# Predicting polarization enhancement in multicomponent ferroelectric superlattices

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*Ab initio* calculations are utilized as an input to develop a simple model of polarization in epitaxial short-period $CaTiO_3/SrTiO_3/BaTiO_3$ superlattices grown on a $SrTiO_3$ substrate. The model is then combined with a genetic algorithm technique to optimize the arrangement of individual $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ layers in a superlattice, predicting structures with the highest possible polarization and a low in-plane lattice constant mismatch with the substrate. This modelling procedure can be applied to a wide range of layered perovskite-oxide nanostructures providing guidance for experimental development of nanoelectromechanical devices with substantially improved polar properties.

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Modern epitaxial thin film techniques make it possible to synthesize artificial multicomponent perovskite oxide superlattices whose polar properties can be precisely tailored for a wide variety of applications.[1,2,3] For example, it was recently demonstrated that hundreds of atomically thin individual layers of $CaTiO_3$ (CT), $SrTiO_3$ (ST) and $BaTiO_3$ (BT) could be grown on a perovskite ST substrate, yielding superlattices with compositionally abrupt interfaces and atomically smooth surfaces.[2,3] It was also shown that — since relaxed lattice constants of CT and BT are 0.07 Å smaller and 0.11 Å larger than that of ST ($a_{\rm ST}$ =3.905 Å), respectively — epitaxial strain in the constituent layers of these structures can be substantial. Due to the strong coupling between strain and polarization in ferroelectric perovskites, this can result in substantial enhancement of the polarization relative to that of the bulk constituents, as has been observed[3] in accordance with theoretical predictions[4].

We recently studied such strain-induced polarization enhancement in two- and three-component ferroelectric CT/ST/BT superlattices epitaxially matched to a cubic ST substrate.[5] First principles methods, namely density-functional theory and the modern theory of polarization,[6] were used to compute the structure and polarization of a small number of short-period structures with the same or similar compositions as those grown and characterized by Lee *et al.*[3,7] Unfortunately, the substantial computational costs associated with these first-principles techniques, growing rapidly as the period of the superlattice increases, make it impossible to perform the calculations necessary to answer a broader and more interesting question: how should we arrange individual CT, ST and BT layers in a given superlattice to obtain the largest possible polarization enhancement? In this paper we address this question by using our *ab initio* results[5] as an input to create a simple model for polarization in CT/BT/ST superlattices, and then employing this model in conjunction with a genetic optimization algorithm technique to identify the optimal candidate structures.

In previous work,[4] a simple continuum model was introduced based on first-principles calculations of ST/BT superlattices; a similar model was subsequently applied to ST/PT superlattices.[8] The main premise was to assume that the constituent layers were linear dielectrics (in the case of the ferroelectric constituent, possessing also a nonzero spontaneous polarization), and to obtain the value of the uniform polarization in each layer by solving the equations of macroscopic electrostatics. With appropriate choices for the two dielectric constants, this model could reproduce the approximate constancy of the local polarization in the superlattice, giving a nonzero polarization in the ST layer, and the dependence of the polarization on the ratio of the thickness of the ST and BT layers. However, the electrostatic continuum character of this model could not reproduce the dependence of the polarization on the absolute thickness of the constituent layers, clearly present in our first-principles results for CT/ST/BT superlattices. For example, the polarization of the $(ST)_1(BT)_1$ superlattice is noticeably smaller than that of $(ST)_2(BT)_2$.

Here, we introduce a model that includes this "size effect," based on the following expression for the energy of the superlattice as a function of the scalar polarization $p_i$ of individual unit-cell layers $i$:

$$E = \sum_i (\alpha_i p_i^2 + \beta_i p_i^4) + \sum_i J_{i,i+1}\, p_i\, p_{i+1} \ . \qquad (1)$$

Here $\alpha_i$ and $\beta_i$ describe the anharmonic potential of a single unit-cell layer, and $J_{i,i+1}$ represents the coupling between nearest-neighbor layers. These parameters take values that depend on the identity of the layer; for example, $\alpha_i$ takes the values $\alpha_C,\ \alpha_S,\ \alpha_B$ for a CT, ST, or BT layer respectively. Similarly, $\beta_i$ takes the values $\beta_C,\ \beta_S,\ \beta_B$, and there are six interface terms $J_{CC}$, $J_{BB}$, $J_{SS}$, $J_{SC}$, $J_{SB}$, and $J_{BC}$.

