Ab Initio Calculations for the BaTiO$_3$ (001) Surface Structure

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The ab initio method within the local density approximation is applied to calculate cubic BaTiO$_3$ (001) surface relaxation and rumpling for two different terminations (BaO and TiO$_2$). Our calculations demonstrate that cubic perovskite BaTiO$_3$ crystals possess surface polarization, accompanied by the presence of the relevant electric field. We analyse their electronic structures (band structure, density of states and the electronic density redistribution with emphasis on the covalency effects). The results are also compared with that of the previous ab initio calculations. Considerable increases of Ti–O chemical bond covalency nearby the surface have been observed. The band gap reduces especially for the TiO$_2$ termination.

Size effects on phase transition in ferroelectrics have been known since the 1950s.[1,2] Recently there has been much attention directed to this area again, because of the development and application of thin-film ferroelectrics and composite materials. Barium titnanate (BaTiO$_3$) is a ferroelectric as well as a wideband-gap semiconductor, and has many applications such as non-volatile ferroelectric memory. Grain boundaries and the state of the surface are supposed to play a major role in these applications, and a large number of studies of BaTiO$_3$ surface have been carried out to understand surface structure variations under different conditions. Previous scanning tunnelling microscopy (STM) and low-energy electron diffraction (LEED) investigations of the BaTiO$_3$ (100) surface have indicated (2×1) and $(\sqrt{5} \times \sqrt{5})$ R26.6° surface superstructure.[3−5] Experimental studies of perovskite surfaces are complicated by the presence of surface defects,[6] which make it difficult to verify the surface stoichiometry. Therefore, most experimental observations have not been conclusive. On SrTiO$_3$ surfaces, the situation is slightly better; studies of SrTiO$_3$ surfaces show evidence for minor relaxations by motions of atoms perpendicular to the surfaces[7] but do not show any evidence for states in the gap.[8] For BaTiO$_3$ surfaces, the experimental reports seem to be less conclusive.

Ab initio calculations have been successfully employed to study properties of bulk ferroelectrics[9,10] and have deepened our understanding of the origin of ferroelectricity. However, applications of the ab initio method to surface properties are daunting due to the giant computational burden. Several ab initio theoretical calculations[11−13] have been published to study the (001) and (111) surface relaxations of BaTiO$_3$ crystals. In all of the research, the (001) surface is found to be much more stable than the (111) surface. There exist Ti- and Ba-containing top layers in the (001) BaTiO$_3$ surfaces. The Ti-containing top layer is slightly more stable than the Ba-containing one, and large polarization of ions in the first two layers of the surface is found. In the present study, we calculate the relaxed atomic structure and electronic structure of the BaTiO$_3$ (001) surface for the cubic phase. One motivation is to see if there is enhancement of the Ti–O covalent bonding near the surface in BaTiO$_3$, since this kind of enhancement has been reported in SrTiO$_3$.[14]

The periodic first-principles calculations are performed using the CASTEP computer code,[15] which is based on density functional theory using a plane-wave pseudopotential formalism, aided by the Materials Studio graphical front-end.[16] The computations are performed via the local density approximation (LDA) using revised CA-PZ functionals[17] and ultra-soft pseudopotentials. The geometries for all the systems are optimized by using a conjugated gradient technique in a direct minimization of the Kohn–Sham energy functional.[18] The pseudopotential atomic configurations for Ti, Ba, and O are identical in surface slab and bulk perovskite, chosen for the Ti $3s2$ $3p6$ $3d2$ $4s2$ states, the O $2s2$ $2p4$ states and the Ba $5s2$ $5p6$ $6s2$. A plane-wave cutoff energy of 300 eV has been used throughout, which has shown that the results are well converged at this cutoff. For the crystal reciprocal-lattices, integrations over the symmetrized Brillouin zone were performed by a sum over special k-points generated via the Monkhorst–Pack scheme.[19]

