

Oxygen-vacancy defects on BaTiO₃ (001) surface: a quantum chemical study

Carlos Duque and Arvids Stashans

Centro de Investigación en Física de la Materia Condensada, Corporación de Física Fundamental y Aplicada, Apartado 17-12-637, Quito, Ecuador

Abstract

A quantum-chemical study of technologically important BaTiO₃ crystal and oxygen-vacancy defects on its (001) surface is reported in the present work. The computations are made using a quantum-chemical method developed for periodic systems (crystals), which is based on the Hartree-Fock theory. The atomic rearrangement due to the surface creation is obtained for a pure BaTiO₃ by means of the periodic large unit cell (LUC) model and using an automated geometry optimisation procedure. The same technique is employed to study the electronic and structural properties of the material due to the presence of an O vacancy and F centre (two electrons trapped in an oxygen vacancy). The computations are carried out for both cubic and tetragonal lattices.

Keywords: Oxygen-vacancy defects; BaTiO₃; (001) surface; Quantum-chemical study

1. Introduction

The properties of metal oxides span as wide as those of any class of materials. One of the most important classes of metal oxides is titanates having the perovskite-type structure. Barium titanate (BaTiO_3) crystal nowadays is one of the most used titanates. It has a high dielectric constant at ambient temperature [1] and also shows piezoelectric properties. Other important features are its chemical and mechanical stability in a wide temperature range, which facilitates its fabrication in bulk polycrystals and both epitaxial and polycrystalline thin films. All of these properties make this material very useful in a number of applications such as dynamic random-access memories, piezoelectric transducers, thermistors and actuators [2-5]. In addition this titanate has large electro-optic coefficients and high photorefractive sensitivity, therefore can be used as an optical sensor [6].

Despite the fact that many studies have been done so far on this crystal our knowledge of its fundamental properties is not satisfactory. It is also worth to mention that the main properties of titanate crystals are strongly influenced by the presence of point defects. However, mainly studies on pure titanate surfaces have been reported so far. Some examples include advanced *ab initio* computations of ferroelectric BaTiO_3 surfaces [7-11] as well as similar SrTiO_3 and PbTiO_3 crystal terminations [8, 12, 13]. One of the most common point defects in oxide crystals is the so-called F centre (two electrons in an oxygen vacancy) as well as the O vacancy itself. That is why we investigate the electronic structure of a pure BaTiO_3 (001) surface and the surface containing oxygen-vacancy defects. An advanced quantum-chemical method developed for crystals and based on the molecular orbital (MO) formalism is used throughout the study.

2. Computational method

The employed method of periodically repeated large unit cells (LUCs) [14] is designed for the calculation of the total energy and electronic structure of crystals. We preferred to use the LUC model because of its advantage compared to different cluster models, for instance, a better treatment of the exchange interaction. A full discussion of the computational relations for calculating the total energy of a given crystal within the framework of the LUC approach is given in Refs. 14-16. In the present work we shall only outline the basic ideas of the method.

In the LUC $k = 0$ approximation, the Fock matrix elements are made self-consistent through the density matrix elements obtained in the following manner:

$$P_{pq}^0 = \frac{1}{N} \sum_k P_{pq}(k) \exp(ikR_v) \quad (1)$$

Here the summation is carried out over all k values in the reduced Brillouin zone (BZ) of the LUC. In this way the information regarding the density matrix $P_{pq}(k)$ is obtained only in the point $k = 0$. However, it has been proven [14, 15] that the computation of the electronic structure of the unit cell at $k = 0$ in the reduced BZ is equivalent to a band structure calculation at those BZ k points, which transform to the reduced BZ centre on extending the unit cell. As indicated by numerous studies [17-21], eight-fold or even four-fold-symmetric extension of the primitive unit cell proves to be completely sufficient to reproduce correctly the electronic band structure of a given crystal. In the present work we exploited 40-atom LUC (8-fold, 2 x 2 x 2 extension) for a pure surface studies while only a 135-atom LUC (27-fold, 3 x 3 x 3 extension) was used for defect computations. It is

important to mention that in the case of surface computations, the 2D periodicity was implemented. Thus the surface was modelled as a single slab applying two-dimensional periodicity along the $\langle 100 \rangle$ and $\langle 010 \rangle$ directions. The translation vector in the direction $\langle 001 \rangle$ was defined to be equal to zero.

