Polarization Enhancement in Short Period Superlattices via Interfacial Intermixing

Valentino R. Cooper, Karen Johnston, and Karin M. Rabe

1Department of Physics and Astronomy, Rutgers University, 136 Frelinghuysen Rd, Piscataway, New Jersey 08854-8019, USA
2Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015, Finland

(Dated: February 1, 2008)

The effect of intermixing at the interface of short period PbTiO$_3$/SrTiO$_3$ superlattices is studied using first-principles density functional theory. The results indicate that interfacial intermixing significantly enhances the polarization within the superlattice. This enhancement is directly related to the off-centering of Pb and Sr cations and can be explained through a discussion of interacting dipoles. This picture should be general for a wide range of multicomponent superlattices and may have important consequences for the design of ferroelectric devices.

Ferroelectric superlattices are a promising paradigm for creating novel materials for device applications. In ideal superlattices with perfectly flat, compositionally abrupt interfaces, first-principles calculations and experimental studies have shown how factors such as strain due to lattice mismatches, charge compensation, and bonding at the interface can be controlled to enhance the ferroelectric properties of the superlattice. Work by Dawber and coworkers show that the behavior of very short period superlattices may deviate from that extrapolated from longer period superlattices. While, these effects may be the result of a number of different factors, it seems likely that changes at the interface dominate at these length scales. Recent high resolution COBRA studies on SrTiO$_3$ (STO) supported PbTiO$_3$ (PTO) thin films further suggest that cation intermixing may be present at the interface of such superlattices.

Knowledge of how interfacial cation intermixing influences the aggregate properties of a superlattice can be useful in tuning its properties. As the superlattice period decreases, these effects become more important and, depending on their strength, may dominate. In this paper, we present a first principles study on the effect of interfacial cation intermixing on the polarization of short period PTO/STO superlattices. Our results demonstrate that intermixing significantly enhances the polarization and that this enhancement is directly linked to larger Pb displacements in the intermixed layers.

We use density functional theory (DFT) to examine the effects of interlayer cation mixing on the polarization within PTO/STO superlattices. We compare superlattices with sharp interfaces with three different compositionally equivalent intermixed systems of $m$=1-3 PTO layers and $n$=1-3 STO layers (figure 1). Checkered, striped and 25%/75% intermixed layers were studied. Intermixed layers were placed at each of the mixed PTO/STO interfaces; giving a total composition of 50% PTO / 50% STO. The two intermixed layers account for one PTO and one STO layer.

Polarization was computed from the center of their respective oxygen cages (i.e. 6 nearest oxygen neighbors for Ti and 12 for Pb and Sr). The bulk PTO lattice constants were computed as $a=3.863$ Å (experiment: 3.905 Å) and $c=4.152$ Å (experiment: $a=3.904$ Å and $c=4.152$ Å). This agreement is typical of LDA calculations for ferroelectric perovskites. In all calculations the in-plane lattice constant $a$ of the superlattice was constrained to that of the STO substrate (3.863 Å) while the c lattice vectors were optimized within the $P4mm$ space group. All ionic coordinates were fully relaxed until the Hellman-Feynman forces on the ions were less than 5 meV/Å. For bulk PTO constrained to the STO in-plane lattice constant of 3.863 Å the c axis lattice parameter was 4.039 Å and the polarization was 0.79 C/m$^2$. Polarizations were computed using the Berry phase method.

Figure 2 shows a comparison between the Berry phase polarization and the polarization calculated using bulk Born effective charges ($Z^*$) and cation off-centering for all the intermixed and unmixed superlattices studied. Cation displacements were computed from the center of their respective oxygen cages (i.e. 6 nearest oxygen neighbors for Ti and 12 for Pb and Sr). The bulk $Z^*$s were: $Z^*_{Pb,8r} = 2.7$ and $Z^*_{Ti} = 4.6$. The remarkable agreement between both methods suggests that the bulk $Z^*$s remain relatively unchanged in all superlattices. This analysis allows us to relate changes in the total polarization to the off-center displacements of the individual cations.

