

Chapter 11

Ab Initio Calculations of SrTiO₃ (111) Surfaces

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Abstract The paper presents the results of calculations of SrTiO₃ polar (111) surface relaxations and energetics using the ab initio code CRYSTAL and a hybrid description of exchange and correlation. Using a hybrid B3LYP approach, the surface relaxation has been calculated for the two possible Ti and SrO₃ SrTiO₃ (111) surface terminations. For both Ti and SrO₃-terminated SrTiO₃ (111) surfaces upper layer atoms, with the sole exception of SrO₃-terminated surface Sr atom, relax inwards. The calculated surface relaxation energy for Ti-terminated SrTiO₃ (111) surface is almost five times larger, than the surface relaxation energy for SrO₃-terminated SrTiO₃ (111) surface. The surface energy for Ti-terminated SrTiO₃ (111) surface (4.99 eV) is smaller, than the surface energy for SrO₃-terminated SrTiO₃ (111) surface (6.30 eV).

Keywords Ab initio calculations • SrTiO₃ • (111) surface • B3LYP

11.1 Introduction

Thin films of SrTiO₃ perovskite ferroelectrics are important for many industrial applications including high capacity memory cells, catalysis, optical wave guides, integrated optics applications, and substrates for high- T_c cuprate superconductor growth [1, 2]. For all these SrTiO₃ applications, the surface structure and the related surface electronic and chemical properties are of primary importance.

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In view of this technological importance, it is not surprising that SrTiO₃ (001) surface has been extensively studied both theoretically by means of *ab initio* methods [3–14] and experimentally using low-energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), medium energy ion scattering (MEIS), and surface x-ray diffraction (SXRD) measurements [15–20]. The most recent experimental studies on the SrTiO₃ surfaces include a combination of XPS, LEED, and time-of-flight scattering and recoil spectrometry [21] (TOF-SARS) as well as metastable impact electron spectroscopy [22].

In contrast to widely investigated SrTiO₃ (001) surfaces, only a small number of *ab initio* studies exist dealing with atomic and electronic structure calculations of SrTiO₃ (011) surface [23–27]. The first *ab initio* study of polar SrTiO₃ (011) surfaces was performed by Bottin et al. [23]. In this paper the electronic and atomic structures of several (1 × 1) terminations of the (110) polar orientation of the SrTiO₃ has been studied by *ab initio* calculations. The electronic structure of the two stoichiometric SrTiO and O₂ terminations has been characterized by marked differences with respect to the bulk, as a consequence of the polarity compensation [23]. Half year later Heifets et al. by means of *ab initio* Hartree-Fock (HF) method calculated the surface energies, near surface atomic displacements for four possible terminations of the polar SrTiO₃ (011) surface, as well as Mulliken atomic charges and dipole moments of atoms characterizing their polarization [24]. Recently, Eglitis and Vanderbilt have performed an *ab initio* study of SrTiO₃ (011) surfaces [7] using a hybrid HF and density-functional theory (DFT) exchange-correlation functional, in which HF exchange is mixed with Beckés three-parameter DFT exchange and combined with the nonlocal correlation functional of Perdew and Wang (B3PW) [25, 26]. Finally, Enterkin et al. reported a solution to the 3 × 1 SrTiO₃ (110) surface structure obtained through transmission electron diffraction and direct methods, and confirmed through density functional theory calculations and scanning tunneling microscopy images and simulations, consisting of rings of six or eight corner-sharing TiO₄ tetrahedra [27].

There exist several experimental studies dealing with SrTiO₃ (111) surfaces. For example, Tanaka and Kawai have obtained clean surfaces of reduced SrTiO₃ (111) crystals and observed them by means of scanning tunneling microscopy (STM) combined with reflection high energy diffraction. They have observed two different surface structures. One obtained by annealing at the temperature ~1,180°C, is assigned to have a SrO₃ outermost layer. The other, obtained by annealing at the temperature ~1,220°C, is assigned to have a Ti outermost layer [28]. More than 10 years later Chang et al. [29] also reproducibly obtained an atomically well-defined SrTiO₃ (111) surface by a combined chemical etching and thermal annealing process. On the theory side, Pojani et al. [30] relying on the results obtained by a total energy, semi-empirical Hartree-Fock method, discuss polarity effects at the (111) and (110) surfaces of SrTiO₃. For these orientations, they consider some prototypical (1 × 1) configurations, which differ by their surface composition and the coordination number of the surface atoms. They argue that the compensation for these polar orientations is achieved through anomalous filling of surface states, which, in principle, should be detectable by surface spectroscopies.

