First-principles study of symmetry lowering and polarization in BaTiO$_3$/SrTiO$_3$ superlattices with in-plane expansion

Karen Johnston,* Xiangyang Huang,† J. B. Neaton,‡ and Karin M. Rabe

Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA

The crystal structure and local spontaneous polarization of $(\text{BaTiO}_3)_m/(\text{SrTiO}_3)_n$ superlattices are calculated using first-principles density-functional theory. The in-plane lattice constant is constrained to be 1% larger than the SrTiO$_3$ (ST) substrate to take into account the in-plane expansion observed in recent experiments. The symmetry is lowered to monoclinic space group *Cm* allowing for polarization along the [110] and [001] directions. The polarization component in the [110] direction is found to develop only in the SrTiO$_3$ layers and falls to zero in the BaTiO$_3$ (BT) layers, whereas the polarization in the [001] direction is approximately uniform throughout the superlattice. These findings are consistent with recent experimental data and first-principles results for epitaxially strained BT and ST.

PACS number(s): 68.65.Cd, 77.80.−e, 81.05.Zx

I. INTRODUCTION

Perovskite materials, such as BaTiO$_3$ (BT) and SrTiO$_3$ (ST), are of considerable interest due to their polarization-related properties. Short-period superlattices of these materials have switchable polarization, ferroelectric Curie temperature, and dielectric and piezoelectric coefficients distinct from those of their individual constituents, and the freedom to choose from a variety of constituent materials, layer thicknesses, and sequences can be exploited to optimize selected desirable properties.[1–9]

The $(\text{BaTiO}_3)_m$-$(\text{SrTiO}_3)_n$ (BT/ST m/n) superlattice has been extensively investigated by experimentalists primarily because of the possible enhancement of the switchable polarization arising from strain effects. Due to the lattice mismatch with ST, there is a compressive in-plane strain on BT that increases the tetragonal strain and, through polarization-strain coupling, the [001] polarization. Several groups[1,6,10] studied the structure and dielectric properties of symmetric and asymmetric BT/ST superlattices with periods ranging from 4 to 500 unit cells. Measurements of these superlattice structures were consistent with tetragonal symmetry. Depending on the BT/ST ratio, the polarization can be enhanced over that of unstrained BT and the Curie temperature elevated.

Neaton and Rabe[8] performed first-principles calculations to study the structure and polarization of BT/ST superlattices lattice matched to an ST substrate. With this epitaxial constraint the systems studied (m/n superlattices with $m+n=5$) were found to be stable with *P4mm* symmetry, with polarization along [001]. The total polarization was decomposed into contributions from individual 5-atom, Ti-centered cells. It was found that the unstrained ST layers were polarized along [001] and the strain-enhanced polarization of BT reduced such that the polarization was nearly constant in the [001] direction. This was attributed to the minimization of electrostatic energy costs associated with the buildup of polarization charge at the interfaces, suggesting a simple model that provided a good fit to the first-principles results.

Recently, Jiang *et al.*[5] and Ríos *et al.*[11] investigated the structure of BT/ST superlattices, grown on ST substrates, with periods ranging from 4 to 100. Through a combination of second-harmonic generation and x-ray diffraction measurements, they found that below a critical periodicity of 30/30, the system has symmetry lower than tetragonal, consistent with a nonzero polarization in the ST layers along the [110] direction. The in-plane lattice constants were reported to be ≈0.8% larger than that of bulk ST, implying that the films are at least partially relaxed.

In this paper we describe first-principles calculations that explore the idea that it is precisely this increase in in-plane lattice constant that is responsible for the observed change in structure. For several BT/ST superlattices with periods up to 10, we expand the in-plane lattice constant to 1.01 times the theoretical lattice constant of bulk ST and relax the tetragonal symmetry constraint to allow polarization to develop along the [110] direction as well as along [001]. We show that the ST layers exhibit both the [001] polarization which, as in the coherent tetragonal superlattices, minimizes the electrostatic energy due to charge accumulation at the BT-ST interfaces, as well as a nonzero component of the polarization along [110], lowering the symmetry as observed. The details of the methods used are given in Sec. II, and in Sec. III we present our results and discussion.

