

Enhancing piezoelectricity through polarization-strain coupling in ferroelectric superlattices

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(Received 16 March 2009; published 7 May 2009)

Short-period ferroelectric/ferroelectric PbTiO_3 (PTO)/ BaTiO_3 (BTO) superlattices are studied using density functional theory. Contrary to the trends in paraelectric/ferroelectric superlattices the polarization remains nearly constant for PTO concentrations below 50%. In addition, a significant decrease in the c/a ratio below the PTO values was observed. Using a first-principles superlattice model we predict an enhancement in the d_{33} piezoelectric coefficient peaking at $\sim 75\%$ PTO concentration due to the different polarization-strain coupling in PTO and BTO layers. Further analysis reveals that these trends are bulk properties which are a consequence of the reduced P brought about by the polarization saturation in the BTO layers.

DOI: 10.1103/PhysRevB.79.180101

PACS number(s): 77.65.-j, 77.84.-s, 31.15.A-, 68.65.Cd

Perovskite superlattices present a new paradigm for engineering ferroelectrics and piezoelectrics for modern device applications. Epitaxial strains (resulting from lattice mismatches) and induced changes in polarization (resulting from electrostatic considerations) can have significant effects on the macroscopic properties of these artificial structures.^{1,2} Superlattices combining a paraelectric (PE), such as SrTiO_3 (STO), with a ferroelectric (FE), such as PbTiO_3 (PTO) or BaTiO_3 (BTO), have been well studied both by experiment and theory.³⁻⁷ Their main features can be modeled by considering them as layers of strained bulklike material with appropriate electrostatic boundary conditions;³ in some systems, interface effects have also been shown to be important in the limit of ultrathin layers.⁶ In this Rapid Communication, we extend this first-principles modeling approach to superlattices combining two ferroelectrics, which we expect to exhibit distinctive features arising from the interplay of the different bulk spontaneous polarizations and dielectric and piezoelectric coefficients of the two constituents.

We perform first-principles calculations, using density functional theory (DFT) (Refs. 8 and 9) for PTO/BTO superlattices with $m=1-5$ and $n=1-5$ layers (keeping $m+n \leq 6$) of PTO and BTO, respectively. All calculations used projector augmented wave (PAW) potentials^{10,11} with the Vienna *ab initio* simulation package (VASP v4.6.26),¹² with the local density approximation for the exchange correlation functional. A 700 eV (22 Ha) cutoff and a $6 \times 6 \times 1$ k -point mesh were used (where $l=4$ for period 2 and 3 superlattices, 2 for periods 4 and 5, and 1 for period 6). For BTO in the tetragonal $P4mm$ five-atom unit-cell structure, the computed lattice constants are $a=3.947$ Å and $c=3.996$ Å. The tetragonal PTO lattice constants were computed as $a=3.867$ Å and $c=4.033$ Å (experiment: $a=3.904$ Å and $c=4.152$ Å).¹³ This agreement is typical of LDA calculations for ferroelectric perovskites. In all superlattice calculations, the in-plane lattice constant was constrained to that of the theoretical value for an STO substrate (3.863 Å), while the c lattice vectors were optimized within the $P4mm$ space group with 1×1 in-plane periodicity. Additional calculations for a doubled $\sqrt{2} \times \sqrt{2}$ in-plane unit cell for $m=n=1$ show no instability to octahedral tilts of the type discussed in Ref. 7. All ionic coordinates were fully relaxed until the Hellman-Feynman forces on the ions were less than 5 meV/Å. Polar-

izations were computed using the Berry phase method.¹⁴ At this in-plane lattice constant of 3.863 Å, in contrast to previous experimental studies of PTO/BTO superlattices under tensile strain,¹⁵ polarization along \hat{z} is favored both in PTO and in BTO.¹⁶ For epitaxially strained PTO, the out-of-plane lattice constant was 4.039 Å and the polarization was 0.79 C/m². The epitaxial constraints placed on the BTO layers result in a BTO c/a ratio (1.063) much larger than that of the more polar PTO layers. The BTO polarization was 0.39 C/m², substantially enhanced over the computed bulk value of 0.26 C/m².

