Vol 17 No 1, January 2008
1674-1056/2008/17(01)/0274-07

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Surface rumples and band gap reductions of cubic $BaZrO_3$ (001) surface studied by means of first-principles calculations*

Zhang Chao(张 超)†, Wang Chun-Lei(王春雷), Li Ji-Chao(李吉超), Yang Kun(杨 鲲), Zhang Yan-Fei(张艳飞), and Wu Qing-Zao(吴清早)

School of Physics and Microelectronics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, *China*

(Received 25 December 2006; revised manuscript received 11 June 2007)

Electronic properties of the (001) surface of cubic $BaZrO_3$ with BaO and ZrO_2 terminations have been studied using first-principles calculations. Surface structure, partial density of states, band structure and surface energy have been obtained. We find that the largest relaxation appears in the first layer of atoms, and the relaxation of the BaO-terminated surface is larger than that of the ZrO_2-terminated surface. The surface rumpling of the BaO-terminated surface is also larger than that of the ZrO_2-terminated surface. Results of surface energy calculations reveal that the $BaZrO_3$ surface is likely to be more stable than the $PbZrO_3$ surface.

Keywords: surface, band gap, $BaZrO_3$, first-principles
PACC: 6820, 7300, 7115M

1. Introduction

Because of the importance of the surface effect in their film structures, the surface structures of ferroelectric ABO_3 perovskite have been investigated extensively. Successful application of first-principles calculations in bulk perovskite ferroelectrics[1−5] has encouraged the application of this method to the surface properties of ferroelectrics.[6−11] Meyer *et al*[8] have performed first-principles calculations for the surfaces of $PbTiO_3$, $SrTiO_3$ and $BaTiO_3$. They have found that $BaTiO_3$ and $SrTiO_3$ have a rather similar surface electronic structure, while $PbTiO_3$ has a different surface electronic structure because of the partially covalent character of the Pb–O bonds. The largest relaxations are found in the first layer atoms on the TiO_2-terminated surface of $BaTiO_3$[6] and $SrTiO_3$.[7] However, the largest relaxations are in the second layer atoms of $PbTiO_3$[8] on a TiO_2-terminated surface. From analysing the band structure of the AO-terminated (A = Ba or Sr) surfaces, it has been found that the surface state appears at the M point of the Brillouin zone. Also it has been found that for $BaTiO_3$ and $SrTiO_3$ surfaces,[6,7] both kinds of surface terminations, i.e., BaO- or SrO-terminated and TiO_2-terminated surfaces can be thermodynamically stable. Only the PbO-terminated surface is stable in $PbTiO_3$. The structure relaxation and the electronic structure of (001) surface of cubic $PbZrO_3$ (PZO) and $PbTiO_3$ (PTO) have been calculated using the full potential linearized augmented plane wave (FLAPW) method.[10] The largest relaxations are also found in the second layer of atoms on the ZrO_2-terminated surface of $PbZrO_3$. This result is similar to that in $PbTiO_3$ but differs from that found in $SrTiO_3$ and $BaTiO_3$. Analysis of the structure relaxation parameters reveals that the rumpling of the (001) surface of $PbZrO_3$ with the PbO-terminated surface is stronger than that of $PbTiO_3$. For the PbO-terminated surface of $PbZrO_3$, the surface state appears at the X point in the band structure. Meanwhile, the surface state appears at M point for ZrO_2-terminated surface.

Barium zirconate ($BaZrO_3$, BZO) is a perovskite oxide with a large lattice constant. Due to its particular physical properties, e.g., a high melting point, small thermal expansion coefficient, low dielectric loss and low thermal conductivity, BZO finds application in many fields.[12−23] In addition, BZO does not undergo a structural transition in the whole temperature

*Project supported by the National Basic Research Program of China (Grant No 2007CB607504) and the National Natural Science Foundation of China (Grant No 10474057).
†E-mail: zhangchao40@mail.sdu.edu.cn

range. It remains in cubic paraelectric phase when the temperature is cooled down to 2 K. These properties make BZO a very good candidate used as an inert crucible in crystal growth techniques,[18,22] an excellent material for wireless communications,[12,21] and a very good substrate in thin film techniques.[12,14] Noticeably, BZO is one of the two parent compounds in the Ba(Zr, Ti)O_3 solid solutions, which are promising for manufacturing high Q materials with a variety of applications in microwave devices. The surface effect of BZO plays an important role in these applications, especially as a substrate for thin film deposition. So the understanding of the BZO surface structure on the atomic scale is quite helpful for film fabrication and device design. In the present work, the (001) surface structure of cubic BZO is studied using first-principles calculations. The remainder of the paper is divided as follows. In Section 2, we describe the technical aspects of first-principles calculations. In Section 3, the results are reported and discussed. Finally, the main conclusions are summarized.