Our method is based on a semi-empirical modification of the molecular orbital (MO) theory with a specific parametrization scheme [22]. Some atomic parameters are used to reproduce main features of a given crystal and to reduce considerably the computational time. Thus our method is not cumbersome and it is applicable to diverse extended systems with a complex structure and a mixed chemical bonding. The BaTiO_3 crystal has been parametrized by us before [23] where also details of the bulk crystal computations are given. The numerical values of atomic parameters are shown in tables 1 and 2. We would like to note that our method has been used before successfully to calculate surfaces. Some examples include study of charge and potential distribution near the GaP (110) surface [24], OH^- adsorption on the perfect rutile (TiO_2) (001) surface [18], and also calculation of organic adsorbates on the rutile (110) surface [25, 26].

Our method already has been applied to study the BaTiO_3 crystal giving encouraging results. Some examples include study of the self-trapped and impurity-trapped hole polarons [23, 27-29], calculation of Nb- and La-doped crystal [20, 30-32] as well as the determination H impurity influence upon the ferroelectricity in this material [33]. It is important to mention that the method has been also used to study F centres and O vacancies in a number of systems, for example, SrTiO_3 crystal bulk [34] and surface [35, 36], BaTiO_3 crystal bulk [37], corundum ($\alpha\text{-Al}_2\text{O}_3$) crystals [38, 39], etc.

It is important to mention that the difference between the cubic and tetragonal phases, e.g. atomic positions within the LUC, electronic band structure and density of states (DOS) patterns, was reproduced applying slightly different set of parameters for two structures. The details of this procedure are depicted in Ref. [23]. The lattice parameters obtained for the bulk of both phases were maintained fixed for the surface computations.

3. Results and discussion

3.1. A perfect BaTiO₃ (001) surface

In order to characterise the perfect BaTiO₃ (001) surface, a LUC of 40 atoms was used and the equilibrium geometry was calculated allowing all atoms to displace. An important point to be addressed is the choice of the LUC size. Normally, in density-functional studies rather dense (4 x 4 x 4) and (6 x 6 x 6) *k*-point meshes are used to reproduce reliably electronic band structure and geometry of such complex systems as BaTiO₃. However, in the case of the Hartree-Fock formalism, the supercell size might be smaller if the Coulomb and especially the exchange interaction are calculated adequately. In the case of the tetragonal phase of BaTiO₃, it was found that the lattice parameters are $a = 3.99 \text{ \AA}$ and $c = 4.03 \text{ \AA}$ [20]. Thus *c/a*-ratio is 1.01 as expected and the lattice parameters are very close to the experimental values of $a = 3.9947 \text{ \AA}$ and $c = 4.0336 \text{ \AA}$ [40]. We can also mention that recently a study using both the density-functional-theory (DFT) and our CLUSTERD computer code were performed for the ferroelectric BaTiO₃ and O-vacancy defects in the bulk of the tetragonal phase of this material [37, 41]. The DFT method used the local density approximation [42] as it is considered in the CASTEP computer code [43]. In order to model the peculiar bulk-ferroelectric properties, the CASTEP program exploited

the Vanderbilt ultrasoft-pseudopotential/plane-wave technique [7] using cut-off energy of 360 eV with (6 x 6 x 6) Monkhorst-Pack k -point mesh. Both computer programs, CLUSTERD and CASTEP, gave practically the same results not only on the bulk-ferroelectric distortions, but also on the atomic displacements around the O-vacancy defects. Therefore, our method surely is adequate to study O-vacancy defects on the BaTiO₃ (001) surfaces.

