

# Calculations of Perovskite Polar Surface Structures

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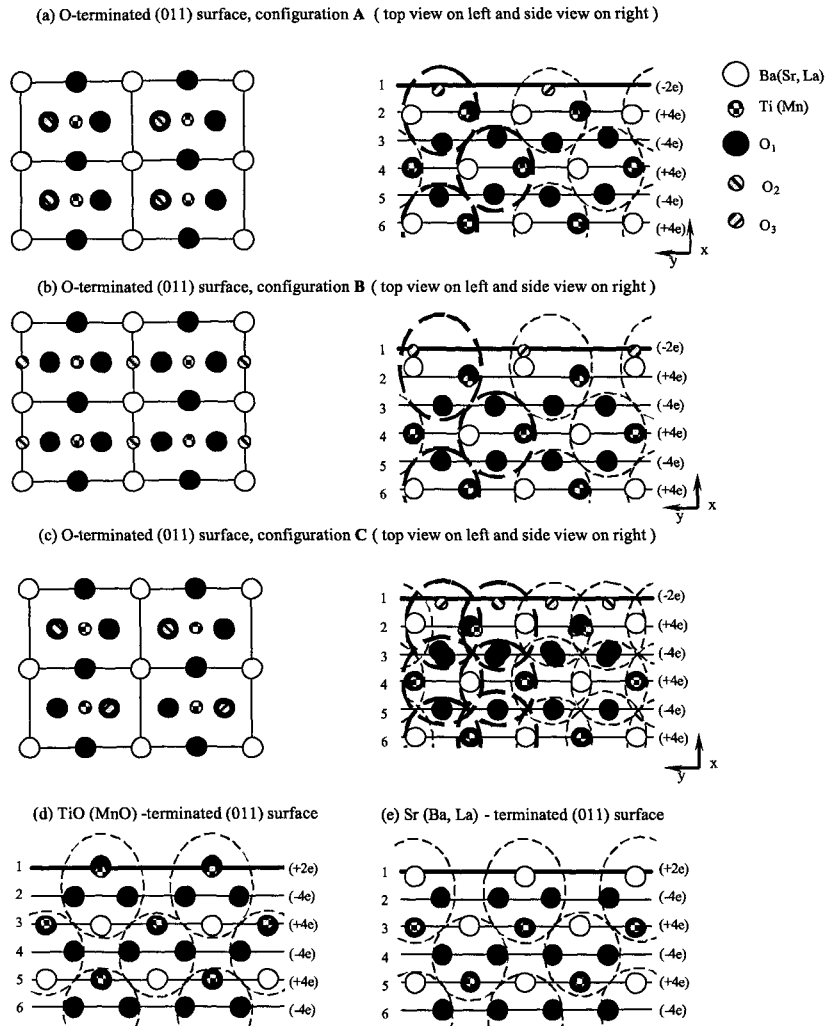
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**Abstract.** Results of calculations for the (110) polar surfaces of three ABO<sub>3</sub> perovskites – STO, BTO and LMO – are discussed. These are based on *ab initio* Hartree-Fock method and classical Shell Model. Both methods agree well on both surface energies and on near-surface atomic displacements. A novel model of the “zig-zag” surface termination is suggested and analyzed. Considerable increase of the Ti–O chemical bond covalency nearby the surface is predicted for STO.

## I INTRODUCTION

Thin films of ABO<sub>3</sub> perovskite ferroelectrics are important for many technological applications, including catalysis, microelectronics, substrates for growth of high T<sub>c</sub> superconductors, where surface structure and its quality are of primary importance [1,2]. Several *ab initio* quantum mechanical [3–9] and classical Shell Model (SM) [10,11] theoretical studies were published recently for the (100) surface of BaTiO<sub>3</sub> and SrTiO<sub>3</sub> crystals (hereafter BTO and STO). In order to study dependence of the surface relaxation properties on exchange–correlation functionals and localized/plane wave basis sets used in calculations, we performed recently a detailed comparative study based on a number of different quantum mechanical techniques [12–14]. The main conclusion was drawn there that the Hartree-Fock (HF), Density Functional Theory (DFT), and even SM calculations give quite similar results for the atomic structure relaxation and surface energies.