2. Theoretical details

Our calculations have been carried out using ESPRESSO package,[24] which is based on the density functional theory with plane-wave pseudopotential (PWP) formalism. Local density approximation (LDA) with ultra-soft pseudopotential is used. Ceperley–Alder's exchange–correlation potential parametrized by the Perdew–Zunger scheme (CA–PZ)[25] is employed. Vanderbilt ultra-soft pseudopotentials[26] are adopted for each type of ions, in which the 5s, 5p and 6s electrons of Ba, the 4s, 4p, 4d and 5s electrons of Zr, the 5d, 6s and 6p electrons of Pb, and the 2s and 2p electrons of O are treated as in valence states. Brillouin zone integrations are performed with $10 \times 10 \times 2$ Monkhorst–Pack[27] k-point mesh for the surface structure. A plane-wave cutoff energy is set at 30 Ry, and correspondingly the charge density cutoff is at 120 Ry. This is four times the plane-wave cutoff energy,[28,29] and shows that the results are well converged.

Slab model are used in BZO surface calculations.[8] The slabs are symmetrically terminated and typically contain seven atomic layers. Two types of surface termination are selected in our calculations: BaO-terminated and ZrO_2-terminated. For a normal ABO_3 perovskite, AO and BO_2 layers are charge neutral, so that both kinds of terminated surfaces are non-polar. For the BaO-terminated surface, the slab consists of four BaO layers and three ZrO_2 layers, including 17 atoms; and for the ZrO_2-terminated surfaces, the slab consists of four ZrO_2 layers and three BaO layers, holding 18 atoms. The slab thickness is five-lattice-constant for both kinds of terminations. Two neighbouring slabs are separated by a two-lattice-constant vacuum region. The whole structure is of tetragonal symmetry with a space group P4mmm. Also calculations have been carried out for the $PbZrO_3$ (PZO) surface using a similar slab model for comparison. The unit cell of the (001) surface structure of BZO slab model is displayed in Fig.1. During the surface structure optimization, all atoms are fully relaxed with forces less than 0.5 mRy/bohr. To test the validity of our slab model, we enlarge the vacuum region to four times the thickness of the theoretical lattice constant and increase the number of layers to nine. Only a very slight difference in structure parameters has been yielded. This result shows that the vacuum region and the number of layers used in our slab model are adequate for the calculations.

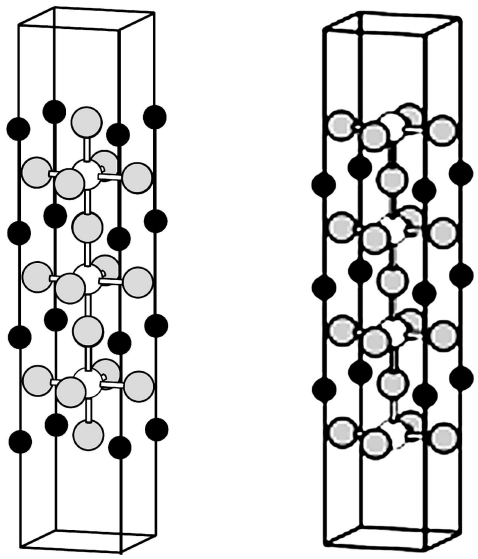


Fig.1. Unit cell for (001) surface structure of cubic $BaZrO_3$: the black, grey and white spheres represent the Ba, O and Zr atoms respectively. (a) BaO-terminated surface, (b) ZrO_2-terminated surface.

Before starting with the calculations for the surface structures, we have optimized the high-symmetry cubic (Pm3m) phase of BZO and PZO using the same scheme with the $8 \times 8 \times 8$ Monkhorst-Pack k-

point mesh. Thereby the calculated lattice constant is 0.415 nm for BZO and 0.411 nm for PZO, both are a little smaller than the experimental value 0.419 nm of BZO and 0.413 nm of PZO.[30] The underestimated lattice constant is an artifact of the LDA. Theoretical lattice constants will be used in our calculations of surface structures in this work.

