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The first-principles study of ferroelectric behaviours of $PbTiO_3/SrTiO_3$ and $BaTiO_3/SrTiO_3$ superlattices*

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We have performed the first-principles calculation to investigate the origins of ferroelectricities and different polarization behaviours of superlattices $BaTiO_3/SrTiO_3$ and $PbTiO_3/SrTiO_3$. The density of state (DOS) and electronic charge profiles show that there are strong hybridizations between atoms Ti and O and between atoms Pb and O which play very important roles in producing the ferroelectricities of superlattices $BaTiO_3/SrTiO_3$ and $PbTiO_3/SrTiO_3$. Owing to the decline of internal electric field in $SrTiO_3$ (ST) layer, the tetragonality and polarizations of superlattices decrease with increasing the fraction of $SrTiO_3$ in the superlattices. We find that the polarization of $PbTiO_3/SrTiO_3$ is largerthan that of $BaTiO_3/SrTiO_3$ at the same ratio of components, because the polarization mismatch between $PbTiO_3$ and $SrTiO_3$ is larger than that between $BaTiO_3$ and $SrTiO_3$. The polarization and tetragonality are enhanced with respect to those of bulk tetragonal $BaTiO_3$ in the superlattices $BaTiO_3/SrTiO_3$, while the polarization and tetragonality are reduced with respect to those of bulk tetragonal $PbTiO_3$ in superlattices $PbTiO_3/SrTiO_3$.

Keywords: ferroelectricity, spontaneous polarization, polarization mismatch, internal electric field
PACC: 7780, 7115M, 7730

1. Introduction

Artificial superlattices (ASLs) of ferroelectric oxide have aroused great interest, because they not only present exciting possibilities for the development of new materials with extraordinary properties, but also are ideal probes of the fundamental physics of ferroelectric materials.

At present, the studies about ASLs mainly focus on various superlattices, such as $BaTiO_3/SrTiO_3$,[1−7] $KTaO_3/KNbO_3$,[8−12] $PbTiO_3/SrTiO_3$,[13,14] Pb–$TiO_3/PbZrO_3$,[15,16] $PbTiO_3/BaTiO_3$,[17] $PbZrO_3$/Ba–ZrO_3,[18,19] etc. And a three-component superlattice $(SrTiO_3)/(BaTiO_3)/(CaTiO_3)$ has been investigated recently.[20] In these ASLs, some researchers show that the ferroelectric property is directly related to the periodicity and structure of ASL. The most commonly observed phenomenon is an enhancement in dielectric constant as the periodicity of ASL reduces. Typically, small-periodicity ASLs will demonstrate their dielectric constants to be about twice those of coarse ones.[21−25] The ratios of components in superlattices have a profound influence on ferroelectric properties of superlattices, because there are various tetragonalities in these superlattices. It is found that the polarizations of $(SrTiO_3)_2/(BaTiO_3)_x/(CaTiO_3)_2$ superlattices increase with x increasing from 1 to 4.[20] The phenomenon is predominantly attributed to the change of tetragonality in these superlattices. If we can control tetragonality by adjusting the structure of superlattice, we can design the superlattice with the desired properties according to our demands. Thus the investigation of polarizations and tetragonalities in superlattices becomes very meaningful. $BaTiO_3/SrTiO_3$ (BST) is a much studied system due to its improved ferroelectric and dielectric properties compared with those of bulk $BaTiO_3$ crystal and film, which is ascribed to a misfit strain of 2% in the BST superlattices. Furthermore, the high-quality $PbTiO_3/SrTiO_3$(PST) superlattices have been prepared on $SrTiO_3$ substrates by reactive molecule beam epitaxy (MBE).[13]

In this work, we investigate the electronic structures and effects of tetragonality on spontaneous polarization behaviours of superlattices BST and PST by using the first-principles calculations. We discuss ferroelectric origin of superlattice by calculating the

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densities of states and electronic charge densities of 1×1 PST and BST superlattices. Strong hybridization between Ti and O atoms can make a great contribution to the ferroelectricities of superlattices BST and PST. The strong interaction between Pb and O atoms also favours the ferroelectricity in PST. We also analyse in detail the polarization behaviours in PST and BST superlattices with four 5-periodicity. The results show the polarization behaviours in the two kinds of superlattices are consistent with the measured ones.