In figure 3 we see that the striped interface shows a marked increase in the total polarization as a function of percent PTO for nearly all short-period superlattices studied. While the striped interface is certainly the most dramatic example of

FIG. 1: Representative 2 PTO / 2 STO structures with intermixed interfaces. Grey squares are PTO unit cells and white squares are STO. Intermixed layers have a total composition of 50% PTO / 50% STO. The two intermixed layers account for 1 PTO and 1 STO layer.
polarization enhancement in an intermixed system, both the 25/75 and checkered interfaces display significant increases in their polarization relative to the sharp interface, suggesting that this trend is the consequence of interfacial cation intermixing. This polarization enhancement can be understood by considering the magnitude of the average cation displacements in both intermixed and sharp superlattices. Figure 2 depicts the average cation off-center displacements for Pb, Sr and Ti ions as a function of PTO concentration for superlattices with striped (right) and unmixed interfaces (left). These results indicate little change in the average Sr and Ti off-center displacements and clearly demonstrate that the changes in the polarization within the intermixed superlattices are due to changes in the off-centering of Pb cations. Once again, this trend is common to all intermixed configurations studied.

To further elucidate the changes induced by interfacial cation intermixing we compared the changes in the average layer-by-layer cation off-centering for Pb, Sr and Ti cations in striped interfaces to those in pure layers (Figure 5). Here we see that the magnitude of the average layer-by-layer Pb off-center displacements in unmixed Pb layers is essentially equal to that of Sr cations in unmixed Sr layers. In addition, the average layer-by-layer Sr cation off-center displacements decrease when comparing an unmixed layer to an intermixed layer. Conversely, Pb cations off-center more in the intermixed layers.

Now we turn to the discussion of how the differences between unmixed and intermixed superlattices arise. First, we recall the present understanding of polarization in unmixed superlattices. PTO is a well-studied ferroelectric material with a double well potential which results in a spontaneous polarization in zero electric field. STO, on the other hand, is an incipient ferroelectric with a very shallow potential energy well centered around the paraelectric state. Previous first principles superlattice studies have shown that in ideal ferroelectric-paraelectric superlattices with compositionally sharp interfaces the ferroelectric layers, e.g. PTO, with polarization along the stacking direction, induce a polarization within the paraelectric layers. Furthermore, the magnitude of the layer-by-layer polarization throughout the superlattice was nearly constant8,14,26; a direct consequence of the minimization of the electrostatic energy associated with the buildup of polar-
Our results for unmixed short-period PTO/STO superlattices are fully consistent with these previous results. In particular, the STO and PTO layers have nearly the same polarization, which is exemplified by considering the 75/25 mixed layer (see Figure 6 inset). Here we see that there are two distinct types of Pb cations in the 75 PTO/25 PTO layer. Empty squares (□) are for Sr cations, filled circles (●) represent Pb cations with four nearest neighbors, and hashed circles are Pb cations with 6 in-plane neighbors (2 nearest neighbors and 4 second nearest neighbors). This plot was generated using data from all three intermixed superlattices as well as unmixed superlattices.

A more precise understanding of this argument can be obtained by examining the Pb off-center displacements as a function of the number of nearest in-plane Pb neighbors. To isolate the intermixing effect, we report these values relative to the average Pb displacements in compositionally identical unmixed superlattices with the same period. As seen in Figure 6, the observed enhancement depends on the composition of the intermixed layer and the number of Pb in-plane neighbors in the layer. First, there is a rough negative correlation between the Pb fraction in the intermixed layer and the enhancement of the Pb off-centering. Second, at a given Pb fraction there is a negative correlation between the number of Pb in-plane neighbors and enhancement of the Pb off-center displacements.

These trends can be understood by considering the dipole-dipole repulsions within the intermixed layer. Each pair of aligned Pb dipoles costs electrostatic energy, which increases as the spacing between the dipoles decreases or as the magnitude of the dipoles increases. A smaller Pb fraction in the layer decreases the relative importance of this contribution, favoring an increase in the magnitude of the Pb dipole. At a fixed fraction, the size of this energy will depend on the arrangement of the Pb dipoles in the layer, with a smaller number of close (first and second) Pb-Pb neighbors decreasing the relative importance of this contribution and similarly favoring an increase in the magnitude of the Pb dipole. This final point is exemplified by considering the 75/25 mixed layer (see Figure 6 inset). Here we see that there are two distinct types of Pb cations, the 4-Pb and the 6-Pb cation. Figure 6 shows that in this case the 4-Pb cation has a much larger enhancement, consistent with the decreases in dipole-dipole repulsions with decreasing first and second Pb nearest in-plane neighbors. Similarly, Pb dipoles in striped (2-Pb nearest neighbors) layers are enhanced relative to those in the compositionally equivalent checkered (4-Pb neighbors) layers. In all cases, larger Pb dipoles in the intermixed layers increase the average polarization of that layer, which, through the same electrostatic arguments presented for the sharp interface superlattices, favors an enhancement of the total polarization. From this it can be understood that the striped interface superlattices, in which the Pb cations have fewer Pb neighbors than the checkered and the combined 25/75-75/25 superlattices, should exhibit more enhanced polarization, as observed in the first principles calculations.