3. Results and discussion

3.1. Structure relaxation

In the surface structure calculations, atoms are allowed to relax along the z-axis of the (001) surface of cubic BZO from its ideal structure. The obtained atomic relaxation parameters of the BaO-terminated and ZrO_2-terminated surfaces are listed in Table 1, and corresponding parameters of PZO are listed in Table 2 together with early results of the (001) surface of cubic PZO from FLAPW method[10] in parentheses.

Table 1. Atomic displacements (relative to the ideal position) δz for the BaO-terminated and ZrO_2-terminated surfaces of $BaZrO_3$. Units are in percent of the theoretical lattice constant $a_0 = 0.415$ nm. δz is positive for the displacement toward the bulk.

layer	BaO-terminated	δz	ZrO_2-terminated	δz
1	Ba	4.1	Zr	2.8
	O	0.2	O	2.5
2	Zr	−1.0	Ba	−1.5
	O	0.2	O	0.04
3	Ba	0.9	Zr	0.4
	O	0.08	O	0.3

Table 2. Atomic displacements (relative to the ideal position) δz for the PbO-terminated and ZrO_2-terminated surfaces of $PbZrO_3$. Units are in percent of the theoretical lattice constant $a_0 = 0.411$ nm. The results from Ref.[10] using FLAPW are shown in parentheses for comparison.

layer	PbO -terminated	δz	ZrO_2 -terminated	δz
1	Pb	6.5 (6.9)	Zr	2.8 (2.9)
	O	−0.2 (0.02)	O	1.6 (1.8)
2	Zr	−2.0 (−1.7)	Pb	−4.3 (−4.2)
	O	−0.2 (0.04)	O	−0.5 (−0.4)
3	Pb	1.6 (1.7)	Zr	0.6 (0.7)
	O	0.03 (0.1)	O	0.07 (0.3)

Generally, the relaxation parameters show that for both kinds of surface termination, a substantial inward contraction towards the bulk occurs for the outmost surface layers, whereas for the second layers an outward relaxation of atoms relative to the ideal position is found. As can be seen from Table 1, for the BaO-terminated surface, Ba atoms move inward (toward the bulk) and the Zr atoms move outward (toward the vacuum). Therefore the lattice constant, if it can still be named, of the first atom layer is reduced. By analysing the relaxation parameters, we find that the closer the metal atoms are to the surface, the larger the displacement of the metal atoms is. For the BaO-terminated surface, the Ba atoms in the surface layer move inward by about 4.1% of the lattice constant, Zr atoms in the second layer move outward by about 1.0%. The Ba atoms in the third layer move inward by only about 0.9%, much less than that of the first layer Ba atoms. The same trend is true for the ZrO_2-terminated surface, where the inward displacement of Zr atoms in the first layer is 2.8%, and the outward displacement of Ba atoms in the second layer is 1.5%. Another interesting feature we can see from Table 1 is that the largest relaxations occur in the outmost surface layer of atoms for both types of surface terminations. However, the second layer atoms in BZO with ZrO_2 termination still have relatively large relaxations. By contrast, the relaxation decreases very quickly for BZO with the BaO-terminated surface. For the two types of surface terminations, the magnitude of the displacement of metal atoms is much larger than that of O atoms in the same layer. Therefore, the atoms in the same plane as in the bulk will not be staying at the very plane if the plane is near the surface. This leads to surface rumpling when the atoms are in the surface layer. As the displacement of O atoms in the first layer of the ZrO_2-terminated surface is comparable to that of the Zr atoms, this causes a small rumpling of the ZrO_2-terminated surface, which is quite different from the first layer of the BaO-terminated surface.

The structural parameters obtained in this work show the same trend as previous calculations[10] for atomic displacement during the relaxation, although the values of parameter are slightly different. As can be seen from Table 2, the largest relaxation in PZO with PbO-termination appears at the surface layer, while for ZrO_2-termination surface the largest relaxation appears at the second layer. The dramatic difference of the relaxation behaviour between BZO and that of PZO happens on the ZrO_2-terminated surface, as can be seen from Tables 1 and 2. The largest relaxation for the BZO surface occurs with the Zr atoms

in the first layer, while for PZO it occurs with the Pb atoms in the second layer. Another major difference between the BZO and PZO surface is the behaviour of O atoms in the first and second layers of the BaO- or PbO-terminated surface. In the BZO surface, the O atoms at the first two layers move inwards, while they move outwards in the PZO surface.