2. Method

In order to calculate the electronic structures and polarizations of superlattices, the first-principles calculation was used in BST and PST superlattices. The first-principles density-functional calculations[26] were performed within local-density approximation (LDA)[27] as implemented in the PWSCF[28] package. The exchange-correlation energy was evaluated using the Ceperley–Alder form with Perdew–Zunger parametrization.[29,30] We used Vanderbilt ultrasoft pseudopotentials [31] for all ions, treating as valence states the 6s and 6p electrons of Ba; the 5d, 6s, and 6p electrons of Pb; the 3s, 3p, 3d, and 4s electrons of Ti; the 4s, 4p, 5s electrons of Sr; the 2s and 2p electrons of O. The inclusion of the semi-core electrons in the valence states is necessary for an accurate description of these oxides. A kinetic energy cut-off of 30 Ry was used and the augmentation charges were expanded up to 270 Ry. Integrals over the Brillouin zone were performed using the Monkhorst–Pack scheme[32−34] where the k-point mesh used was $6\times6\times3$ and $6\times6\times6$ for superlattice and bulk ferroelectric material, respectively. The spontaneous polarizations have been calculated by the Berry-phase method.[35,36]

During relaxation, atomic coordinates within a supercell were relaxed along [001] within space group $P4mm$ until the Hellmann–Feynman force was less than 5.0×10^{-4}Ry/Bohr, while the in-plane lattice constant was fixed as the calculated lattice constant of $SrTiO_3$, and the out-of-plane lattice constant c was allowed to vary. In the Berry-phase calculation, we used 12 k points/string along [001] in the irreducible wedge to gain well-converged results.

3. Results

3.1. Structural properties

The lattice parameters of prototype cubic perovskite structures of the pure materials $BaTiO_3$, $SrTiO_3$ and $PbTiO_3$ have been calculated as listed in Table 1. All theoretic lattice parameters are 1%–2% smaller than the corresponding experimental values, which is a typical underestimation in the LDA approximation. Our results are in good agreement with the previous calculations.[35,37] A large lattice misfit of 2.29% is obtained in BST, while 0.75% of lattice misfit in PST is very small. The misfit strain is larger in BST than in PST. Oxygen atoms in cubic perovskite have two inequivalent directions: perpendicular and parallel to the cubic face, labelled with O_1 and O_2 in Table 1, respectively. As shown in Table 1, Born effective charges $Z^*(\mathrm{Ti})$ and $Z^*(\mathrm{O_1})$ are anomalously large. With the exception of Pb atom, $Z^*(\mathrm{A})$ and $Z^*(\mathrm{O_2})$ are close to their nominal ionic valences. The anomalous values of $Z^*(\mathrm{Ti})$ and $Z^*(\mathrm{O_1})$ indicate that a strong dynamic charge transfer takes place along the Ti–O bond as the bond varies, which can be understood to arise from the strong covalence character of the Ti–O bond. The Pb–O bond also has a similar character. It is indicated that there are strong electronic interactions in bond Ti–O and in bond Pb–O which are the main factors resulting in ferroelectricities of the three compounds.[38]

Table 1. Lattice parameters (in Bohr) and Born effective charges in cubic perovskite $ATiO_3$, where A represents ion Ba, Pb and Sr correspondingly.

compound	a_0	$Z^*(A)$	$Z^*(\mathrm{Ti})$	$Z^*(\mathrm{O_1})$	$Z^*(\mathrm{O_2})$
$BaTiO_3$	7.452	2.76	7.13	−5.66	−2.21
$PbTiO_3$	7.338	3.93	7.01	−5.8	−2.58
$SrTiO_3$	7.285	2.55	7.08	−5.62	−2.02

