Modeling challenges in ceramic materials innovations
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Advances in the modeling of modern ceramics have been made in the areas of ferroelectric oxides, interfaces, solid solutions, fracture, and microstructures. The more difficult problems lie in areas where local bonding changes are encountered, high energy excitations are generated, nonlocal interactions in heterogeneous media are demanded, and when integrations of very wide time and length scales are required.

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Introduction

The simulation of ceramics helps materials innovations. It sometimes provides a precise understanding of the modeled materials in terms of first-principles. At other times, it provides a set of numerical 'experiments' which enables the effects of different underlying variables to be isolated. The high reproducibility of numerical simulations, the relative ease with which models can be varied, and the large quantity of data and the detail which can be obtained enable such calculations and experiments to be readily analyzed by trained experts and reviewers. Of course, depending on the basis of the model and the task it is expected to perform, the material simulated may or may not be realistic. Nevertheless, well-conducted simulations free of artifacts are valuable resources for ceramic scientists and technologists.

Ceramics are complicated in some respects. Their bonding ranges from ionic to covalent, sometimes in a single ceramic, they contain many atomic species, and as they are often made from fine powders they inherit many interfaces and impurities. On the other hand, ceramics are simple in some respects. Dislocations are relatively inactive so many problems are simply elastic ones and electrons are mostly localized, at least in the ground state. These aspects may require special attention or may be taken advantage of during simulations.

I will review some of the selected literature since 1997 in this field. My selection is based on my sense of the interest of the ceramic community. I also place an emphasis on the ceramics that are of technological importance. I will further comment on the issues and challenges that I perceived while reviewing these subjects.

Phase diagrams

Phase diagrams are essential tools for practicing ceramists. Reproduction by first-principles calculations has been a challenge to theorists. Low temperature phase diagrams that are of special interest, are those that involve diffusionless phase transitions. For pure compounds, first-principles calculations have yielded definitive results for ferroelectric oxides as described below. These oxides have special properties that arise from the dynamic charge transfer which occurs when 'ionic' bonds are distorted [1]. Experimentally, a very large Born effective charge (tensor) with a magnitude well in excess of the formal charge has been implicated. In the past five years, using both the Berry's phase approach in quantum mechanics and linear response theory (or density functional perturbation theory as it is sometimes called), a solid handle for treating this aspect in first-principles calculations at zero temperature has been obtained [2–6]. These calculations have been extended to finite (but low compared to melting) temperatures by first constructing model Hamiltonians to take into account the low-energy excitations of both a localized and of a long-range nature [2,7–10,11•,12]. Monte Carlo simulations then allow the free energy to be computed and the phase transitions predicted. As each term in the model Hamiltonian can be evaluated from the behavior of various 'normal modes' of supercells using first-principles calculations at zero temperature, the model Hamiltonian is first-principles based and so are the predicted phase transitions. Such calculations have been performed for $BaTiO_3$, $PbTiO_3$, $KNbO_3$, and $SrTiO_3$ [7–10,11•,12].

First-principles calculations of the LDA (local density approximation) type always underestimate the lattice parameter by ~1% and hence overestimate the importance of the short-range interaction. This is then 'corrected' by imposing an appropriate negative pressure. Even so, there is a typical underestimate of the absolute transition temperature by ~10 to 25%. The discrepancy is the largest for the high temperature transitions and may be indicative of the need for including the higher-energy excitations in the model Hamiltonian (See below).

Ferroelectric phase diagrams are 'constrained' phase diagrams without compositional partitioning. Thus, the configurational entropy of solid solutioning can be ignored; only an ensemble average of the free energies of the various (indeed infinite) configurations needs to be evaluated. For a small supercell, configurations are finite and cluster expansion techniques can be used in conjunction with first-principles calculations to treat solid solutions. Some preliminary calculations for ferroelectric solid solutions along this line have appeared in the past year but further development is still needed [13•].

First-principles calculations of phase diagrams at high temperatures are difficult. Certainly, the configurational entropy needs to be considered. The methodology for this task is well developed and has been commonly incorporated in modern calculations [14]. A larger difficulty lies in the inadequacy of the low-energy perturbation expansion of the Hamiltonian at high temperatures, especially for those ceramics that exhibit interesting electronic, ionic and other transport properties. (Even for alkali halides, very rich vibrational and elastic properties have been found at high temperatures when the potentials are far from harmonic and strong effects due to anisotropy are manifest [15].) Meanwhile, computationally, high temperature first-principles calculations incorporating dynamics are not yet able to span the time scale required for reaching thermal equilibrium with long (or even short) range diffusion. Much remains to be done in this area. (Semi-empirical calculations of phase diagrams at high temperatures are reviewed elsewhere in this issue.)