In the cubic phase of the material (Fig. 1) we obtained inward displacements of the atoms placed in the exterior Ba-O and Ti-O₂ layers. The magnitudes of atomic movements were found to be equal to 0.14 Å for Ba and 0.06 Å for O atoms, respectively in the case of the Ba-O layer. The relaxation for the Ti-O₂ exterior layer showed O movements by 0.23 Å and Ti movements by 0.01 Å, respectively. We also intended to optimize the slab's "inner" atoms but without any results, which implies that the surface creation effect does not extend to these atoms.

In the tetragonal phase (Fig. 2) some atomic movements showed somewhat different pattern. The O atoms again exhibited inward displacements by 0.04 Å for the Ba-O layer and 0.15 Å for Ti-O₂ layer, respectively. However, the cationic displacements were found to be outward, 0.11 Å for Ba and 0.06 Å for Ti atoms, respectively. In our mind, the displacements of Ba and Ti atoms situated in the topmost layers of the tetragonal phase slab might be explained by the presence of ferroelectricity. This phenomenon occurs just due to the opposite displacements of cations and anions and this is what we get. It is worth to mention that similar effect already has been observed in the case of SrTiO₃ (001) perfect surface [36].

It is worth to mention that in general our results on perfect surface re-arrangement agree with those of previous theoretical works (see [7-11] and references therein), i.e. the

atomic movements within the planes are negligible while their displacements inward/outward the crystal are considerable. The directions of atomic relaxation are mainly inward again in coincidence with the results reported in previous theoretical works.

3.2. Oxygen vacancies and F centres on the exterior Ba-O layer

In order to avoid any mutual defect-defect interaction, i.e. to study *single defect* within the periodic LUC model, we have enlarged the BaTiO₃ slab up to 135 atoms, which corresponds to the symmetric 3 x 3 x 3 extension of the primitive unit cell of the given crystal. So, a single slab with no periodicity in the z direction was used to study O vacancies and F centres. However, the model remained fully periodic within the xy plane, 2D periodicity.

In order to study the O vacancies we removed one of the O ions from the topmost Ba-O layer. The charge of the O vacancy with respect to the perfect crystalline lattice is +2, i.e., we deal with the so-called charged point defect within the periodic model. The problem for net charge has been discussed in detail in Ref. 44, in which the reliability of the charged periodic model has been shown. According to [44] the Coulomb energy E^c of a periodic array is written as follows:

$$E^c = \frac{1}{2} \sum_{ij} \frac{q_i q_j}{|\mathbf{r}_{j1} - \mathbf{r}_{i0}|} \operatorname{erf}(\gamma^{1/2} |\mathbf{r}_{j1} - \mathbf{r}_{i0}|) + \frac{2\pi}{v_0} \sum_{\mathbf{G} \neq 0} \frac{1}{G^2} |S(\mathbf{G})|^2 \exp(-G^2/4\gamma) - \left(\frac{\gamma}{\pi}\right)^{1/2} \sum_i q_i^2 - \frac{\pi Q^2}{2v_0\gamma} \quad (2)$$

where the term $j = i$ is omitted if $l=0$, q_i is the charge on ion i , γ is the Ewald parameter, v_0 is the volume of the repeating 135-atom LUC, the G is the reciprocal-lattice vector of the

superlattice, the $S(G)$ is the structure factor of the repeating unit, and Q is the net charge of the unit, which is equal to +2 in our case. The last term of equation (2) appearing due to the net charge Q does not depend on the positions of the ions within the LUC. In the present work we compare the total energies of different spatial configurations *within the same* type of defect, i.e., within *the constant* last term of equation (2), as a result it is not necessary to take into account additionally the effect of the last term.

As expected the surrounding atoms experienced displacements due to this perturbation. In the cubic structure the vacancy-nearest O atoms move towards the defect and these displacements are completely symmetric (see Table 3 and Fig. 3). On the other hand, the movements of positively charged Ti and Ba atoms are outward with respect to the O vacancy (Fig. 3). Thus one can conclude that basically the atomic displacements are due to the electrostatic Coulomb interaction. There are some variations in the electronic charge distribution within the defective region, especially one can notice change in the charge of the vacancy-closest Ti(1) atom. Since the O vacancy is a positively charged defect it might polarise slightly the surrounding lattice and lead to the formation of a local dipole moment. The obtained relaxation energy as a difference between the system's total energies for the relaxed equilibrium geometry and the non-relaxed structure is found to be equal to 3.68 eV.

