Advances in First-Principles Studies of Transducer Materials

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Advances in First-Principles Studies of Transducer Materials

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We have used first-principles linear response calculations and molecular dynamics to study the relaxor ferroelectric Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-xPbTiO$_3$ (PMN-xPT). First-principles calculations for ordered PMN show a low-symmetry monoclinic ground state. A new set of phase transitions to lower symmetry rhombohedral and monoclinic structures is predicted for PT at high pressures, showing predicted piezoelectric response as high as is seen in the giant coupling relaxor ferroelectrics. We have developed a transferable shell-model potential for PMN-xPT by fitting to first-principles data. The potential qualitatively reproduces the compositional phase diagram for PMN-xPT. A new exchange-correlation potential, which gives excellent predictions for ferroelectric materials, is discussed.

Keywords PMN; PbTiO$_3$; first-principles; relaxors; ferroelectrics; molecular dynamics; shell model; exchange; linear response; lattice dynamics

I. Introduction

Relaxor ferroelectrics, such as Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-PbTiO$_3$ (PZN-PT) and Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-PbTiO$_3$ (PMN-PT), exhibit superior electromechanical properties [1] and are being developed for the next generation of transducer devices. In addition to their technological usefulness, understanding the fundamental origin of their behavior is a fascinating area of recent research [1–4]. Fu and Cohen showed that the relaxor ferroelectrics obtain their properties from the ease of rotating the polarization direction in an applied electric field [3]. The most useful materials also have a large piezoelectric strain associated with the change in polarization direction. The relaxor endmember PMN has a diffuse phase transition attributed to the existence of polar nanoregions (PNRs), but the exact nature of the PNR is still controversial (see Ref. [5] and references therein). Examining these materials using first-principles methods is not feasible due to the disorder in the B-site. We are developing a multi-scale model for PbMg$_{1/3}$Nb$_{2/3}$O$_3$-xPbTiO$_3$ (PMN-xPT) by fitting a shell model potential to first principles calculations of PT and ordered PMN structures.
The rest of the paper is organized as follows. Section II discusses our linear response studies of ordered PMN and PbTiO$_3$. In Section III we present our shell model potential for PMN-xPT and report on MD simulations of PT, PMN, and PMN-xPT. Finally we discuss a new, more accurate GGA exchange-correlation functional for ferroelectric materials in Section IV.

II. Linear Response and Total Energies

A. PMN Results

We have performed a large number of total energy and linear response computations of ordered 15-atom PMN supercells with 1:2 (Mg:Nb) chemical ordering along the $(111)$ (labeled PMN $111_{\text{MNN}}$) and $(001)$ (PMN $001_{\text{MNN}}$) planes [6]. The ordering along $(111)$ is lower in energy than the ordering along $(001)$. We have identified FE and AFE structures for PMN $111_{\text{MNN}}$ with polarization along $[111]$, but these structures have unstable modes. We find a series of cascading instabilities leading to a low symmetry ground state. The ground state has C$_2$ symmetry with polarization along $[110]$, which would be orthorhombic except for the chemical ordering which reduces the symmetry to monoclinic. We find this structure to be lower in energy than the 30-atom cell found as the ground state by Prosandeev et al. [7]. The energy versus polarization direction is very soft, making it easy to rotate the polarization, leading to relaxor behavior. In addition, the low symmetry ground state allows for 24 domain variants, leading to an apparent pseudocubic symmetry from the fine submicroscopic domains.

B. PbTiO$_3$

We have performed a series of linear response computations for PbTiO$_3$ versus pressure and obtained unexpected results [8]. It was known that PT transformed to cubic at high pressures, but using linear response calculations at the zone center ($\mathbf{q} = 0$) we found a series of transitions from tetragonal to monoclinic, to rhombohedral and then to cubic. More recently we find that the cubic structure may be superseded by a zone boundary instability. Most interestingly, the predicted piezoelectric constants peak in the transition region, giving electromechanical response as large as is observed in the large coupling single crystal piezoelectrics (see Fig. 1). Essentially there is a morphotropic phase transition predicted in a pure material. This result implies that the primary effect of PMN in the PMN-PT solid solution is to tune the transitions to zero pressures, rather than the relaxor behavior of PMN playing a key role.

