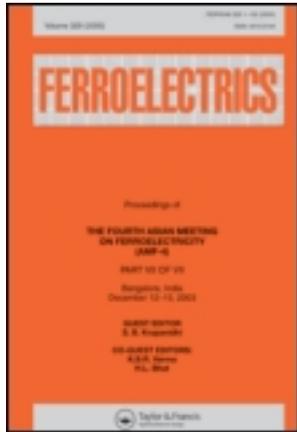


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# First-Principles Calculations of the Atomic and Electronic Structure of $\text{CaTiO}_3$ (111) Surfaces

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*The results of calculations of  $\text{CaTiO}_3$  polar (111) surface relaxations, rumplings, energetics, optical band gaps, and charge distribution using the ab initio code CRYSTAL and a hybrid description of exchange and correlation are presented. Using a hybrid B3LYP approach, the surface relaxation for the two possible Ti and  $\text{CaO}_3$   $\text{CaTiO}_3$  (111) surface terminations are calculated. For both Ti and  $\text{CaO}_3$ -terminated  $\text{CaTiO}_3$  (111) surfaces upper layer atoms relax inwards, while the second layer atoms, with the sole exception of  $\text{CaO}_3$ -terminated surface Ca atom, relax outwards. Calculated surface relaxation energy for Ti-terminated  $\text{CaTiO}_3$  (111) surface is more than five times larger than the surface relaxation energy for  $\text{CaO}_3$ -terminated  $\text{CaTiO}_3$  (111) surface. The surface energy for Ti-terminated  $\text{CaTiO}_3$  (111) surface (4.18 eV/cell) is smaller, than the surface energy for  $\text{CaO}_3$ -terminated  $\text{CaTiO}_3$  (111) surface (5.86 eV/cell).*

**Keywords** *Ab initio* calculations; (111) surface structure;  $\text{CaTiO}_3$ ; B3LYP hybrid exchange-correlation functional

## Introduction

$\text{CaTiO}_3$  is a cubic perovskite that is widely used in electronic ceramic materials and as a key component of synthetic rock to immobilize high-level radioactive waste [1]. Thin films of  $\text{CaTiO}_3$  perovskite are important for many applications [1, 2]. In particular,  $\text{CaTiO}_3$  is interesting material regarding his electrochemical properties and are promising as component for electrodes and sensors. Surface properties of  $\text{CaTiO}_3$  are important for catalysis and for epitaxial growth of high- $T_c$  superconductors. For all these applications, the surface structure and the associated surface electronic and chemical properties are of primary importance.

Taking into account this high technological importance, it is surprng that there have been so few *ab initio* studies of  $\text{CaTiO}_3$  surface atomic and electronic structure. Only three studies by Wang et al. [3] and Zhang et al. [4] and recently also by Eglitis and Vanderbilt [5] exist dealing with  $\text{CaTiO}_3$  (001) surfaces. In contrast, several other  $\text{ABO}_3$  perovskite (001) surfaces have been widely studied. For example, recently *ab initio* studies were published for the (001) surfaces of  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{SrZrO}_3$ ,  $\text{PbZrO}_3$  and  $\text{BZrO}_3$  [6–14].

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CaTiO<sub>3</sub> perovskite (011) surfaces are less studied than (001) surface. On the theory side only two *ab initio* studies exist. The first *ab initio* calculations for CaTiO<sub>3</sub> (011) surfaces were performed by Zhang et al. [15] and recently also by Eglitis and Vanderbilt [5]. Finally, so far only one *ab initio* study exist dealing with atomic and electronic structure calculations for CaTiO<sub>3</sub> (111) surface structure [16].

Taking into account very high technological importance of SrTiO<sub>3</sub> and CaTiO<sub>3</sub> perovskites and their surfaces, as well as very limited number of *ab initio* studies dealing with their (111) surfaces, in this study predictive first-principles calculations dealing with atomic and electronic structure of SrTiO<sub>3</sub> and CaTiO<sub>3</sub> (111) surface structures are performed. The manuscript is organized as follows. In Sec. II computational details are presented. The results of calculations for surface structures, energies, charge distributions, and band populations are reported in Sec. III. Finally, the results are discussed and conclusions are presented in Sec. IV.

### Computational Details and Surface Models

The first-principles DFT-B3LYP calculations are performed by means of the CRYSTAL computer code [17]. 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, are its ability to calculate the electronic structure of materials within both Hartree-Fock (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 SrTiO<sub>3</sub>, BaTiO<sub>3</sub> and PbTiO<sub>3</sub> perovskites was developed in [18]. In this paper, for Ti and O atoms, this new BS which differs from previous calculations [6, 7] by inclusion of polarisable d-orbitals on O ions are used.