### Table I: \( \Delta E_{\text{mixing}} \) relative to bulk for interfacial intermixed and unmixed superlattices

| \( m_{\text{PTO}/n_{\text{STO}}} \) | 25/75 Striped | Checker | Sharp |
|----------------|-------------|--------|-------|
| 1/1           | 33          | 27     | 32    | 45    |
| 1/2           | -6          | -7     | -5    | 5     |
| 1/3           | 1           | 1      | 1     | 2     |
| 2/1           | -35         | -41    | -35   | -18   |
| 2/2           | -16         | 16     | 16    | 5     |
| 2/3           | -6          | 8      | -6    | 5     |
| 3/1           | -46         | 52     | -46   | -29   |
| 3/2           | -23         | 26     | -23   | -20   |
| 3/3           | -14         | 15     | -14   | -11   |

The polarization of the superlattice is then intermediate between zero and the full spontaneous polarization of the ferroelectric layer material, increasing with increasing layer fraction of the ferroelectric phase. Our results for unmixed short-period PTO/STO superlattices are fully consistent with these previous results. In particular, the STO and PTO layers have nearly the same polarization, less than the full bulk spontaneous polarization of PTO, which is exemplified by considering the 75/25 mixed layer (see Figure 6 inset). Here we see that there are two distinct types of Pb cations in the 75 PTO/25 PTO layer. Empty squares (□) are for Sr cations, filled circles (●) represent Pb cations with four nearest neighbors, and hashed circles are Pb cations with 6 in-plane neighbors (2 nearest neighbors and 4 second nearest neighbors). This plot was generated using data from all three intermixed superlattices as well as unmixed superlattices.

A more precise understanding of this argument can be obtained by examining the Pb off-center displacements as a function of the number of nearest in-plane Pb neighbors. To isolate the intermixing effect, we report these values relative to the average Pb displacements in compositionally identical unmixed superlattices with the same period. As seen in Figure 6, the observed enhancement depends on the composition of the intermixed layer and the number of Pb in-plane neighbors in the layer. First, there is a rough negative correlation between the Pb fraction in the intermixed layer and the enhancement of the Pb off-centering. Second, at a given Pb fraction there is a negative correlation between the number of Pb in-plane neighbors and enhancement of the Pb off-center displacements.

These trends can be understood by considering the dipole-dipole repulsions within the intermixed layer. Each pair of aligned Pb dipoles costs electrostatic energy, which increases as the spacing between the dipoles decreases or as the magnitude of the dipoles increases. A smaller Pb fraction in the layer decreases the relative importance of this contribution, favoring an increase in the magnitude of the Pb dipole. At a fixed fraction, the size of this energy will depend on the arrangement of the Pb dipoles in the layer, with a smaller number of close (first and second) Pb-Pb neighbors decreasing the relative importance of this contribution and similarly favoring an increase in the magnitude of the Pb dipole. This final point is exemplified by considering the 75/25 mixed layer (see Figure 6 inset). Here we see that there are two distinct types of Pb cations, the 4-Pb and the 6-Pb cation. Figure 6 shows that in this case the 4-Pb cation has a much larger enhancement, consistent with the decreases in dipole-dipole repulsions with decreasing first and second Pb nearest in-plane neighbors. Similarly, Pb dipoles in striped (2-Pb nearest neighbors) layers are enhanced relative to those in the compositionally equivalent checkered (4-Pb neighbors) layers. In all cases, larger Pb dipoles in the intermixed layers increase the average polarization of that layer, which, through the same electrostatic arguments presented for the sharp interface superlattices, favors an enhancement of the total polarization. From this it can be understood that the striped interface superlattices, in which the Pb cations have fewer Pb neighbors than the checkered and the combined 25/75-75/25 superlattices, should exhibit more enhanced polarization, as observed in the first principles calculations.
Finally we consider whether interfacial cation intermixing is energetically favorable. Table [I] shows the $\Delta E_{mixing}$ relative to bulk PTO and STO for the three interfacial intermixed cells and the sharp interface. In all cases, we see that intermixing is preferred over sharp interfaces.