In order to study F centres we have added two extra electrons into the system. The obtained atomic movements for this case show similar pattern. However, the magnitude of their displacements is smaller compared to the case of the above-discussed O vacancy. Complete analysis of the atomic displacements is given in Table 3 and Fig. 3. The calculated relaxation energy for this case is about 2.95 eV. This value is smaller compared to the case of the O vacancy due to the smaller movements. The analysis of the atomic charges (Table 3) points out to the localised nature of the F centre, it is well localised

within the defective region, mainly on the nearest Ti(1) atom. We also observe an occurrence of the local energy level within the band-gap situated around 1.1 eV below the edge of the conduction band. In our mind, this explains some experimental results [45, 46] obtained by scanning tunnelling spectroscopy and claiming the existence of in-gap electronic states at about 1.0 eV below Fermi level.

Similar results were obtained for the O vacancy and F centre on the Ba-O topmost layer in the tetragonal BaTiO₃ structure. The atomic displacements are described in Table 3 and Fig. 4. As it is possible to see the magnitude of lattice distortion in the defective region is similar to the one obtained before for the cubic structure. However, contrary to the completely symmetric movements in the cubic phase, we observe some asymmetry in the tetragonal structure. As it is shown in Fig. 4, O(6) to O(9) atoms experience rotation by around 1.5° in a peculiar way as demonstrated in the figure. In our mind, due to the lower symmetry of the tetragonal phase compared to the cubic structure, some local phase transitions occur leading to the observed asymmetric movements of the O atoms. The calculated relaxation energies are found to be equal to 1.30 eV and 1.81 eV for the O vacancy and F centre, respectively. The F centre finds itself localised on the Ti(1) atom as in the cubic phase but the magnitude of localisation is somewhat smaller, i.e. its wave function is found to be more diffuse. The local energy level originated from the F centre is obtained to be about 0.9 eV below the conduction band edge.

3.3. Oxygen vacancies and F centres on the exterior Ti-O₂ layer

O vacancy on the Ti-O₂ layer finds itself in somewhat different surrounding. As a result we obtain some peculiarities in atomic movements and electronic charge

redistribution (see Table 4 and Fig. 5). In the case of the cubic lattice all Ti and Ba atoms move outwards while the O atoms towards the O vacancy according to the electrostatic Coulomb interaction. It is important to note that we observe a displacement for the distant O(18) atom. Obviously, this testifies the importance of the correlation effects in BaTiO₃ crystal and a possible formation of an electronic dipole. The obtained relaxation energy is found to be equal to 2.79 eV. In the case of the F centre we find somewhat smaller atomic movements maintaining their directions of relaxation. The displacements of Ti atoms along the $\langle 001 \rangle$ axis considerably larger compared to their movements along the $\langle 100 \rangle$ and $\langle 010 \rangle$ directions. This implies symmetry reduction and a possible formation of a new phase in the defective region due to the F centres. The obtained relaxation energy is found to be around 1.65 eV. A noticeable difference compared to the defects on the Ba-O layer is found for the localization nature of the F centres. As it follows from Table 4, the state of the F centre is delocalised. We also do not observe any local energy level within the band-gap with extra electrons being within the conduction band.

The same results are obtained in the tetragonal phase of the material. The computed relaxation energies are about 2.16 eV and 1.46 eV for the O vacancy and F centre, respectively. The F centre is delocalised and possibly can contribute into the augmentation of electric conductivity in the BaTiO₃.

Our calculations are similar to SrTiO₃ surface [36] if we note the difference between these two crystals.