To compute the energy for arbitrary values of the unit-cell layer polarizations $p_i$ would thus require knowledge of twelve parameters. However, the approximate constancy of the polarization across unit-cell layers observed in the first-principles results suggests a simplification in which, for each superlattice, $p_i$ is taken to be uniform and equal to the overall polarization. Substituting $p_i = p$ into Eq. (1), we find that

$$E(p) = Ap^2 + Bp^4 \qquad (2)$$

where

$$A = \sum_\nu N_\nu \alpha_\nu + \sum_{\langle \nu\nu' \rangle} N_{\nu\nu'} J_{\nu\nu'} \ , \qquad (3)$$

$$B = \sum_\nu N_\nu \beta_\nu \ , \qquad (4)$$

and $N_\nu$ and $N_{\nu\nu'}$ are the number of layers of type $\nu$ and the number of interfaces of type $\nu\nu'$ appearing in the superlattice

TABLE I: Columns two and three contain expressions for quadratic ($A$) and quatric ($B$) energy-decomposition coefficients for the two- and three-component superlattices of Ref. 5. The *ab initio* ground-state superlattice energies relative to the nonpolar structures, the values of *ab initio* and fitted superlattice polarizations, as well as the differences between the two, are shown in columns four, five, six and seven respectively.

| System | $A$ | $B$ | $\Delta E$ (eV) | $\lvert p_{\min}\rvert$ (C/m$^2$) | $\lvert p_{\min}^{\rm fit}\rvert$ (C/m$^2$) | $\lvert\Delta p_{\min}\rvert$ (%) |
|---|---|---|---|---|---|---|
| Strained bulk: | | | | | | |
| CT | $\widetilde{J}_{CC}$ | $\beta_C$ | -0.019 | 0.434 | 0.370 | 14.85 |
| BT | $\widetilde{J}_{BB}$ | $\beta_B$ | -0.044 | 0.368 | 0.363 | 1.30 |
| Two-component: | | | | | | |
| $(CT)_1(ST)_1$ | $2\widetilde{J}_{CS}$ | $\beta_C+\beta_S$ | -0.005 | 0.026 | 0.026 | |
| $(ST)_1(BT)_1$ | $2\widetilde{J}_{SB}$ | $\beta_S+\beta_B$ | -0.025 | 0.231 | 0.231 | |
| $(CT)_1(BT)_1$ | $2\widetilde{J}_{CB}$ | $\beta_C+\beta_B$ | -0.039 | 0.231 | 0.231 | |
| $(CT)_2(ST)_2$ | $\widetilde{J}_{SS}+\widetilde{J}_{CC}+2\widetilde{J}_{CS}$ | $2\beta_C+2\beta_S$ | -0.007 | 0.168 | 0.168 | |
| $(ST)_2(BT)_2$ | $\widetilde{J}_{SS}+\widetilde{J}_{BB}+2\widetilde{J}_{SB}$ | $2\beta_S+2\beta_B$ | -0.039 | 0.245 | 0.245 | |
| $(CT)_2(BT)_2$ | $\widetilde{J}_{CC}+\widetilde{J}_{BB}+2\widetilde{J}_{CB}$ | $2\beta_C+2\beta_B$ | -0.081 | 0.306 | 0.306 | |
| Three-component: | | | | | | |
| $(CT)_1(ST)_1(BT)_1$ | $\widetilde{J}_{CS}+\widetilde{J}_{SB}+\widetilde{J}_{CB}$ | $\beta_C+\beta_S+\beta_B$ | -0.034 | 0.200 | 0.194 | 2.98 |
| $(CT)_2(ST)_2(BT)_2$ | $\widetilde{J}_{CC}+\widetilde{J}_{SS}+\widetilde{J}_{BB}+\widetilde{J}_{CS}+\widetilde{J}_{SB}+\widetilde{J}_{CB}$ | $2\beta_C+2\beta_S+2\beta_B$ | -0.057 | 0.242 | 0.249 | 2.94 |
| $(CT)_2(ST)_2(BT)_4$ | $\widetilde{J}_{CC}+\widetilde{J}_{SS}+3\widetilde{J}_{BB}+\widetilde{J}_{CS}+\widetilde{J}_{SB}+\widetilde{J}_{CB}$ | $2\beta_C+2\beta_S+4\beta_B$ | -0.131 | 0.298 | 0.287 | 3.83 |
| $(CT)_3(ST)_3(BT)_3$ | $2\widetilde{J}_{CC}+2\widetilde{J}_{SS}+2\widetilde{J}_{BB}+\widetilde{J}_{CS}+\widetilde{J}_{SB}+\widetilde{J}_{CB}$ | $3\beta_C+3\beta_S+3\beta_B$ | -0.082 | 0.260 | 0.265 | 1.91 |

