Electroceramics: Modeling of Grain Boundaries, Interfaces, and Defects

The process of designing and fabricating functional electroceramic devices on an ever-smaller size scale, and with demanding performance standards, leads to a need for detailed theoretical analyses. The simple “brick-wall” circuit model of a capacitor built from a granular material can yield at best a macroscopic parametrization of bulk and grain boundary electrical properties. Discrete circuit element models for more complex devices such as ferroelectric memory cells are useful at the engineering level, but nanometer- and angstrom-scale models are needed in order to control chemical properties, diffusion rates, thermal expansion, heat transfer, etc. The parallel development of microscopic theoretical methodologies, along with site-specific and spatially resolved spectroscopic experimental techniques, has provided the necessary tools for analyses which span the angstrom- to nanometer- to micron-size scales relevant to device technology.

Modeling complex systems with several size scales necessarily leads to amalgamation of different theoretical techniques, with differing levels of sophistication. At the most basic level, first-principles quantum theory is required to resolve electronic structures, atomic configurations, and interatomic forces. However, first principles or ab initio calculations are complex, computationally demanding, and not yet capable of resolving many important dynamics issues. Semiempirical quantum schemes can extend the size scale to nanometers, but require parametrizations which must be obtained by rigorous theory on the smaller scale, or by fitting to very limited experimental data. Fortunately, atomistic simulations making use of classical parametrized interatomic potentials have proven capable of filling the “midrange” scale, where the atomic arrangements are still important, but detailed electronic interactions are seen in only an average sense. Classical reaction kinetics schemes have been rapidly evolving to provide a continuum approach which matches well to the atomic- and nanometer-scale modeling, and can deal with such phenomena as microporous fluid flow, crack formation and propagation, interface debonding, and particle migration.

1. Atomistic Simulations

It may seem surprising that a classical interatomic potential function \( U(R_1, R_2, \ldots) \) with a rather small number of parameters can embody sufficient information to reproduce structural, electrical, and thermal properties of a complex structure like an electroceramic. Nevertheless, molecular dynamics (MD), lattice statics, and stochastic Monte Carlo (MC) approaches based on a model potential have proven quite useful in interpreting defect structures (Catlow et al. 1976), grain boundaries (GB), and free surfaces (Wolff 1984), at least in “simple” materials like MgO. At present, scanning transmission electron microscopy (STEM) with the use of Z-contrast imaging and spatially resolved electron energy loss spectroscopy (SREELS) make it possible to obtain atomic resolution images of grains at an interface or GB, which can be combined with simulations to yield a model with consistent theoretical and experimental interpretations (Ravikumar et al. 1996, Pennycook et al. 1999). Images of spatially varying potential and charge density across interfaces have been obtained by electron holography, e.g., for pristine and doped SrTiO\(_3\) GB (Ravikumar et al. 1997). Such combined atomic-scale experimental imaging and atomistic simulation approaches provide a challenge to structural models derived from less detailed discrete element or continuum models, which may not be easy to resolve. For example, the width of the charge compensation region on either side of a doped grain boundary may be \( > 50 \text{nm} \) according to continuum modeling, and may be measured as \( < 15 \text{nm} \) by holography. Are they measuring the same quantity? This becomes a challenge for the first-principles theory, to generate and map detailed electron and ion distributions, and is of consequence for device design, showing how the different levels of size and modeling interact.

The basic principles of MD and MC atomistic modeling are very well known (Ciccoti et al. 1987, Binder and Heerman 1988, Yoneya and Simmons et al. 1997). In MD, one establishes a set of initial atomic positions and velocities, determines the force on each atom as the gradient of the potential with respect to the atomic coordinates, and solves Newton’s equations of motion using finite time-step algorithms. Fixed temperature \((T)\) and programmed temperature algorithms are used to either follow lattice dynamics and ion migration, or to search (by annealing or quenching) for basins of potential energy containing the stable or metastable configurations of the system. To maintain numerical precision, the typical time step of 1 fs (10\(^{-15}\)s) is required; with a GB or surface geometry sampling volume of several thousand atoms, it may be convenient to run the simulation for \( 10^4\)–\(10^5 \) steps. Of course, a single “run” with a given set of initial conditions does not give adequate statistics for reliable conclusions. This reveals a limitation of MD: with vibrational periods of \( \sim 10^{-12}\)s and diffusion times of interest of perhaps \( 10^{-8}\)–\(10^{-9}\)s, straightforward MD accesses too short a time scale to study many important processes. Acceleration methods exist, but are not yet very general, nor easy to implement and verify. Nevertheless, MD-related lattice statics and T-quenching approaches have been extremely useful in predicting defect geometries and energetics, interface composition, and surface relaxation of ceramics (Gale 1997), with especial attention
given to oxides, e.g., by Grimes and coworkers (McCoy et al. 1997a, 1997b, Yan et al. 1995).