Structural parameters and polarizations of bulk $BaTiO_3$, $PbTiO_3$, BST (1/1) and PST (1/1) superlattices are provided in Table 2, where 1/1 represents the unit cell of superlattice consisting of one $SrTiO_3$ layer and one $BaTiO_3$ ($PbTiO_3$) layer. In Table 2, it is shown that the polarizations of bulk $BaTiO_3$ and $PbTiO_3$ are 23.75 and 74.76 μC/cm^2 respectively, and they are consistent with previous calculated results.[39,40] The lattice parameter c/a of PST (2.03) is smaller than that of BST (2.052), which results from a larger misfit strain in BST as mentioned above. It is seen that the polarization of BST is slightly larger than that of bulk $BaTiO_3$, while there is a sharp decline for polarization of PST with respect to that of bulk $PbTiO_3$ due to a smaller misfit strain existing in PST.

Table 2. The tetragonalities and polarizations of $BaTiO_3$, $PbTiO_3$, BST and PST.

compound	$BaTiO_3$	$PbTiO_3$	BST	PST
c/a	1.01	1. 035	2.052	2.03
polarization/(μC/cm^2)	23.75	74.76	24.51	32.18

3.2. Electronic properties

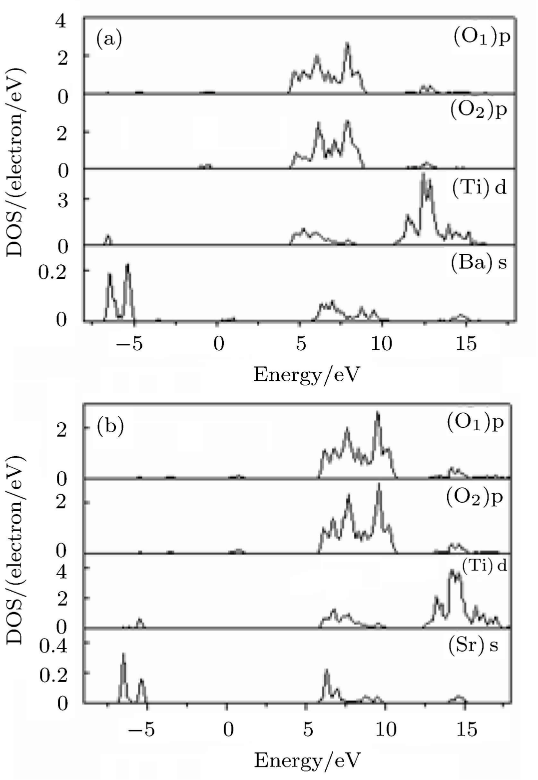


Fig.1. DOS profiles of $BaTiO_3$ layer (a) and $SrTiO_3$ layer (b) in BST superlattices.

In order to understand the role that each atom plays in a ferroelectric BST superlattice, we calculate its electronic structure. The density-of-state (DOS) profiles of $BaTiO_3$ (BT) and $SrTiO_3$ (ST) layers in superlattices are shown in Fig.1, where DOS profiles of Ti 3d and O 2p range from 5 to 16 eV. Their DOS distributions are similar, which implies the strong hybridization existing between Ti and O atoms. It is well known that, in ferroelectric materials, there are a long-range coulomb force and a short-range repulsion force, and they compete with each other according to the previous first-principles calculations.[39,40] Contrary to the short-range repulsion, the Coulomb force can stabilize the ferroelectric property. In ABO_3 perovskite, the strong hybridization between B atom and O atom suppresses the repulsion force, which stabilizes the ferroelectric properties. Therefore, the strong hybridization between Ti and O atoms in superlattice BST drives the occurrence of ferroelectricity similar to the case of bulk $BaTiO_3$.[41,42] For Ba and Sr atoms, there exist three peaks. Only one peak ranges from 5 to 10 eV, which indicates the weak hybridization between Ba (Sr) and O atoms.

