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Multiscale Modeling of Materials

The rotating reflector antenna associated with airport traffic control systems is giving way in some applications to a newer technology called the phased array antenna system (sometimes called a beamformer, *example shown at right*). Thousands of closely spaced, individual radiating elements produce a composite beam that can be shaped and directed electronically in microseconds, enabling it to track hundreds of targets simultaneously. Using a phased array, one radar system can be used for both missile guidance and target detection/tracking functions, rather than requiring separate dedicated systems, and no moving parts are required.

The Cobra Judy phased-array radar system on the missile range instrumentation ship USNS Observation Island. (Wikimedia Commons)

Each antenna element requires its own associated radio frequency (RF) phase shifter. The cost of the phase shifters is a limiting factor to the adoption of phased array antenna technology: the price of a system with thousands of elements can be prohibitive.

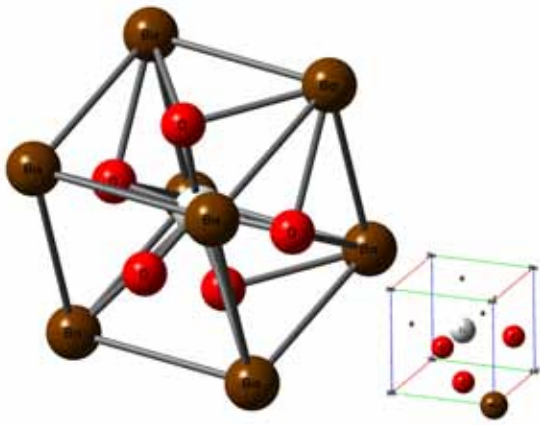
Phase shifters may be made from tunable dielectric materials, including the ferroelectric material barium titanate (BTO, or $BaTiO_3$). The magnitude and direction of electrical polarization in ferroelectric materials can be manipulated using an applied electrical field. *(See box, next page.)* Thus, the relative phases of the respective signals feeding the antennas can be varied so as to reinforce or suppress the effective radiation pattern of the array in specific directions.

Eric Darve, mechanical engineering professor at Stanford University, and his students, are developing new modeling methods in order to facilitate the rational design and evaluation of ferroelectrics and related materials. These methods combine a modeling component at the atomistic scale and a numerical component, with techniques to solve linear systems arising from finite-element and finite-volume analyses at the macroscopic scale.

Material models

Molecular dynamics (MD) methods can be used to model BTO crystals, using existing computational force fields. However, the existing force fields and parameterization cannot accurately model the crystal in different solid phases at various temperatures, making it impossible to predict accurately the most stable phase at a given temperature. In addition, no force field is currently capable of modeling defects in the crystal. This significantly restricts the ability to model and predict the behavior of BTO.

Developing force fields is a challenging task; Darve's group has created a unique set of tools to address this challenge. The first goal of the project is to apply genetic algorithm (GA) approaches to create a novel parameterization of the shell model potential as applied to BTO perovskite-structured crystals *(illustrations, this page and next page, and explanation, next page)*.



Perovskite-type crystal structure typical of barium titanate. Atoms at corners of cube: barium; white atom: titanium; red atoms: oxygen. The five atoms that form the unit basis are shown in the inset. (Graphic courtesy of José Solomon, Stanford.)

By re-parameterizing the shell model potential to tailor it specifically for BTO, the behavior of the crystal can be modeled with a high degree of fidelity under a diverse range of physical and electrical loading conditions. Predicting the behavior and response of materials often requires coupling atomistic and macroscopic models—for example, quantum models, molecular dynamics, Monte Carlo, and finite-element analysis. The resulting mathematical systems can be difficult to solve. The geometry of the domain is often very complicated.

In order to derive the BTO-specific parameterization, density functional theory (DFT) analysis is coupled with a GA-based technique by which the multidimensional parameter space can be explored efficiently. First, DFT is used to perform a single-point energy calculation on numerous deformed configurations of BTO's unit basis *(figure, below left)*. The numerous configurations examined with DFT are various deformations from the stable state of the perovskite structure in each of its four crystalline phases, *(cubic, tetragonal, orthorhombic, and rhombohedral: see figure, page 12)*. These calculations provide various energy configuration curves, which the GA then uses as a reference database.

The GA uses evolutionary algorithms derived loosely from Darwinian concepts. The starting point is a population of parameter sets for the functional form of the potential. The potential is evaluated using each population member (i.e., parameter set), and the resulting difference between the energy produced from the potential and that of the reference DFT database is used to establish the fitness of the given member. Members of a population are consequently combined, using either crossover or mutation techniques, with the objective of creating offspring with increased fitness. As the GA produces generation after generation, the algorithm strives to produce parameter sets with ever-greater fidelity to the quantum energy calculations.