Before starting the surface calculations, we check the method on the cubic perovskite properties of the BaTiO$_3$ crystal. The lattice constant calculated for bulk BaTiO$_3$ is $a = 3.977$ Å, which is almost as much as the experimental value. The surface initial parameters used in the surface slabs are those found to give the minimum energy for bulk cubic BaTiO$_3$. For a perfect (001) terminated surface, two configurations are possible: (a) Ba and O termination with a ratio of 1:1 (essentially BaO) (type I); or (b) Ti and O

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termination with a ratio of 1:2 (TiO_2 stoichiometry) (type II). In both types, the slabs consist of seven BaO and TiO_2 layers with a 10 Å vacuum region in our calculations. Before surface relaxation, we fix the atomic fractional position of the four-lowest-layer atoms of the slab. Only the three topmost layers are relaxed in the calculations. Then the two slabs can be regard as a half-infinity crystal.

The atomic displacements in the three outmost $BaTiO_3$ planes are listed in Table 1. From the table, we can see that the largest relaxations are on the surface layer atom. In both cases, the surface ions are displaced inwards in the direction perpendicular to the surface, whereas the ionic displacements in the second and third layers are smaller than that in the first layer. The magnitudes of the ionic displacements decrease significantly for the deeper layers. Relaxation of atoms in the third layer is quite small. Also, due to the crystal termination, the two O atoms associated with the Ti atom are no longer equivalent in the surface layers. For the case of the BaO terminated surface, the surface Ba ions shift inwards by 6% of the bulk lattice constant ($a_0 = 3.977$ Å), whereas in the third layer the reduction is 2.2%. Ti ions are displaced inwards by $\approx 0.56\%$ in the second layer. The O ions also displace inward but their displacement magnitude is different from that of Ba and Ti ions. The displacement of every ion in the $x - y$ plane is nearly zero. On the other hand, for the TiO_2 terminated surface, the inward displacement of the surface Ti ions is $\sim 5.0\%$, and the outward displacement of the Ba ions in the second layer is 1.0%. The O ions displace inward but Ba ions displace outward in the second layer. Except for the displacement in the direction perpendicular to the surface, lateral displacement exists in the uppermost three layers in the TiO_2 terminated surface. The asymmetry between the two types of O atoms lying in a common TiO_2 surface plane is significant. The Ti displaces toward the positive directions of the x and y axes and O displaces toward the negative directions of the x and y axes. This causes order arrangement of the Ti and the four O around it.

Cohen[11] has computed the surface relaxations of $BaTiO_3$ slabs in the cubic phase and with its polarization normal to the surface. Thus, direct comparison with our work is only possible for the cubic phase. Cohen calculated the relaxation only for the case of an asymmetrically terminated slab (BaO on one surface and TiO_2 on the other). Thus, detailed quantitative agreement is probably not to be expected, because only the surface layer atoms were relaxed in his calculation. Nevertheless, we do find qualitative agreement. Cohen found that the Ba and O atoms relax inwards by 4.3% and 3.3% lattice constants, respectively, on the type I surface; and the Ti and O atoms relax inwards by 4.8% and 2.7% respectively on the type II surface. These values are smaller in magnitude, but have the same sign as those we obtain in the calcula-

tion.

Table 1. Calculated absolute atomic displacements of uppermost three layers for $BaTiO_3$ (001) from the ab initio LDA. Positive (negative) values refer to the displacements in the direction outwards (inwards) the surface. Note that in the calculations only atomic positions in the three outmost planes were optimized.

	Layer	Ion	Displacements (Å)		
			x	y	z
Slab I	1	Ba^{2+}	0	0	−0.263
		O^{2-}	0	0	−0.154
	2	Ti^{4+}	0	0	−0.022
		O^{2-}	0	0	−0.066
		O^{2-}	0	0	−0.066
	3	Ba^{2+}	0	0	−0.088
		O^{2-}	0	0	−0.066
Slab II	1	Ti^{4+}	0.083	0.079	−0.200
		O^{2-}	−0.103	−0.064	−0.080
		O^{2-}	−0.056	−0.103	−0.080
	2	Ba^{2+}	0.024	0.008	0.040
		O^{2-}	−0.024	0.008	−0.060
	3	Ti^{4+}	0.075	−0.068	−0.060
		O^{2-}	−0.024	0.052	−0.040
		O^{2-}	−0.028	0.075	−0.040