Stochastic MC and related methods sample the configuration space of the system by making random jumps in the independent variables such as atomic positions. A "cost function" \( W \), which may be as simple as the potential energy \( U \) itself, is evaluated, and the new system state is accepted or rejected based upon a probability distribution \( g(W, T) \). Here the temperature variable \( T \) plays the role of a constraint; hot systems are permitted frequent excursions away from the minimum-\( W \) state, while cold systems tend to remain trapped within (local or global) minima of \( W \). In principle, the system will eventually sample all available states, thus reducing the chance (all too common in MD) of trapping at a local minimum. In the so-called simulated annealing (SA) scheme, the system is cooled as it performs jumps, and with an optimized cooling rate can be expected to find the configuration of minimal structural energy fairly rapidly. Variants of MC/SA have been successfully employed to search molecular structures, examine protein folding, relax interfaces, and "grow" low energy grain boundaries between ceramics such as MgO:CaWO\(_4\) (Ellis and Guenzburger 1999, Mundim and Ellis 1999).

2. First-principles Theory

Quantum mechanics forms the rigorous basis for first-principles methodology, and the Schrödinger equation (or its relativistic counterpart the Dirac equation) governs the behavior of electrons and nuclei in solids. For any materials system of interest, drastic approximations are required in order to obtain computationally feasible procedures. These approximations typically include: the Born–Oppenheimer (B–O) approximation, in which the electronic states are treated in the (instantaneously static) field of the nuclei; the self-consistent field (SCF) approximation, in which a one-electron equation is obtained describing the motion of each electron in the average field of all others; and a model many-body wavefunction—such as the Hartree–Fock single determinant, or a specified mult-determinant configuration scheme based upon a many-body correlation model. The B–O approximation defers the treatment of dynamics to a later stage, and leads to a successful description (though approximate and tedious in the case of low symmetry) of molecular and solid vibrations and rotations. The SCF or one-electron approximation is a great conceptual aid, in that the single-particle functions can be used to represent a variety of states of the many-body system, and in an appropriate mathematical formulation can satisfy the desire for chemically intuitive orbital descriptions of atomic configurations, bonding interactions, and excitation modes. The problem of choosing an appropriate many-body wavefunction model is more difficult, since the important electronic correlations may not be known before the fact, and an "inappropriate" choice would require an astronomical number of terms in the wavefunction expansion. Fortunately, this problem has largely been bypassed by the development of density functional (DF) approaches, which concentrate upon the discovery of an electronic density-dependent energy functional \( E(\rho, \rho_{\ldots}) \) from which all ground state properties can be derived, including an effective SCF procedure (Parr and Wang 1989 and references therein). Thus, the rapid development of quantum-theoretical methods for materials over recent years has largely taken place in the DF framework.

For idealized periodic systems, translation symmetry can be exploited and band structure representations of electronic single-particle states can be obtained by SCF procedures. Band structures for defect-free bulk crystals and simple crystal surfaces can be obtained routinely, using a variety of numerical and variational techniques. It is feasible, but not routine, to use a large supercell to represent a complex GB, defected volume, or reconstructed surface—in which case an artificial periodicity is imposed upon the system. If the cell is sufficiently large, boundary effects and "ghost" interactions can be made negligible. An important achievement using this approach is the analysis of the energetics of surface reconstruction and its effects upon ferroelectric polarization in materials like SrTiO\(_3\) and BaTiO\(_3\) (Cohen 1996, Padilla and Vanderbilt 1997a, b). Other milestones include the study of relaxation and column-buckling within SrTiO\(_3\) GB (Mu et al. 1999), combined theory and experimental studies of pristine and Y-segregated GB in sapphire (Mo et al. 1996, Ma et al. 1999), and a description of F-center defects (oxygen vacancy with two electrons) in KNaO\(_3\) (Eglitis et al. 1997).