To describe the change of the surface structure after relaxation more clearly, surface rumpling parameter s and interlayer distance Δd_{ij} are introduced. The magnitude of the surface rumpling parameter s measures the displacement of oxygen with respect to metal atoms in the surface layer, which reflects the relative displacement between the surface layer atoms. The parameter Δd_{12} is defined as the change of the interlayer distance measured from the first layer metal atoms to the second layer metal atoms along the z-direction. Similarly, Δd_{23} is defined as the distance between the second and third layers. Structural parameters for the two types of surfaces of BZO are presented in Table 3 together with that of PZO from our present calculations as well as earlier calculations by FLAPW, where one can notice that the values of s, Δd_{12}, and Δd_{23} for the PZO in the present work are in fairly agreement with the results of FLAPW method.[10] It can be easily seen that the surface rumpling of the BaO-terminated surface is much larger than that of the ZrO_2-terminated surface. The lattice constant between the first and second layers is reduced, while the lattice constant between the second and third layers is expanded. Generally, these surface structure features of BZO are similar to that of PZO. However, the surface rumpling in BZO with BaO-termination is much smaller than that in PZO, which implies that the BZO surface is flatter than that of PZO, especially for the BZO surface with ZrO_2-termination.

Table 3. Surface relaxation parameters (in percent of lattice constant) for $BaZrO_3$ and $PbZrO_3$.

		s	Δd_{12}	Δd_{23}
BaO- or PbO-terminated				
BZO	this work	3.86	−5.13	1.92
PZO	this work	6.69	−8.47	3.56
	FLAPW (LDA) [10]	6.88	−8.6	3.4
ZrO_2-terminated				
BZO	this work	0.27	−4.31	1.94
PZO	this work	1.19	−7.15	4.91
	FLAPW (LDA) [10]	1.1	−7.1	4.9

From the third column of Tables 1 and 2, it can be easily seen that the displacement of the Ba atoms in BZO is smaller than that of the Pb atoms in PZO during surface relaxation. To understand this difference, we compute the total energy change of the (001) surface system for BZO and PZO as a function of the displacement of the Ba and Pb atoms along the [001] direction, as shown in Fig.2. For BZO, the total energy of unrelaxed BaO-terminated surface is set at zero. In this calculation, only the Ba atoms in the surface layer move along the [001] direction, other atoms are fixed. So the total energy becomes smaller, and then larger. This result also confirms the fact that the Ba atoms move inward by 4.1% of the lattice constant in the stable structure (see Table 1). The similar explanation can be applied to the case of PZO. It can be seen that the total energy for PZO changes more greatly and rapidly than that for BZO with the same atomic displacement. This means that the Pb atoms in PZO can be more easily moved away from its ideal positions than Ba atoms in BZO.

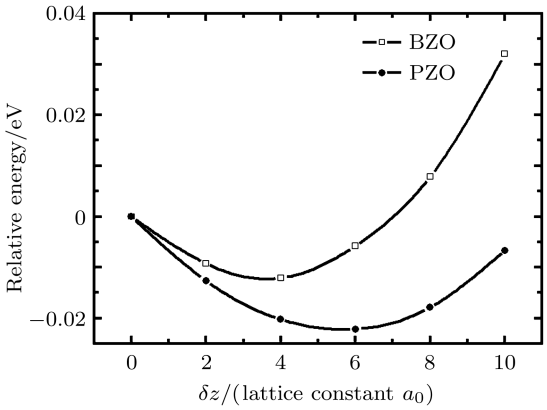


Fig.2. Relative total energy as a function of the atomic displacement δz (relative to the lattice constant a_0) of the Ba or Pb atoms in the first layer along the [001] direction for the BaO- or PbO-terminated surface structures of $BaZrO_3$ and $PbZrO_3$.