sequence. The fact that $N_C = N_{CC} + (N_{CS} + N_{CB})/2$, and similarly for $N_S$ and $N_B$, for any periodic sequence of layers, implies that the three $\alpha_\nu$ parameters and the six $J_{\nu\nu'}$ parameters enter Eq. (3) in a linearly dependent way. We can then define

$$\widetilde{J}_{\nu\nu'} = J_{\nu\nu'} + \frac{\alpha_\nu + \alpha_{\nu'}}{2}, \tag{5}$$

in order to rewrite Eq. (3) as

$$A = \sum_{\langle\nu\nu'\rangle} N_{\nu\nu'} \widetilde{J}_{\nu\nu'} \ . \tag{6}$$

That is, we have eliminated the $\alpha_\nu$ parameters; from now on, we consider our model to be determined by the nine independent parameters $\beta_C$, $\beta_S$, $\beta_B$, $\widetilde{J}_{CC}$, $\widetilde{J}_{SS}$, $\widetilde{J}_{BB}$, $\widetilde{J}_{CS}$, $\widetilde{J}_{CB}$, and $\widetilde{J}_{SB}$.

We obtain the values of the nine model parameters $\{\beta_\nu, \widetilde{J}_{\nu\nu'}\}$ by fitting to the first-principles results for the six two-component superlattices we considered. For each particular superlattice, the quadratic ($A$) and quatric ($B$) energy-decomposition coefficients, which are the linear combinations of $\{\beta_\nu, \widetilde{J}_{\nu\nu'}\}$ (see Table I for explicit formulas), can be determined from first-principles superlattice polarization $p_{\min}$ and its ground-state energy $E(p_{\min})$ relative to the structure constrained to have zero polarization.[9] These quantities are related to coefficients $A$ and $B$ as follows:

$$E(p_{min}) \equiv \Delta E = A p_{\min}^2 + B p_{\min}^4, \tag{7a}$$

$$\left.\frac{dE(p)}{dp}\right|_{p=p_{\min}} = 0 \implies A + 2Bp_{\min}^2 = 0. \tag{7b}$$

The resulting parameters $\{\beta_\nu, \widetilde{J}_{\nu\nu'}\}$ are shown in Table II.[10] The *ab initio* ground-state superlattice energies (relative to the corresponding nonpolar structures) and polarizations are shown in the fourth and fifth columns of Table I. The values of fitted superlattice polarizations as well as the differences between them and their *ab initio* derived counterparts are shown in columns six and seven of the same table. The fitted polarization differences for the two-component superlattices are not presented, since they are, by construction, equal to the *ab initio* ones. For the rest of the structures the model shows a remarkable agreement with first-principles results ($|\Delta p_{\min}| < 4\%$). For the three-component superlattices that possess inequivalent polarizations along [001] and [00$\bar{1}$] due to the breaking of inversion symmetry,[5,11] one could in principle compare with the larger polarization, the smaller one, or their average. We find empirically that the fit is best when compared with the larger polarization, so we have chosen to present these values in the table. The model performs poorly only for the strained bulk CT, whose first-principles value of polarization (computed in Ref. 5) represents an extreme limiting case[12] and cannot be well reproduced by the model, which is fitted to the superlattice calculations.