The obtained structural parameters together with the ab initio theoretical estimates of Padilla and Vanderbilt[13] are listed in Table 2. We define Δd_{12} as the change (with respect to bulk) of the first interlayer spacing, as measured from the surface to the subsurface metal z-coordinate, and similarly for Δd_{23}, quantity s measures the outward displacement of the surface-layer oxygen relative to the surface-layer metal atoms. It is evident that the agreement between our calculations and the result in Ref. [13] is good. Both our result and Padilla and Vanderbilt's give the same signs for both the rumpling and change in interplanar distances. The rumpling s of the surface layer is somewhat larger in magnitude than that of Ref. [13]. We predict a much larger substantial contraction of the interlayer spacing d_{12} than Padilla and Vanderbilt's. We are not aware of any previous experimental surface structure relaxation and rumpling determination for $BaTiO_3$. Our calculations could be important for more detailed experiments on surface rumpling and relaxation.

Table 2. Comparison of surface relaxations. Here Δd_{12} and Δd_{23} are the changes of interlayer spacings for the first and second pair of layers respectively, while s measures the outward displacement of the surface oxygen respect to the first-layer metal atoms. All quantities are in angstroms.

	s	Δd_{12}	Δd_{23}
BaO-terminated			
Present study	0.10	−0.214	0.0385
Ref. [11]	0.06	−0.146	0.059
TiO_2-terminated			
Present study	0.127	−0.234	0.104
Ref. [11]	0.10	−0.205	0.079

Our calculations show that Ti^{4+}, Ba^{2+}, and O^{2-} ions display very different displacements from their perfect-crystalline sites. This leads to the creation of a dipole moment at the surface. The induced dipole