III. Shell Model Potential and Molecular Dynamics simulations

As noted in the Introduction, an accurate and transferable potential is needed to study relaxor ferroelectrics as functions of temperature, pressure, composition, and state of order. Our approach is to develop a transferable shell-model potential for the relaxor ferroelectric PMN-PT based on fits to ab initio data of the endmembers, PMN and PT.

A. Developing Shell Model Potential for PMN-PT

The shell model [9, 10] phenomenologically describes the deformation of the electronic structure of an ion due to the interactions with other atoms. In the model, each atom is described by two charged particles: a massive core and massless shell. Electronic polarization effects are captured by the dipolar moment produced by the relative core-shell displacement.
Figure 1. Computed pressure dependence on piezoelectricity in PbTiO₃. (a) Spontaneous polarization $P_s$. (b) Piezoelectric stress coefficients $e_{15}$ and $e_{33}$. (c) Piezoelectric strain coefficients $d_{15}$ and $d_{33}$.

We use a core linked to the shell by an anharmonic spring, $V(w) = \frac{1}{2}c_2w^2 + \frac{1}{24}c_4w^4$, where $w$ is the relative core-shell displacement. We have found it necessary to add a penalty term $D(w - w_0)^2$ if $w \geq w_0$, where $w_0 = 0.2$ Å and $D$ varied from 2000 to 40000 eV, to the core-shell coupling to prevent the shell from drifting off the core and ensure the potential stability. There are Coulombic interactions between all cores and shells except the core and shell of the same atom. The short-range interactions are described using a Rydberg potential, $V(r) = (A + Br) \exp(-r/\rho)$, and occur between A-O, B-O, and O-O shells. There are a total of 33 parameters for the PMN-PT system.

We have fitted our potential simultaneously for both PT and PMN. We found that developing a PMN-PT potential sequentially by first developing a PT potential and then incorporating PMN, keeping the PT related parameters fixed, resulted in poor potentials for PMN. Fits were performed using our own fitting code that uses a Levenberg-Marquardt (LM) method in conjunction with singular value decomposition, which is necessary due to the highly correlated nature of the parameters. The LM-method was alternated with a simulated annealing method based on the Nelder-Mead simplex algorithm [11] in order to find a more global minimum.

The input DFT-LDA data for PbTiO₃ consisted of the energy, atomic forces, and stress of 55 different configurations with cubic, tetragonal, and rhombohedral symmetry at various volumes and distortions. Phonon information (frequencies and eigenvectors at special $q$ points, effective charges, and high frequency dielectric constants) for the cubic and tetragonal PT structures at experimental volumes were also included in the input data. For PMN
Table 1

Structural and internal parameters for the fully relaxed tetragonal \(P4mm\) \(\text{PbTiO}_3\).
Here \(a\) and \(c\) are lattice constants (Å), and \(V_0\) the volume (Å³).

<table>
<thead>
<tr>
<th></th>
<th>LDA input</th>
<th>Our potential</th>
<th>Exp. (300 K)</th>
<th>Exp. (73 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>3.865</td>
<td>3.843</td>
<td>3.902</td>
<td>3.891</td>
</tr>
<tr>
<td>(c)</td>
<td>4.042</td>
<td>4.155</td>
<td>4.156</td>
<td>4.167</td>
</tr>
<tr>
<td>(c/a)</td>
<td>1.046</td>
<td>1.081</td>
<td>1.065</td>
<td>1.071</td>
</tr>
<tr>
<td>(V_0)</td>
<td>60.37</td>
<td>61.36</td>
<td>63.28</td>
<td>63.08</td>
</tr>
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<td></td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>(z) (Ti)</td>
<td>0.5235</td>
<td>0.5351</td>
<td>0.538</td>
<td></td>
</tr>
<tr>
<td>(z) (O₁,O₂)</td>
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<td>0.6191</td>
<td>0.612</td>
<td></td>
</tr>
<tr>
<td>(z) (O₃)</td>
<td>0.0823</td>
<td>0.1016</td>
<td>0.112</td>
<td></td>
</tr>
</tbody>
</table>

