Polarization enhancement in perovskite superlattices by oxygen octahedral tilts

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ABSTRACT

Interface engineering in perovskite oxide superlattices has developed into a flourishing field, enabling not only further tuning of the exceptional properties, but also giving access to emergent physical phenomena. Here, we reveal a new mechanism for enhancing the electric polarization by the interface-induced oxygen octahedral tilts in $BaTiO_3/CaTiO_3$ superlattices. By combining a novel genetic algorithm with density functional theory (DFT), we predict that the true ground states in 1:1 and 2:2 $BaTiO_3/CaTiO_3$ superlattices grown on $SrTiO_3$ adopt *Pc* symmetry with a large proper electric polarization (32.8 $\mu C/cm^2$ for 1:1 and 35.8 $\mu C/cm^2$ for 2:2 superlattices), which is even larger than that of bulk $BaTiO_3$. The tilt of oxygen octahedron is found to play a key role for the enhancement of out-of-plane polarization in 1:1 superlattices because it reduces greatly the rotation of oxygen octahedron (out-of-phase) which significantly suppresses the out-of-plane polarization.

1. Introduction

Interfaces formed by perovskite oxides offer a tremendous opportunity for fundamental as well as applied research. In this active field of research, interfacial effects on the polarization of the ultra-short superlattices have attracted enormous interests [1–8]. Considering only the out-of-plane ferroelectric modes, Neaton et al. predicted that the polarization of $BaTiO_3/SrTiO_3$ superlattices (*P4mm* structure) with $BaTiO_3$ (BTO) fraction larger than 40% grown on $SrTiO_3$ (STO) substrate was enhanced above that of bulk BTO [1]. The effects of oxygen octahedral rotations around [0 0 1] [an antiferrodistortive (AFD) mode] on the ferroelectricity were examined later: It was shown that a trilinear coupling between the ferroelectric and interfacial (in-phase and out-of-phase) AFD rotation modes results in an enhanced polarization in the 1:1 $PbTiO_3/SrTiO_3$ (PTO/STO) superlattices with octahedral rotations (*P4bm* structure) when compared to *P4mm* structure [7,9]. Recently, the role of another common AFD mode, i.e., oxygen octahedral tilt (rotation of oxygen octahedron around an axis perpendicular to [0 0 1]) played on the polarization has been elucidated [10–15], in which the in-plane polarization was induced by

another type of trilinear coupling between the polarization, oxygen octahedral rotation and tilt. The polarization resulting from the trilinear coupling was then referred as hybrid improper ferroelectricity (HIF) [10]. According to this model, Mulder et al. [13] raised a strategy to design artificial oxides with large electric polarization (*P*) and small energetic switching barriers between +*P* and −*P*.

In this work, we investigate a typical ferroelectric/dielectric superlattice system, i.e., $(BaTiO_3)_n/(CaTiO_3)_n$ (*n* is the number of layers). Previous first principles studies showed that the polarization of $(BaTiO_3)_2/(CaTiO_3)_2$ on STO substrate with the *P4mm* structure was larger than that of the tetragonal bulk BTO [16]. But it decreased greatly in *P4bm* structure and became even smaller than the tetragonal bulk BTO value. This decreasing was attributed to the suppressing of the polarization by an oxygen octahedral rotation [17,18]. It should be noted that all previous studies neglected the tilts of oxygen octahedra, which is one of the most important distortions in bulk *Pbnm* $CaTiO_3$.

In order to consider all possible relevant distortions in perovskites, we propose a global optimization method based on the genetic algorithm (GA) (see Computational Methods) to search the lowest energy structures of BTO/CTO superlattices. By combining the GA with density functional theory (DFT) calculations, the true ground states of 1:1 and 2:2 BTO/CTO superlattices are predicted to adopt the *Pc* symmetry. We find that the enhanced out-of-plane polarization in 1:1 *Pc* structure with the oxygen octahedral tilt occurs because the tilt of oxygen octahedra suppresses dramatically the

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oxygen octahedral rotation (out-of-phase), which disfavors the out-of-plane ferroelectricity. Finally due to the existence of a large in-plane polarization, the total polarizations of 1:1 and 2:2 BTO/CTO on STO are predicted to be 32.8 μC/cm^2 and 35.8 μC/cm^2 respectively, which are larger than the bulk value of tetragonal BTO.

2. Computational methods

Since the 1990s, genetic algorithms (GAs) have been used to search the ground state of nanoclusters [19,20], alloys [21,22], and crystals [23]. They employ a search technique based on principles similar to those of natural selection, singling out the most "adaptive" structures, which have the lowest energies [19,20,23]. In this study, we are dealing with a problem different from the previous studies: Here, the basic lattice structure (i.e., perovskite based structures) is fixed and our purpose is to find out the distortion of the cell and ionic positions which leads to the lowest energy. To this end, we propose a genetic algorithm which differs from the previous algorithms in several aspects: (1) To generate an initial structure of the first generation, we first randomly select a subgroup of the space group of the undistorted perovskite structure for a given superstructure. By symmetrizing a structure with random distortions using the symmetry operation of the subgroup, we can obtain an initial structure with this selected subgroup symmetry. (2) For the mating operation, we propose another crossover operation besides the usual cut-and-splice method proposed by Deaven and Ho [19]: In a cubic perovskite system, there are different unstable phonon modes such as the ferroelectric displacement and the oxygen octahedral rotation. The distortion in the ground state is usually a superposition of different modes. Guided by this physical insight, we introduce the following mating operation: $X_{child} = X_{cubic} + (X_{father} - X_{cubic}) + c(X_{mother} - X_{cubic})$, where X_{father} and X_{mother} are the two parent structures, X_{cubic} and X_{child} are the undistorted cubic structure and new child structure, respectively. For the new distortion, we take either the sum or difference of these two distortions depending on a constant c, which is randomly chosen to be 1 or −1.