In conclusion, our results show that intermixed PTO/STO interfaces enhance the polarization of a superlattice relative to sharp interfaces. This enhanced polarization is strongly linked to larger Pb displacements in the intermixed layers and can be rationalized through a consideration of the dipole-dipole interactions. Since this model is based solely on the interaction of dipoles constrained by potential energy wells, these concepts should be general to all multicomponent superlattices in which there is a significant difference in the ferroelectric and/or dielectric properties of the substituent layers. This study, combined with knowledge from previous studies on strain and internal electric field effects in superlattices, suggests a new mechanism for tailoring short period superlattices for specific applications.

---

1. H. Tabata, H. Tanaka, and T. Kawai, App. Phys. Lett. 65, 1970 (1994).
2. H. M. Christen, L. A. Boatner, J. D. Budai, M. F. Chisholm, L. A. Gea, P. J. Marrero, and D. P. Norton, App. Phys. Lett. 68, 1488 (1996).
3. J. C. Jiang, X. Q. Pan, W. Tian, C. D. Theis, and D. G. Schlom, App. Phys. Lett. 74, 2851 (1999).
4. F. Le Marrec, R. Farhi, M. El Marssi, J. L. DELLIS, M. G. Karkut, and D. Ariosa, Phys. Rev. B 61, R6447 (2000).
5. O. Nakagawara, T. Shimuta, T. Makino, S. Arai, H. Tabata, and T. Kawai, App. Phys. Lett. 77, 3257 (2000).
6. M. Sepliarsky, S. R. Philpot, D. Wolf, M. G. Stachiotti, and R. L. Migoni, J. App. Phys. 90, 4509 (2001).
7. A. Q. Jiang, J. F. Scott, H. B. Lu, and Z. H. Chen, J. App. Phys. 93, 1180 (2003).
8. J. B. Neaton and K. M. Rabe, App. Phys. Lett. 82, 1586 (2003).
9. S. Rios, A. Ruediger, A. Q. Jiang, J. F. Scott, H. Lu, and Z. Chen, J. Phys.:Cond. Matt. 15, L305 (2003).
10. C. Bungaro and K. M. Rabe, Phys. Rev. B 69, 184101 (2004).
11. M. Dawber, C. Lichtensteiger, M. Cantoni, M. Veithen, P. Ghosez, K. Johnston, K. M. Rabe, and J. M. Triscone, Phys. Rev. Lett. 95, 177601 (2005).
12. K. Johnston, X. Huang, J. B. Neaton, and K. M. Rabe, Phys. Rev. B 71, 100103(R) (2005).
13. H. N. Lee, H. M. Christen, M. F. Chisholm, C. M. Rouleau, and D. H. Lowndes, Nature 433, 395 (2005).
14. S. M. Nakhmanson, K. M. Rabe, and D. Vanderbilt, App. Phys. Lett. 87, 102906 (2005).
15. M. Dawber, P. Chandra, P. B. Littlewood, and J. F. Scott, J. Phys.: Cond. Matt. 15, L393 (2003).
16. J. Junquera and P. Ghosez, Nature 422, 506 (2003).
17. C. H. Ahn, K. M. Rabe, and J.-M. Triscone, Science 303, 488 (2004).
18. A. M. Kolpak, N. Sai, and A. M. Rappe, Phys. Rev. B 74, 054112 (2006).
19. D. D. Fong, A. M. Kolpak, J. A. Eastman, S. K. Streiffer, P. H. Fuoss, G. B. Stephenson, C. Thompson, D. M. Kim, K. J. Choi, C. B. Eom, et al., Phys. Rev. Lett. 96, 127601 (2006).
20. D. D. Fong, C. Cionca, Y. Yacoby, G. B. Stephenson, J. A. Eastman, P. H. Fuoss, S. K. Streiffer, C. Thompson, R. Clarke, R. Pindak, et al., Phys. Rev. B 71, 144112 (2005).
21. G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
22. P. E. Blöchl, Phys. Rev. B Rapid Comm. 41, 5414 (1990).
23. G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
24. K. Hellwege and A. M. Hellwege, eds., Landolt-Börnstein, vol. III (Springer-Verlag, Berlin, 1981).
25. R. D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993).
26. X. Wu, O. Diéguez, K. M. Rabe, and D. Vanderbilt, Phys. Rev. Lett. 97, 107602 (2006).