprinted with permission, American Chemical Society)

cannot represent realistic glass-forming processes. Building structural models for solids under external stimuli (eg, 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 multicomponent 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) simulations<sup>292</sup> as well as emerging, further refined computational methods<sup>293</sup> 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 resolution.<sup>294</sup> The direct imaging of two-dimensional silica glass comprising bilayers of SiO<sub>4</sub> tetrahedra using STEM is another salient example.<sup>295</sup> 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 semiempirical 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, for example, 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, 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.

## 7 | 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.

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