3.2. Band structure and density of states

Figure 3 shows the band structure of BZO with BaO- and ZrO_2-terminated relaxed surfaces respectively, the projected band structures of cubic bulk BZO being also shown for comparison. In general, our results for the band structure of the surfaces of $BaZrO_3$ are similar to the case of $BaTiO_3$.[6] On the one hand, there is a tendency of the band structure for the ZrO_2-terminated surface to extend upward near

the M point of the Brillouin zone by comparing with that of the bulk system. On the other hand, the top of the valence band for the BaO-terminated surface is relatively flat throughout the Brillouin zone with the indirect gap between M and Γ points. The gap value is 3.09 eV, which is slightly smaller than the bulk band gap of 3.15 eV.

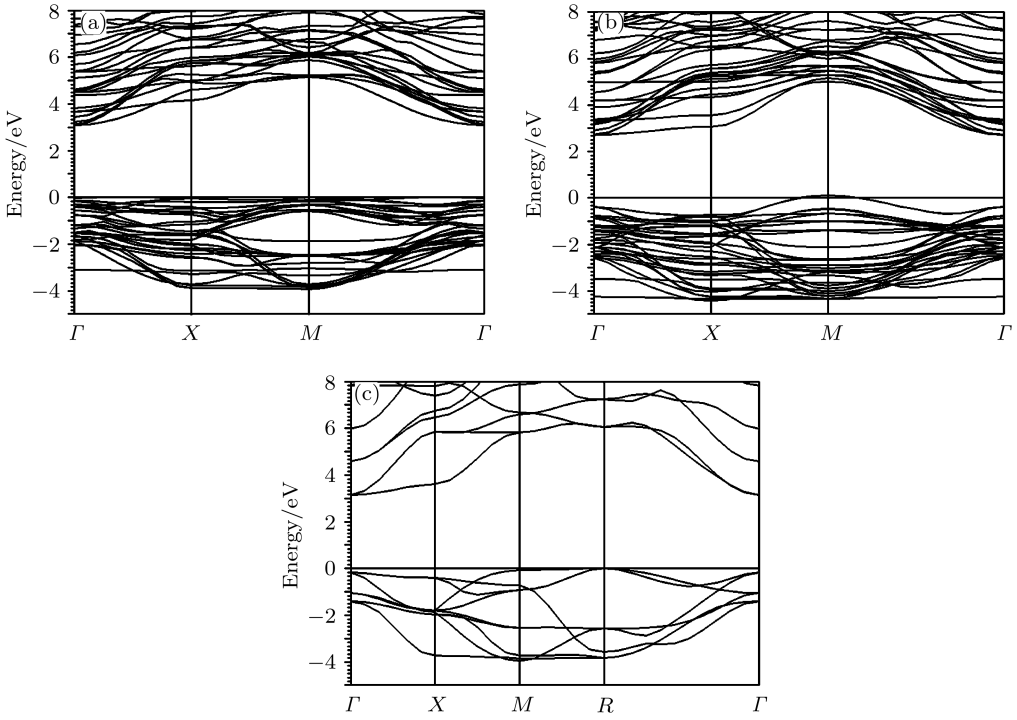


Fig.3. Band structure for $BaZrO_3$: (a) BaO-terminated surface, (b) ZrO_2-terminated surface, (c) Bulk band structure.

Figures 4 and 5 show the density of states (DOS) for the BaO- and ZrO_2-terminated surfaces respectively. By analysing the DOS calculated for the BaO-terminated surface shown in Fig.4, we can see that

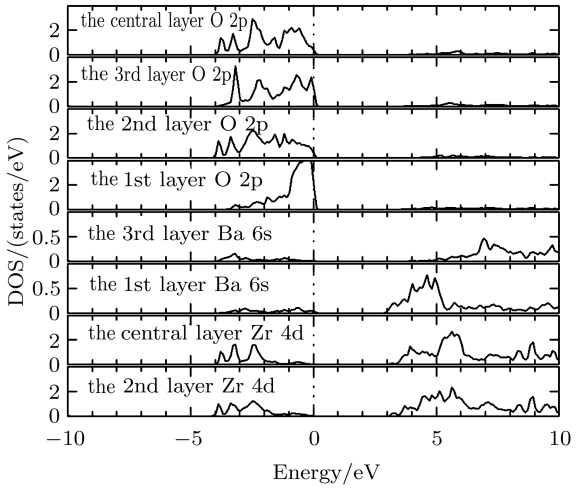


Fig.4. Partial DOS for each layer of the BaO-terminated $BaZrO_3$ surface.