33 structures with 2:1 (Nb:Mg) ordering along the (111), (001), and (110) planes along with phonon information from the AFE and FE 111\(_{\text{NNM}}\) structures discussed in Section I were included as input data. There are a total of 3644 input data points.

Our potential reproduces the relative energy of phases and structures in both PT and PMN. Table 1 shows the ground state structure for PT at zero pressure obtained from our potential versus the LDA input and experimental values. Our potential overestimates the equilibrium volume and \(c/a\) ratio compared to the LDA input. This overestimation actually brings our potential results closer to experimental values because the LDA underestimates these values. This well known difficulty the LDA and GGA functionals have reproducing the experimental volume will be addressed in Section IV. The \(c/a\) ratio obtained from our potential is slightly larger than the experimental value. Overall the potential very closely reproduces the experimental structure.

As shown in Table 2, the model also reproduces the main features of the phonon dispersion curves for both the PT and PMN structures. The soft modes in the cubic PT structure are reproduced. The PT ground state is tetragonal and there are no zone-boundary

Table 2

Select phonon frequencies (cm\(^{-1}\)) for the PT and PMN structures obtained with the potential. The LDA results are given in parentheses. The \(i\) indicates imaginary frequencies (i.e. unstable modes).

<table>
<thead>
<tr>
<th>TO 244(i) (183(i))</th>
<th>TO 437 (452)</th>
<th>LO 70 (50)</th>
<th>LO(_3) 543 (615)</th>
<th>R(_{25}) 30(i) (83(i))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1) TO 155 (146)</td>
<td>E TO 53 (90)</td>
<td>(A_1) LO 198 (178)</td>
<td>(E) TO 123 (112)</td>
<td>(E) (Z) 23 (51)</td>
</tr>
<tr>
<td>(E) TO 4.5i (45i)</td>
<td>(E) LO 134 (107)</td>
<td>(E) LO 270 (261)</td>
<td>(A_1) TO 76 (66)</td>
<td>(A_1) LO 76 (67)</td>
</tr>
<tr>
<td>(E_u) TO 130i (110i)</td>
<td>(E_u) LO 118 (94)</td>
<td>(E_u) LO 305 (349)</td>
<td>(A_{2u}) TO 123i (90i)</td>
<td>(A_{2u}) LO 127(122) (113)</td>
</tr>
</tbody>
</table>
instabilities. All of the soft modes in the AFE and FE PMN 111NNN structure are also reproduced, but some of the highest frequencies modes are underestimated by 100–150 cm$^{-1}$ for the current potential. In the following sections we present preliminary MD results that show our shell model potential reproduces much of the structure and dynamics of PMN-xPT.

B. Molecular Dynamics Results for PbTiO$_3$

We apply the potential to simulate the finite temperature behavior of PbTiO$_3$. Molecular dynamics simulations were carried out using DL-POLY [12] in an (N, $\sigma$, T) ensemble. A supercell size of 6 × 6 × 6 was used with periodic boundary conditions. A mass of 7 a.u. was assigned to the Pb and Ti shells and 2 a.u. to the oxygen shell. The time step was set to 0.2 fs and after equilibration (10000 MD steps) results were collected for 10 ps at each temperature. Figures 2(a) and (b) show the lattice parameters and polarization respectively as a function of temperature for PbTiO$_3$ at zero pressure from our simulations. We find the transition from ferroelectric tetragonal to paraelectric cubic to occur at a temperature of 900 K, which overestimates the experimental $T_c$ value of 763 K. This result can be compared to earlier shell model potentials for PbTiO$_3$ that showed a $T_c$ of 450 K at zero pressure [10]. Based on the LDA input data one would expect an underestimation of $T_c$ since LDA underestimates the equilibrium volume. The improved accuracy of our potential is again due to a fortuitous overestimation of the input LDA structure discussed earlier.