Figure 1 shows the dependence of computed polarization and c/a lattice constant on the concentration of PTO and the superlattice period of short-period PTO/BTO superlattices for the full set of structures with period ≤ 6 . Consistent with the fact that PTO has a greater polarization than BTO, higher concentrations of PTO give rise to larger P of the superlattice. Similarly, decreasing the content of the larger c/a ratio strained BTO reduces the average c/a ratio of the superlat-

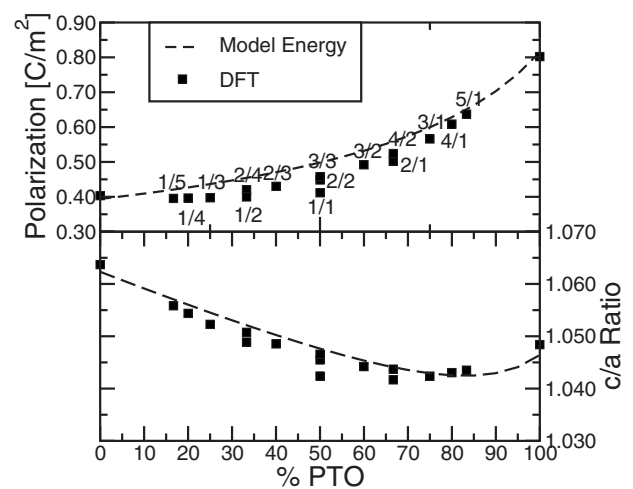


FIG. 1. Polarization along the z axis (top) and c/a ratio (bottom) as a function of PTO concentration for BTO/PTO superlattices with varying superlattice periods. Solid squares represent DFT calculations, and the dashed lines are the values obtained using the superlattice model [see Eqs. (1) and (3)]. Numerical model parameters can be found in Table I.

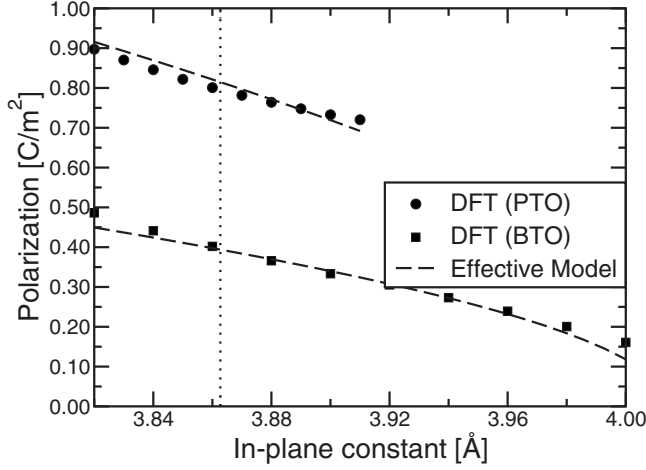


FIG. 2. Polarization along the z axis as a function of in-plane strain for bulk BTO and PTO. Solid circles and squares represent DFT calculations for PTO and BTO, respectively. Dashed lines are the corresponding values obtained using Eq. (1) with the parameters of Table I.

tice. However, closer examination shows some unexpected features. First, the polarization of the superlattices remains almost constant for PTO concentrations below 50% while the c/a ratio is below, rather than above, that of bulk PTO for a wide range of PTO concentrations ($\geq 40\%$). In fact, the derivative of c/a with respect to PTO concentration is positive near 100% rather than negative as would be expected from a simple linear interpolation.

