ATOMIC-LEVEL SIMULATION OF FERROELECTRICITY IN PEROVSKITES

M. SEPLIARSKY\textsuperscript{a,b}, S. R. PHILLPOT\textsuperscript{a}, M. G. STACHIOTTI\textsuperscript{b}, D. WOLF\textsuperscript{a} and R. L. MIGONI\textsuperscript{b}

\textsuperscript{a}Materials Science Division, Argonne National Laboratory, Argonne IL, 60439, USA; \textsuperscript{b}Instituto de Fisica Rosario, CONICET-UNR, Rosario, Argentina.

It is shown that atomistic simulations can provide detailed atomic-level information on the ferroelectric properties of perovskite materials. These capabilities are illustrated by an analysis of the ferroelectric properties of a $\text{KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$ solid solution and $\text{KNbO}_3/\text{KTaO}_3$ superlattices.

Keywords  Ferroelectricity; Perovskites; Simulation; Heterostructure; Solid Solution; Atomic-Level Simulation

INTRODUCTION

The traditional approach to the theoretical study of ferroelectricity based on Ginzburg-Landau-Devonshire (GLD) theory\textsuperscript{[1]} continues to provide important insights into the ferroelectric properties of perovskites. The GLD theory is analytically tractable for many systems of interest and is computationally efficient when a simulation approach is required. However, it cannot provide microscopic information on the ferroelectric response. Moreover, values for some of the parameters in the GLD theory are difficult to obtain and it is not always clear how to choose the boundary conditions for the calculations correctly.

Complementing the phenomenological approach, over the last decade considerable progress has been made in \textit{ab-initio} electronic-structure calculations of ferroelectricity in perovskites.\textsuperscript{[2]} While able to provide detailed information on the ferroelectric, electronic and lattice
properties of single crystals, these methods also have limitations. In particular, due to the heavy computational load, only systems of up to approximately a hundred ions can be simulated. Moreover, such calculations can only be performed at zero temperature. These limitations severely restrict the applicability of electronic-structure methods for the study of the materials science of ferroelectric materials.

There is thus a significant need for a methodology which can provide microscopic information on ferroelectric behavior, and yet is computationally efficient enough to allow materials problems to be addressed. In particular, such an approach should be usable for the study of complex microstructures in which there is a significant amount of structural disorder.

One attempt at such a methodology is the "effective Hamiltonian method".[3,4] In this approach electronic-structure calculations are used to parameterize a model Hamiltonian in which the degrees of freedom of each unit cell correspond to lattice strain and the soft phonon associated with the ferroelectric distortion. Chemical inhomogeneity, as in a solid solution, for example, is treated in an improved Virtual Crystal Approximation, in which all unit cells are assumed to have the average composition of the solid solution, but with on-site fluctuations from the averages due to alloying effects taken into account.

In this paper, we describe a computationally efficient methodology for the simulation of the finite-temperature properties of structurally disordered perovskite ferroelectrics. We illustrate the capabilities of this approach with the examples of the finite-temperature properties of solid solutions and the ferroelectric properties of ferroelectric/paraelectric superlattices.

ATOMIC-LEVEL SIMULATION METHOD

Atomic-level simulation methods involving pair potentials with either a rigid-ion model or the shell model[5] have long been used with considerable success to describe the finite-temperature and defect properties of many ionic systems. In the shell model, atomic polarizability is accounted for by defining a core and a shell for each ion (representing the ion core with the closed shells of electrons, and the valence electrons, respectively), which interact with each other through a harmonic spring (characterizing the ionic polarizability), and interact with the cores and shells of other ions via Coulombic interactions. The
interactions among the valence electrons are characterized by a repulsive, exponentially decaying, pair-potential interaction between shells (the Born-Mayer term). Covalency effects, such as Born effective charges, are at least qualitatively accounted for in the shell model through the ionic polarizabilities, whose magnitudes may be considered to include the effects of hybridization.\cite{6} Covalency effects are included by setting the ion charges to values less than the formal valence, and by adding a van-der-Waals $1/r^6$ attractive term to the O-O shell-shell repulsion.\cite{7} This combination of the Born-Mayer term and the van der Waals interaction is known as the Buckingham potential.

Building on insights gained from electronic-structure calculations and from experience obtained with an earlier anisotropic shell-model approach,\cite{8,9} we have developed a Buckingham potential with an isotropic shell model which describes the phase behavior of KNO.\cite{10}

![Phase Diagram](image.png)

**FIGURE 1** The phase diagram of KNBO$_3$ (solid lines) and KTa$_{0.5}$Nb$_{0.5}$O$_3$ (dotted lines) determined from molecular-dynamics simulation are very similar to those determined experimentally.
The ability of our Buckingham potential with isotropic shell model to provide a good description of the ferroelectric phase behavior of KNO is illustrated in Figure 1 (solid lines), which shows that the single crystal displays the experimentally observed sequence of phases on heating: rhombohedral, orthorhombic, tetragonal and finally cubic with transition temperatures of 225K, 475K and 675K, which are very close to the experimental values of 210K, 488K and 701K respectively.\cite{10} Furthermore, the lattice parameters in the four phases agree with experimental values to better than 1%, and the calculated polarization in the tetragonal phase of $33 \mu \text{C/cm}^2$ is only about 20% larger than the experimental value of $26 \mu \text{C/cm}^2$.\cite{11} Using this approach we have also determined the dielectric properties of KNO through the cubic-to-tetragonal phase transition.\cite{10}

To allow us to simulate microstructures involving a ferroelectric and a paraelectric, we have also developed an interatomic potential to describe KTaO$_3$ (KTO), an incipient ferroelectric with the perovskite structure.