4. Conclusions

The quantum-chemical method developed from crystal studies is used to compute O vacancies and F centres on the different layers of the BaTiO₃ (001) surface considering both cubic and tetragonal structures. The obtained atomic displacements within the defective region point out to the importance of (i) Coulomb interaction and thus the ionic chemical-bonding in this material, and also (ii) polarisation-correlation effects, which occur due to the defect presence. In general, the atomic movements and relaxation energies are larger for the positively charged O vacancy compared to the corresponding values for the F centre. The situation of F centre, either on the Ba-O layer or on the Ti-O₂ layer, is very important in order to understand the nature of localisation/delocalisation of this defect. In the case of the F centres on the Ba-O layer, we find the local energy level and the defects are well localised within the vacancy region in accordance to the experimental results [45, 46]. In the case of the Ti-O₂ layer, the F centres are delocalised and extra electrons are found in the lower part of the conduction band of the material.

References

- [1] D. Balzar, H. Ledbetter, P. W. Stephens, E. T. Park, and J. L. Routbort, *Phys. Rev. B* 59 (1999) 5.
- [2] U. Van Stevendaal, K. Buse, S. Kämpar, H. Hesse, and E. Krätzig, *Appl. Phys. B* 63 (1996) 315.
- [3] H. Song, S. X. Dou, M. Chi, H. Gao, Y. Zhu, and P. Ye, *J. Opt. Soc. Am. B* 15 (1998) 1329.
- [4] D. Mahgerefteh and J. Feinberg, *Modern Phys. Lett. B* 5 (1991) 693.
- [5] G. Rass, G. Montemezzani, P. Bernasconi, and M. Zgionik, *J. Appl. Phys.* 79 (1996) 3665.
- [6] J. Feinberg, D. Heiman, A. R. Tanguay, Jr., and R. W. Hellwarth, *J. Appl. Phys.* 51 (1980) 1297.
- [7] B. Meyer and D. Vanderbilt, *Phys. Rev. B* 63 (2001) 205426.
- [8] B. Meyer, J. Padilla, and D. Vanderbilt, *R. Soc. Chem. Faraday Disc.* 114 (1999) 395.
- [9] J. Padilla and D. Vanderbilt, *Phys. Rev. B* 56 (1997) 1625.
- [10] R. E. Cohen, *Ferroelectrics* 194 (1997) 323.
- [11] W. Zhong, D. Vanderbilt, and K. M. Rabe, *Phys. Rev. B* 52 (1995) 6301.
- [12] J. Padilla and D. Vanderbilt, *Surf. Sci.* 418 (1998) 64.
- [13] P. Ghosez and K. M. Rabe, *Appl. Phys. Lett.* 76 (2000) 2767.
- [14] A. Shluger and E. Stefanovich, *Phys. Rev. B* 42 (1990) 9664.
- [15] E. V. Stefanovich, E. K. Shidlovskaya, A. L. Shluger, and M. A. Zakharov, *Phys. Status Solidi (b)* 160 (1990) 529.
- [16] P. V. Smith, J. E. Szymanski, and J. A. D. Matthews, *J. Phys. C* 18 (1985) 3157.

- [17] A. Stashans, S. Lunell, R. Bergström, A. Hagfeldt, and S.-E. Lindquist, *Phys. Rev. B* 53 (1996) 159.
- [18] A. Stashans, S. Lunell, and R. W. Grimes, *J. Phys. Chem. Solids* 57 (1996) 1293.
- [19] A. Stashans and S. Lunell, *Int. J. Quant. Chem.* 63 (1997) 729.
- [20] E. Patiño and A. Stashans, *Ferroelectrics* 256 (2001) 189.
- [21] P. Sánchez and A. Stashans, *Phil. Mag. B* 81 (2001) 1963.
- [22] A. Shluger, *Theor. Chim. Acta* 66 (1985) 355.
- [23] H. Pinto and A. Stashans, *Comput. Mater. Sci.* 17 (2000) 73.
- [24] E. V. Stefanovich and A. L. Shluger, *J. Phys.: Condens. Matter* 6 (1994) 4255.
- [25] P. Persson, A. Stashans, R. Bergström, and S. Lunell, *Int. J. Quant. Chem.* 70 (1998) 1055.
- [26] L. Patthey, H. Rensmo, P. Persson, K. Westermark, L. Vayssieres, A. Stashans, Å. Petersson, P. Brühwiler, H. Siegbahn, S. Lunell, and N. Mårtensson, *J. Chem. Phys.* 110 (1999) 5913.
- [27] A. Stashans and H. Pinto, *Rad. Measurements* 33 (2001) 553.
- [28] A. Stashans and H. Pinto, *Int. J. Quant. Chem.* 79 (2000) 358.
- [29] H. Pinto and A. Stashans, *Phys. Rev. B* 65 (2002) 134304.
- [30] E. Patiño, F. Erazo, and A. Stashans, *Mater. Lett.* 50 (2001) 337.
- [31] E. Patiño and A. Stashans, *Comput. Mater. Sci.* 22 (2001) 137.
- [32] E. Patiño, A. Stashans, and R. Nieminen, *Key Engin. Mater.* 206/213 (2002) 1325.
- [33] A. Stashans and J. Chimborazo, *Phil. Mag. B* 82 (2002) 1145.
- [34] A. Stashans and F. Vargas, *Mater. Lett.* 50 (2001) 145.
- [35] A. Stashans and S. Serrano, *Surf. Sci.* 497 (2002) 285.
- [36] A. Stashans, F. Erazo, J. Ortiz, and P. Valverde, *Phil. Mag. B* 81 (2001) 1977.