To interpret our DFT data and to distinguish between interface effects and bulk properties, we constructed a parametrized energy expression for the superlattice following Refs. 16 and 17. The expression is a Taylor expansion around the cubic perovskite structure in terms of the six independent components, η_i , of the strain tensor (i is a Voigt index; $i=1-6$) and the three Cartesian soft mode amplitude components u_α ($\alpha=x, y, z$) parametrized from DFT calculations. Restricted to $P4mm$ symmetry, the effective stress-strain elastic enthalpy for a pure constituent ferroelectric under epitaxial strain (i.e., $\eta_1 = \eta_2 = \bar{\eta}$) with external out-of-plane stress, σ_3 , can be written as

$$G(\bar{\eta}, \eta_3, u_z, \sigma_3) = \frac{1}{2}B_{11}(2\bar{\eta}^2 + \eta_3^2) + B_{12}(\bar{\eta}^2 + 2\eta_3\bar{\eta}) + \kappa u_z^2 + \alpha u_z^4 + \frac{1}{2}B_{1xx}\eta_3 u_z^2 + B_{1yy}\bar{\eta} u_z^2 - \sigma_3 \eta_3, \quad (1)$$

where B_{11} and B_{12} are related to the elastic constants of the crystal, κ and α are two independent symmetry-allowed fourth-order coefficients describing the cubic anisotropy, and B_{1xx} and B_{1yy} are the phonon-strain coupling coefficients. In the systems we consider, $\sigma_3=0$.

Figure 2 shows the polarization versus in-plane lattice constant for the pure end-point compounds BTO and PTO. The model parameters (Table I) were fit to DFT data for PTO with in-plane lattice constants within $\pm 1\%$ of the STO in-plane lattice constant of 3.863 Å. For BTO, the fitting range was extended to include the computed bulk tetragonal lattice

constant of 3.947 Å. The excellent agreement between the model and our DFT calculations is an indication of the quality of the model.

For a given $m_{\text{PTO}}/n_{\text{BTO}}$ superlattice we assume uniform soft mode amplitude u_z within each constituent layer. Further, we impose the constraint that the corresponding polarizations

$$P_z^i = \frac{e}{\Omega^i} Z^{*,i} u_z^i, \quad (2)$$

of the two constituent layers, $i=\text{BTO, PTO}$, are equal so that polarization is uniform throughout the superlattice. (Here, e is the absolute value of the electron charge, Ω^i is the layer unit-cell volume, and $Z^{*,i}$ is the Born effective charge of the soft mode.) Strictly speaking, it is the displacement field, $D=P+\epsilon E$, which remains uniform throughout the superlattice. However, this uniform polarization approximation has previously been shown to be valid for short-period superlattices^{18,19} and is supported in the present case by unit-cell-layer polarization profiles computed using bulk Born effective charges (not shown).

The effective elastic enthalpy for the two-component superlattice with m_{PTO} layers and n_{BTO} layers is then

$$G^{\text{Total}} = \frac{1}{(m+n)} [mG^{\text{PTO}} + nG^{\text{BTO}}]. \quad (3)$$

The superlattice values of P and η_3 are determined by minimizing Eq. (3) with respect to η_3^i and u_z^i , imposing the uniform polarization approximation through the relation

$$u_z^{\text{BTO}} = \Gamma u_z^{\text{PTO}}, \quad \text{with } \Gamma = \frac{\Omega^{\text{BTO}} Z^{*,\text{PTO}}}{\Omega^{\text{PTO}} Z^{*,\text{BTO}}}. \quad (4)$$

This model can also be used to compute the piezoelectric coefficient, $d_{33} = \frac{dP}{d\sigma_3}$,

$$\frac{dP}{d\sigma_3} = - \frac{meZ^{*,\text{PTO}}B_{1xx}^{\text{PTO}}}{2\Omega^{\text{PTO}}u_z^{\text{PTO}} \left[2B_{11}^{\text{PTO}}\alpha^{\text{PTO}} - \frac{1}{4}(B_{1xx}^{\text{PTO}})^2 \right]} - \frac{meZ^{*,\text{BTO}}B_{1xx}^{\text{BTO}}}{2\Omega^{\text{BTO}}u_z^{\text{BTO}} \left[2B_{11}^{\text{BTO}}\alpha^{\text{BTO}} - \frac{1}{4}(B_{1xx}^{\text{BTO}})^2 \right]}. \quad (5)$$

Figure 3 shows the dependence of d_{33} on composition as predicted from Eq. (5). The model is in good agreement with the DFT d_{33} values for bulk BTO (32 pC/N), bulk PTO (55 pC/N) and the 3 PTO/1 BTO superlattice (58 pC/N). Surprisingly, we find a 5% enhancement of the d_{33} coefficient at 75% PTO, where the c/a is a minimum.