The availability of such a convenient expression for computing polarization with nearly *ab initio* precision allows us to predictively identify the arrangements of CT, ST and BT layers in a superlattice that would result in the largest possible polarization enhancement. While for short period superlattices ($N \leq 10$), this could be done by straightforward enumeration, the number of configurations increases rapidly with $N$, necessitating a more sophisticated optimization procedure for longer-period superlattices. Here, we use a genetic algorithm,[13] in which a particular CT/ST/BT superlattice of a given period $N$ is represented by a "chromosome" containing a sequence of $C$, $S$ and $B$ "genes". For example, a $(CT)_2(BT)_1(ST)_2(BT)_1$ superlattice of period 6 is encoded as a $CCBSSB$ chromosome. The genetic algorithm also makes it easy for us to impose constraints on the optimization, such as limiting the thickness of individual layers or the average in-plane lattice constant of the superlattice, as discussed further below.

TABLE II: Fitting parameters used to predict polarization in CT/ST/BT superlattices. See text and Table I for more details.

| $\beta_C$ | $\beta_S$ | $\beta_B$ | $\widetilde{J}_{CC}$ | $\widetilde{J}_{SS}$ | $\widetilde{J}_{BB}$ | $\widetilde{J}_{CS}$ | $\widetilde{J}_{CB}$ | $\widetilde{J}_{SB}$ |
|---|---|---|---|---|---|---|---|---|
| 0.584562 | 0.648676 | 0.833222 | -0.159671 | 0.022111 | -0.219844 | -0.000834 | -0.075701 | -0.079061 |

Our specific implementation of the genetic optimization algorithm is as follows. We create an initial population of $M$ chromosomes ($M$ is usually in between $2N$ and $3N$) by randomly assigning $C$, $S$ or $B$ values to each gene in each chromosome. The polarization of each chromosome is computed using Eq. (7b), and the chromosome's "fitness" is taken to be equal to the polarization. The current generation of chromosomes is then replaced by the offspring-chromosome generation, created as follows. First, the three chromosomes with the highest fitness (the so-called elite chromosomes) are copied into the offspring generation without change to preserve the best solutions from the previous generation. Second, the remaining $M-3$ members of the next generation are created by applying the following three-step procedure. (i) Two "parent" chromosomes are selected from the current generation by the so-called "roulette wheel" selection procedure,[14] which chooses a chromosome with a probability proportional to its fitness. (ii) With probability 10%, the offspring is taken to be identical to the parent with better fitness. The remaining 90% of the time, a "crossover" procedure is applied. We use a single-point crossover operator that randomly selects a single crossover point on the chromosome and copies the genes from one parent up to that point, and from the other after that point. (iii) Finally, the offspring is subjected to a "mutation" operator, which changes the current value of each gene into one of the two other available variants — i.e., gene $S$, for example, could be changed to either $C$ or $B$ — with a low probability (in our case: 1%). This entire selection and breeding process is continued for five hundred or more generations, after which the best available chromosomes are identified. For each set of parameters, i.e., the superlattice period and possible layer-sequencing restrictions, we perform five separate optimization runs to ensure convergence to a consistent solution.

For any given $N$, if we impose no restrictions on the number of consecutively repeating layers of the same type, then the optimal configuration turns out to be pure CT or BT (the fitted polarizations of bulk CT and BT are very close, see Table I). The former solution dominates in long period superlattices, while in shorter period ones ($N \leq 10$) the latter solution is found more often. This happens because, as shown in Table I, in thin superlattice layers BT has larger polarization than CT, which biases the optimization procedure towards BT. However, as it is well known, neither of these configurations can be experimentally realized because, when grown beyond a critical thickness, CT or BT relaxes to its natural in-plane lattice constant and the strain-induced polarization enhancement is lost. Thus, we constrain our optimization procedure so that only superlattices containing up to a given number $k$ of consecutive layers of the same type are allowed.