- [37] Pinto, M. Yoshino, M. Morinaga, A. Stashans, and R. Nieminen, *Bull. Soc. Discrete Variational X α Japan* 14 (2001) 114.
- [38] A. Stashans, E. Kotomin, and J.-L. Calais, *Phys. Rev. B* 49 (1994) 14854.
- [39] E. A. Kotomin, A. Stashans, L. N. Kantorovich, A. I. Lifshitz, A. I. Popov, and I. A. Tale, *Phys. Rev. B* 51 (1995) 8770.
- [40] R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1960).
- [41] H. Pinto, S. Elliott, and A. Stashans, *SPIE Proceedings*, 5122 (2003) 308.
- [42] P. Hohenberg and W. Kohn, *Phys. Rev.* 136 (1964) 864.
- [43] V. Milman, B. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatkaya, and R. H. Nobes, *Int. J. Quant. Chem.* 77 (2000) 895.
- [44] M. Leslie and M. J. Gillan, *J. Phys. C* 18 (1985) 973.
- [45] H. Bando, T. Shimitzu, Y. Aiura, Y. Haruyama, O. Oka, and Y. Nishihara, *J. Vac. Sci. Techn.* 14 (1996) 1060.
- [46] T. Shimitzu, H. Bando, Y. Aiura, Y. Haruyama, O. Oka, and Y. Nishihara, *Japan J. Appl. Phys.* 34 (1995) L1305.

Tables

Table 1. Semi-empirical parameter sets used in the present work: ζ (au), E_{neg} (eV), P^0 (e) and β (eV).

Atom	AO	ζ	E_{neg}	P^0	β
Ba	6s	1.65	6.2	0.2	-0.4
	5p	2.8	34.6	2.0	-4.0
Ti	4s	1.4	3.7	0.65	-0.5
	4p	1.1	-15.0	0.04	-0.5
	3d	1.93	7.2	0.55	-9.0
O	2s	2.27	4.5	1.974	-16.0
	2p	1.86	-12.6	1.96	-16.0

Table 2. Two-centre parameters $\alpha_{\mu\text{B}}$ (au^{-1}), numbers in the parenthesis show the corresponding values of this parameter for the tetragonal phase.

A	B		
	Ba	Ti	O
Ba	0.20	0.10	0.57
Ti	0.53	0.13 (0.16)	0.38 (0.362)
O	0.36	0.10 (0.14)	0.15

Table 3. Atomic displacements, d (in Å) and changes in atomic charges, ΔQ (in e) for the atoms within the defective region if the defect is situated on the Ba-O plane. The atomic numeration corresponds to the one in Figs. 3 and 4.