Studies of thermodynamic properties yield information, as a by-product, on the structure and energetics of point defects or other excitations, either in the ground state or in the saddle point state. This information has not always been presented in the literature. For example, it would be very useful to know, explicitly, the path and the energy barrier for Ti-switching between the eight equivalent (111) sites in $BaTiO_3$, at various temperatures. The required Monte Carlo calculations can be performed using the model Hamiltonian already established. Presently, such data can be more easily obtained by high fidelity simulations than by definitive experiments. These data could further our understanding of ferroelectric oxides more than a mere reaffirmation of the transition temperatures can do.

Interfaces

Many polycrystalline ceramics contain a SiO_2-rich thin amorphous film between grains. Such films also exist at heterophase junctions, where one side is crystalline quartz [16]. Thus, apparently, it is energetically more favorable for silica to remain amorphous than to crystallize. The film can be squeezed out from between the grains by applying a certain compressive stress, but even when it becomes thinner some amount still remains to support stress as if it forms an absorbed layer (or Stern layer) [17–19]. At much higher compressive stresses, patches of 'dry', desorbed boundaries can emerge, as was recently observed in superplastically deformed ceramics [18,19]. More commonly, in the sintered, stress free state, an apparent 'equilibrium' thickness independent of the type of grain junctions is attained [20,21]. It has been proposed that the equilibrium thickness arises from the balance of attractive van der Waals forces and various repulsive interactions [22]. The latter include an electrostatic (double layer) repulsion between the grains and a shorter range interaction due to the inability of the amorphous layer to instantaneously align itself with the two different crystallographic surface orientations of the adjacent grains.

Simulations of single-crystal/glass couples, bicrystal grain boundaries, bicrystal/glass sandwiches, and nanocrystalline polycrystals have been reported in the past year for Si [23*,24]. The simulations were performed using empirical three-atom potentials, which did not include van der Waals forces. At large twist angles, grain boundaries are energetically unstable and amorphous films form: the thickness of the amorphous layer being independent of the twist angles. Interestingly, this 'equilibrium' thickness is twice the thickness of the transition layer between amorphous Si and an Si crystal of 100, 110, or 111 orientation [23*]. (The transition can be identified because the average amorphous layer energy is lowest at the interface and monotonically rises with the distance from the interface.) These results suggest that the interfacial layer should be treated as two absorbed layers on the adjacent grains. The apparent attraction to keep a minimum thickness is caused by the need to expel the higher energy excess amorphous phase that is not sufficiently close to the interface. In particular, van der Waals forces are not necessary for the stabilization of the amorphous film. As Si shares the same covalent bonding nature with the constituents of amorphous grain boundary films (SiO_2 and Bi_2O_3), these simulation findings are pertinent to ceramics. Note, however, that the angles in the SiO_2 tetrahedron are not all the same as in the Si tetrahedron, and that SiO_2 is partly ionic which gives rise to a long range polarization effect that is not seen in Si. Thus, further validation using more realistic potentials for glass-forming oxides is desirable.

Substitutional and interstitial impurities

One focus in ceramic science and technology is the use of additives to alter the physical and chemical characteristics of ceramics. Sinterability, grain boundary mobility, creep resistance, fracture toughness, electrical and ionic conductivity, and environmental stability can all be significantly influenced by impurity doping. Additives have been extensively studied for alumina and silicon nitride. The alumina in use today is mostly α-Al_2O_3 which has very little solubility for most impurities [25]. Nevertheless, dramatic dopant effects in alumina have been well documented. The silicon nitride in use today is mostly β-Si_3N_4 which forms a solid solution with Al and O. The recently discovered *in situ* toughened α-Si_3N_4 solid solution (α'-SiAlON) has an even broader range of solid solution with Al, O, and many other cations [26].

According to conductivity measurements yttrium is a donor in alumina, even though the formal charge of Y is the same as Al. Calculations using orthogonalized linear combinations of atomic orbitals in the local density approximation have been carried out assuming that Y occupies the octahedral site in the α-Al_2O_3 structure [27]. The results show that Y introduces three defect states in the energy gap near the conduction band edge, thus explaining the donor effect. These defect states are quite localized and are derived from the Y 4d orbitals, coupled to the O 2p and Al 3d orbitals. There are also strong covalent bonding characteristics

between Y and the neighboring atoms. It remains to be seen whether these features are unique to Y or are shared by other oversized, 4d and 5d trivalent (or even tetravalent) dopants, such as the rare earth cations (Ln) and Zr or Hf.

In the case of Si_3N_4, molecular orbital calculations by the discrete variational $X\alpha$ method have been applied to α-Si_3N_4 and β-Si_3N_4 containing rare-earth ions as interstitials [28]. These calculations were performed using (unrelaxed and charged) clusters that are nitrogen terminated. The results showed that the antibonding between Ln^{3+} interstitials and Si/N atoms increased with the ionic size of Ln, and this was thought to lower the solubility of the larger Ln ion in Al–O substituted α-Si_3N_4. Meanwhile, stronger Si–N bonding was found in α-Si_3N_4 than in β-Si_3N_4 upon the introduction of Ln. This was thought to explain the lack of Ln solubility in β-Si_3N_4.