We performed also SM calculations of the atomic relaxation for the polar (110) surfaces of STO and BTO [11]. To our knowledge, only semi-empirical quantum mechanical calculations [15] exist so far for such perovskite surfaces. In this paper, we present a novel, “zig-zag” model for the polar (110) surface termination, and



**FIGURE 1.** The top and side view of the (110) perovskite surfaces. (a), (b), (c) are three possible configurations of O-terminated surface, (d) and (e) same for TiO- and Sr (Ba) terminations, see details in the text.

perform calculations of the relaxed atomic structure of the STO, BTO and LaMnO<sub>3</sub> (LMO) (110) surfaces, combining the *ab initio* HF and classical SM methods.

## II METHODS AND SURFACE MODELS

In this study, we restrict ourselves to simulations of ABO<sub>3</sub> perovskites in the cubic crystalline phase, stable at high temperatures. Description of SM and its parameterization is available in Ref. [11]. Use of this model permits us to find the atomic relaxation for several hundreds of atoms, surface energies, along with the surface polarization, characterized by dipole moments perpendicular and parallel to the surface. This information is of great importance for analysis of dielectric properties of thin ferroelectric films. We allow atoms in a given number of near-surface planes (varied from 2 to 16) to relax to the minimum of total energy, and then analyze, how the major properties are affected by a number of relaxed planes. This is important since in time-consuming *ab initio* calculations only 2-3 near-surface planes are typically allowed to relax.

In HF calculations for STO, performed to check accuracy of the SM calculations, we use the CRYSTAL-98 computer code (see [16] and references therein for description of all mentioned techniques), in which both (HF/DFT) types of calculations are implemented on equal grounds. Unlike previous plane-wave calculations, this code uses the localized Gaussian-type basis set. In our simulations we applied the basis set recommended for SrTiO<sub>3</sub> [16]. Another advantage of the CRYSTAL-98 code is its treatment of purely 2D slabs, without an artificial periodicity in the direction perpendicular to the surface, commonly employed in all previous surface-band structure calculations (e. g., [3,9]). In HF calculations, along with the atomic displacements in several planes near the surface, we calculate effective (Mulliken) atomic charges, bond populations between nearest atoms, characterizing the covalency effects, and dipole, quadrupole moments characterizing atomic polarization and deformation. In particular, the dipole moments  $p_z$  and  $p_y$  characterize atomic deformation and polarization along the  $z$  axis and the  $y$  axis perpendicular and parallel to the surface, respectively.

For optimization of atomic coordinates through minimization of the total energy per unit cell, we use our own computer code that implements the Conjugated Gradients optimization technique with numerical computation of derivatives. Using this code, we optimized the atomic positions in three top layers of a STO slab consisting of seven planes.

The problem of the (110) polar surface modeling is that it consists of charged planes. This is why, if the (110) surface were to be modeled exactly as one would expect after crystal cleavage, it would have in *infinite* dipole moment perpendicular to the surface, which makes such the surface unstable [17]. To avoid this problem, in our calculations we removed half the O atoms from from the O-terminated surface, the Sr(Ba) atoms from the Ti-terminated surface, and both the Ti and O atoms from the Sr (Ba) - terminated surface. As a result, we obtain the surface with

**TABLE 1.** Atomic relaxation of three top layers (in percent of the lattice constant) for four terminations, calculated by means of the *ab initio* HF and Shell Model [11].

Ti-O terminated		SM		HF	
Layer	Atom	$\delta z$	$\delta y$	$\delta z$	$\delta y$
1	Ti	-5.99		-6.49	
1	O	8.48		6.85	
2	O	-1.72		-1.47	
3	O	-4.10		-3.85	
3	Ti	2.14		2.20	
3	Sr	-6.96		-5.78	
O-terminated		A-type			
1	O	-14.2	-8.54	-10.41	-10.53
2	Ti	-2.37	-8.27	-1.36	-7.71
2	Sr	4.10	-10.79	2.20	-7.30
2	O	5.71	8.20	6.65	6.15
3	O	-11.06	-11.01	-7.02	-7.46
O-terminated		B-type			
1	O	-2.78		-3.95	
2	Ti	-5.14		-4.26	
2	Sr	30.32		22.67	
2	O	9.68		8.23	
3	O	-2.41		-1.68	
O-terminated		C-type			
1	O	-13.76	-9.08		
2	Ti	-4.87	-5.52		
2	Sr	4.31	0.0		
2	O	1.21	0.0		
3	O	-9.60	7.54		
Sr-terminated					
1	Sr	-19.07		-17.38	
2	O	3.18		2.72	
3	Sr	4.67		3.95	
3	O	-0.25		-0.21	
3	Ti	-0.89		-0.86	

charged planes but a zero dipole moment (before atomic relaxation). The relevant surface cells are built from neutral five-atom elements from three successive planes which are shown as encircled dashed ellipses in Fig.1.