#	atom	Cubic phase				Tetragonal phase			
		O Vacancy		F centre		O Vacancy		F centre	
		ΔQ	d	ΔQ	d	ΔQ	d	ΔQ	d
1	Ti	-0.23	0.22	-0.92	0.16	-0.26	0.15	-0.78	0.17
2	O	-0.04	0.19	-0.06	0.15	-0.03	0.16	-0.05	0.14
3	O	-0.03	0.19	-0.06	0.15	-0.03	0.16	-0.05	0.14
4	O	-0.03	0.19	-0.06	0.15	-0.03	0.16	-0.05	0.14
5	O	-0.04	0.19	-0.06	0.15	-0.03	0.16	-0.05	0.14
6	O	0.04	0.14	-0.05	0.11	0.02	0.15	-0.04	0.12
7	O	0.04	0.14	-0.04	0.11	0.02	0.15	-0.04	0.12
8	O	0.04	0.09	-0.05	0.11	0.02	0.15	-0.04	0.07
9	O	0.04	0.09	-0.05	0.11	0.02	0.15	-0.04	0.07
10	Ba	-0.01	0.20	-0.03	0.05	0.00	0.13	-0.03	0.14
11	Ba	-0.01	0.20	-0.03	0.05	-0.01	0.13	-0.03	0.14
12	Ba	-0.01	0.20	-0.03	0.05	-0.01	0.13	-0.04	0.14
13	Ba	-0.01	0.20	-0.03	0.05	0.00	0.13	-0.03	0.14
14	O	0.06	0.00	0.05	0.04	0.08	0.04	0.05	0.07

Table 4. Atomic displacements, d (in Å) and changes in atomic charges, ΔQ (in e) for the atoms within the defective region if the defect is situated on the Ti-O₂ plane. The atomic numeration corresponds to the one in Fig. 5.

#	Atom	Cubic phase				Tetragonal phase			
		O Vacancy		F centre		O Vacancy		F centre	
		ΔQ	d	ΔQ	d	ΔQ	d	ΔQ	d
1	O	-0.01	0.10	-0.02	0.03	-0.01	0.12	-0.01	0.08
2	O	0.26	0.06	0.24	0.07	0.23	0.13	0.25	0.16
3	O	0.26	0.06	0.24	0.07	0.23	0.13	0.25	0.16
4	O	0.01	0.09	-0.02	0.11	-0.04	0.09	-0.03	0.10
5	O	0.01	0.09	-0.02	0.11	-0.04	0.09	-0.02	0.10
6	O	0.00	0.17	-0.04	0.09	-0.04	0.17	-0.04	0.21
7	O	0.00	0.17	-0.03	0.09	-0.04	0.17	-0.04	0.21
8	O	0.00	0.17	-0.03	0.09	-0.04	0.17	-0.02	0.21
9	O	0.00	0.17	-0.03	0.09	-0.04	0.17	-0.02	0.21
10	Ti	0.05	0.06	0.03	0.09	0.17	0.20	0.00	0.21
11	Ti	0.05	0.06	0.03	0.09	0.17	0.20	0.00	0.21
12	Ti	-0.15	0.14	-0.26	0.17	-0.05	0.24	-0.15	0.23
13	Ti	-0.15	0.14	-0.26	0.17	-0.05	0.24	-0.15	0.23
14	Ti	0.05	0.06	0.03	0.09	0.17	0.20	-0.06	0.21
15	Ti	0.05	0.06	0.03	0.09	0.17	0.20	-0.07	0.21
16	Ba	0.00	0.06	0.00	0.07	-0.01	0.12	-0.01	0.17
17	Ba	0.00	0.06	0.00	0.07	-0.01	0.12	-0.02	0.17
18	O	0.00	0.04	-0.01	0.05	0.00	0.08	-0.04	0.04

Figure captions

Fig. 1. Atomic relaxation of the cubic BaTiO₃ (001) perfect surface.

Fig. 2. Atomic relaxation of the tetragonal BaTiO₃ (001) perfect surface. Please note that the tetragonal phase is chosen with c-axis perpendicular to the surface in all cases.

Fig. 3. Atomic relaxation around the O vacancy and F centre in the cubic structure of the BaTiO₃ (001) surface if defects are placed on the Ba-O layer. Atomic displacements obey the Coulomb law since the negatively charged O atoms move towards the positively charged O vacancy while the positively charged Ti and Ba atoms experience movements in the opposite direction. Movement of O(14) atom is observed only in the case of the F centre.