The good agreement between the DFT results and the superlattice energy functional, shown in Fig. 1, suggests that the observed trends in P and c/a are a consequence of bulk electrostatics and strain effects and that interfaces do not play an essential role. The success of the model allows us to elucidate the origin of the nearly constant P for low PTO concentration through an examination of the evolution of the FE potential energy well (Fig. 4, left panel). A comparison of the FE potential energy wells of the epitaxially strained par-

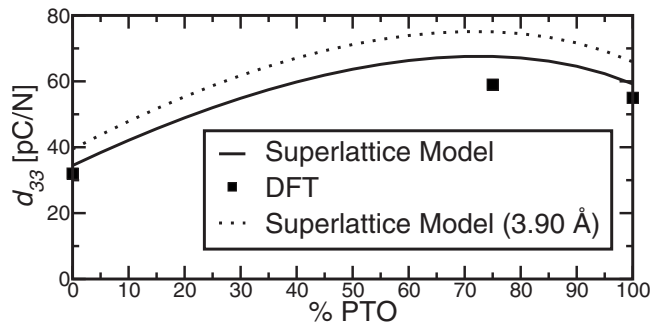


FIG. 3. Dependence of d_{33} on PTO concentration for PTO/BTO superlattices. The dashed line represents the results of the superlattice model at the bulk STO in-plane lattice constant of 3.863 Å, and the dotted line represents that for an in-plane lattice constant of 3.90 Å. The solid squares are computed from DFT.

ent compounds shows that BTO has a much stiffer FE well with a minimum at a P of less than half of PTO. For polarizations much greater than 0.39 C/m² the effective enthalpy of BTO sharply increases while PTO has a much gentler dependence. Here the P in the BTO layers is saturated, requiring larger electric fields to further polarize them. Similar polarization saturation effects have been observed in compressively strained PZT and PTO.²⁰ In a superlattice, this translates into the need for a higher percentage of the more polar PTO in order to increase the macroscopic polarization of the superlattice. This fact is borne out in the evolution of the FE wells with PTO concentration (Fig. 4, left panel). Even up to PTO concentrations of 80% the FE well still resembles that of BTO, severely limiting the total P in the superlattice and accounting for the suppression in expected P enhancement with increasing PTO concentration.

This suppressed layer-by-layer polarization can be linked to the abnormal decrease of c/a below that of the PTO parent compound (Fig. 4) as well as the enhancement in the d_{33} coefficient. The model indicates that if P were to increase linearly with increasing PTO concentration then the c lattice parameter would have a corresponding linear decrease to the PTO values. However, as previously stated, the P throughout the superlattices is severely suppressed due to the presence of the BTO layers. Since P is coupled to the c lattice parameter this results in a drastic reduction in the average c lattice parameter (see Fig. 4). This BTO effect is only overcome at extremely high concentrations of PTO, where the electric field generated by the PTO layers is capable of counteracting the BTO potential energy well constraints. Furthermore, BTO has a much steeper dependence of c on P than PTO; i.e., the c lattice parameter increases more with increasing P in the BTO layers than in the PTO layers. As such, it is the balance between the stronger polarization-strain coupling in