11.2 Computational Details

To perform the first-principles DFT-B3LYP calculations, we used the CRYSTAL computer code [31]. This code employs Gaussian-type functions (GTF) localized at atoms as the basis for an expansion of the crystalline orbitals. Features of the CRYSTAL code, which are most important for the study of perovskite surfaces, present its ability to calculate the electronic structure of materials within both HF and Kohn-Sham (KS) Hamiltonians and implementation of the isolated 2D slab model without its artificial repetition along the z -axis. However, in order to employ the linear combination of atomic orbitals (LCAO)-GTF method, it is desirable to have optimized basis sets (BS). The optimization of such BSs for SrTiO₃, BaTiO₃ and PbTiO₃ perovskites was developed and discussed in Piskunov et al. [32]. In the present paper, for O atoms, we have used this new BS which differs from the previous calculations [5, 11] by inclusion of polarizable d-orbitals on O ions. For Ca atoms we used the same basis set as in Ref. [33].

Our calculations have been performed using the hybrid exchange-correlation B3LYP functional involving a hybrid of nonlocal Fock exact exchange, LDA exchange and Beckés gradient corrected exchange functional [25], combined with the nonlocal gradient corrected correlation potential by Lee-Yang-Parr [34]. The Hay-Wadt small-core effective core pseudopotentials (ECP) have been adopted for Sr, Ca and Ti atoms [35, 36]. The small-core ECPs replace only inner core orbitals, but orbitals for sub-valence electrons as well as for valence electrons are calculated self-consistently. Light oxygen atoms have been treated with the all-electron BS [32].

The reciprocal space integration has been performed by sampling the Brillouin zone of the five-atom cubic unit cell with the $5 \times 5 \times 1$ Pack-Monhorst net [37], that provides the balanced summation in direct and reciprocal spaces. To achieve high accuracy, large enough tolerances of 7, 8, 7, 7, 14 have been chosen for the Coulomb overlap, Coulomb penetration, exchange overlap, the first exchange pseudo-overlap, and for the second exchange pseudo-overlap, respectively [31].

The SrTiO₃ (111) surfaces have been modeled with two-dimensional (2D) slabs, consisting of several planes perpendicular to the [111] crystal direction. The CRYSTAL code has allowed us to avoid artificial periodicity along the Oz direction and to perform simulations for stand-alone 2D slabs. To simulate SrTiO₃ (111) surfaces, we have implemented symmetrical (with respect to the mirror plane) slabs consisting of nine alternating Ti and SrO₃ layers. One of these slabs is terminated by Ti planes and consists of a supercell containing 21 atoms. The second slab is terminated by SrO₃ planes and consists of a supercell containing 24 atoms. These slabs are non-stoichiometric, with unit cell formulas Sr₄Ti₅O₁₂ and Sr₅Ti₄O₁₅, respectively. These two (Ti and SrO₃) terminations are the only two possible flat and dense (111) surfaces in SrTiO₃ perovskite lattice structure.

As a next step, we have calculated cleavage and surface energies. It is obvious that Ti and SrO₃-terminated (111) surfaces are mutually complementary. The cleavage energy of the complementary surface $E_{c1}(\beta)$ ($\beta = \text{Ti or SrO}_3$) can be

Table 11.1 The calculated lattice constant (in Å) for the SrTiO₃ bulk using the hybrid B3LYP method

Material	Calculated lattice constant	Experimental lattice constant
SrTiO ₃	3.914	3.89

The experimental bulk lattice constant [38] are listed for comparison

obtained from the total energies computed for the unrelaxed slabs through the following equation:

$$E_{\text{cl}}(\beta) = \frac{1}{4} [E_{\text{slab}}^{\text{unrel}}(\text{Ti}) + E_{\text{slab}}^{\text{unrel}}(\text{SrO}_3) - 9E_{\text{bulk}}] \quad (11.1)$$

where $E_{\text{slab}}^{\text{unrel}}(\beta)$ is the total energy of unrelaxed β -terminated slab, E_{bulk} is the bulk energy per formula unit in the cubic structure, and $\frac{1}{4}$ means that totally four surfaces are created upon the crystal cleavage.

When both sides of the slab are allowed to relax, the relaxation energies for each of the surfaces can be obtained by the equation:

$$E_{\text{rel}}(\beta) = \frac{1}{2} [E_{\text{slab}}^{\text{rel}}(\beta) - E_{\text{slab}}^{\text{unrel}}(\beta)] \quad (11.2)$$

where $E_{\text{slab}}^{\text{rel}}(\beta)$ is the β -terminated slab energy after relaxation, $\frac{1}{2}$ means that two surfaces are created upon the crystal cleavage. Now when the cleavage and relaxation energies are calculated, the surface energy is just a sum of them:

$$E_{\text{surf}}(\beta) = E_{\text{cl}}(\beta) + E_{\text{rel}}(\beta). \quad (11.3)$$

11.3 Main Results

As a starting point of the calculations, the SrTiO₃ bulk lattice constant has been calculated. The received calculated lattice constant for SrTiO₃ (3.914 Å) is slightly larger than the experimental value of 3.89 Å [39] (see Table 11.1). Thus, the computational approach used in the present study can be established as appropriate. We used the theoretical SrTiO₃ bulk lattice constant in the following (111) surface structure calculations.