While these conclusions may appear reasonable, their validity cannot be taken for granted without further scrutiny. The paper [28] describing the Si_3N_4 results also reported that the Si–N bonding increased monotonically and substantially when the Si–N bond length was lengthened from 1.67 to 1.84 Å by stretching the $(Si_3N_{10})^{18-}$ cluster [28]. This result is chemically unreasonable. It is quite likely that it simply reflects the overriding influence of the electrostatic energy of the charged cluster which decreases when the cluster expands. If so, it is a mere artifact, and all the calculated results in this series of studies are suspect [28–30]. In the case of the Al_2O_3 study, [27] it is noted that the LDA calculations greatly underestimate the magnitude of the bandgap, and the computed Y–O and Y–Al bond distances do not quantitatively agree with the experimental data (which additionally needs to be independently confirmed). As the covalent character and defect states are sensitive to the bond distance, further investigation is needed before a definitive resolution of the effects of Y can be reached.

Physical properties

Two challenges in simulating physical properties of ceramics have already been mentioned: the difficulty in incorporating high-energy excitations when they are needed at high temperatures, and how to account for bonding changes in excitations and distortions. The former is especially important for transport properties, the latter when covalency is in a subtle balance with ionicity. Other than ferroelectricity, such a subtle balance is probably also present in the transformations of ZrO_2 [31,32] and around some impurities in otherwise strongly ionic compounds. These aspects need to be considered for both linear and nonlinear properties. A further challenge concerns the integration of length and time scales. This is particularly important for nonlinear properties such as fracture, [33] as reviewed elsewhere in this issue.

First-principles calculations of permittivity and piezoelectric coefficients have been reported for $BaTiO_3$ and

$PbTiO_3$ using effective Hamiltonians and correlation functions [5,34,35]. These calculations were performed using the linear response theory, and at relatively low temperatures (but encompassing the Curie temperature [34,35]). A more detailed analysis of the components of the piezoelectric stress tensor in the context of Berry's phase approach has also been formulated for $PbTiO_3$ and PZT ($PbZrTiO_3$) at zero temperature [36,37]. These results are presumably rigorous having taken into account the bonding changes during excitations. The investigation of solid solutions, however, may require further validation. It is well known that the properties and phase stabilities of ferroelectrics are extremely sensitive to the constraints imposed. Therefore, the small supercell calculations of limited solid solution configurations with some assumed symmetry might not be sufficiently representative [38–40].

Compared with mixed ionic/covalent ceramics, calculations of linear properties of strongly covalent or strongly ionic ceramics are easier and pair or three-body potentials may suffice [15]. However, the same cannot be said for nonlinear physical properties, such as fracture. Even at low temperatures, bonding changes along the path to the saddle point are possible given the large degree of bond distortion prior to bond rupture. Likewise, property simulations of highly distorted structures, such as grain boundaries, dislocations, metal ceramic interfaces (for which image charge is of paramount importance [41]), and atomic transport with and without a field could encounter the same complication regarding bonding changes especially when impurities are involved. In addition, for nonlinear problems, the relaxation and reconstruction of the final state configurations demand attention.

Less rigorous quantum chemical simulations can nevertheless yield interesting results when the statement of the problem is simplified to one of molecular configurations. Slow crack growth in amorphous silica is thought to be just that, involving sequential fracture of three-, four-, five- and six-member silica rings in some statistical combination [42]. Using semiempirical quantum molecular orbital calculations, the transition state probabilities can be calculated for the above events. The slow crack growth kinetics can then be computed by evaluating the matrix of transition state probability for a characteristic distribution of silica ring sizes. (The need to bridge the length scale is less acute here because amorphous silica is supposed to lack any recognizable microstructure beyond the molecular scale.) This approach has also been extended to slow crack growth in various environments (vacuum, carbon monoxide, water and nitrogen) that are known to affect the kinetics. Although questions remain regarding the need to consider charge distribution at the crack tip and the screening effect of the environment, let alone the adequacy of the methodology, the above study nevertheless marks an encouraging advance in our understanding of one of the 'simplest' problems in fracture.

Microstructures

Innovations in ceramic technology are as often due to the creation of unique microstructures as to the discovery of new phenomena, new compounds or new compositions. Examples range from pore-free translucent alumina lamp envelops and the core-shell structure of $BaTiO_3$ X7R capacitors, to the recent discovery of whisker-like α-SiAlON [26]. I will comment on some recent progress in microstructure simulations, emphasizing classical microstructures of macroscopically homogeneous ceramics. Microstructures of graded ceramics are of current interest but will not be commented upon here. Another current focus of research, the integration of length and time scales over many orders of magnitude, is not covered here either. The latter aspect is important for simulating thin film microstructures in a manufacturing setting and is reviewed elsewhere in this issue.

