Ab initio calculations of the BaTiO$_3$ (100) and (110) surfaces

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Abstract We present and discuss the results of calculations of BaTiO$_3$ (100) surface relaxation and surface rumpling with two different terminations (BaO and TiO$_2$) and BaTiO$_3$ (110) surface relaxation with three different terminations (Ba, TiO and O). These are based on a *hybrid* B3PW exchange-correlation technique. The O-terminated *A*-type BaTiO$_3$ (110) surface has a surface energy close to that for the (100), which indicates that both (110) and (100) BaTiO$_3$ surfaces can exist simultaneously in perovskite ceramics.

Keywords *Ab initio* calculations · BaTiO$_3$ · Surface relaxation · Surface energies · B3PW method

1 Introduction

Numerous high technology applications, including catalysis, microelectronics, substrates for growth of high T_c superconductors etc., are based on thin films of ABO$_3$ perovskite ferroelectrics [1, 2]. Several *ab initio* quantum mechanical [3–8] and classical shell model (SM) [9–11] studies have dealt with the (100) surface of BaTiO$_3$ and SrTiO$_3$ crystals. In order to study the dependence of the surface relaxation properties on exchange-correlation functionals and localized/plane wave

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basis sets used in calculations, we recently performed a detailed comparative study of SrTiO$_3$ (100) surfaces based on ten different quantum mechanical techniques [12–14].

Due to intensive development and progressive miniaturization of electronic devices, the electronic properties and atomic structure of the ABO$_3$ perovskite thin films have been extensively studied experimentally during the last years. The SrTiO$_3$ (100) surface structure has been analyzed by means of low energy electron diffraction (LEED) [15], reflection high energy electron diffraction (RHEED), X-ray photoelectron spectroscopy (XPS) and ultraviolet electron spectroscopy (UPS) [16], medium energy ion scattering (MEIS) [17], and surface X-ray diffraction (SXRD) [18]. The most recent experimental studies on the SrTiO$_3$ (100) surfaces include a combination of XPS, LEED, and time-of-flight scattering and recoiling spectrometry (TOF-SARS) [19], as well as metastable impact electron spectroscopy (MIES) [20]. The BaTiO$_3$ and PbTiO$_3$ surfaces are less well studied.

2 Computational method

To perform the first-principles density functional theory (DFT) calculations using Becke's three parameter method, combined with the non-local correlation functionals by Perdew and Wang (B3PW), we used the CRYSTAL computer code [21]. Unlike the plane-wave codes employed in many previous calculations [22, 23], CRYSTAL uses localized Gaussian-type basis sets. In our calculations we used the basis set recommended for BaTiO$_3$ [24]. An additional advantage of the CRYSTAL code is that it treats isolated 2D slabs, without an artificial periodicity in the z direction perpendicular to the surface, as commonly employed in most previous surface-band structure calculations (e.g., [8]).

Table 1 Atomic displacements with respect to atomic positions on unrelaxed BaTiO$_3$ (100) surfaces (in percent of bulk lattice constant)

Termination	Layer number	Ion	This study	SM [11]	LDA [4]
BaO	1	Ba^{2+}	−1.99	−3.72	−2.79
	1	O^{2-}	−0.63	1.00	−1.40
	2	Ti^{4+}	1.74	1.25	0.92
	2	O^{2-}	1.40	0.76	0.48
	3	Ba^{2+}		−0.51	0.53
	3	O^{2-}		0.16	0.26
TiO$_2$	1	Ti^{4+}	−3.08	−2.72	−3.89
	1	O^{2-}	−0.35	−0.94	−1.63
	2	Ba^{2+}	2.51	2.19	1.31
	2	O^{2-}	0.38	−0.17	−0.62
	3			−0.33	−0.75
	3			−0.01	−0.35

Table 2 Calculated surface rumpling s, and relative displacements Δd_{ij} (in percent of lattice constant) of three near-surface planes for the BaO and TiO$_2$ terminated BaTiO$_3$ (100) surfaces

	BaO-terminated BaTiO$_3$ (100) surface			TiO$_2$-terminated BaTiO$_3$ (100) surface		
	s	Δd_{12}	Δd_{23}	s	Δd_{12}	Δd_{23}
This study	1.37	−3.74	1.74	2.73	−5.59	2.51
LDA [4]	1.39	−3.71	0.39	2.26	−5.2	2.06
SM [11]	4.72	−4.97	1.76	1.78	−4.91	2.52

The difficulty in modelling the BaTiO$_3$ (110) polar surface is that it consists of charged planes, O-O or BaTiO. Consequently, modelling the (110) surface exactly as would be obtained from a perfect crystal cleavage, leads to an *infinite* dipole moment perpendicular to the surface, when it is terminated by different kinds of planes (O-O and BaTiO), or it leads to infinite charge per surface unit cell, when it is terminated by the same type of crystalline planes. Obviously, these crystal terminations make such a surface unstable [3]. To avoid this problem in our calculations, we removed half the O atoms from the O-terminated surface, simulated by the 7-plane slab, as well as Ba or both Ti and O atoms from the BaTiO-terminated surface. As a result, our (110) surface with charged planes has a zero macroscopic dipole moment (before atomic relaxation). The initial atomic configuration for the O-terminated surface, where every second surface O atom is removed and others occupy the same sites as in the bulk structure, we call *asymmetric* (A).