With this "epitaxial growth" constraint, the optimal superlattices that we find fall into two families depending on the relation between $N$ and $k$. For even $N$ and $k \geq N/2$ or for odd $N$ and $k \geq (N-1)/2$, the best solutions have the form of $(XT)_k(YT)_{N-k}$ or $(XT)_k(YT)_{N-k-1}(ST)_1$, where (X, Y) is (B, C) or (C, B). On the other hand, optimal superlattices for smaller $k$ (relative to the same period $N$) contain a number of CT/ST/BT stripes and can be reduced to combinations of the best solutions of the same form as above but with smaller periods. For example, for $(N,k)$ = (12,4) we find three optimal superlattices with polarizations in the range of 0.32–0.33 C/m$^2$: $(CT)_4(BT)_4(CT)_2(BT)_2$, $(CT)_3(BT)_4(CT)_2(BT)_3$ and $(CT)_2(BT)_4(CT)_2(BT)_4$. Each of these superlattices splits into two shorter ones with smaller $N$ and $k$. These are (8,4) $(CT)_4(BT)_4$ and (4,2) $(CT)_2(BT)_2$ for the first, (7,4) $(CT)_3(BT)_4$ and (5,3) $(CT)_2(BT)_3$ for the second, and two instances of (6,4) $(CT)_2(BT)_4$ for the third optimal superlattice, respectively. In what follows we restrict the discussion to solutions for large $k$ only, assuming that in the opposite case optimal superlattices for any particular $N$ could be constructed by merging together an appropriate number of the best large-$k$ solutions for shorter periods.

We have carried out first-principles calculations for a few short-period optimal superlattices to check that their *ab initio* polarizations agree well with those predicted by the model. We use a plane-wave based DFT-LDA method[15] with ultrasoft pseudopotentials[16] for structural relaxation of the superlattices and the Berry-phase method of the modern polarization theory[6] to compute their total polarization. The details of the calculations are the same as in Ref. 5. The results are presented in Table III and show that the good agreement between *ab initio* and fitted values of polarization in short-period CT/ST/BT superlattices is preserved.

Another feature of the superlattice relevant to the feasibility of its experimental realization is the mismatch between the equilibrium in-plane lattice constant of the superlattice (estimated by averaging over the unstrained lattice constants of individual layers) and the lattice constant of the ST substrate. The low substrate mismatch restriction tends to balance the number of CT ($a_{\rm CT} < a_{\rm ST}$) and BT ($a_{\rm BT} > a_{\rm ST}$) layers in the superlattice. With this additional screening step, we find that the most polar CT/ST/BT superlat-

TABLE III: Comparison between *ab initio* polarizations $p_{\min}$ and fitted polarizations $p_{\min}^{\rm fit}$ for a few polar short-period superlattices identified by the genetic algorithm optimization procedure.

| System | $(N,k)$ | $\lvert p_{\min}\rvert$ (C/m$^2$) | $\lvert p_{\min}^{\rm fit}\rvert$ (C/m$^2$) | $\lvert\Delta p_{\min}\rvert$ (%) |
|---|---|---|---|---|
| $(CT)_1(BT)_3$ | (4,3) | 0.315 | 0.310 | 1.6 |
| $(ST)_2(BT)_3$ | (5,3) | 0.279 | 0.275 | 1.2 |
| $(CT)_2(BT)_4$ | (6,4) | 0.342 | 0.328 | 4.1 |
| $(CT)_3(ST)_1(BT)_3$ | (7,3) | 0.313 | 0.305 | 2.6 |

TABLE IV: Short-period superlattices identified by the genetic algorithm optimization procedure as being the most polar and simultaneously having the lowest lattice constant mismatch $|\Delta a|$ with the substrate.

