

This article was downloaded by: [MPI Max-Planck-Institute]

On: 28 November 2013, At: 01:00

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phase Transitions: A Multinational Journal

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gpht20>

Ab initio calculations of BaTiO₃ (111) surfaces

R.I. Eglitis^a

^a Institute of Solid State Physics, University of Latvia, Riga, Latvia
Published online: 16 Jan 2013.

To cite this article: R.I. Eglitis (2013) Ab initio calculations of BaTiO₃ (111) surfaces, Phase Transitions: A Multinational Journal, 86:11, 1115-1120, DOI: [10.1080/01411594.2012.759220](https://doi.org/10.1080/01411594.2012.759220)

To link to this article: <http://dx.doi.org/10.1080/01411594.2012.759220>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Ab initio calculations of BaTiO₃ (111) surfaces

R.I. Eglitis*

Institute of Solid State Physics, University of Latvia, Riga, Latvia

(Received 25 October 2012; final version received 11 December 2013)

The article presents the results of calculations of 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 BaO₃ BaTiO₃ (111) surface terminations. For both Ti- and BaO₃-terminated BaTiO₃ (111) surfaces, the upper layer atoms relax inward. The second layer atoms, with the sole exception of Ti-terminated BaTiO₃ (111) surface Ba atom, relax outward. The calculated surface relaxation energy for Ti-terminated BaTiO₃ (111) surface is more than two times larger than the surface relaxation energy for BaO₃-terminated BaTiO₃ (111) surface. The surface energy for Ti-terminated BaTiO₃ (111) surface (7.28 eV/cell) is smaller, than the surface energy for BaO₃-terminated (111) surface (8.40 eV/cell).

Keywords: *ab initio* calculations; BaTiO₃; (111) surface; B3LYP

1. Introduction

Thin films of BaTiO₃ 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 BaTiO₃ applications, the surface structure and the related surface electronic and chemical properties are of primary importance.

In view of this technological importance, it is not surprising that BaTiO₃ (001) surface has been extensively studied theoretically by means of *ab initio* and shell model methods [3–9]. In contrast to widely investigated BaTiO₃ (001) surfaces, only a small number of studies exist dealing with atomic and electronic structure calculations of BaTiO₃ (011) surface [4,5,9]. For example, recently, Eglitis and Vanderbilt [9] have performed an *ab initio* study of BaTiO₃ (011) surfaces using a hybrid Hartree–Fock (HF) and density-functional theory (DFT) exchange–correlation functional, in which HF exchange is mixed with Beckes three-parameter DFT exchange and combined with the nonlocal correlation functional of Perdew and Wang (B3PW) [9].

There are no experimental studies reported dealing with BaTiO₃ (111) surfaces, but several experimental studies exist dealing with related SrTiO₃ (111) surfaces. For example, Tanaka and Kawai [10] have obtained clean surfaces of reduced SrTiO₃ (111) crystals and observed them by means of scanning tunneling microscopy combined with the reflection high-energy diffraction. They have observed two different surface structures. One, obtained by annealing at the temperature $\sim 1,180^\circ\text{C}$, is assigned to have a SrO₃ outermost layer. The other, obtained by annealing at the temperature $\sim 1,220^\circ\text{C}$, is assigned to have a Ti outermost layer [10]. More than 10 years later, Chang et al. [11] also

*Email: reglitis@yahoo.com

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. [12], relying on the results obtained by a total energy, semi-empirical Hartree–Fock method, discussed 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.

2. Computational details

To perform the first-principles DFT-B3LYP calculations, the CRYSTAL computer code [13] was used. 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 the 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 two-dimensional (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 (BSs). The optimization of such BSs for SrTiO₃, BaTiO₃, and PbTiO₃ perovskites was developed and discussed by Piskunov et al. [14]. In the present article, this new BS was used for BaTiO₃ (111) surface calculations.

Numerical calculations have been performed using the hybrid exchange–correlation B3LYP (Becke three-parameter Lee–Yang–Parr) functional involving a hybrid of nonlocal Fock exact exchange, LDA exchange, and Beckes gradient corrected exchange functional [15], combined with the nonlocal gradient corrected correlation potential by Lee–Yang–Parr [16]. The Hay–Wadt small-core effective core pseudopotentials (ECPs) have been adopted for Ba and Ti atoms [17,18]. 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 [14].