The calculations were performed using the hybrid exchange-correlation B3LYP functional involving a hybrid of nonlocal Fock exact exchange, LDA exchange and Becke's gradient corrected exchange functional [19], combined with the nonlocal gradient corrected correlation potential by Lee-Yang-Parr [20]. The reciprocal space integration was performed by sampling the Brillouin zone of the five atom primitive unit cell for CaTiO<sub>3</sub> perovskite with the  $5 \times 5 \times 1$  Pack-Monkhorst net [21], that provides the balanced summation in direct and reciprocal spaces. To achieve high accuracy, large enough tolerances of 7, 8, 7, 7, 14 were chosen for the Coulomb overlap, Coulomb penetration, exchange overlap, the first exchange pseudo-overlap, and for the second exchange pseudo-overlap, respectively [22].

The CaTiO<sub>3</sub> (111) surfaces were modeled with two-dimensional (2D) slabs, consisting of several planes perpendicular to the [111] crystal direction. The CRYSTAL code allowed to avoid artificial periodicity along the *Oz* direction and to perform simulations for stand-alone 2D slabs. To simulate CaTiO<sub>3</sub> (111) surfaces, symmetrical (with respect to the mirror plane) slabs consisting of nine alternating Ti and CaO<sub>3</sub> layers are used. One of these slabs was terminated by Ti planes and consisted of a supercell containing 21 atoms. The second slab was terminated by CaO<sub>3</sub> planes and consisted of a supercell containing 24 atoms.

As a next step, cleavage and surface energies [5–11] are calculated using following equations. It is obvious that Ti and CaO<sub>3</sub>-terminated (111) surfaces are complementary

mutually. The cleavage energy of the complementary surface  $E_{(\text{cl})}(\beta)$  ( $\beta = \text{Ti}$  or  $\text{CaO}_3$ ) can be obtained from the total energies computed for the unrelaxed slabs through the following equation:

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

where  $E_{(\text{slab})}^{(\text{unrel})}(\beta)$  is the total energy of unrelaxed  $\beta$ -terminated slab,  $E_{(\text{bulk})}$  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 equation:

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

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

$$E_{(\text{surf})}(\beta) = E_{(\text{cl})}(\beta) + E_{(\text{rel})}(\beta). \quad (3)$$

## Main Results

As a starting point of calculations, the CaTiO<sub>3</sub> bulk lattice constant (3.851 Å) are calculated. Calculated lattice constant (3.851 Å) is slightly smaller than the experimental value of 3.895 Å [23]. To characterize the chemical bonding and covalency effects, a standard Mulliken population analysis for the effective atomic charges  $Q$ , bond populations  $P$ , and other local properties of electronic structure as described, for example, in [24] are used. The calculated effective charges for the CaTiO<sub>3</sub> bulk are (+1.773e) for the Ca atom, (+2.334e) for the Ti atom, and (−1.369e) for the O atom (see Table 1). The bond population of the chemical bonding between Ti and O atoms is (+0.084e) in CaTiO<sub>3</sub>. The bond population

**Table 1**  
Calculated effective charges  $Q$  and bond populations  $P$  (in e) for bulk CaTiO<sub>3</sub>

Ion or bond	CaTiO <sub>3</sub>	
	Property	Value
Ca	$Q$	1.773
O	$Q$	−1.369
Ti	$Q$	2.334
Ca-O	$P$	0.006
Ti-O	$P$	0.084
O-O	$P$	−0.050

**Table 2**

Calculated relaxation of Ti-terminated  $\text{CaTiO}_3$  (111) surface upper three layer atoms (as a percentage of the bulk crystal lattice constant  $a = 3.851 \text{ \AA}$ ). Positive (negative) values refer to displacements in the direction outwards (inwards) the surface

Layer	Ion	Displacement ( $\Delta z$ )
1	Ti	-6.23
2	Ca	-14.02
	O	1.30
3	Ti	-0.26

between Ca and O atoms is much smaller (+0.006e). Finally, the bond population between O and O atoms in  $\text{CaTiO}_3$  (-0.050e) is negative, which indicates repulsion between O-O atoms (see Table 1). The calculated optical band gap for the  $\text{CaTiO}_3$  bulk is 4.20 eV. Experimentally reported value of the optical band gap in  $\text{CaTiO}_3$  is equal to 3.5 eV [25].