Another theme in quantum mechanics dating back to the origins of crystal field theory and its successor, ligand field theory, is the development of localized representations of electronic properties. Beginning in the 1970s, advances in computer power made it possible to develop embedded cluster models, and specifically embedded cluster density functional (ECDF) models of sufficient size to represent chemical and electronic properties to satisfactory accuracy (Ellis et al. 1978, Ellis and Guo 1995, Ellis and Guenzburger 1999). There now exist a variety of ECDF implementations demonstrating the utility of the approach, especially for extended systems with low symmetry. Recent extensions of methodology lead to parallel computational schemes in which the computational time and effort only increase linearly with system size, permitting first-principles surveys of "landscapes" consisting of thousands of atoms. Typical applications have ranged from defect clusters in wustite Fe\(_{1-x}\)O, TiO, and MnO (Press and Ellis 1987, Khawash and Ellis 1989) to defected ceramic nanoclusters (Grimes 1999).
Figure 1. For legend see opposite page.
3. Examples
The foregoing general principles can best be illustrated by further examples where a considerable interaction between theory and experiment permits cross checks, and where there also exists some technical significance. Oxide-oxide interfaces are of growing importance in applications where mixed ionic and electronic conductivity can be exploited, as in oxygen and molecular sensors, fuel-cell electrolytes and supports, thin-film superconducting circuit elements, transparent conductors, etc. The deposition and growth of metal particles and films on oxides and adhesion of metals to oxides are essential elements to the further development of integrated circuit structures, micro-motive components, and the emerging area of bio-metallo-inorganic sensors and self-organized nanostructures.

3.1 Zirconia/Nickel Oxide Interface
The cubic $\text{ZrO}_2(100) \parallel \text{NiO}(111)$ interface provides an opportunity for comparison between atomic-scale measurements, atomistic simulations, and theoretical electronic structures. This interface is especially interesting since, along the “a” in-plane direction the mismatch is extremely small (0.4%), while along the “b” in-plane direction the mismatch is several percent. High-resolution electron microscopy indicates that the oxides share a common oxygen layer, and that the small lattice strain is largely taken up by NiO, near the interface. Using atomistics simulations with simple Coulomb plus Born-type pairwise interatomic potentials,

$$U = \sum_{i<j} \frac{q_i q_j}{r} + A e^{-\alpha r} - \frac{B}{r^6}$$

one obtains a still more focused picture, revealing two types of boundary. The potential parameters ($q_i, q_j, A, B, \alpha$) for each distinct pair were found in this case by fitting to the known lattice parameters, cohesive energy, elastic constants, and dielectric constant of the bulk constituent crystals. The lowest energy interface
is highly planar, nearly ideal in structure; a second interface is found, of higher energy, which shows a rumpled structure with strain taken up by deformation of nickel chains as shown in Fig. 1. Depth profiling of atomic site energies permits calculation of interface versus bulk and surface energies, and shows that the interface effects only penetrate 2–3 atomic layers. Embedded cluster density functional studies of bulk and interface-region sites permit characterization of perturbations of electronic density around the boundaries. The ionic charge on the metal sites is somewhat less than the Zr$^{4+}$, Ni$^{5+}$ nominal configuration, due to covalent charge-sharing with oxygen ligands, as is generally observed in oxides. More importantly, it is found that the metal valency is only slightly altered in the interface region, where the oxygen coordination is moderately deformed. The oxygen atoms forming the interface core suffer the greatest changes, giving up a fraction of an electron due to the “frustration” of being unable to complete the four-fold bonding structure to zirconium on one side, or the six-fold coordination to nickel on the other side of the interface. This modified oxygen valency at the interface will have an effect on oxygen transport across/along the interface, which would be the subject of an interesting study.

3.2 Growth of Nickel on Rutile(110) Surface

The bonding structure and binding character for the initial stage of thin film growth of nickel on a TiO$_2$ rutile(110) surface were studied using first-principles density functional theory (DFT) (Cao et al. 1999). In this case, electron diffraction data clearly defined the (essentially unreconstructed) surface geometry, and the primary questions concerned the relative energetics and bonding schemes of available metal adsorption/bonding sites at differing levels of coverage. The results show that, in the first monolayer, nickel atoms are preferentially adsorbed on top of bridging oxygen atoms, and upon secondary surface oxygen. The bond strength between nickel adatom and substrate oxygen is much stronger than that between nickel adatoms. About 0.3 electrons are transferred from nickel atoms to substrate in low coverage; the adsorption of additional nickel atoms on neighboring sites decreases this transfer, consistent with workfunction data. In addition to the bonding component, some covalent character is found in the nickel adatom–substrate bond. The Stransky–Kraskov mechanism has been proposed for the growth habit, among others: i.e., initial formation of nickel clusters, followed eventually by complete overlayers. The DFT study clearly shows how this takes place, given the “row-and-ditch” geometry of the TiO$_2$ surface and the relative energetics of Ni–O and Ni–Ni bonding interactions.

4. Future Directions

The balance between first-principles quantum analyses, parametrized atomistic simulation, and discretized/continuum classical modeling is dynamic and will continue to evolve as algorithms and computer capabilities develop. It is evident that integration of the different approaches, and improvement of feedback mechanisms which also involve atomistic-scale experimental data, are non-trivial tasks. The dream of “materials by design” is very much alive, and a major milestone in the modeling of electroceramics would be the reliable prediction of electromigration phenomena of components “under load.”

See also: Dielectric and Ferroelectric Ceramics: Interfaces

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