3 Main results

In the present BaTiO$_3$ (100) surface structure calculations we allowed atoms of the two outermost surface layers to relax along the z-axis (surfaces of perfect cubic crystals by symmetry have no forces along the x- and y-axes). Displacements of the third layer atoms were found to be negligibly small in our calculations and thus are not treated. Our calculated atomic displacements are presented in Table 1. A comparison with the surface atomic displacements obtained by other theoretical calculations performed by Padilla and Vaderbilt [4]

by means of the local-density approximation (LDA) and by Heifets et al. [11] using the shell model (SM) is also made in Table 1. The relaxation of surface metal atoms is much larger than that of oxygen ions what leads to a considerable *rumpling* (the relative displacement of oxygen with respect to the metal atom in the surface layer) of the outermost plane (see Table 2). According to our calculations, atoms of the first surface layer relax inwards, i.e. towards the bulk. At the latter point, our calculations disagree with the SM calculations [11]. Namely, according to SM calculations [11], the first layer oxygen ions for BaO terminated BaTiO$_3$ (100) surface relax upwards. However the magnitudes of calculated displacement is relatively small, −0.63% of lattice constant (a_o) inwards, according to our calculations, and 1.00% of a_o outwards according to SM calculations [11].

In order to compare the calculated surface structures with further experimental results, the surface rumpling s and the changes in interlayer distances Δd_{12} and Δd_{23} (1, 2, and 3 are the numbers of near-surface layers) are presented in Table 2. Our calculations of the interlayer distances are based on the positions of relaxed metal ions, which are known to be much stronger electron scatters than oxygen ions [15]. Qualitative agreement between all theoretical methods is observed. The rumpling of BaTiO$_3$ TiO$_2$-terminated surface is predicted to exceed by a factor of two that for BaO-terminated surface. This finding is in line with the result reported by Padilla and Vanderbilt [4] for BaTiO$_3$ (100) surface rumpling.

Ab initio B3PW calculated atomic relaxations for BaTiO$_3$ (110) surfaces, shown in Table 3, confirm the results of much more simple SM calculations. The agreement between *ab initio* B3PW and SM for all three (110) terminations is

Table 3 Atomic relaxation of BaTiO$_3$ (110) surface (in percent of the lattice constant) for three terminations, calculated by means of the *ab initio* B3PW and shell model (Ref. [11]). Positive sign corresponds to outward atomic displacements (toward the vacuum)

Layer number	Ion	B3PW, Δz	B3PW, Δy	SM, Δz [11]	SM, Δy [11]
Ti-O terminated					
1	Ti^{4+}	−7.86		−6.93	
1	O^{2-}	2.61		6.45	
2	O^{2-}	−1.02		−1.66	
3	Ba^{2+}	−0.88		−3.85	
3	O^{2-}			−2.40	
3	Ti^{4+}			1.59	
Ba terminated					
1	Ba^{2+}	−8.67		−13.49	
2	O^{2-}	0.80		2.80	
3	Ti^{4+}	0.16		−1.20	
3	O^{2-}	−0.43		−2.94	
3	Ba^{2+}			2.52	
O terminated, *A* type					
1	O^{2-}	−5.40	−1.67	−11.16	−6.70
2	Ti^{4+}	−0.15	−6.38	−1.83	−5.33
2	Ba^{2+}	1.54	−1.27	4.84	−2.21
2	O^{2-}	1.95	2.97	4.54	5.90
3	O^{2-}	0.90	4.49	6.52	5.58

Table 4 Calculated surface energies (in electronvolt per unit cell area) using the *hybrid* B3PW and shell model (Ref. [11])

Surface	Type	B3PW	SM [11]
(100)	TiO$_2$ terminated	1.07	1.40
	BaO terminated	1.19	1.45
(110)	TiO terminated	2.04	2.35
	Ba terminated	3.24	4.14
	O terminated, *A* type	1.72	1.81

satisfactory. This demonstrates that semiempirical classical calculations with a proper parametrization can serve as a useful tool for modelling perovskite thin films. According to our calculations, Ti ions on the TiO-terminated BaTiO$_3$ (110) surface move inwards (towards the bulk), whereas O ions move outward (towards the vacuum), by a 0.0261 a_o. Ba atoms in the top layer of the Ba-terminated surface move inward more, by 0.0867 a_o.

The calculated surface energies of the relaxed BaTiO$_3$ (100) and (110) surfaces are presented in Table 4. The energies calculated for BaO and TiO$_2$-terminated BaTiO$_3$ (100) surfaces (1.19 eV per surface cell) and (1.07 eV) respectively demonstrate only a small difference. Unlike the BaTiO$_3$ (100) surface, different terminations of the (110) surface show great differences in the surface energies. The lowest energy has the *A*-type O-terminated surface (1.72 eV). This is close to the energy of BaTiO$_3$ (100) surfaces. That means that *A*-type O-terminated BaTiO$_3$ (110) surface and BaTiO$_3$ (100) surfaces can co-exist. The Ba-terminated BaTiO$_3$ (110) surface shows much higher surface energy of 3.24 eV, while the BaTiO$_3$ TiO-terminated (110) surface energy is 2.04 eV.

4 Conclusion

Using a *hybrid* B3PW approach, we have calculated the surface relaxation of the two possible terminations of the BaTiO$_3$ (100) surfaces (TiO$_2$ and BaO), and three possible terminations of the BaTiO$_3$ (110) surfaces (Ba, TiO and O-terminated *A*-type). The data obtained for the surface structure are in a good agreement with previous LDA calculations by Padilla and Vanderbilt [4] and in a satisfactory agreement with the shell model calculations by Heifets et al. [11]. We find that the O-terminated *A*-type BaTiO$_3$ (110) surface has the lowest surface energy among all (110) terminations studied. This energy is close to that for the BaTiO$_3$ (100) surface, i.e. both (100) and (110) BaTiO$_3$ surfaces could simultaneously exist in BaTiO$_3$ ceramics.

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