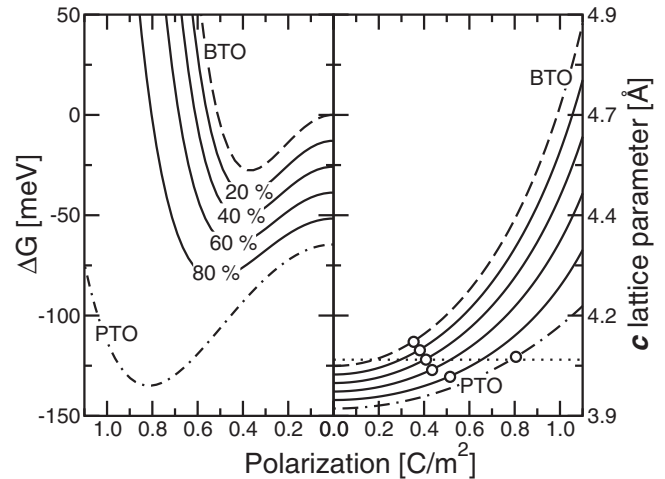


FIG. 4. Effective enthalpy (left) and c lattice parameter (right) as a function of polarization for various compositions of PTO/BTO superlattices obtained from the superlattice energy functional. Dashed lines represent pure BTO, dashed-dotted lines are for pure PTO, and solid lines indicate the ferroelectric wells for the superlattices at 20% PTO intervals. Open circles mark the c lattice parameter for each composition at the predicted P . The dotted line in the right figure indicates c for epitaxially strained tetragonal PTO. Energies are relative to epitaxially strained bulk BTO.

the BTO layers and the amount of PTO present to pole these layers which gives rise to the peak in d_{33} at $\sim 75\%$ PTO concentration. These results suggest that it may be possible to further enhance d_{33} by reducing the saturation in the BTO layers either by decreasing the in-plane compressive strain (see Fig. 4; dotted line: $a=3.90$ Å) or through other factors such as intermixing at the interface between PTO and BTO layers.⁶

A final point of interest is the consideration of the effect of interfaces. In Fig. 1, there are three different concentrations for which results for multiple superlattice periods are shown: $\frac{1}{3}$ (1 PTO/2 BTO and 2 PTO/4 BTO), $\frac{1}{2}$ (1 PTO/1 BTO, 2 PTO/2 BTO, and 3 PTO/3 BTO), $\frac{2}{3}$ (2 PTO/1 BTO and 4 PTO/2 BTO). In each case, it is clear that as the superlattice period is increased there is an increase in the polarization. Furthermore, the longer-period polarizations approach that of the model. This suggests that the sharp interfaces function to suppress polarization in these materials. Similar behavior was seen previously in BTO/STO superlattices.²¹ Work on PTO/STO superlattices suggests that this may be reduced through cation intermixing at the interface.⁶

In conclusion, we have used density functional theory to explore the dependence of P and c/a on PTO concentration for short-period PTO/BTO superlattices. Our extensive DFT

TABLE I. Energy expansion coefficients [Eq. (1)] and soft mode Born effective charges for PTO and BTO in atomic units, fit to the DFT results in Fig. 2, as described in the text.

	B_{11}	B_{12}	B_{Lxx}	B_{Lyy}	κ	α	Z^*	a_o
BaTiO ₃	5.13	3.05	-1.00	-0.100	-0.007	0.14	9.94	7.48
PbTiO ₃	4.69	1.15	-0.705	0.207	-0.0132	0.0364	9.40	7.385

calculations reveal two intriguing phenomena: nearly constant P for PTO concentrations less than 50% and a dramatic decrease in c/a to values below that of the smaller PTO. Using a superlattice model we demonstrate that these trends are a consequence of P saturation in the BTO layers which, by limiting the magnitude of P , results in abnormally large decreases in the c lattice parameter. The competition between the polarization saturation effects of BTO and the high polarization in the PTO layers results in a corresponding peak in the d_{33} coefficients in the PTO/BTO superlattices, suggesting a way of enhancing the piezoelectric properties of the superlattices; other material combinations may yet be found

which show an even greater enhancement based on this mechanism. In addition, this model can be easily extended to multicomponent systems, to different phases, and to model strain effects on these phases, allowing for the easy exploration of materials properties.

We would like to thank David Vanderbilt and Scott Beckman for valuable discussions. This work was supported by ONR (Grant No. N0014-00-1-0261). Part of this work was carried out at the Aspen Center for Physics. Work at ORNL was supported by DOE, Division of Materials Sciences and Engineering.

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