Monte Carlo methods using multiple-state Potts models have been well developed for microstructure simulations. They have the advantage of providing a direct visualization of the microscopic mechanisms describable in terms of standard Boltzmann kinetics, even though each Monte Carlo step is not to be equated to an atomic step because the 'lattice' size employed in these simulations is generally much coarser than the atomic size. These simulations have been carried out for grain growth, grain coarsening, and final stage sintering [43–45]. This technique, however, is mostly limited, in its present form, to a fixed 'lattice' that is mechanically rigid. Thus, while the local interactions can be conveniently considered in the model Hamiltonian, nonlocal interactions caused by, say, elastic interactions between strain distributions at different points in the simulated microstructure, are very difficult to treat. Khachaturyan [46] has shown that solving the time-dependent Ginsburg–Landau equations for a mean field free energy functional sometimes provides a more efficient way of simulating microstructure. This is because when the field equations are solved in reciprocal space, standard long-range nonlocal (elastic and electrostatic) interactions transform to simple $1/k$ terms (k being a wave vector) that require no special treatment. For applications such as domain formation in martensitic transformations and ferroelectric transitions, the latter method is advantageous even though its visualization is sometimes clouded.

Simulations can easily separate the effects of various kinetic and energetic contributions to microstructural evolution. As an example, 3D simulations have now shown that there is a significant elastic contribution to the formation of twins, often seen in ferroelectric domains [47]. This is similar to the case in martensitic transformations, even though electrostatic (dipole–dipole and depolarization) energies are the main causes for forming domains in ferroelectric transitions. As another example, in some ceramic systems such as ZrO_2/Al_2O_3, the Zener pinning effect (grain growth being arrested by second phase particles) is found to be three to four times stronger than expected [48] from simple analytical theories, [49] albeit the theories correctly predicted the scaling relations. A recent 2D simulation study found that the enhanced Zener effect is associated with those particles that are able to coarsen themselves [50]. Apparently, it is much more difficult for grain boundaries to escape a 'moving target'. One should be cautioned, though, because particle pinning dynamics are known to depend on the dimensionality and further 3D simulations would be required to settle this issue.

One of the most complex but important phenomena in ceramic science and technology is sintering. Despite some early effort on final stage sintering, [45] simulations of sintering with a realistic microstructure remain an essentially unmet challenge. It is difficult, not because of the multiple kinetic paths (diffusion along surfaces, grain boundaries, and the lattice) and complex microstructures (particle packing, contacts, pore distributions and migration) involved, but because of the nonlocal elastic interactions that arise from differential shrinkage and grain boundary plating. The latter actions are especially important in earlier stage sintering when the diffusion distance is short, and they could be responsible for the rearrangement and separation of particles as well as the enhancement and retardation of sintering that is observed [51,52]. As the modulus of the porous microstructure is spatially inhomogeneous, the Green's function of elastic interactions is not simple and cannot be converted into a single term in reciprocal space. Thus, both the Potts model and mean field theory have great difficulties in attacking this problem. In fact, I believe concurrent iterative elastic solutions have to be sought at the same time as executing Monte Carlo steps or solving Ginsburg–Landau equations. Moreover, it has to be done with a high accuracy over many length scales because stress concentrations can be quite important at the necks causing enhanced diffusion and even particle rearrangement. This approach has not yet been undertaken.

Liquid phase sintering is sometimes thought to be simpler because of the absence of elastic stresses. This advantage is offset by the complications arising from such processes as pore filling and particle relocation made possible by the liquid. So it is by no means simpler. The only simple problem is viscous sintering which is entirely a mechanical problem. This has been treated by the finite element method in a straightforward way [53].

Conclusions

First-principles calculations of ferroelectric oxides have made rapid progress, carrying implications beyond ferroelectricity on which they are currently focused. New issues in ceramic interfaces and impurity defects have also been raised, and their resolutions appear to be promising but further simulation efforts are needed. Outstanding and open questions in relatively classic problems are many and have been outlined for high temperature structures and phases, transport properties, deformation and fracture, and sintering. These problems are difficult and will require continued attention.

Simulations are most valuable in yielding 'data' which are hard to obtain experimentally, and in separating the roles of different mechanisms in complex thermodynamic and kinetic problems. Pleasing examples of this kind are provided and further suggestions made. In this connection, I feel that sometimes modelers generate data which experimentalists find hard to relate to. Examples in which modeling and experiments are truly integrated are few and far between [54,55]. A closer integration between modelers and experimentalists is thus recommended, which would help the fruits of their labor benefit the innovation and improvement of ceramics.

Acknowledgements

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