| System | $(N, k)$ | $\lvert p^{\rm fit}_{\rm min}\rvert$ (C/m$^2$) | $\lvert\Delta a\rvert$ (%) |
|---|---|---|---|
| $(CT)_3(BT)_3$ | (6,3) | 0.327 | 0.34 |
| $(CT)_3(ST)_1(BT)_2$ | (6,3) | 0.292 | 0.03 |
| $(CT)_3(ST)_1(BT)_3$ | (7,3) | 0.305 | 0.29 |
| $(CT)_4(BT)_3$ | (7,4) | 0.333 | 0.12 |
| $(CT)_4(BT)_4$ | (8,4) | 0.337 | 0.34 |
| $(CT)_4(ST)_1(BT)_4$ | (9,4) | 0.320 | 0.30 |
| $(CT)_5(ST)_1(BT)_4$ | (10,5) | 0.324 | 0.15 |
| $(CT)_{10}(ST)_1(BT)_9$ | (20,10) | 0.346 | 0.24 |

tices that emerge from the genetic optimization procedure have the following form: $(CT)_{N/2}(BT)_{N/2}$ for even $N$ and $(CT)_{(N-1)/2}(ST)_1(BT)_{(N-1)/2}$ for odd $N$. It is worth pointing out that adding one or two ST layers to CT and BT containing superlattices destroys their inversion symmetry without seriously reducing polarization. The lack of the center of inversion makes the superlattice polarizations along [001] and $[00\bar{1}]$ unequal, which provides for even greater flexibility in fine-tuning of the polar properties of such structures.

In Table IV we assemble a number of short-period CT/ST/BT superlattices that were identified by the genetic algorithm optimization procedure as being the most polar superlattices with a lattice mismatch of less than 0.5%, which should allow them to be grown coherently.[7] The following first-principles lattice constants were used for the substrate-mismatch analysis: $a_{\rm CT} = 3.813$ Å (cubic), $a_{\rm ST} = 3.858$ Å (cubic) and $a_{\rm BT} = 3.929$ Å (tetragonal). On average, the polarizations of the superlattices presented in Table IV are predicted to be 10–30% higher than the computed polarizations of the previously investigated structures[5] shown in Table I.

To conclude, we have used a first-principles-based one-dimensional chain model for polarization in multicomponent perovskite-oxide ferroelectric superlattices combined with a genetic algorithm optimization procedure to study the connection between the polar properties of a superlattice and its layer sequence. We predict specific layering arrangements that produce superlattices simultaneously possessing the highest possible polarization and a low in-plane lattice-constant mismatch with the substrate. Our method could be applied to superlattices containing individual components other than CT, ST and BT, or more than three components, as long as the polarization profile across the superlattice remains sufficiently flat. Various additional restrictions on the arrangement of components could easily be added to the genetic algorithm optimization to design structures that are custom-tailored for specific applications. Our predictions are for ideal structures that are defect-free and fully switchable. Since the remanent polarization of experimentally grown perovskite-oxide ferroelectric superlattices is substantially reduced due to structural defects and incomplete switching of ferroelectric domains, the computed values are expected to be higher than those observed. Nevertheless, since our technique does identify the most polar layer sequences (regardless of the absolute polarization) as well as quickly eliminating unfavorable arrangements, it can be used as a valuable tool to guide the experimental efforts in the quest for more efficient nanoelectromechanical devices with tailored and/or substantially enhanced properties.

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[9] For each superlattice we create a corresponding non-polar structure with the ferroelectric displacement removed by "unbuckling" the AO and BO planes and moving the "middle" planes back to the center of each primitive cell.

[10] We use both equations (7a) and (7b) for each two-component superlattice in the fit, which doubly overdetermins the set of $\{\beta_\nu\}$.

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[12] We consider bulk CT under epitaxial tensile strain — which actually favors in-plane polarization — but with ferroelectric displacement along the film-growth direction (symmetry restricted to space group P4mm) and all the zone boundary distortions that are present in its actual ground-state crystal structure suppressed. On the other hand, it is reasonable to assume that in a superlattice CT layers do develop substantial ferroelectric displacements in the film-growth direction by being polarized by the neighboring BT layers.

[13] See, for example, A. E. Eiben and J. E. Smith, *Introduction to Evolutionary Computing* (Springer-Verlag, 2003).

[14] For the detailed description of the roulette wheel selection procedure see, for example, section 3.7 in Ref. 13.

[15] We used PWscf code (available from http://www.pwscf.org) for the calculations presented here.

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