The reciprocal space integration has been performed by sampling the Brillouin zone of the five-atom cubic unit cell with the 5 × 5 × 5 Pack–Monkhorst net for the BaTiO₃ bulk and the 5 × 5 × 1 Pack–Monkhorst net for the BaTiO₃ (111) surface [19], which provides the balanced summation in direct and reciprocal spaces. To achieve high accuracy, large enough tolerances of 7, 8, 7, 7, and 14 have been chosen for the Coulomb overlap, Coulomb penetration, exchange overlap, the first exchange pseudo-overlap, and the second exchange pseudo-overlap, respectively [13].

The BaTiO₃ (111) surfaces have been modeled with 2D slabs, consisting of several planes perpendicular to the [111] crystal direction. The CRYSTAL code has allowed to avoid artificial periodicity along the *Oz* direction and to perform simulations for stand-alone 2D slabs. To simulate BaTiO₃ (111) surfaces, I have implemented symmetrical (with respect to the mirror plane) slabs consisting of nine alternating Ti and BaO₃ layers. One of these slabs is terminated by Ti planes and consists of a supercell containing 21 atoms. The second slab is terminated by BaO₃ planes and consists of a supercell containing 24 atoms. These slabs are nonstoichiometric, with unit cell formulas Ba₄Ti₅O₁₂ and Ba₅Ti₄O₁₅, respectively. These two (Ti and BaO₃) terminations are the only two possible flat and dense (111) surfaces in BaTiO₃ perovskite lattice structure.

As it is well known from previous studies dealing with CaTiO_3 , BaZrO_3 , and SrTiO_3 polar (111) surfaces [20–24], a strong electron redistribution takes place for such terminations in order to cancel the polarity, but the Ti- or BaO_3 -terminated BaTiO_3 (111) surface keeps its insulating character and such calculations are possible. Of course, it is impossible to perform calculations for asymmetric slabs with different terminations, for example, $\text{Ti-BaO}_3\text{-Ti-BaO}_3\text{-Ti-BaO}_3\text{-Ti-BaO}_3$, since this would lead to a large dipole moment for an asymmetric slab.

As a next step, I have calculated cleavage and surface energies. It is obvious that Ti- and BaO_3 -terminated (111) surfaces are mutually complementary. The cleavage energy (per surface cell) of the complementary surface $E_{\text{cl}}(\zeta)$ ($\zeta = \text{Ti}$ or BaO_3) can be obtained from the total energies computed for the unrelaxed slabs through the following equation:

$$E_{\text{cl}}(\zeta) = \frac{1}{4}[E_{\text{slab}}(\text{Ti}) + E_{\text{slab}}(\text{BaO}_3) - 9E_{\text{bulk}}], \quad (1)$$

where $E_{\text{slab}}^{\text{unrel}}(\zeta)$ is the total energy of unrelaxed ζ -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 following equation:

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

where $E_{\text{slab}}^{\text{rel}}(\zeta)$ is the ζ -terminated slab energy after relaxation and $\frac{1}{2}$ 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:

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

3. Main results

As a starting point of the calculations, I calculated the BaTiO_3 (4.021 Å) bulk lattice constant for the cubic phase. The calculated bulk lattice constant for BaTiO_3 (4.021 Å) is slightly larger than the experimental value of 4.00 Å [25]. Thus, the computational approach used in the present study can be established as appropriate. I used the theoretical BaTiO_3 bulk lattice constant in the following (111) surface calculations.

To characterize the chemical bonding and covalency effects, I 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 [26,27]. The calculated effective charges for the BaTiO_3 bulk are (+1.797 e) for the Ba atom, (+2.365 e) for the Ti atom, and (−1.387 e) for the O atom (see Table 1). The bond population of the chemical bonding between Ti and O atoms is (+0.100 e) in BaTiO_3 . The bond population between O and O atoms is negative (−0.038 e), which indicates repulsion between O and O atoms (see Table 1).

According to the results of the calculations, the upper layer Ti atom for Ti-terminated BaTiO_3 (111) surface strongly (by 11.19% of bulk lattice constant a_0) relaxes inward (see Table 2). The second layer Ba atom also rather strongly relaxes inward (by 6.22% of a_0),

Table 1. Calculated effective charges Q and bond populations P (in e) for bulk BaTiO₃.

| BaTiO ₃ | | |
|--------------------|----------|--------|
| Ion or bond | Property | Value |
| Ba | Q | +1.797 |
| O | Q | -1.387 |
| Ti | Q | +2.365 |
| Ba-O | P | -0.032 |
| Ti-O | P | +0.100 |
| O-O | P | -0.038 |

Table 2. Calculated relaxation of Ti-terminated BaTiO₃ (111) surface upper three layer atoms (as a percentage of the bulk crystal lattice constant $a_0 = 4.021$ Å). Positive (negative) values refer to displacements in the direction outward (inward) of the surface.

| BaTiO ₃ | | |
|--------------------|-----|-----------------------|
| Layer | Ion | Displ. (Δz) |
| 1 | Ti | -11.19 |
| 2 | Ba | -6.22 |
| | O | +2.74 |
| 3 | Ti | -0.25 |

while the second layer O atom relaxes outward by 2.74% of a_0 . Inward relaxation of the third layer Ti atom is rather weak, only 0.25% of a_0 .