moment in the BaO-terminated case is perpendicular to the surface, and in the TiO_2-terminated case it can be divided into ones perpendicular and parallel to the surface. For the TiO_2-terminated surface, the negative sign of the dipole moment perpendicular to the surface comes from a larger inward displacement of Ti^{4+} ions, in comparison with those for the O^{2-} ions. The opposite direction of the displacement of Ba^{2+} ions in the second layer only partly reduces the large dipole moment created by Ti displacements. In the surface, the order arrangement of Ti ions and O ions induces a dipole moment along the positive direction on the x and y axes. For the BaO-terminated surface the displacements of Ba ions are large and the same direction displacements of Ti ions in the second layer increase the surface dipole moment. In both cases, a large polarization in the near-surface layer takes place, which manifests itself through the displacements of the ions in the near-surface layer. The observed large polarization of the ions in the $BaTiO_3$ crystal indicates the existence of a strong electric field near the surface of this paraelectric crystal. The ab initio study on the $SrTiO_3$[20] (001) surface indicated that there does exist a small ferroelectric surface distortion for both the surface terminations. This dipole moment derived from the surface ion displacement in the $SrTiO_3$ surface is much smaller than that of $BaTiO_3$.
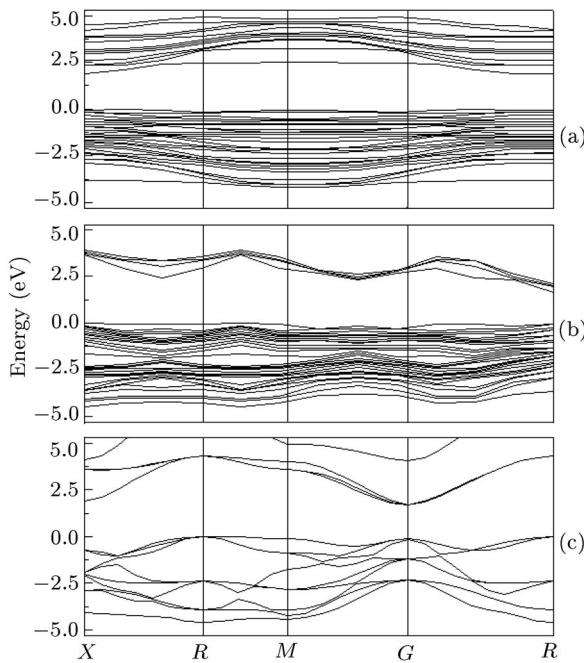
we can ensure that the results given here are at least qualitatively correct. The band gap obtained for bulk $BaTiO_3$ is 1.9 eV. Compared with the experimental value of 3.2 eV, this level of disagreement is typical for the LDA. Therefore, our results for the band structures of the surfaces of $BaTiO_3$ are very similar to the case of $SrTiO_3$ surfaces.[20] The computed LDA electronic energy band structure is shown in Fig. 1. It can be seen that the band gap for the BaO-terminated surface almost does not change with respect to that in the bulk case, and no in-gap state occurs. For the TiO_2 surface, there is a substantial reduction of the band gap. From Fig. 1(a) we can see that there is a
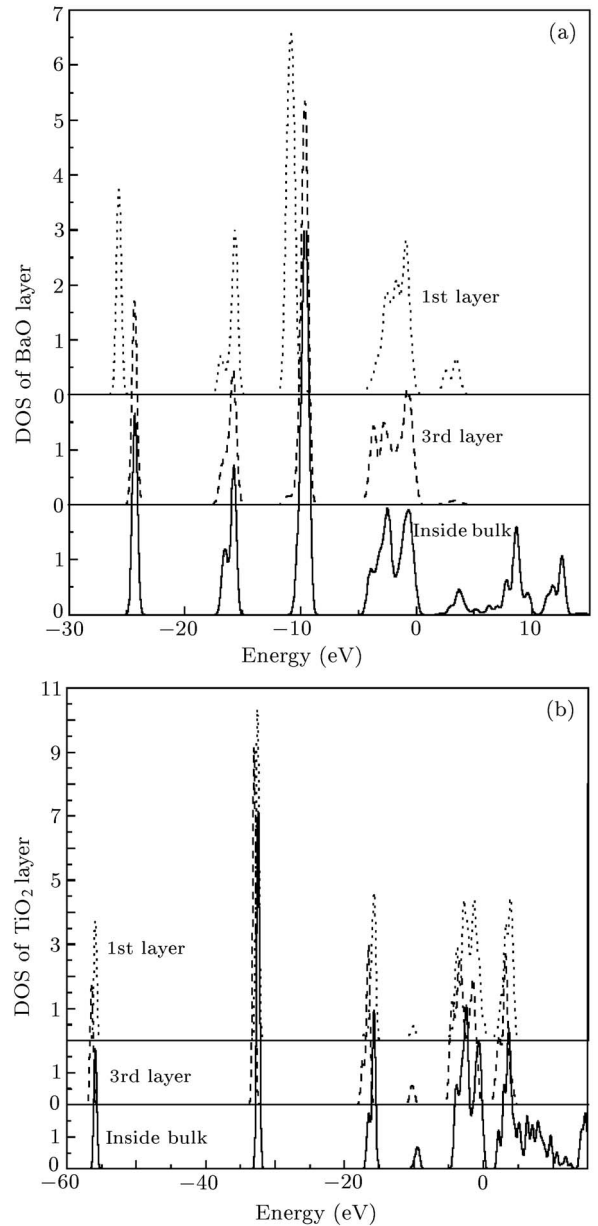

Fig. 1. Band structure for $BaTiO_3$ in the cubic phase (a) for TiO_2-terminated surface (slab II), (b) for BaO-terminated surface (slab I), and (c) for bulk. The zero energy corresponds to the bulk valence band maximum. Only the lowest few conduction bands and the upper valence bands are presented.