To characterize the chemical bonding and covalency effects, we have applied a standard Mulliken population analysis for the effective atomic charges Q and other local properties of electronic structure as described, for example, in [39, 40]. The calculated effective charges for the SrTiO₃ bulk are (+1.869e) for the Sr atom, (+2.356e) for the Ti atom, and (−1.408e) for the O atom (see Table 11.2). The bond population of the chemical bonding between Ti and O atoms is (+0.088e) in SrTiO₃. The bond populations between Sr and O atoms and O and O atoms are negative, which indicates repulsion between Sr–O and O–O atoms (see Table 11.2).

Table 11.2 Calculated effective charges Q and bond populations P (in e) for the bulk SrTiO₃

SrTiO ₃		
Ion or bond	Property	Value
Sr	Q	1.869
O	Q	-1.408
Ti	Q	2.356
Sr-O	P	-0.010
Ti-O	P	0.088
O-O	P	-0.046

Table 11.3 Calculated relaxation of Ti-terminated SrTiO₃ (111) surface upper three layer atoms (as a percentage of the bulk crystal lattice constant $a = 3.914$ Å)

Layer	Ion	Displacement (Δz)
1	Ti	-3.58
2	Sr	-11.24
	O	1.53
3	Ti	0.26

Table 11.4 Calculated relaxation of SrO₃-terminated SrTiO₃ (111) surface upper three layer atoms (as a percentage of the bulk crystal lattice constant $a = 3.914$ Å)

Layer	Ion	Displacement (Δz)
1	Sr	1.33
	O	-0.03
2	Ti	1.81
3	Sr	-0.03
	O	-0.26

Table 11.5 Calculated cleavage, relaxation, and surface energies for SrTiO₃ (111) surfaces (in electron volt per surface cell)

Surface	Termination	E_{cl}	E_{rel}	E_{surf}
SrTiO ₃ (111)	Ti-term	6.65	-1.66	4.99
	SrO ₃ -term	6.65	-0.35	6.30

According to the results of the calculations, the upper layer Ti atom for Ti-terminated SrTiO₃ (111) surface strongly (by 3.58% of bulk lattice constant a_0) relaxes inwards (see Table 11.3). The second layer Sr atom relaxes inwards even more strongly (by 11.24% of a_0), while the second layer O atom relaxes outwards by 1.53% of a_0 . Outward relaxation of the third layer Ti atom is rather weak, less than 1% of a_0 .

For SrO₃-terminated SrTiO₃ (111) surface the upper layer metal atom relaxes outwards by 1.33% of a_0 , but the upper layer O atom relaxes very slightly inwards by 0.03% of a_0 (see Table 11.4). The second layer Ti atom outward relaxation (1.81% of a_0) is larger than upper layer Sr atom relaxation. Both third layer Sr and O atoms relax inwards by a very small magnitude (0.03% of a_0 and 0.26% of a_0), respectively.

The calculated surface relaxation energy for Ti-terminated SrTiO₃ (111) surface (-1.66 eV) is almost five times larger, than the surface relaxation energy for SrO₃-terminated SrTiO₃ (111) surface (-0.35 eV) (see Table 11.5). The calculated surface energy for Ti-terminated SrTiO₃ (111) surface is equal to 4.99 eV, while the surface energy for SrO₃-terminated SrTiO₃ (111) surface is equal to 6.30 eV.

11.4 Conclusions

Using the *hybrid* B3LYP approach, the surface relaxation for the two possible SrTiO₃ (111) surface terminations has been calculated. For both Ti and SrO₃-terminated SrTiO₃ (111) surfaces the upper layer atoms, with the sole exception of SrO₃-terminated surface Sr atom, relax inwards. The second layer atoms, with the exception of Ti-terminated surface Sr atom, relax outwards. The Ti-terminated SrTiO₃ (111) surface second layer Sr atom exhibits the strongest relaxation between all Ti and SrO₃-terminated SrTiO₃ (111) surface atoms.

The calculated surface relaxation energy for Ti-terminated SrTiO₃ (111) surface is almost five times larger than the surface relaxation energy for SrO₃-terminated SrTiO₃ (111) surface. The surface energy for Ti-terminated SrTiO₃ (111) surface (4.99 eV) is smaller, than the surface energy for SrO₃-terminated (111) surface (6.30 eV).

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