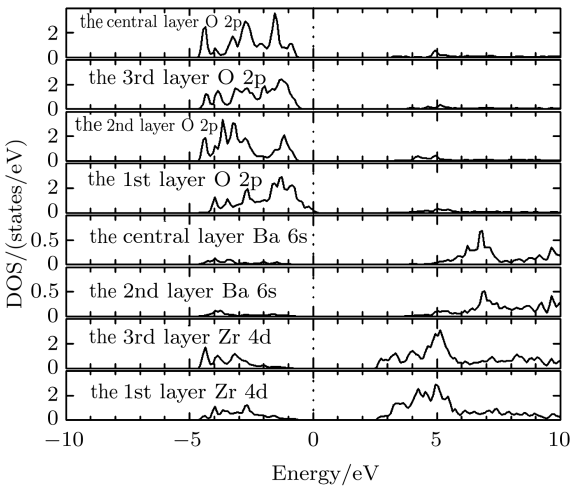


Fig.5. Partial DOS for each layer of the ZrO_2-terminated $BaZrO_3$ surface.

the O-2p electronic states make a great contribution to the valence band top. Moreover, the conduction band bottom is largely composed of Zr-4d and Ba-6s electronic states. The electronic states of O-2p in the first layer move up to the top of the valence band

more than O atoms in the other layers. The first layer Ba-6s electronic states move to the lower energy side. The partial DOS of the second layer of Zr-4d electronic states seems to be the same as that of central layer Zr-4d electronic states. Therefore, the reduction of the band gap of the BaO-terminated surface is mainly a result of the first layer atoms, especially Ba-6s electronic states. Consequently, the presence of this surface, especially the surface of Ba and O atoms, changes the band electronic structure.

3.3. Surface energy

The surface energy $E_{\rm s}$ of BZO is defined as the average surface energy of the two slabs[8]

$$E_{\rm s} = \frac{1}{4}[E_{\rm slab}({\rm I}) + E_{\rm slab}({\rm II}) - 7E_{\rm bulk}], \qquad (1)$$

where $E_{\rm slab}$(I), $E_{\rm slab}$(II), and $E_{\rm bulk}$ are the total energies of the relaxed BaO-terminated slab, the relaxed ZrO_2-terminated slab and the bulk crystal per unit cell respectively. A factor of 1/4 is derived from the fact that we have created four surfaces during the cleavage procedure. The factor of 7 in the above expression comes from the fact that the two seven-layer BaO- and ZrO_2-terminated surfaces together representing seven bulk unit cells. The cleavage energy $E_{\rm cle}$ and the relaxation energy $E_{\rm rel}$ are defined as,

$$E_{\rm cle} = \frac{1}{4}\left[E_{\rm slab}^{\rm (unrel)}({\rm I}) + E_{\rm slab}^{\rm (unrel)}({\rm II}) - 7E_{\rm bulk}\right], \qquad (2)$$

$$E_{\rm rel}({\rm I}) = \frac{1}{2}\left[E_{\rm slab}({\rm I}) - E_{\rm slab}^{\rm (unrel)}({\rm I})\right], \qquad (3)$$

where $E_{\rm slab}^{\rm (unrel)}$(I), $E_{\rm slab}^{\rm (unrel)}$(II) and $E_{\rm slab}$(I) are the total energies for the unrelaxed BaO-terminated slab, the unrelaxed ZrO_2-terminated slab and the relaxed BaO-terminated slab respectively. The average surface energy, the cleavage energy and the relaxation energy of BZO and PZO are listed in Table 4. We can easily see that the cleavage energy of BZO is higher than that of PZO. The absolute values of the relaxation energy of the two types of terminations in BZO both are smaller than that in PZO. In a word, the surface energy of BZO is higher than that of PZO. A smaller surface energy means an easier cleavability under the condition that the migration of atoms can be neglected. Therefore, the surface of BZO might be more difficult to construct than the PZO surface. In other words, the results of surface energy imply that the BZO surface may be more stable than PZO surface.

Table 4. Average surface energy (in eV/a_0^2) for $BaZrO_3$ and $PbZrO_3$.