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), Fig. 1.a. Since such a removal of half of O atoms disturb the balance of interatomic forces along the surface, we also studied another, symmetric initial surface configuration (B) in which the O<sub>2</sub> atom is placed in the *middle* of the distance between two equivalent O atoms in the bulk (Fig. 1.b). The A-type surface reveals considerable atomic displacements not only perpendicular to the surface, but also parallel to the surface. Preliminary results for the A-, B-cases were discussed in Ref. [11]. In this paper, we study one more configuration (C) which corresponds to the 2 × 1 surface reconstruction where O atoms are removed in pairs of nearest surface cells in a “zig-zag” way (O<sub>2</sub> and O<sub>3</sub> in Fig. 1.c). In this case, there is no artificial dipole moment parallel to the surface, in contrast to the case A.

The effective charges for Ti and O ions, both in the bulk and on the (100) surface, calculated by means of the HF and DFT methods [13], are much smaller than formal ionic charges (4 e, -2 e, respectively). This arises due to partly covalent nature of the Ti-O chemical bond. In contrast, Sr charge remains close to the formal charge, +2 e. The Ti-O chemical bond covalency is confirmed by calculated bond populations, which vary from 0.05 e (DFT-LDA) to 0.11 e (HF), dependent on the particular method. Obviously, there is no chemical bonding between any other types of atoms, e.g. Sr-O or O-O.

Our atomic displacements in the (100) outermost SrTiO<sub>3</sub> planes, obtained by means of various *ab initio* methods, were analyzed recently [13,14].

In all calculations of the (100) surface energy, that for the SrO termination is only slightly smaller than for the TiO<sub>2</sub> termination. Thus, both (100) surfaces can co-exist, in agreement with the experimental observation [13].

### III MAIN RESULTS

#### A Shell Model

Atomic relaxation of the first three top layers are given in Table 1. SM calculations predict large, ≈ 14 % a<sub>0</sub> *rumpling* for the TiO-terminated surface (the distance along the z axis between O and Ti atoms displaced from the first plane in opposite directions). Atomic displacements in the third plane are still considerable, unlike the (100) case. For the Sr-termination, top Sr atoms are displaced inwards, by ≈ 19 %, whereas the O atoms in the second plane go outwards, by ≈ 3 %.

The top O atom on the O-terminated symmetric surface (A) is strongly displaced inwards, by ≈ 14 %, whereas the Ti atom in the second plane is also displaced inwards, but only by ≈ 2 %. Along with the displacements along the z axis per-

pendicular to the surface, all atoms here reveal also considerable displacements parallel to the surface. This results in the dipole moments  $p_y$ , to be discussed below.

In contrast, for the symmetric termination B, atoms are displaced only along the  $z$  axis and reveal much smaller displacements (e.g., the top O atoms go inward, by  $\approx 3\%$ .) However, Sr atoms in the second plane are strongly ( $\approx 30\%$ ) displaced outwards the surface. Similar effect was observed by us for the (100) surface [11]. The (110) surface polarization, characterized by the relaxation-induced dipole moments (per surface unit cells)  $p_z$  and  $p_y$  perpendicular and parallel to the surface, respectively, is shown in Fig. 2. For the asymmetric termination (A) the surface polarization  $p_z$  oscillates around  $1.1 e \text{ \AA}$ , with an increase of a number of relaxed near-surface planes (varied between 2 and 16). This is accompanied by a considerable dipole moment  $p_y$  parallel to the surface. In contrast, the  $p_z$  dipole moment for the B-type termination rapidly saturate at  $1.13 e \text{ \AA}$  whereas  $p_y$  strives for zero, with an increase of a number of relaxed layers. Lastly, for the “zig-zag” termination C,  $p_z$  oscillates around  $1.1 e \text{ \AA}$  similarly to the asymmetric case (A) but without any dipole moment parallel to the surface. In other words, surface relaxation of cubic perovskite structure leads to the considerable polarization perpendicular to the surface which results from near-surface relaxation. This could considerably affect the dielectric properties of thin films.