II. METHOD

First-principles calculations were performed with the Vienna *ab initio* simulations package (VASP),[12] which implements density-functional theory within the local-density approximation. Projector augmented-wave potentials were used[13,14] with the Ba $(5s,5p,6s)$, Sr $(4s,4p,5s)$, Ti $(3s,3p,3d,4s)$, and O $(2s,2p)$ treated as valence states. A plane-wave energy cutoff of 600 eV and a $6 \times 6 \times 2$ Monkhorst-Pack k-point sampling of the Brillouin zone were used.

The superlattices have structure m/n, where m and n represent the thickness in unit cells of BT and ST, respectively. The structures considered in this paper are 3/3, 4/4, 4/6, 5/5, and 6/4, with unit cells $1 \times 1 \times (n+m)$. The structures

TABLE I. Variation of c/a (layout consistent with Fig. 1). The average c/a ratios for the BT and ST layers are shown, as well as the two components of the total polarization, P, of each superlattice.

	Present results				
	3/3	4/4	6/4	5/5	4/6
		c/a for 5-atom cells			
	0.9999	1.0000	1.0003	0.9999	1.0000
	0.984	0.984	0.986	0.984	0.983
	0.987	0.987	0.989	0.987	0.985
	1.010	0.988	0.990	0.987	0.985
	1.028	1.010	1.014	0.988	0.986
	1.026	1.029	1.031	1.011	0.985
		1.027	1.029	1.029	1.006
		1.027	1.028	1.027	1.026
			1.028	1.027	1.024
			1.028	1.027	1.025
		Average c/a			
BT	1.027	1.027	1.029	1.027	1.025
ST	0.986	0.986	0.988	0.987	0.985
		P (μC cm^{-2})			
[001]	17.1	17.9	22.8	18.5	10.8
[110]	5.0	6.0	2.9	7.1	9.0

are optimized in the monoclinic space group *Cm*, which allows nonzero polarization of the form $P_1(\hat{x}+\hat{y})+P_3\hat{z}$. Because the deviation from the in-plane square lattice observed in the x-ray experiment is very small,[11] we constrain the angles between the lattice vectors to 90°. The c lattice parameter and the ions are allowed to fully relax within the symmetry of the *Cm* space group. The in-plane lattice parameter is fixed to $a=1.01a_{ST}=3.902$ Å, with the calculated values of the lattice constants for the constituent materials being $a_{ST}=3.863$ Å for bulk cubic ST and $a_{BT}=3.943$ Å and $c/a=1.012$ for bulk tetragonal BT. This results in a compressive, in-plane strain of -1.04% on the tetragonal BT layer. The ionic relaxation was considered to be complete when the Hellman-Feynman forces on the ions were less than 5 meV Å^{-1}.

As discussed in Sec. I, this value of in-plane lattice constant was chosen to take account of the in-plane expansion of the superlattice as observed in recent experiments. This expansion implies that the BT/ST superlattices, although epitaxial, are not coherent with the substrate and dislocations are present. It is assumed that these dislocations are confined to the region near the substrate interface and therefore we are modeling the defect-free superlattice far from the substrate interface.

To investigate the spatial variation of the polarization and strain within the superlattice, we compute the local polarization in each 5-atom, Ti-centered cell of the superlattices, defined as

$$P_{\alpha,\text{local}} = \frac{1}{\Omega}\left\{ Z^*_{\alpha,\text{Ti}}u_{\alpha,\text{Ti}} + Z^*_{\alpha,\text{O}_1}u_{\alpha,\text{O}_1} + Z^*_{\alpha,\text{O}_2}u_{\alpha,\text{O}_2} \right.$$
$$\left. + \frac{1}{2}(Z^*_{\alpha,\text{O}_{3_-}}u_{\alpha,\text{O}_{3_-}} + Z^*_{\alpha,\text{O}_{3_+}}u_{\alpha,\text{O}_{3_+}}) \right\},$$

where Ω is the volume of the 5-atom cell, α is a Cartesian direction, $Z^*_{\alpha,i}$ is the dynamical charge of atom i along α (Ref. 19), and $u_{\alpha,i}$ is the displacement along α of atom i with respect to the centrosymmetric cell defined by the Ba/Sr atoms. O_{3_+} and O_{3_-} represent the O_3 atoms at the top and bottom of the 5-atom cell, respectively. The local strain c/a is obtained by using the A atoms to define the corners of the local unit cell, i.e., $c/a=[z(A_+)-z(A_-)]/a$.