Our total energy calculations are based on the density functional theory (DFT) [24] within the local density approximation (LDA) on the basis of the projector augmented wave method [25] encoded in the Vienna ab initio simulation package [26]. Calcium 3s, 3p and 4s electrons, Ba 5s, 5p and 6s electrons, Ti 3p, 3d and 4s electrons and O 2s and 2p electrons are treated as valence states. The plane-wave cutoff energy is set to 600 eV for calculating phase diagram and 450 eV for searching the ground state using the GA method. And $4 \times 4 \times 3$ k-point mesh is used for the 20-atom $\sqrt{2} \times \sqrt{2} \times 2$ cell and $4 \times 4 \times 1$ k-point mesh for the 40-atom $\sqrt{2} \times \sqrt{2} \times 4$ cell. For the electric polarization calculations, the berry phase method [27] is used.

3. Results and discussion

The lattice vectors used in this study are $\boldsymbol{a} = a_s\boldsymbol{x} - a_s\boldsymbol{y}$, $\boldsymbol{b} = a_s\boldsymbol{x} + a_s\boldsymbol{y}$ and $\boldsymbol{c} = \delta_1\boldsymbol{x} + \delta_2\boldsymbol{y} + (2a_s + \delta_3)\boldsymbol{z}$ for 20-atom cell and $\boldsymbol{c} = \delta_1\boldsymbol{x} + \delta_2\boldsymbol{y} + (4a_s + \delta_3)\boldsymbol{z}$ for 40-atom cell, where a_s is the in-plane lattice constant of the studied system at a given strain, and ($\boldsymbol{x}$, $\boldsymbol{y}$, $\boldsymbol{z}$) are defined within the pseudocubic setting. Epitaxial strain is then defined as ($a_s - a_0/a_0$), where a_0 (3.856 Å) is the theoretical lattice constant of bulk STO within LDA optimization in Ref. [17].

The total energies of the lowest energy phases in 1:1 BTO/CTO superlattices from the GA simulations, as a function of epitaxial strain from −4% to 4%, are shown in Fig. 1a. For comparison, the previous suggested $P4bm$, $P4mm$ and Pm[28] phases are also shown. Fig. 1b displays the dependence of the total polarizations
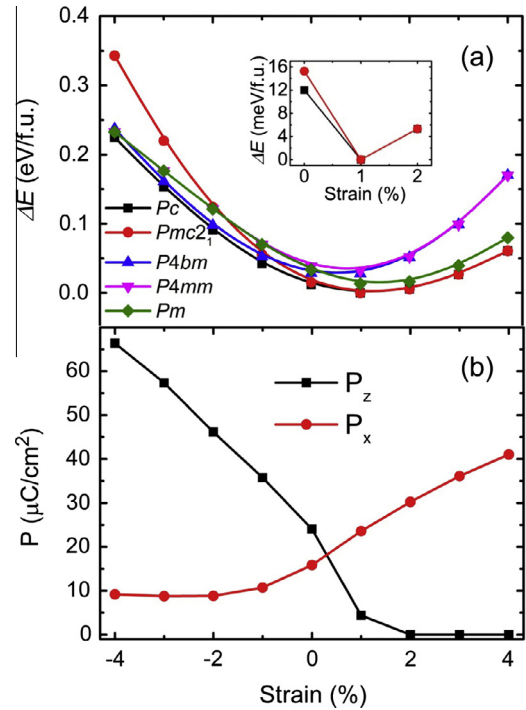

Fig. 1. (a) Calculated total energies versus the epitaxial strain (−4% to 4%) for 1:1 BTO/CTO superlattices. Previously suggested $P4bm$, $P4mm$ and Pm phases are also shown for comparison. Inset shows a zoomed view in the strain range of 0–2%. (b) Calculated ferroelectric polarizations ($P_y = P_x$) of the lowest energy phases at each strain.

Table 1
Calculated frequencies of modes [30] at Γ and M in $P4mmm$ structure of 1:1 BTO/CTO superlattices at different strains.

Strain (%)	ω (cm^{-1})	k-Points	Modes
−4	0.3i	Γ	FE$_{xy}$
	259i	Γ	FE$_z$
	162i	M	AFD$_{xy}$
	192i	M	AFD$_{zi}$
	207i	M	AFD$_{zo}$
0	101i	Γ	FE$_{xy}$
	96i	Γ	FE$_z$
	137i	M	AFD$_{xy}$
	82i	M	AFD$_{zi}$
	119i	M	AFD$_{zo}$
4	230i	Γ	FE$_{xy}$
	91	Γ	FE$_z$
	118i/62i[a]	M	AFD$_{xy}$
	83	M	AFD$_{zi}$
	38i	M	AFD$_{zo}$

[a] There are more than one unstable modes corresponding to a certain distortion-type.

of the lowest energy phases on the epitaxial strain for 1:1 superlattices. The results for 2:2 superlattices are given in Ref. [29].

As can be seen in Fig. 1a, in the strain range of −4% to 1%, Pc phase is stabilized, which is lower in energy by an average of 14 meV per formula unit with respect to $P4bm$ phase. This is also confirmed by the phonon calculations indicating that $P4bm$ structure is unstable. In Pc structure, the tilts of oxygen octahedra and the in-plane ferroelectric distortion occur which lower the energy when compared with $P4bm$ structure. These rotations and tilts of oxygen octahedra related to CTO bulk-like layers can be attributed to the interfacial effects, which do not exist in BTO bulk. As the strain is higher than 1%, Pc phase is gradually transformed into