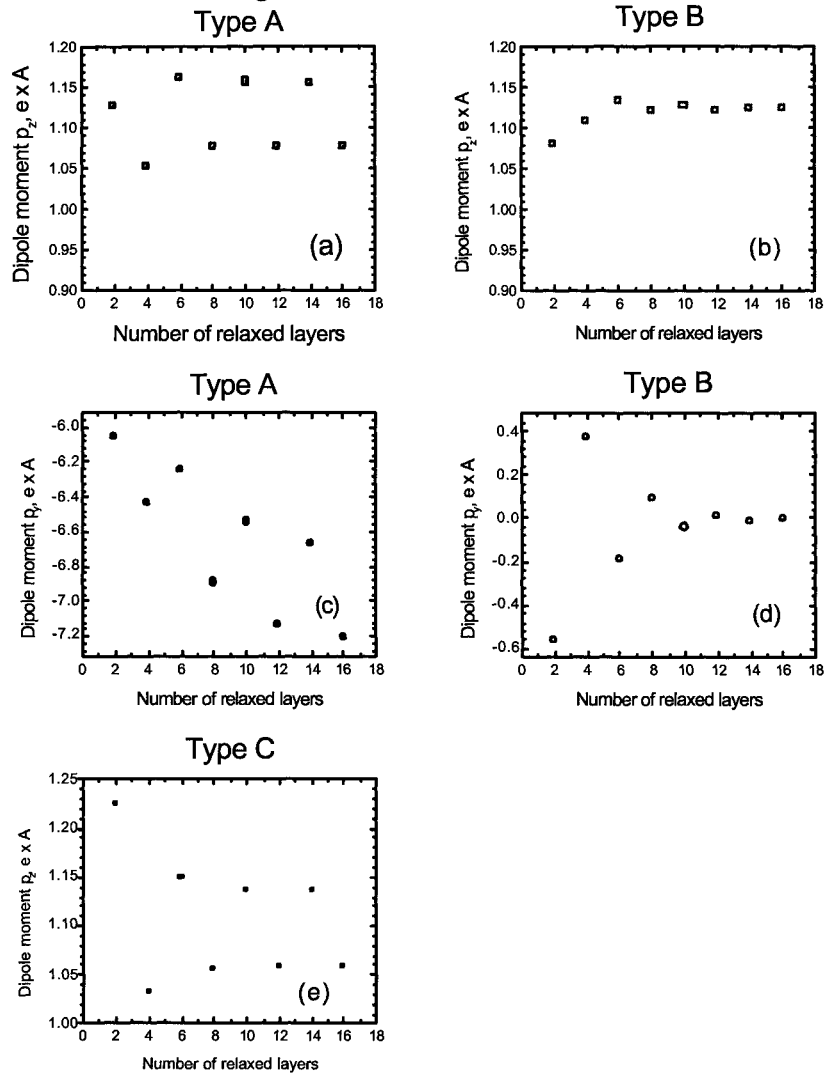
Table 2 shows considerable difference for surface energies for STO, BTO and LMO (110) surfaces, obtained for two and 16 relaxed layers. (Our calculations show that the (110) surface energy saturates at about 6-8 relaxed layers only, whereas in *ab initio* calculations only 1-2 layers are typically relaxed.) Unlike the (100) surface, different (110) surface terminations strongly differ in energies. For all three perovskites, the novel, “zig-zag” termination (C) is lowest in surface energy.

## B Hartree-Fock Calculations

The HF-calculated atomic relaxations for STO, shown in Table 1, confirm results of much simpler SM calculations. The agreement for all four termination is remarkable, indeed. This demonstrates that semi-empirical classical calculations with a proper parameterization could serve as a very useful tool for modeling perovskite thin films. Table 2 demonstrates also a good agreement between the HF calculated surface energies and those obtained by means of the SM (comparing in both cases results for two relaxed planes.)

We calculated also the effective atomic charges, dipoles and quadrupole moments for atoms near the surface. For the TiO termination, the Ti atom charge is reduced by 0.14 e, as compared to that in the bulk, due to the additional electron charge transfer from O atoms. The effective charge for O atoms turns out to be more positive, by 0.11 e. The Sr effective charge on the Sr-terminated surface is also reduced by 0.13 e, as for the TiO terminated (110) surface, and metal-terminated (100) surfaces. Changes in atomic charges in deeper layers become small. On

# Polarization of O-terminated SrTiO<sub>3</sub> (110) Surface



**FIGURE 2.** Surface polarization and dipole moments perpendicular and parallel to the STO (110) surface with different terminations.