According to the results of calculations, upper layer Ti atom for Ti-terminated  $\text{CaTiO}_3$  (111) surface strongly (by 6.23% of bulk lattice constant  $a_0$ ) relax inwards (see Table 2). The second layer Ca atom relax inwards even more strongly (by 14.02% of  $a_0$ ), while the second layer O atom relax outwards by 1.30% of  $a_0$ . Inward relaxation of third layer Ti atom is rather weak, less than 1% of  $a_0$ .

For  $\text{CaO}_3$ -terminated  $\text{CaTiO}_3$  (111) surface both upper layer atoms Ca and O relax inwards (0.52% of  $a_0$  and 0.81% of  $a_0$ , respectively), but their relaxation is rather small (see Table 3). The outward relaxation of second layer Ti atom is 2.13% of  $a_0$ . Even third layer Ca atom exhibits strong outward relaxation by 2.60% of  $a_0$ , while the third layer O atom relaxation is almost negligible, only 0.07% of  $a_0$ .

Calculated surface relaxation energy for Ti-terminated  $\text{CaTiO}_3$  (111) surface (-2.06 eV) is more than 5 times larger, than the surface relaxation energy for  $\text{CaO}_3$ -terminated  $\text{CaTiO}_3$  (111) surface (-0.38 eV) (see Table 4). Calculated surface energy for Ti-terminated  $\text{CaTiO}_3$  (111) surface is 4.18 eV/cell, while the surface energy for  $\text{CaO}_3$ -terminated  $\text{CaTiO}_3$  (111) surface is equal to 5.86 eV/cell.

**Table 3**

Calculated relaxation of  $\text{CaO}_3$ -terminated  $\text{CaTiO}_3$  (111) surface upper three layer atoms (as a percentage of the bulk crystal lattice constant  $a = 3.851 \text{ \AA}$ )

Layer	Ion	Displacement ( $\Delta z$ )
1	Ca	-0.52
	O	-0.81
2	Ti	2.13
3	Ca	2.60
	O	-0.07

**Table 4**

Calculated cleavage, relaxation, and surface energies for  $\text{CaTiO}_3$  (111) surfaces (in electron volt per surface cell)

Surface	Termination	$E_{(\text{cl})}$	$E_{(\text{rel})}$	$E_{(\text{surf})}$
$\text{CaTiO}_3$ (111)	Ti-term.	6.24	-2.06	4.18
	$\text{CaO}_3$ -term.	6.24	-0.38	5.86

## Conclusions

Using a *hybrid* B3LYP approach, the surface relaxation for the two possible  $\text{CaTiO}_3$  (111) surface terminations are calculated. For both Ti and  $\text{CaO}_3$ -terminated  $\text{CaTiO}_3$  (111) surfaces upper layer atoms relax inwards, while the second layer atoms, with the sole exception of  $\text{CaO}_3$ -terminated surface Ca atom, relax outwards. The  $\text{CaO}_3$ -terminated  $\text{CaTiO}_3$  (111) surface second layer Ca atom exhibits the strongest relaxation between all Ti and  $\text{CaO}_3$ -terminated  $\text{CaTiO}_3$  (111) surface atoms.

Calculated surface relaxation energy for Ti-terminated  $\text{CaTiO}_3$  (111) surface is more than five times larger than the surface relaxation energy for  $\text{CaO}_3$ -terminated  $\text{CaTiO}_3$  (111) surface. The surface energy for Ti-terminated surface (4.18 eV/cell) is smaller, than the surface energy for  $\text{CaO}_3$  terminated (111) surface (5.86 eV/cell).