**PROXIMITY vs. STRAIN EFFECTS IN A KTa$_{0.5}$Nb$_{0.5}$O$_3$ SOLID SOLUTION**

In this Section and in the next, we very briefly illustrate the ability of our atomic-level approach to provide insights into ferroelectric behavior at atomic level. Here we elucidate the local polarization structure of a KTa$_{0.5}$Nb$_{0.5}$O$_3$ (KTN) solid solution; there is significant interest in such solid solutions to obtain ferroelectric responses unobtainable in single-component systems.

The calculated phase diagram of a KTN random solid solution, shown as the dotted lines in Figure 1 is qualitatively identical to that of KNO.\cite{10} In particular, in agreement with experiment,\cite{12} the transition temperatures of the cubic-to-tetragonal and tetragonal-to-orthorhombic phase transitions are reduced from that of pure KNO by approximately one-half to 380K and 280K respectively, while the transition temperature of the orthorhombic-to-rhombohedral phase transition of 190K is only slightly lower than that of KNO.

To understand the ferroelectric response of KTN at the microscopic level, it is useful to examine the distribution in the polarizations of the Nb-containing and Ta-containing unit cells. Figure
2 shows polarization distribution functions (PDFs) of the Nb and Ta unit cells in the rhombohedral phase of KTN at zero temperature. While the average polarization of the Nb cells is significantly reduced from the polarization of single-crystal KNO (22 µC/cm² vs. 32 µC/cm²), the Ta cells now also show a significant polarization (~18 µC/cm²).

Many of the features of these extremely broad PDFs can be understood in terms of the lattice strain and the effects arising from the proximity of Nb and Ta unit cells. For example, the zero-temperature lattice parameter of the rhombohedral phase of KTN is ~0.4% greater than the lattice parameter of cubic KTO and ~0.4% smaller than that of rhombohedral KNO. We find that under these tensile strains, single-crystal KTO is actually rhombohedral with \( p_x = p_y = p_z = 10 \) µC/cm²; this corresponds to the lower bound of the PDF of the Ta cells. Likewise, these compressive strains on single-crystal KNO reduce the polarization

\( p_x = p_y = p_z \)

KTN
Rhombohedral
\( T = 0 \) K

Ta - cells
Nb - cells

FIGURE 2 Polarization distribution function (PDF) for one component of the polarization in the Nb-containing unit cells (solid line) and the Ta-containing unit cells (dotted line).
to \( p_x = p_y = 25 \, \mu\text{C/cm}^2 \); presumably the slightly larger upper bound of the PDF of the Nb cells (\( \sim 28 \, \mu\text{C/cm}^2 \)) reflects the local strains, which may be somewhat different from the average strains. Similarly, the other two limits of the PDFs can be understood on the basis of the polarization of a single unit cell of one type in a matrix of the other. Finally, the PDFs of both the Ta and the Nb cells show shoulders at \( \sim 19\mu\text{C/cm}^2 \), similar to their polarizations (18.9 and 19.4 \( \mu\text{C/cm}^2 \)) in a completely ordered solid solution; these shoulders thus reflect the presence of regions of local chemical ordering in the simulation cell.

FERROELECTRICITY IN K\text{NbO}_3/K\text{TaO}_3 SUPERLATTICES

Current interest in superlattices containing ferroelectric materials is driven by the vision of building nanostructures with ferroelectric, dielectric and optical properties unachievable in either the bulk or in solid solutions. We have simulated the zero-temperature structure and properties of coherent (001) K\text{NO}/K\text{TO} superlattices of equal layer thicknesses and various modulation lengths, \( \Lambda \), (i.e., the total thickness of a K\text{NO}/K\text{TO} bilayer, measured in unit cells); each interface lies at a KO plane shared by neighboring layers and thus all interfaces are crystallographically identical to each other. To mimic the effects of the KTO substrate used in experiment, the lattice parameters in the plane normal to the modulation direction, the x-y plane, are fixed to those of KTO at \( T=0\text{K} \). To be consistent with the imposition of periodic border conditions on the simulation cell, we simulated a four-layer stack with the in-plane polarizations of the KNO layers being equal and opposite.