For BaO₃-terminated BaTiO₃ (111) surface, the upper layer metal atom relaxes inward by 1.24% of a_0 , but the upper layer O atom relaxes inward even more strongly by 3.98% of a_0 (see Table 3). The second layer Ti atom outward relaxation (2.49% of a_0) is larger than the upper layer Ba atom relaxation. The third layer Ba atom rather strongly relaxes outward, but the third layer O atom relaxes inward by a very small magnitude (0.25% of a_0).

The calculated surface relaxation energy for Ti-terminated BaTiO₃ (111) surface (-1.94 eV) is more than two times larger than the surface relaxation energy for

Table 3. Calculated relaxation of BaO₃-terminated BaTiO₃ (111) surface upper three layers (as a percentage of the bulk crystal lattice constant $a_0 = 4.021$ Å). Positive (negative) values refer to displacements in the direction outward (inward) of the surface.

| BaTiO ₃ | | |
|--------------------|-----|-----------------------|
| Layer | Ion | Displ. (Δz) |
| 1 | Ba | -1.24 |
| | O | -3.98 |
| 2 | Ti | +2.49 |
| 3 | Ba | +1.49 |
| | O | -0.25 |

Table 4. Calculated cleavage, relaxation, and surface energies for BaTiO₃ (111) surfaces (in electron volt per surface cell).

| Surface | Termination | E_{cl} | E_{rel} | E_{surf} |
|--------------------------|-------------------------|----------|-----------|------------|
| BaTiO ₃ (111) | Ti-term. | 9.22 | -1.94 | 7.28 |
| | BaO ₃ -term. | 9.22 | -0.82 | 8.40 |

BaO₃-terminated BaTiO₃ (111) surface (-0.82 eV) (see Table 4). The calculated surface energy for Ti-terminated BaTiO₃ (111) surface is equal to 7.28 (eV/cell), while the surface energy for BaO₃-terminated BaTiO₃ (111) surface is equal to 8.40 (eV/cell).

4. Conclusions

Using the hybrid B3LYP approach, the surface relaxation for the two possible BaTiO₃ (111) surface terminations has been calculated. For both Ti- and BaO₃-terminated BaTiO₃ (111) surfaces, the upper layer atoms relax inward. The second layer atoms, with the sole exception of Ti-terminated BaTiO₃ (111) surface Ba atom, relax outward. The Ti-terminated BaTiO₃ (111) surface upper layer Ti atom exhibits the strongest relaxation between all Ti- and BaO₃-terminated BaTiO₃ (111) surface atoms.

The calculated surface relaxation energy for Ti-terminated BaTiO₃ (111) surface is more than two times larger than the surface relaxation energy for BaO₃-terminated BaTiO₃ (111) surface. The surface energy for Ti-terminated BaTiO₃ (111) surface (7.28 eV/cell) is smaller than the surface energy for BaO₃-terminated (111) surface (8.40 eV/cell). My calculated BaTiO₃ (111) surface energies are considerably larger than the another ABO₃ perovskite (001) and (011) surface energies [4,5,7-9,28-31].

Acknowledgement

This work was supported by European Social Fund Project Nr. 2009/0202/1DP/1.1.12.0/09/APIA/VIAA/141 and the Latvian Council of Science.

References

- [1] Noguera C. Physics and chemistry at oxide surfaces. New York: Cambridge University Press; 1996.
- [2] Auciello O, Scott JF, Ramesh R. The physics of ferroelectric memories. Phys. Today. Jul 1998;51:22.
- [3] Padilla J, Vanderbilt D. *Ab initio* study of BaTiO₃ surfaces. Phys. Rev. B. 1997;56:1625.
- [4] Eglitis RI, Borstel G, Heifets E, Piskunov S, Kotomin E. *Ab initio* calculations of the BaTiO₃ (100) and (110) surfaces. J. Electroceramics. 2006;16:289.
- [5] Heifets E, Kotomin EA, Maier J. Semi-empirical simulations of surface relaxation for perovskite titanates. Surf. Sci. 2000;462:19.
- [6] Fu L, Yaschenko E, Resca L, Resta R. Hartree-Fock studies of surface properties of BaTiO₃. Phys. Rev. B. 1999;60:2697.
- [7] Eglitis RI, Piskunov S, Heifets E, Kotomin EA, Borstel G. *Ab initio* study of the SrTiO₃, BaTiO₃ and PbTiO₃ (001) surfaces. Ceramics International. 2004;30:1989.
- [8] Piskunov S, Kotomin EA, Heifets E., Maier J., Eglitis RI, Borstel G. Hybrid DFT calculations of the atomic and electronic structure for ABO₃ perovskite (001) surfaces. Surf. Sci. 2005;575:75.