III. RESULTS AND DISCUSSION

The local c/a ratio for each cell is given in Table I. The BT layers, being under compressive in-plane strain, have c/a larger than the bulk tetragonal value, whereas the ST layers are under tensile in-plane strain and have $c/a<1$. The two interface cells are inequivalent, with the polarization being directed towards the Ba in one and towards the Sr in the other. Both interfaces have c/a values intermediate between the average BT and ST values.

Figures 1 and 2 show the variation of P_{local} in each superlattice. The [001] component remains approximately uniform throughout the superlattice, dipping slightly in the ST layers. As the relative thickness of the BT layer increases, the magnitude of the [001] polarization increases. In the ST layers, a
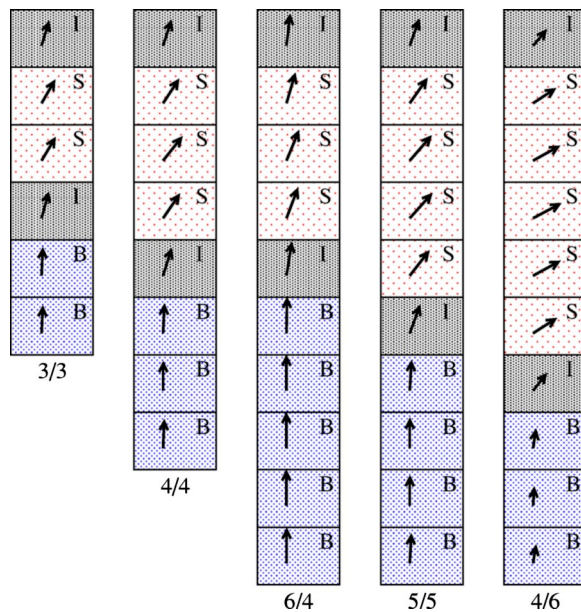
FIG. 1. (Color online) Magnitude of P_{local} in the [110] and [001] directions. SrTiO$_3$, BaTiO$_3$, and interface cells are labeled as S, B, and I, respectively.

nonzero polarization develops along [110]. It grows smoothly from zero at the interface over about two lattice constants, reaching its maximum value in the center of the layer. As the relative thickness of the ST layer increases, the magnitude of the polarization along [110] increases. The [001] and [110] components are not independent. This can be seen by comparing the 4/4 and 6/4 superlattices, in which the ST layer has the same thickness. Relative to the 4/4 superlattice, in the 6/4 superlattice the [001] component is larger and the [110] component is smaller. An analogous be-

FIG. 2. (Color online) [001] and [110] components and magnitude of P_{local}.

havior is seen in the 4/4 and 4/6 superlattices. In the 4/6 superlattice, the [001] component is smaller and the [110] component is larger. In all superlattices studied except the shortest period (3/3), the magnitude of the total polarization in the center of the ST layer is quite similar.

The local variation of polarization and strain can be understood by applying the model discussed in Ref. 8 to the superlattice with expanded in-plane lattice constant. The first step is to consider the effect of epitaxial strain on the polarization and c/a. In the expanded BT/ST superlattice the BT layers are subject to compressive in-plane strain whereas the ST layers are subject to tensile in-plane strain. Diéguez *et al.*[15] studied the epitaxial strain phase diagram of bulk BT in zero macroscopic field using a first-principles approach. They found that for compressive strains greater than 0.64% BT is in the c phase (tetragonal structure $P4mm$), in which the polarization points along the [001] direction. By extrapolating their structural parameters to the expanded lattice constant $a=3.902$ Å we calculate the local polarization and local c/a of BT to be 28.4 μC cm^{-2} and 1.036, respectively. A similar study of the effect of strain on ST was carried out by Antons *et al.*[16] They found that for tensile strains greater than 0.54% ST has orthorhombic structure $Amm2$ with polarization in the [110] direction. The predicted polarization and c/a of bulk ST with an in-plane tensile strain of 1% are ≈ 20 μC cm^{-2} and 0.985, respectively.[16]