**TABLE 2.** Surface energies for four different O (110) terminations shown in Fig.1, as calculated for STO, BTO and LMO perovskites, using the Shell Model (SM) [11] and *ab initio* HF method (for STO only). SM-2, SM-16 refer to the number of near-surface planes allowed to relax.

Type	HF	SM-2	SM-16
STO-A-type	1.40	1.54	0.92
B	3.08	3.13	3.31
C		1.63	0.76
TiO	2.10	2.21	2.36
Sr	2.97	3.04	3.37
BTO-A-type		1.58	1.83
B		4.66	4.84
C		1.84	1.82
TiO		2.11	2.36
Ba		3.79	4.16
LMO-A-type		2.59	2.06
B		4.11	4.06
C		2.81	1.95

the TiO- and Sr-terminated (110) surfaces both Ti and Sr atoms reveal negative dipole moments, directed outwards the surface which means a contraction of the near-surface cations.

The interatomic bond populations for three terminations are given in Table 3. The major effect observed here is a strong increase of the Ti-O chemical bonding near the surface as compared to (already large) bonding in the bulk (112 me). The Ti-O bond population for the O-terminated A-type surface is as large as 294 me, i.e. by a factor larger than 2 larger than in the bulk. (This factor for the (100) surface was 1.5.) The Ti-O bond population reaches practically the bulk value for atoms in a third plane. An increased Ti-O bond population near the (110) surface obviously does not arise from the surface relaxation. As shows Table 3, for the TiO termination and *unrelaxed* surface  $P[\text{Ti(I)}-\text{O(II)}]=182$  me, which increases up to 240 me after surface relaxation. Second, for the same interatomic distance, the Ti-O bond populations are larger in the direction perpendicular to the surface (182 me) than on-plane (126 me).

## IV CONCLUSIONS

Our *ab initio* calculations indicate a considerable increase of the Ti-O bond covalency near the (110) surface, much larger than that for the (100) surface. This should have impact on the electronic structure of surface defects (e.g.,  $F$  centers), as well as affect an adsorption and surface diffusion of atoms and small molecules



**TABLE 3.** The A-B bond populations, P (in milli e= me) and the relevant interatomic distances R (in Å) for three different O (110) terminations in STO. I to IV are number of planes enumerated from the surface. The nearest neighbour Ti-O distance in the unrelaxed lattice is 1.945 Å. Numbers in brackets are bond populations for unrelaxed lattice.

Atom A	Atom B	P	R
Ti-O terminated			
Ti(I)	O(I)	176 (126)	2.01
	O(II)	240 (182)	1.81
O(II)	Ti(III)	140 (130)	1.85
	Sr(III)	-10	2.84
Ti(III)	O(III)	-22	2.80
	Sr(III)	0	3.38
Sr(III)	O(III)	126 (136)	1.96
	O(IV)	-22	2.75
Ti(III)	O(IV)	-24	2.64
	O(IV)	108 (112)	2.00
O(III)	O(IV)	-24	2.68
O-terminated			
A-type			
O(I)	Sr(I)	-28	2.47
	Ti(II)	294	1.80
	O(II)	-26	2.90
Sr(II)	O(II)	-30	2.23
	Ti(II)	0	3.36
Ti(II)	O(II)	90	2.04
	O(III)	104	2.10
O(II)	O(III)	-28	2.85
Sr(II)	O(III)	-6	2.94
O(III)	O(IV)	-20	2.48
	Ti(IV)	110	2.00
	Sr(IV)	-14	2.48
O-terminated			
B-type			
O(I)	Sr(I)	-30	1.97
	Ti(II)	16	3.08
	O(II)	-4	3.49
Sr(II)	O(II)	-20	2.81
	Ti(II)	0	3.53
Ti(II)	O(II)	130	2.00
	O(III)	204	1.87
O(II)	O(III)	-18	2.96
Sr(II)	O(III)	4	3.33
O(III)	O(IV)	-22	2.72
	Ti(IV)	114	1.90
	Sr(IV)	-22	2.72

relevant for catalysis. Atomic displacements calculated by means of classical SM are in surprisingly good agreement with the *ab initio* HF calculations for STO. The lowest surface energies in all three perovskites studied are found for the novel “zig-zag”  $2 \times 1$  reconstructed surface termination. This surface termination reveals no dipole moment parallel to the surface, but considerable dipole moment perpendicular to the surface, which certainly can affect the dielectric properties of thin perovskite films.

## V ACKNOWLEDGEMENTS

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