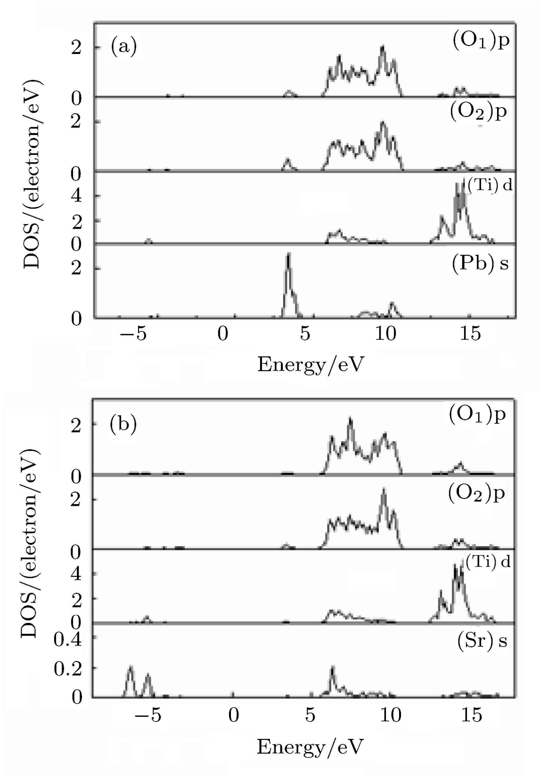
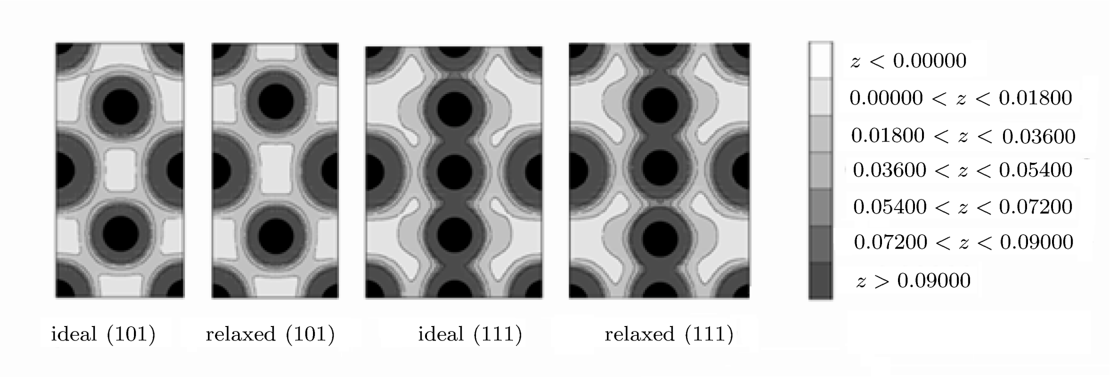


Fig.2. DOS profiles of $PbTiO_3$ layer (a) and $SrTiO_3$ layer (b) in PST superlattices.

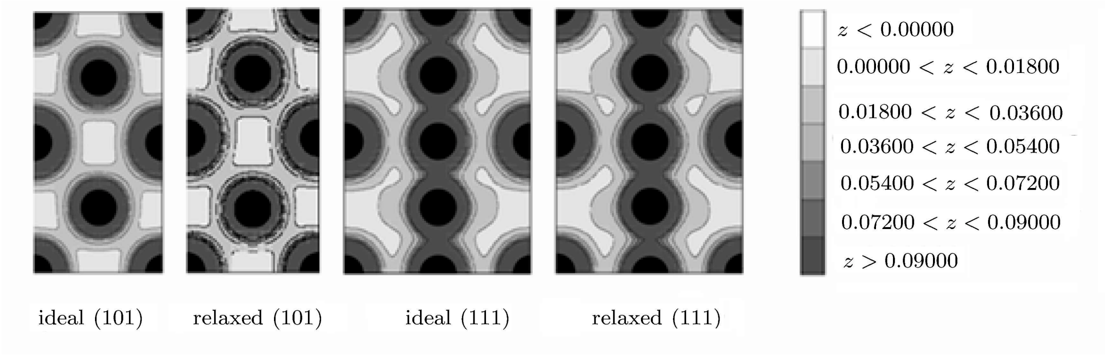
Figure 2 shows the DOS profiles of $PbTiO_3$ (PT) layer and ST layer in PST superlattices. The DOS profiles of Ti and O atoms distribute in a range from 5 to 16 eV. Similar to that in the BST superlattice, the strong orbital hybridization between Ti and O atoms leads to the ferroelectric property in the PST. For Pb atoms, there are mainly two peaks: one ranges from 7 to 11 eV and the other is around 4 eV, while DOS profile peaks of Sr atom exist around −5.5, −6.5 and 6.5 eV. For O atoms, the DOS profile peaks mainly distribute in a range from 5 to 16 eV, and the additional DOS profile peak in PT layer appears around 4 eV. Obviously, distributions of DOS profiles of O and Pb atoms are similar. Thus the interaction between Pb and O atoms is stronger than that between Sr and O atoms. In ABO_3 ferroelectric perovskite, the strong interaction between Pb and O atoms favours the ferroelectricity. [38] The Strong interaction between Pb and O atoms in superlattice PST induces the ferroelectricity, which is consistent with the description in Table 1.