The next step is to take into account the electrostatic energy of combining these two strained layers into a superlattice. In particular, a discontinuity in the [001] component of the polarization is energetically costly. The energy is reduced by concomitant polarization of the highly polarizable ST layer and reduction in the polarization of the BT layer to achieve continuity. The final value of the polarization is strongly dependent on the relative thicknesses of the two layers. The thicker the BT layer relative to the ST layer, the higher the polarization. These trends are evident in the computed polarizations of each layer shown in Fig. 2.

Through polarization-strain coupling, these changes in the polarization lead to changes in the c/a ratio. This can at least roughly account for the differences of the local BT and ST c/a from the strained bulk values, and for the trends between c/a and polarization in Table I.

In the ST layer, increasing polarization along [001] reduces the component along [110], minimizing changes in the total magnitude. This coupling has previously been noted in a first-principles study[16] of phonon modes in strained ST, wherein the $Amm2$ phase, nonzero polarization along [110] is associated with a hardening of the ferroelectric mode along [001]. This observation allows us to account for the observed variation in the maximum [110] component in Fig. 2.

In comparing these results with experiment, it is important to select only systems with in-plane expansion, such as the superlattices in Refs. 5 and 11. The shortest period system in these experimental studies is the 10/10 superlattice. In order to compare with this system we extrapolate the results from the three symmetrical superlattices, namely the 3/3, 4/4, and 5/5. The c/a values for each superlattice are remarkably similar so we can expect the 10/10 superlattice to have similar c/a values, as indeed it does. We can esti-
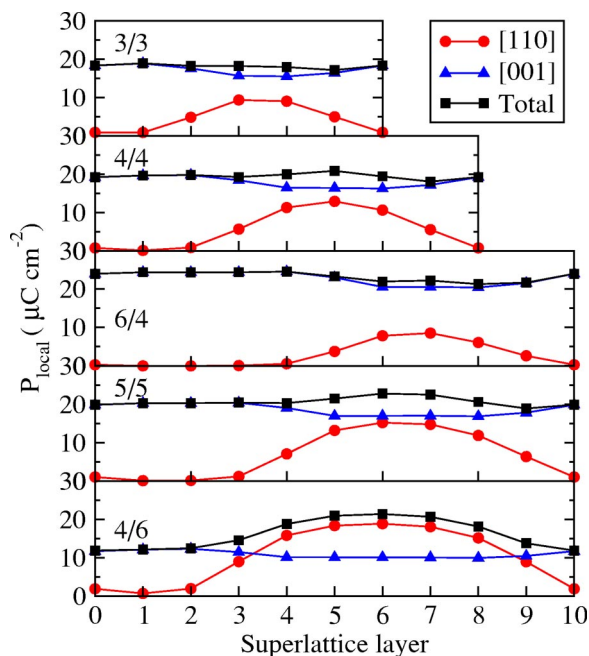
mate the period of the 10/10 superlattice by scaling the periods of the 3/3, 4/4, and 5/5 superlattices. This gives ≈ 78.5 Å which compares well with measured values of 78.1 (Ref. 11) and 79 Å (Ref. 6). Consistent with the simple electrostatic model, the [001] component increases only very slightly with increasing period, and saturates to an estimated value of ≈ 22–23 $\mu C \, cm^{-2}$, about 90% of the computed free bulk polarization of BT.[8] The [110] component at the center of the ST layers increases from less than 10 $\mu C \, cm^{-2}$ for the 3/3 to ≈ 13 $\mu C \, cm^{-2}$ for the 4/4, to ≈ 15 $\mu C \, cm^{-2}$ for the 5/5. This should be close to the saturation value; smaller than the strained bulk ST polarization of ≈ 20 $\mu C \, cm^{-2}$, as expected, due to the coupling to the nonzero [001] component.