Figure 3 shows the variation in the polarization in the modulation direction, \( p_z \), (thick line) and in the x-y plane, \( p_x = p_y \), (thin line) averaged over unit-cell-thick slices through the \( \Lambda=36 \) superlattice. In analyzing these polarization profiles, we first address the strain effects produced by the KTO substrate, which result in a compressive strain of \( \sim 0.7\% \) on the KNO layers. To compensate for this in-plane compression, the KNO layers expand in the z-direction thereby breaking the strict rhombohedral symmetry of the polarization of KNO; nevertheless, these strains are not sufficient to force the KNO to become tetragonally polarized. Moreover, the magnitudes of the polarization in the interiors of the KNO layers (\( |p_x| = 21.7 \, \mu\text{C/cm}^2 \), \( p_z = 33.4 \, \mu\text{C/cm}^2 \))
are the same as those calculated independently for a perfect crystal under the same strain conditions; the opposite signs of $p_x$ in the two layers arise from the equal and opposite rhombohedral distortions of the KNO layers. Similarly, the absence of any in-plane polarization for the KTO layer is consistent with the absence of any strain arising from the KTO substrate. The finite value of $p_z$ in the interior of the KTO layer, however, is different from the expected value of $p_z=0$ for this unstrained layer which, as we discuss below, has important consequences for the switching behavior of the heterostructure.

![Figure 3: Polarization](image)

**FIGURE 3** Polarization in the x-y plane (thin line) and parallel to the modulation direction (thick line) for a superlattice with $\Lambda=36$ and in-plane lattice parameters corresponding to a KTO substrate.

The components of polarization in the x-y plane and in the modulation direction show remarkably different behaviors at the interfaces. The rather abrupt transitions in $p_x$ at the interfaces are indicative of only weak coupling between the in-plane components of the polarization along the modulation direction. In addition, the presence of a weak
coupling between $p_x$ and $p_z$ results in $p_x$ in the interface regions being slightly different in the cases of $p_z$ is pointing into and out of the ferroelectric layer (see Figure 3).

By contrast with $p_x$, $p_z$ varies continuously through the interfaces, a signature of strong coupling. The penetration length, determined from the approximately exponential change in $p_z$ in the interface region, is only about two lattice parameters in the KNO layer for all values of $\Lambda$ simulated, but appears to increase with increasing $\Lambda$ for the KTO layer. From an analysis of the $\Lambda$-dependence of the polarization and strain in the center of the KTO layer, we estimated that the polarization at the center of the KTO layer would reach zero only for $\Lambda_{\infty} \geq 160$ (~640 Å). Thus the strain in the interior of a KTO layer only vanishes for layers of more than 80 unit cells thick. This marked difference between the penetration lengths in the layers is consistent with the large difference in the dielectric constants, $\varepsilon$, of the two materials, which measure the ease with which they can be polarized: while $\varepsilon$(KNO) is ~50, $\varepsilon$(KTO) is ~3000. Despite this long-ranged

![Figure 4](image-url)

**FIGURE 4** Hysteresis loops for the KNO and KTO layers in superlattices with $\Lambda=36$ (solid lines) and the $\Lambda=6$ (dotted lines).
penetration of $p_z$ into the KTO layers, we find that the values of $p_z$ at the interfaces themselves are remarkably independent of $\Lambda$ and take a value very similar to that of a KTN solid solution under these strain conditions.

We have simulated the ferroelectric switching of superlattices of varying modulation lengths. Fig. 4 shows calculated hysteresis curves for unit-cell-thick slices at the center of the KNO and KTO layers for the representative cases of $\Lambda=6$ and $\Lambda=36$. For $\Lambda=6$, the loops for KNO and KTO are almost identical, indicating that the superlattice acts as a single artificial ferroelectric structure with the response of the KTO layers being controlled by the ferroelectric KNO layers. For $\Lambda=36$, the KNO layers show a square hysteresis loop characteristic of a good ferroelectric. The KTO layers also appear to show a ferroelectric hysteresis loop; however, this is simply an effect of coupling to the KNO layers. In particular, no hysteretic behavior appears in the KTO layers under a cyclic electric field when the KNO layers are not allowed to switch. Thus, the KTO layers actually behave as a paraelectric material.

OUTLOOK

The two examples given above are merely illustrative of what we can learn from atomic-level simulations; this approach has broad applicability for addressing issues related to the correlation of structure and ferroelectric properties. For example, important insights into ferroelectricity in thin films and at surfaces can be obtained. The atomistic approach is also ideal for investigating the structure and dynamics of $180^\circ$ and $90^\circ$ domain walls. Also amenable to atomic-level simulation is the interaction of microstructure with ferroelectricity, including the effects of grain boundaries on ferroelectric properties and the effects of confinement in nanostructures. This methodology is currently being extended to the BaTiO$_3$-SrTiO$_3$ systems with plans to also consider PbTiO$_3$ - PbZrO$_3$. The latter is a significantly more difficult task because charge transfer from the Pb ions is expected to be important. This atomistic approach is by no means a panacea however. In particular, since the atomistic approach does not explicitly model the electrons in the system, it can provide no information on the electronic structure or optical properties. Despite such limitations, we anticipate
that atomic-level simulation methods will provide important insights into
the ferroelectric, dielectric and piezoelectric properties of perovskite
ferroelectrics unobtainable by any other means.

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