We now focus on the LDA-calculated electronic structure for the surfaces slabs. Although it is well known that the LDA underestimates the band gaps,

Fig. 2. (a) DOS projected BaO layer in the BaO-terminated surface and bulk $BaTiO_3$. (b) DOS projected TiO_2 layer in the TiO_2-terminated surface and bulk $BaTiO_3$. The solid, dashed, and dotted lines are for the layer in the bulk, third layer, and surface layer.

tendency for valence-band states to intrude upwards into the lower part of the band gap. For a more detailed study of the surface character, we performed calculation of DOS projected on different layers for the two slabs. Figure 2(b) demonstrates that the upper valence-band states of the surface TiO_2 layer have a visible shift to the higher energy region, and the lower conduction states shift to the lower energy region compared with that of the TiO_2 layer in the bulk. All of these shifts result in the reduction of the band gap of slab II. The lower part states of the valence band of the surface TiO_2 layer have no obvious changes compared with the TiO_2 layer in the bulk. Contrary results are observed for the BaO-terminated slab (see Figs. 1(b) and 2(a)). The valence and conduction states near the Fermi surface in the surface BaO layer are qualitatively the same as that of the bulk, but the DOS increases in the upper part of the valence band with resulting increase of number of valence band in Fig. 1(b). The lower part states of the valence band shift to the further lower energy region.
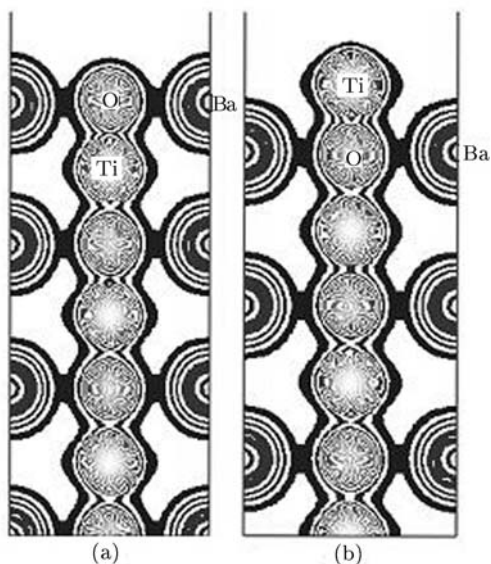

Fig. 3. Charge-density map for (110) cross section perpendicular to the (001) surface with (a) BaO and (b) TiO_2 terminations. The contour interval is 0.17 electron/Å^3.

The most intriguing results are the charge densities in Fig. 3. The electron densities confirm that the Ti–O covalency bond effects and the increase of covalency in the surface layers. These maps (calculated with respect to Ba^{2+}, Ti^{4+}, and O^{2-} ions) demonstrate considerable charge density redistribution for both the $BaTiO_3$ surface terminations. For both the slabs, the Ti–O bond nearest to the surface becomes stronger, but the next nearest bond becomes weaker. This electronic density phenomenon is in agreement with interplanar distances, namely a substantial contraction of the interlayer spacing d_{12} and an expansion of d_{23}.

There is no trace of covalent bonding between Ba and O atoms. The electronic density is shifted inwards the bulk on the slab-II surface and outwards on the slab-I surface. This can lead to surface polarization. Most interesting is the collapse of the surface Ti bond. Instead of dangling, the charge moves back onto the Ti and Ti–O surface bonds. This self-healing leaves the surface highly reactive and is probable for the utility of $BaTiO_3$ as a substrate for epitaxial growth and for surface catalysis. These results suggest that the Ti–O surface of $BaTiO_3$ is highly reactive due to the possibility of covalent bonding on the surface, whereas any reactivity Ba–O surface is entirely due to ionic bonding. The non-bonding O p surface state may also enhance surface reactivity.

In summary, from LDA density functional calculations of BaO- and TiO_2-terminated (001) surfaces of $BaTiO_3$ in a periodic half-infinity crystal, we have obtained large displacements of ions from their crystalline sites, which leads to the creation of the so-called surface rumpling, a dipole moment, and electric field in the near-surface region. This arises due to an atomic relaxation accompanying the surface creation, and affects layers near the surface. This surface turns out to be ferroelectric with properties different from those of the bulk material. Also, considerable increase of the Ti–O bond covalency near the surface is found. This could be important for the electronic structure of surface defects, as well as for adsorption and surface diffusion of atoms and small molecules relevant for catalysis.

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