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## References

1. A. E. Ring, S. E. Kesson, K. D. Reeve, D. M. Levins, and E. J. Ramm, *Radioactive Waste Forms for the Future*. Edited by W. Lutze and R. C. Ewings, North-Holland, Amsterdam; 1987.
2. J. F. Scott, *Ferroelectric Memories*. Springer: Berlin; 2000.
3. Y. X. Wang, M. Arai, T. Sasaki, and C. L. Wang, First-principles study of the (001) surface of cubic  $\text{CaTiO}_3$ . *Phys. Rev. B* **73**, 035411 (2006).
4. J. M. Zhang, J. Cui, K. W. Xu, V. Ji, and Z. Y. Man, *Ab initio* modelling of  $\text{CaTiO}_3$  (110) polar surfaces. *Phys. Rev. B* **76**, 115426 (2007).
5. R. I. Eglitis and D. Vanderbilt, *Ab initio* calculations of the atomic and electronic structure of  $\text{CaTiO}_3$  (001) and (011) surfaces. *Phys. Rev. B* **78**, 155420 (2008).
6. E. Heifets, R. I. Eglitis, E. A. Kotomin, J. Maier, and G. Borstel, *Ab initio* modeling of surface structure for  $\text{SrTiO}_3$  perovskite crystals. *Phys. Rev. B* **64**, 235417 (2001).
7. E. Heifets, R. I. Eglitis, E. A. Kotomin, J. Maier, and G. Borstel, First-principles calculations for  $\text{SrTiO}_3$  (100) surface structure. *Surf. Sci.* **513**, 211–220 (2002).
8. S. Piskunov, E. A. Kotomin, E. Heifets, J. Maier, R. I. Eglitis, and G. Borstel, Hybrid DFT calculations of the atomic and electronic structure for  $\text{ABO}_3$  perovskite (001) surfaces. *Surf. Sci.* **575**, 75–88 (2005).
9. R. I. Eglitis and D. Vanderbilt, First-principles calculations of atomic and electronic structure of  $\text{SrTiO}_3$  (001) and (011) surfaces. *Phys. Rev. B* **77**, 195408 (2008).
10. E. A. Kotomin, R. I. Eglitis, J. Maier, and E. Heifets, Calculations of the atomic and electronic structure for  $\text{SrTiO}_3$  perovskite thin films. *Thin Solid Films* **400**, 76–80 (2001).

11. R. I. Eglitis and D. Vanderbilt, Ab initio calculations of BaTiO<sub>3</sub> and PbTiO<sub>3</sub> (001) and (011) surface structures. *Phys. Rev. B* **76**, 155439 (2007).
12. R. I. Eglitis, G. Borstel, E. Heifets, S. Piskunov, and E. A. Kotomin, Ab initio calculations of the BaTiO<sub>3</sub> (100) and (110) surfaces. *J. Electroceram.* **16**, 289–292 (2006).
13. R. I. Eglitis, First-principles calculations of BaZrO<sub>3</sub> (001) and (011) surfaces. *J. Phys.: Condens. Matter.* **19**, 356004 (2007).
14. R. I. Eglitis and M. Rohlfing, First-principles calculations of the atomic and electronic structure of SrZrO<sub>3</sub> and PbZrO<sub>3</sub> (001) and (011) surfaces. *J. Phys.: Condens. Matter.* **22**, 415901 (2010).
15. J. M. Zhang, J. Cui, K. W. Xu, V. Ji, and Z. Y. Man, Ab initio modelling of CaTiO<sub>3</sub> (110) polar surfaces. *Phys. Rev. B* **76**, 115426 (2007).
16. W. Liu, C. Wang, J. Cui, and Z. Y. Man, Ab initio calculations of the CaTiO<sub>3</sub> (111) polar surfaces. *Solid State Commun.* **149**, 1871–1876 (2009).
17. V. R. Saunders, R. Dovesi, C. Roetti, M. Causa, N. M. Harrison, R. Orlando, and C. M. Zicovich-Wilson, *CRYSTAL-2006 User Manual*. University of Torino. Torino, Italy; 2006.
18. S. Piskunov, E. Heifets, R. I. Eglitis, and G. Borstel, Bulk properties of SrTiO<sub>3</sub>, BaTiO<sub>3</sub> and PbTiO<sub>3</sub> perovskites: an *ab initio* HF/DFT study. *Comput. Mater. Sci.* **29**, 165–180 (2004).
19. A. B. Becke, Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648–5652 (1993).
20. C. Lee, W. Yang, and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785–789 (1988).
21. P. J. Hay and W. R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys.* **82**, 270–283 (1985).
22. H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations. *Phys. Rev. B* **13**, 5188–5192 (1976).
23. B. J. Kennedy, C. J. Howard, and B. C. Chakoumakos, Phase transitions in perovskite at elevated temperatures—a powder neutron diffraction study. *J. Phys.: Condens. Matter.* **11**, 1479–1488 (1999).
24. C. R. A. Catlow and A. M. Stoneham, Ionicity in solids. *J. Phys. C: Solid State Phys.* **16**, 4321–4338 (1983).
25. K. Ueda, H. Yanagi, R. Noshiro, H. Hosono, and H. Kawazoe, Vacuum ultraviolet reflectance and electron energy loss spectra of CaTiO<sub>3</sub>. *J. Phys.: Condens. Matter* **10**, 3669–3677 (1998).