The electronic density profiles of the ideal and relaxed BSTs in vertical and diagonal planes are shown in Fig.3, which we can see a large electronic charge density between Ti and O atoms. This means that there is a strong hybridization existing between Ti and O atoms, which is in agreement with the description in Fig.1. Comparing the charge density of ideal BST with that of relaxed BST, we find that the charge density of ferroelectric BST is distorted due to the displacement of atoms induced by the misfit strain in BST. Figure 4 describes the profiles of the ideal and relaxed PSTs in vertical and diagonal planes. Charge density of PST in Fig.4 shows a similar character to that of BST.



ideal (101) relaxed (101) ideal (111) relaxed (111)

Fig.3. The electronic density profiles of ideal and relaxed BSTs in vertical and diagonal planes.



ideal (101) relaxed (101) ideal (111) relaxed (111)

Fig.4. The electronic density profiles of ideal and relaxed PSTs in vertical and diagonal planes.

3.3. Polarization behaviours in superlattices

The tetragonalities c/a and polarizations of various period-5 superlattices of PST and BST are indicated in Table 3. With the fraction of $SrTiO_3$ increasing, c/a and polarization of superlattice decline. We conclude that the superlattice with a larger c/a has a larger polarization. In a 5/0 PST superlattice, the polarization is 80.81 $\mu C/cm^2$, which is slightly larger than that of bulk $PbTiO_3$. The slight enhancement in polarization is attributed to the small misfit strain in PST. When only one $SrTiO_3$ exists in 4/1 superlattice unit cell, c/a decreases from 5.24 to 5.14 and the polarization declines to a value of 57.75 $\mu C/cm^2$. When the number of ST layer n increases from 1 to 5 in unit cell of period-5 superlattice, the polarization and c/a can evenly decrease. The polarization of 1/4 PST becomes 8.9 μC/cm^2. Similar polarization behaviours have been found in $KNbO_3/KTaO_3$ superlattice,[12] because it has a small misfit strain (0.5%), which is close to the misfit strain of PST. In BST superlattices, there is a similar tendency of polarization with increasing the content of $SrTiO_3$, which is similar to the result in Ref.[4]. The superlattices in our calculations grow on the $SrTiO_3$ substrates. More fractions of $SrTiO_3$ in superlattices PST and BST can reduce the polarization energy, which leads to a decrease in the polarization. According to an electrostatic model, the paraelectric ST layers in superlattices are polarized by an internal electric field induced by the polarization mismatch between $PbTiO_3$ ($BaTiO_3$) and $SrTiO_3$, and the polarization in PT (BT) layer is reduced by the internal electric field. With the fraction of ST layer increasing in period-5 superlattices PST (BST), the internal electric field in each ST layer decreases due to the larger distance between PT (BT) layers. So the polarization of ST layer declines with ST layer increasing. The internal electric field in superlattices eliminates the polarization mismatch between ST layer and PT (BT) layer.[43,44] Thus the polarization of PST (BST) decreases with the fraction of ST layer increasing.