A similar plot to Fig. 2 is shown in Fig. 3 except the transition with pressure is examined at $T = 300$ K. The potential captures the qualitative behavior of a transition from tetragonal to cubic structure with pressure at around 10 GPa, which underestimates the experimental transition pressure of 12.1 GPa [13]. The above results demonstrate that our potential accurately captures PT behavior, despite the incorporation of information on PMN.

C. Molecular Dynamics Results for PMN

PMN is a relaxor with perovskite structure and disorder on the B sites. There have been several models proposed for the distribution of the B site over Nb$^{5+}$ and Mg$^{2+}$. For our MD
Figure 3. Average (a) lattice parameters and (b) polarization for PbTiO$_3$ as a function of pressure at 300 K obtained from MD simulations. The experimental transition pressure is 12.1 GPa [13].

Simulations we have used the random site model [14], where PMN can be represented by A(B'B'')O$_3$, where B'' is located in the nearest neighbor cells of B' and B' is equal to Nb and B'' is a random mixture of Mg and Nb but maintaining 1:1 ratio. The random site model has a macroscopic cubic symmetry, but local correlated distortions or chemical order may produce polar nanoregions. MD parameters and cell size are the same as the PT simulations discussed earlier.

In Fig. 4 we show the pair distribution function (PDF) for small $r$ obtained from our MD simulations as a function of temperature at zero pressure. This result can be compared to the recent experimental PDF’s obtained by Jeong et al. [15] (see Fig. 1 in Ref. [15] for experimental results). Overall we observe a good match between the simulated and experimental PDF. Similar to the experimental PDF, we observe a decline in the shoulder at 2.5 Å with an increase in temperature. The shoulder is associated with splitting of the Pb-O peaks indicating that at lower temperatures there is a wider dispersion of these distances. Jeong et al. observed a split of the peak at 2.0 Å at temperatures below 300 K. This peak is associated with Mg/Nb-O interactions and indicates differences in Mg-O and

Figure 4. Pair distribution function (PDF) at small $r$ for PMN as a function of temperature obtained from MD simulations. The pressure was set to 0 GPa.
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Figure 5. Phonon density of states as a function of pressure at \( T = 300 \) K from our MD simulations of PMN.

Nb-O interactions at lower temperatures. We do not observe this splitting at 2.0 Å, but an examination of the PDF associated with the individual Mg-O and Nb-O distances indicates that the two differ by 0.1 Å. The agreement between our simulated PDF and the experimental PDF indicates that our potential captures the general dynamics in PMN. The changes in PDF due to local order and different arrangements will require simulations of larger supercells.

We have examined the phonon density of states (PDOS) at different pressures at a temperature of 300 K and the results are shown in Fig. 5. These results can be compared with Raman spectra for PMN obtained by Kriesel et al. [16]. We see a qualitative agreement in the distribution of frequencies, but the high frequency peak from our MD simulations is approximately 180 cm\(^{-1}\) lower than seen experimentally. This is not surprising since we observed this type of error in our fits for the high frequency mode.

D. Molecular Dynamics results for PMN-PT

The relaxor ferroelectric PMN-xPT was shown to have ultra-high electromechanical coupling in a range of compositions that consisted of a morphotropic boundary between rhombohedral and tetragonal phases [17]. There have been numerous experimental studies to clarify the temperature-composition phase diagram, especially near the morphotropic boundary [17, 18]. We have simulated the temperature-composition phase diagram at zero pressure for PMN-PT. The random site model is used with Ti atoms substituted randomly in the B\(^{\prime}\) and B\(^{\prime\prime}\) sites but maintaining a Nb:Mg ratio of 2:1. The system size and MD parameters are the same as used in the above PT and PMN simulations.