Validating the Technique

In order to validate their technique, as well as optimize the selection of which crystal geometries to explore with the DFT, a series of synthetic energy curves was produced from a known shell model parameter set for BTO. The researchers hoped to reproduce the original parameter set that was used to create these synthetic curves, and thus have a direct quantification of the accuracy and effectiveness of the technique. A series of two-ion displacements was performed on the crystal

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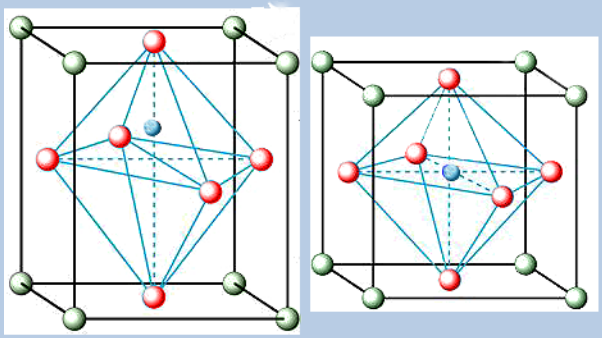

Ferroelectric Materials

Ferroelectric materials exhibit a nonlinear response to an applied electrical field. That is, the electrical polarization of a ferroelectric material increases or decreases suddenly at a particular electrical field strength. This transition point is characteristic of the specific material. Slight alterations in material composition or other characteristics can "tune" the transition point to a desired electrical field strength.

Additionally, ferroelectrics exhibit hysteresis—the transition point in an increasing applied field is not the same as the transition point for a decreasing applied field. This property is useful for application in memory devices.

The polarization effects in BTO arise from the distortion of the titanium oxide sublattice due to the large size of the barium ions that occupy the large cavities in the lattice *(silver atoms in the figure above)*. The titanium atoms are forced off-center in the TiO_6 octahedra *(blue and red atoms in the figure)*, producing an uneven distribution of electrical charges, creating a dipole effect. Applying pressure forces the titanium atoms back toward the centers of the octahedra, reducing the dipole strength. This sensitivity to pressure is called piezoelectricity.

Shell Model Potential

The shell model describes the deformation of the electronic structure of an ion (electrically non-neutral atom) as a result of interactions with other atoms. Each atom in a solid is described in terms of a massive core and a massless shell. Core–shell displacements create dipole moments (uneven distribution of electrical charges) that serve as a means of storing energy (potential).

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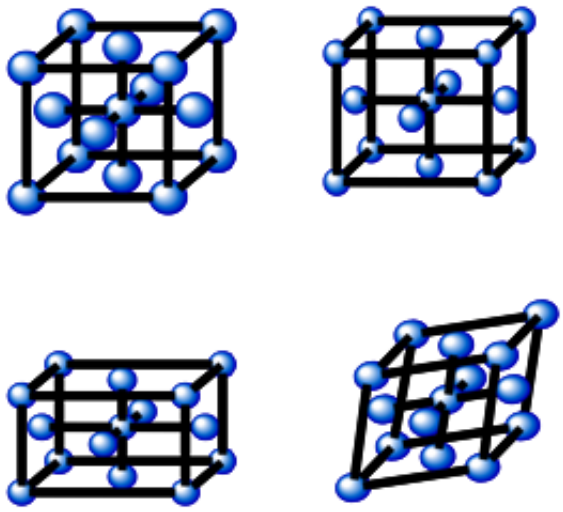
unit basis of the lattice to determine the symmetries inherent to the geometry. Each ion was displaced from –0.5 Å to +0.5 Å from its empirically determined stable configuration in the cubic phase.

Ninety displacements were compared, comprising a total of ten two-ion combinations displaced in nine orthogonal symmetries. A subset of 18 displacements was identified that covers the entire set of displacements. Energy curves produced from these 18 displacement configurations were fed to the GA. This is a fairly stringent test, because fitting the GA force field parameters to this data set guarantees that all thermal fluctuations of the system around the equilibrium point are reproduced correctly by the force field. Using this geometry, a series of evolutions was performed on the Buckingham parameters A and ρ. The agreement between the exact and evolved parameter sets was close over a wide energy range. The general results of the current GA analysis are satisfactory and served as a general validation of this approach.

In parallel to efforts to optimize the GA technique, various energy configuration curves were created for use with the novel parameter derivations. Using the DFT code Abinit, the same coupled displacements that were explored in the synthetic analysis are being reproduced within the quantum framework. In fact, a key benefit of the synthetic study was to identify equivalent displacement configurations so as to minimize the computational overhead required in the fitting procedure with the quantum data.

Darve's group has begun to implement a "hybrid" technique, by which a steepest descent optimization method (such as the conjugate gradient, CG) is coupled to the GA algorithm. In this novel approach, the GA will begin a partial evolution process followed by application of CG iterations. By iterating this procedure, they hope to improve the accuracy of GA still further.



Crytal phases for the perovskite-type crystal structure typical of barium titanate (clockwise from top left): cubic, orthorhombic, rhombohedral, and tetragonal.

Moving Ahead

The initial objective of the force field development is to model the phase transition cycle of the crystal lattice as the BTO is heated thermally, capturing the transition temperatures between phases with a high degree of fidelity to empirical results. Experimental measurements are available to verify and validate the code. In addition, they will tune the force field to reproduce properly the formation of an oxygen vacancy, which is of pivotal importance. This allows for MD simulations of oxygen vacancy diffusion in the crystal. Further objectives include the modeling of dislocation energies of all three atomic species in the perovskite, along with the ability of an MD calculation to determine the dielectric constant of the crystal in response to an applied electric field.

Army researchers familiar with this work have complimented the quality of the math and science behind it. The electronic potentials developed here are of particular interest, and will assist in developing more cost-effective phased-array antenna components. ✯