To extrapolate to still longer periods, it is necessary to recognize that the behavior will change once the thickness of the layers exceeds the polarization coherence length and/or the elastic critical thickness of the individual layers. The uniformity of the [001] polarization is expected only for short-period superlattices, as for thicker layers the energy cost of nonzero $\nabla \cdot P$ competes with the energy cost for polarizing the paraelectric ST. As a result, the [001] component decays into the interior of the ST layers and for sufficiently thick layers will become zero. This behavior is demonstrated in

$KNbO_3/KTaO_3$ superlattice shell-model studies by Sepliarsky *et al.*[2,3] In addition, as the individual layers exceed their elastic critical thickness, they would be expected to contract or expand to their separate in-plane lattice constants through the formation of misfit dislocations. The precise value depends on the method of synthesis; it has been shown that coherent films can be grown well over the critical thickness under appropriate conditions.[17,18]

In summary, it seems that the overall strain state is crucial to the properties of the superlattice. If the superlattice expands in plane, as in the work of Rios *et al.*, the ferroelectric properties can be dramatically different than in a superlattice where the strain is preserved. For BT/ST, a simple model of electrostatics and bulk strain effects works very well, with the very gentle interface between BT and ST being relatively unimportant.

---

*Electronic address: karenjoh@physics.rutgers.edu

†Present address: Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455.

‡Present address: The Molecular Foundry, Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720.

[1] H. Tabata, H. Tanaka, and T. Kawai, Appl. Phys. Lett. **65**, 1970 (1994).

[2] M. Sepliarsky, S. R. Phillpot, D. Wolf, M. G. Stachiotti, and R. L. Migoni, Phys. Rev. B **64**, 060101(R) (2001).

[3] M. Sepliarsky, S. R. Phillpot, D. Wolf, M. G. Stachiotti, and R. L. Migoni, J. Appl. Phys. **90**, 4509 (2001).

[4] H. M. Christen, E. D. Specht, S. S. Silliman, and K. S. Harshavardhan, Phys. Rev. B **68**, 020101(R) (2003).

[5] A. Jiang, J. Scott, H. Lu, and Z. Chen, J. Appl. Phys. **93**, 1180 (2003).

[6] T. Shimuta, O. Nakagawara, T. Makino, S. Arai, H. Tabata, and T. Kawai, J. Appl. Phys. **91**, 2290 (2002).

[7] J. Kim, L. Kim, D. Jung, Y. S. Kim, and Jaichan Lee, Integr. Ferroelectr. **47**, 235 (2002).

[8] J. B. Neaton and K. M. Rabe, Appl. Phys. Lett. **82**, 1586 (2003).

[9] H. Tabata and T. Kawai, Appl. Phys. Lett. **70**, 321 (1997).

[10] H. Tabata, H. Tanaka, T. Kawai, and M. Okuyama, Jpn. J. Appl. Phys., Part 1 **34**, 544 (1995).

[11] S. Ríos, A. Ruediger, A. Q. Jiang, J. F. Scott, H. Lu, and Z. Chen, J. Phys.: Condens. Matter **15**, L305 (2003).

[12] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[13] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[14] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[15] O. Diéguez, S. Tinte, A. Antons, C. Bungaro, J. B. Neaton, K. M. Rabe, and D. Vanderbilt, Phys. Rev. B **69**, 212101 (2004).

[16] A. Antons, J. B. Neaton, K. M. Rabe, and D. Vanderbilt, Phys. Rev. B **71**, 024102 (2005).

[17] J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy, and D. G. Schlom, Nature (London) **430**, 758 (2004).

[18] K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L.-Q. Chen, D. G. Schlom, and C. B. Eom, Science **306**, 1005 (2004).

[19] The dynamical charges are approximated by those of bulk cubic BT in the BT layers, bulk cubic ST in the ST layers, and average values in the two TiO_2 interface layers. The values of the dynamical charges were taken from Refs. 20 and 21. The variation of P_{local} depends on the choice of Z^*. Even though the effect is small it should be noted that P_{local} is only a guide to the variation of the polarization and should not be treated as an exact quantity.

[20] P. Ghosez, X. Gonze, and J.-P. Michenaud, Ferroelectrics **206–207**, 205 (1998).

[21] W. Zhong, R. D. King-Smith, and D. Vanderbilt, Phys. Rev. Lett. **72**, 3618 (1994).