Atomic-level simulation of ferroelectricity in perovskite solid solutions

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Building on the insights gained from electronic-structure calculations and from experience obtained with an earlier atomic-level method, we developed an atomic-level simulation approach based on the traditional Buckingham potential with shell model which correctly reproduces the ferroelectric phase behavior and dielectric and piezoelectric properties of KNbO$_3$. This approach now enables the simulation of solid solutions and defected systems; we illustrate this capability by elucidating the ferroelectric properties of a KTa$_{0.5}$Nb$_{0.5}$O$_3$ random solid solution. © 2000 American Institute of Physics. [S0003-6951(00)04526-5]

Over the last few years new applications have opened up for ferroelectric perovskites as the systems exploited have become both chemically more complex, e.g., solid solutions such as Ba$_x$Sr$_{1-x}$TiO$_3$, PbZr$_x$Ti$_{1-x}$O$_3$, KTa$_x$Nb$_{1-x}$O$_3$, and microstructurally more complex, e.g., thin films and superlattices. While the overall properties of such systems can be relatively easily investigated experimentally, it is difficult to obtain local structural or electrical information. Computer simulation can provide such microscopic insights, complementing the information which can be obtained experimentally.

It is only during the last decade that electronic-structure calculations have provided a fundamental theoretical understanding of the nature of bonding in ferroelectric perovskites (ABO$_3$).$^{1-4}$ In particular, these calculations have shown that: (i) both the B and O ions are highly polarizable, each playing a critical role in the ferroelectric response; (ii) the B–O interactions are partially covalent, with the B and O ions being only partially ionized and there being a significant hybridization of the $d$ orbitals of the B ion with the $p$ orbitals of O; and (iii) because the A ion is almost completely ionized (unless it is Pb), with very little hybridization with the B and O ions, it contributes to the ferroelectric response mainly through lattice strain.$^2$ Unfortunately, electronic-structure calculations, from which these insights have been derived, are essentially limited to zero temperature and to very small system sizes; this severely limits their ability to elucidate the ferroelectric properties of multicomponent and defected systems.

Atomic-level simulation methods involving pair potentials with either a rigid-ion model or the shell model$^6$ 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.$^5$ Covalency effects are also included by setting the ion charges to values less than the formal valence, and by adding a van-der-Waals$^6$ attractive term to the O–O shell–shell repulsion.$^7$ This combination of the Born–Mayer term and the van der Waals interaction is known as the Buckingham potential. Here we address the question as to whether such a simple Buckingham potential with the shell model can be developed so as to reproduce the phase diagram of perovskite systems.

That even a rigid-ion model is capable of describing complex phase behavior has been demonstrated, for example, in SiO$_2$$^8$,$^9$ and TiO$_2$.$^{10}$ Moreover, some of us have previously shown that atomic-level methods using pair potentials can correctly describe the phase behavior of perovskites.$^{11,12}$ Indeed, these simulations showed that an anisotropic shell model can correctly reproduce the phase behavior of KNbO$_3$ (KNO).$^{11}$ In this more sophisticated shell model, in addition to a usual harmonic shell model on the K and Nb, an anisotropy is imposed on the O polarizability to reflect the underlying anisotropy of the crystallographic environment of O ions. While this anisotropy does have the desired effect of stabilizing the ferroelectric phases it can only be used in crystallographically well-defined environments. Unfortunately, in lattice defects it is not always possible to unambiguously characterize the crystallographic environment of any given ion. For simulations of such disordered systems an isotropic model is required.
values of 0.8, 9.1, and 20.1, and the calculated polarization in
the tetragonal phase of \( 33 \mu C/cm^2 \) is only about 20% larger
than the experimental value of 26 \( \mu C/cm^2 \).

Building on the insights gained from electronic-structure
calculations and from experience obtained with this aniso-
tropic shell-model approach, we have succeeded in develop-
ing a Buckingham potential with an isotropic shell model
which also describes the phase behavior of KNO. This iso-
tropic shell model differs from the anisotropic shell model
only in that the anisotropic fourth-order core-shell interaction
on the O ions is replaced by an isotropic fourth-order core-
shell interaction on both the Nb and the O ions, which both
stabilizes the ferroelectric phases and prevents the very large
local electric fields associated with the breaking of the cubic
symmetry from making the core-shell displacements too
large. As we shall illustrate, this advance allows us to elici-
tate the interplay among ferroelectric behavior, chemistry
and structural disorder present, e.g., in solid solutions, thin
films and superlattices.

As a first test of the ability of this model to describe
electronic polarization effects, we have calculated\(^1\) the
dynamical Born effective charges \( \tilde{Z}(k) \) for comparison with
first principles calculations. We obtain \( \tilde{Z}(K) = 1.6, \tilde{Z}(\text{Nb}) = 10.64, \tilde{Z}(\text{O}_1) = -1.42, \) and \( \tilde{Z}(\text{O}_2) = -8.78, \) where \( \text{O}_1 \) and \( \text{O}_2 \) denote motion of the oxygen in the direction of the niobium.
These are in quite good agreement with the first-principles
values of 0.8, 9.1, -1.7, and -6.6, respectively,\(^1,4\) indicating
that the model captures the effects of electronic polarization
quite well.