From Table 3, we find that the polarization of PST is larger than that of BST, when they have the same ratio of components m/n. The polarizations of BSTs with various ratios of components agree with the results in previous investigation,[4] which confirms our results to be reasonable. It is also indicated that the ferroelectric natures of $BaTiO_3$ and $PbTiO_3$ have an important effect on the polarization of superlattice. Our results confirm that the polarization of $PbTiO_3$ is much larger than that of $BaTiO_3$, implying that there exists a larger polarization mismatch between PT layer and ST layer in PST than between BT layer and ST layer in BST. Thus comparing with the polarization of ST layer in BST, we find that a large polarization of ST layer in PST is induced by a bigger internal electric field. So the polarization of PST is larger than that of BST with the same m/n.

Table 3. Structural parameters for superlattices with in-plane lattice constant $a = 7.285$ Bohrs, m layers of $BaTiO_3$ ($PbTiO_3$) and n layers of $SrTiO_3$.

PST			BST		
m/n	c/a	$P/(\mu C/cm^2)$	m/n	c/a	$P/(\mu C/cm^2)$
5/0	5.24	80.81	5/0	5.32	37.65
4/1	5.14	57.75	4/1	5.235	34.92
3/2	5.09	40.28	3/2	5.17	30.84
2/3	5.05	24.75	2/3	5.12	26.29
1/4	5.015	8.9	1/4	5.05	14.35
0/5	5	0	0/5	5	0

In order to investigate the polarizations of PST and BST more accurately, the ratios between the polarization of PST superlattice and the polarization of bulk $PbTiO_3$ and between the polarization of BST superlattice and the polarization of bulk $BaTiO_3$ are calculated, which are shown in Fig.5. In Fig.5, it can be seen that the polarization ratio P/P_0 of BST superlattices exceeds 1, indicating that there appears a polarization improvement in BST as responding to $BaTiO_3$, which is supported by previous experiments.[45,46] In contrast, the polarization values of PST superlattices are smaller than those of bulk $PbTiO_3$. This is because the misfit strain in BST superlattice is much larger than that in PST superlattice.

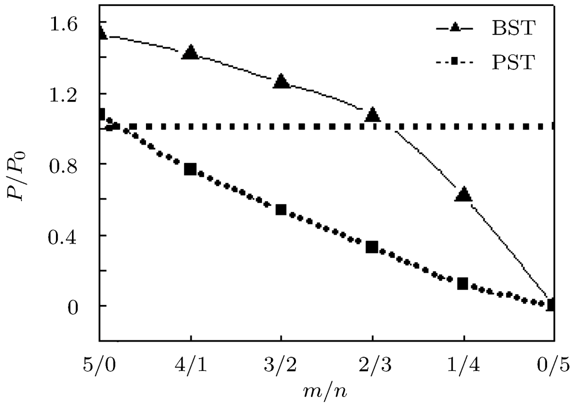


Fig.5. Polarization ratio P/P_0 of PST (BST) as a function of constituents ratio m/n (P is polarization of PST (BST), P_0 is polarization of bulk $PbTiO_3$($BaTiO_3$).)

4. Summary and conclusions

We have utilized the first-principles calculation to investigate the electronic structures and polarization behaviours of PST and BST superlattices. The conclusions drawn from the results are summarized as follows:

1. According to DOS and electronic charge profiles, the strong hybridization between Ti and O atoms is critical in the formation of ferroelectricities of PST and BST superlattices. Besides the hybridization between Ti and O atoms, hybridization between Pb and O atoms favours the ferroelectricity in PST superlattices.

2. With the fraction of $SrTiO_3$ increasing, the internal electric field in ST layer decreases, inducing a reduction in polarization and tetragonality c/a for BST and PST superlattices.

3. The misfit strain in BST induces an improvement in polarization compared with the polarization of bulk $BaTiO_3$, and the polarization in PST reduces as compared with the polarization of bulk $PbTiO_3$. But due to the larger polarization mismatch in PST, the polarization in PST is larger than that in BST at the same ratio of components.

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