The lattice parameters and polarization as a function of Ti composition at 300 K is shown in Figs. 6(a) and (b) respectively. We observe a series of transitions from cubic at the PMN limit to rhombohedral phase at low concentrations of PT and then an intermediate phase before finally around 50% PMN-PT becomes clearly tetragonal. The intermediate
IV. New Exchange-Correlation Potential

We have developed a new non-empirical density functional generalized gradient approximation (GGA) that gives significant improvements for lattice constants and crystal structures over existing GGA’s [20]. This is particularly important for ferroelectrics, since they are very sensitive to volume. LDA gives too small a volume, which decreases ferroelectric well depths and GGA generally gives too large a volume, resulting in too large distortions. PbTiO$_3$ illustrates the severity of the problem. The PBE GGA [21] gives c/a of 1.24 rather than 1.07, and a huge volume [22]. Due to these problems, most calculations to date for ferroelectrics have used the LDA at the experimental lattice. In contrast, the new GGA gives excellent lattice parameters for PbTiO$_3$, (see Table 3) as well as all materials so far tested, so that the theoretical equilibrium lattice can be used.

The new GGA has an enhancement factor fit to a smooth cutoff for a diffuse exchange-correlation hole. We have studied the differences from the exchange correlation hole for PbTiO$_3$. The largest changes are around the atom cores, where densities and gradients are high. There are also chemically significant differences in the bonding region, though in magnitude much smaller than in the core regions. This new functional is no more computationally intensive than the PBE GGA, and should allow more accurate predictions for ferroelectrics, especially for materials with unknown lattice constants.
Table 3

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PBE</th>
<th>New GGA</th>
<th>Exp. (300 K)</th>
<th>Exp. (73 K)</th>
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<tbody>
<tr>
<td>LDA PBE New GGA</td>
<td>Exp.</td>
<td>Exp.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
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<td>3.891</td>
</tr>
<tr>
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</tr>
<tr>
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<td>63.47</td>
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</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>z (Ti)</td>
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<td>0.5532</td>
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<td></td>
</tr>
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<td>z (O1, O2)</td>
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<td>0.612</td>
<td></td>
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<tr>
<td>z (O3)</td>
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<td>0.1884</td>
<td>0.1083</td>
<td>0.112</td>
<td></td>
</tr>
</tbody>
</table>

V. Conclusions

First-principles linear response calculations of ordered PMN show that PMN is likely composed of microscopic monoclinic phases with 24 possible polarization directions. New transitions from tetragonal to monoclinic to rhombohedral were discovered for PT at high pressures. PT shows large piezoelectric constants near the tetragonal to monoclinic transition. We have developed a shell model potential for PMN-PT based on fitting to first-principles calculations of ordered PMN and PT. MD calculations of PT, PMN, and PMN-xPT show that the potential is able to qualitatively reproduce the behavior of these materials across a wide range of pressures, temperatures, and compositions. A new GGA exchange functional was discussed that is very accurate for ferroelectric materials.

Acknowledgments

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dielectric tensors for the relaxor PMN (PbMg1/3Nb2/3O3). Computational Materials Science in press (2005).


12. DL$_{POLY}$ is a parallel molecular dynamics simulation package developed at Daresbury Laboratory by W. Smith and T. R. Forrester under the auspices of the Engineering and Physical Sciences Research Council (EPSRC) for the EPSRC’s Collaborative Computational Project for the Computer Simulation of Condensed Phases (CCP5) and the Advanced Research Computing Group (ARCG) at Daresbury Laboratory. The package is the property of Daresbury Laboratory. http://www.cse.clrc.ac.uk/msi/software/DL$_{POLY}$/