- [9] Eglitis RI, Vanderbilt D. *Ab initio* calculations of BaTiO₃ and PbTiO₃ (001) and (011) surface structures. Phys. Rev. B. 2007;76:155439.
- [10] Tanaka H, Kawai T. Surface structure of reduced SrTiO₃ (111) observed by scanning tunneling microscopy. Surf. Sci. 1996;365:437.
- [11] Chang J, Park YS, Kim, SK. Atomically flat single-terminated SrTiO₃ (111) surface. Appl. Phys. Lett. 2008;92:152910.
- [12] Pojani A, Finocchi F, Noguera C. Polarity on the SrTiO₃ (111) and (110) surfaces. Surf. Sci. 1999;442:179.
- [13] Saunders VR, Dovesi R, Roetti C, Causa M, Harrison NM, Orlando R, Zicovich-Wilson CM. CRYSTAL-2006 user manual. Torino, Italy: University of Torino; 2006.
- [14] Piskunov S, Heifets E, Eglitis RI, Borstel G. Bulk properties and electronic structure of SrTiO₃, BaTiO₃, PbTiO₃ perovskites: an *ab initio* HF/DFT study. Comput. Mater. Sci. 2004;29:165.
- [15] Becke AD. Density-functional thermochemistry. 3. The role of exact exchange. J. Chem. Phys. 1993;98:5648.
- [16] Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B. 1988;37:785.
- [17] Hay PJ, Wadt WR. *Ab initio* effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. J. Chem. Phys. 1984;82:284.
- [18] Hay PJ, Wadt WR. *Ab initio* effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. J. Chem. Phys. 1985;82:299.
- [19] Monkhorst HJ, Pack JD. Special points for Brillouin-zone integrations. Phys. Rev. B. 1976;13:5188.
- [20] Eglitis RI. First-principles calculations of the atomic and electronic structure of CaTiO₃ (111) surfaces. Ferroelectrics. 2011;424:1.
- [21] Liu W, Wang C, Cui J, Man ZY. *Ab initio* calculations of the CaTiO₃ (111) polar surfaces. Solid State Commun. 2009;149:1871.
- [22] Eglitis RI. *Ab initio* calculations of the atomic and electronic structure of BaZrO₃ (111) surfaces. Solid State Ionics. 2013;230:43.
- [23] Pojani A, Finocchi F, Noguera C. Polarity on the SrTiO₃ (111) and (110) surfaces. Surf. Sci. 1999;442:179.
- [24] Pojani A, Finocchi F, Noguera C. A theoretical study of the unreconstructed polar (111) face of SrTiO₃. Appl. Surf. Sci. 1999;142:177.
- [25] Hellwege KH, Hellwege AM, editors. Ferroelectrics and related substances. New Series, Vol. 3. Berlin: Landolt-Bornstein, Springer Verlag; 1969.
- [26] Catlow CRA, Stoneham AM. Ionicity in solids. J. Phys. C Solid State Phys. 1983;16:4321.
- [27] Bochicchio RC, Reale HF. On the nature of crystalline bonding: extension of statistical population analysis to two- and three-dimensional crystalline systems. J. Phys. B At. Mol. Opt. Phys. 1993;26:4871.
- [28] Eglitis RI, Vanderbilt D. *Ab initio* calculations of the atomic and electronic structure of CaTiO₃ (001) and (011) surfaces. Phys. Rev. B. 2008;78:155420.
- [29] Eglitis RI, Vanderbilt D. First-principles calculations of atomic and electronic structure of SrTiO₃ (001) and (011) surfaces. Phys. Rev. B. 2008;77:195408.
- [30] Eglitis RI. First-principles calculations of BaZrO₃ (001) and (011) surfaces. J. Phys. Condens. Matter. 2007;19:356004.
- [31] Eglitis RI, Rohlfig M. First-principles calculations of the atomic and electronic structure of SrZrO₃ and PbZrO₃ (001) and (011) surfaces. J. Phys. Condens. Matter. 2010;22:415901.