The ability of our Buckingham potential with isotropic
shell model to provide a good description of the ferroelectric
properties of KNO is illustrated in Fig. 1, which shows that
the single crystal displays the experimentally observed se-
quence of phases on heating: rhombohedral, orthorhombic,
tetragonal, and finally cubic, with transition temperatures
very close to the experimental values. 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 \( 33 \mu C/cm^2 \) is only about 20% larger
than the experimental value of 26 \( \mu C/cm^2 \).\(^1,4\)

While it is critical to correctly reproduce the ferroelectric
phase behavior, it is equally important to correctly describe
the dielectric and piezoelectric properties, particularly close
to the phase transitions. Therefore, we have determined the
temperature dependence of the dielectric and piezoelectric
responses of KNO by calculating the change in the polarization
and the elastic strain of the perfect crystal under an
applied electric field. Figure 2 shows the dielectric constant,
\( \varepsilon_{33} \), through the cubic-to-tetragonal phase transition (the c
axis of the tetragonal phase lies along the three direction).
The value of \( \varepsilon_{33} \) thus obtained is \( \sim 700–800 \) in the cubic
phase, peaks at \( \sim 2900 \) at the transition temperature, decreas-
ing to \( \sim 100 \) in the tetragonal phase; this is consistent with
the experimental values of \( \sim 500–700 \) in the cubic phase and
\( \sim 3000 \) at the phase transition.\(^1,5\) Figure 2 also shows the
converse piezoelectric constant, \( d_{33} \), whose value in the te-
tragonal phase of \( \sim 10^{-10} \) C/N is reasonably consistent with
the experimentally determined room-temperature values (i.e.,
in the orthorhombic phase) of 2.4–2.9 \( 10^{-11} \) C/N;\(^1,6\) as ex-
cpected, it also diverges at the transition temperature.

Having demonstrated that our Buckingham potential, al-
beit with an anharmonic shell model, can indeed capture the
phase behavior of the KNO single crystal, we now illustrate
how it can also describe the ferroelectric behavior of a
KTa\(_{0.5}\)Nb\(_{0.5}\)O\(_3\) (KTN) random solid solution. In order to
study this system, we have also developed and validated an
interatomic potential for KTaO\(_3\) (KTO), which is cubic at all
temperatures.\(^1,7\) Our potentials for KNO and KTO have iden-
tical K–O and O–O interactions and K and O polarizabil-
ities; the only differences between them are in the Nb–O and
Ta–O interactions, and in the different polarizabilities of the
Nb and Ta ions. Thus, the two potentials can be used to-
gether for the simulation of systems containing any relative
proportion of KNO and KTO, e.g., KTa\(_x\)Nb\(_{1-x}\)O\(_3\) over the
full composition range.

As also shown in Fig. 1, the calculated phase diagram of

\[\text{FIG. 1. The phase diagram of KNbO}_3 \text{ (solid lines), determined from molecular-dynamics simulation using a Buckingham potential with shell model, is very similar to that seen experimentally, with the same sequence of phase transitions at temperatures of 675, 475, and 225 K. Which are very close to the experimental values of 701, 488, and 210 K, respectively. The phase diagram of KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3 \text{ (dashed lines) is qualitatively identical to that of KNbO}_3.}\]

\[\text{FIG. 2. The calculated dielectric constant, } \varepsilon_{33}, \text{ and the converse piezoelectric coefficient, } d_{33}, \text{ of KNbO}_3 \text{ show strong divergences at the cubic-to-
tetragonal phase transition.}\]
FIG. 3. The width of the PDF of the components of the polarization in the Nb cells (solid line) and the Ta cells (dotted line) of the KTN random solid solution reflect the varying local environments.

a KTN random solid solution is qualitatively identical to that of KNO. In particular, in agreement with experiment, 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 380 K and 280 K, respectively, while the transition temperature of the orthorhombic-to-rhombohedral phase transition of 190 K is only slightly lower than that of KNO.

To elucidate the ferroelectric response of KTN, it is useful to examine the distribution in the polarizations of the Ta-containing and Nb-containing unit cells. Figure 3 shows polarization distribution functions (PDFs) of the Nb cells and Ta 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 coupling of the ferroelectric response with the local lattice strain. 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 \( p_x = p_y = p_z = 10 \mu C/cm^2 \); this corresponds to the lower bound of the PDF of the Ta cells. Likewise, these compressive strains on single-crystal KNO reduce the polarization to \( p_x = p_y = p_z = 25 \mu C/cm^2 \); presumably the slightly larger upper bound of the PDF of the Nb cells (~28 μC/cm²) reflects the local strains, which may be somewhat different from the overall strains. Similarly, the other two limits of the PDFs can be rationalized 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 cells and the Nb cells show shoulders at ~19 μC/cm², similar to their polarizations (18.9 and 19.4 μC/cm²) in a completely ordered solid solution; these shoulders reflect the presence of regions of local chemical ordering in the simulation cell.

Our atomic-level simulations can also provide insights into the nature of the phase transitions in these solid solutions. It is well known that the cubic-to-tetragonal phase transition in KNO has a more order-disorder character than displacive character, as is reproduced by our Buckingham potential and by the anisotropic shell model. We find that the PDF for the Nb cells in the high-temperature cubic phase of KTN exhibits two peaks, clear evidence that the Nb cells still display largely order-disorder behavior. By contrast, the PDF for the Ta cells shows a single broad peak centered around zero polarization, evidence that the Ta cells undergo largely displacive behavior.

As illustrated by the above example, the ability to describe perovskite materials by an isotropic Buckingham potential with a shell model allows the ferroelectric properties of multicomponent and/or defected systems to be elucidated at the atomic scale. Of particular current interest are the structure and dynamics of ferroelectric domains, ferroelectric heterostructures, and the interaction of ferroelectricity with structural defects such as point defects, dislocations, and grain boundaries. In addition, atomic-level simulations will also be able to provide parameterizations to phase-field models based on Ginzburg–Landau theory which have long been used to investigate ferroelectricity at the phenomenological level.

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