	$E_{\rm cle}$	$E_{\rm rel}$(I)	$E_{\rm rel}$(II)	$E_{\rm s}$
BZO	1.49	–0.12	–0.14	1.36
PZO	1.35	–0.23	–0.20	1.14

4. Conclusion

From LDA-PWP calculations of the structure and the electronic properties of the BaO- and ZrO_2-terminated (001) $BaZrO_3$ surfaces, we find that the largest relaxations appear on the first layer atoms for both ZrO_2- and BaO-terminated surfaces. The analysis of the structure relaxation parameters reveals that the rumpling of the surface structure for $BaZrO_3$ is relatively small, at least in comparison with that of the $PbZrO_3$ surface. The rumpling of the ZrO_2-terminated surface is smaller than that of BaO-terminated surface, suggesting that surface termination with ZrO_2 is relatively flatter than that with BaO. A comparison of the band structure of the ZrO_2-terminated surface with that of the bulk $BaZrO_3$ reveals that the surface state appears near the M point of Brillouin zone. A relatively large surface energy has been found for $BaZrO_3$, which gives evidence that the $BaZrO_3$ surface is not so easily constructed as the $PbZrO_3$ surface.

References

[1] Cohen R E 1992 *Nature* **358** 136

[2] Singh D J 1997 *Ferroelectrics* **194** 299

[3] Xue W D, Chen Z Y, Yang C and Li Y R 2005 *Acta Phys. Sin.* **54** 0857 (in Chinese)

[4] Meng X, Xu X G, Liu W, Sun Y and Chen G 2004 *Acta Phys. Sin.* **53** 3873 (in Chinese)

[5] Zhang C, Wang C L, Li J C and Yang C 2007 *Chin. Phys.* **16** 1422

[6] Padilla J and Vanderbilt D 1997 *Phys. Rev.* B **56** 1625

[7] Padilla J and Vanderbilt D 1998 *Sur. Sci.* **418** 64

[8] Meyer B, Padilla J and Vanderbilt D 1999 *Faraday Discuss* **114** 395

[9] Xue Y X, Wang C L and Zhong W L 2004 *Chin. Phys. Lett.* **21** 825

[10] Wang Y X, Arai M, Sasaki T, Wang C L and Zhong W L 2005 *Sur. Sci.* **585** 75
[11] Yang K, Wang C L, Li J C, Zhang C, Wu Q Z, Zhang Y F, Yin N and Liu X Y 2006 *Chin. Phys.* **15** 1580
[12] Dobal P S, Dixit A, Katiyar R S, Yu Z, Guo R and Bhalla A S 2001 *J. Appl. Phys.* **89** 8085
[13] Azad A-M and Subramaniam S 2002 *Mater. Res. Bull.* **37** 11
[14] Azad A-M, Subramaniam S and Dung T W 2002 *J. Alloy Compd.* **334** 118
[15] Robertz B, Boschini F, Cloots R and Rulmont A 2001 *Int. J. Inorganic Mater.* **3** 1185
[16] Lecerf N, Mathur S, Shen H, Veith M and Hufner S 2001 *Scripta Mater.* **44** 2157
[17] Taglieri G, Tersigni M, Villa P L and Mondelli C 1999 *Int. J. Inorganic Mater.* **1** 103
[18] Celik E, Akin Y, Mutlu I H, Sigmund W and Hascicek Y S 2002 *Physica* C **382** 355
[19] Koopman M, Duncan S, Chawla K K and Coffin C 2001 *Compos.* Part A **32** 1039
[20] Brzezinska-Miecznik J, Haberko K and Bucko M M 2002 *Mater. Lett.* **56** 273
[21] Chai L, Akbas M A, Davies P K and Parise J B 1997 *Mater. Res. Bull.* **32** 1261
[22] Erb A, Walker E and Flukiger R 1995 *Physica* C **245** 245
[23] Langhorn J B and McGinn P J 1999 *Physica* C **323** 79
[24] Baroni S, Corso D A, Gironcoli S, Giannozzi P, Cavazzoni C, Ballabio G, Scandolo S, Chiarotti G, Focher P, Pasquarello A, Laasonen K, Trave A, Car R, Marzari N and Kokalj A http://www.pwscf.org/
[25] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
[26] Vanderbilt D 1990 *Phys. Rev.* B **41** 7892
[27] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
[28] Pasquarello A, Laasonen K, Car R, Lee C and Vanderbilt D 1992 *Phys. Rev. Lett.* **69** 1982
[29] Laasonen K, Pasquarello A, Car R, Lee C and Vanderbilt D 1993 *Phys. Rev.* B **47** 10142
[30] King-Smith R D and Vanderbilt D 1993 *Phys. Rev.* B **47** 1651