Fig. 4. Atomic relaxation around the O vacancy and the F centre in the tetragonal structure of the BaTiO₃ (001) surface if defects are placed on the Ba-O layer. Movements of atoms are similar to the case of the cubic structure but we observe additionally a rotation of four O atoms as shown in the figure.

Fig. 5. Atomic relaxation around the O vacancy and F centre in both cubic and tetragonal structures of the BaTiO₃ (001) surface if defects are placed on the Ti-O₂ layer. Displacements for O(2) and O(3) atoms are different for the F centre from those of the O vacancy. Displacement of O(18) atom situated far away from the surface is observed, which implies a possible correlation-polarisation effect along the direction perpendicular to the surface.

Cubic Phase

Surface of crystal

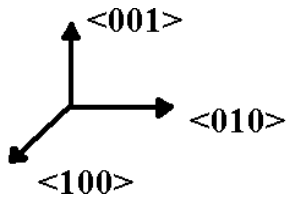
Ti-O Surface

- Oxygen
- Barium
- Titanium

Inside of crystal

Ba-O Surface

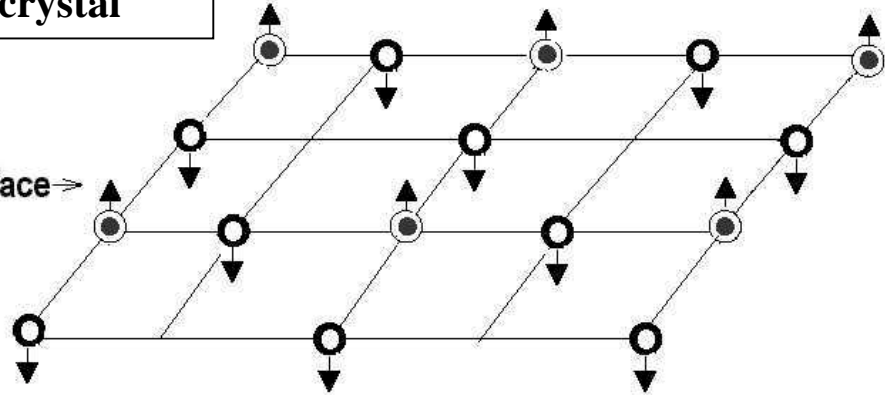
Surface of crystal



Tetragonal Phase

Surface of crystal

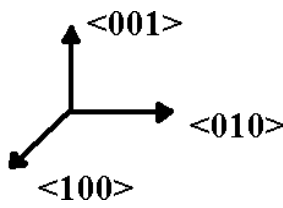
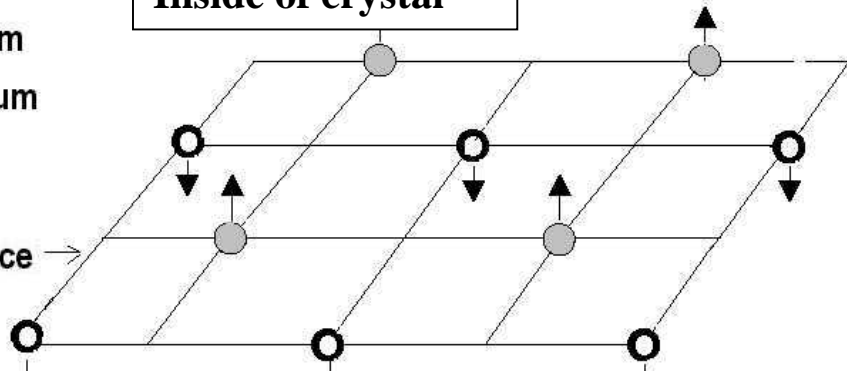
Ti-O Surface



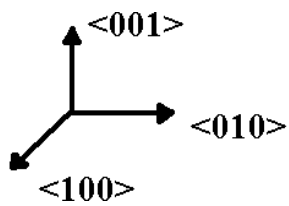
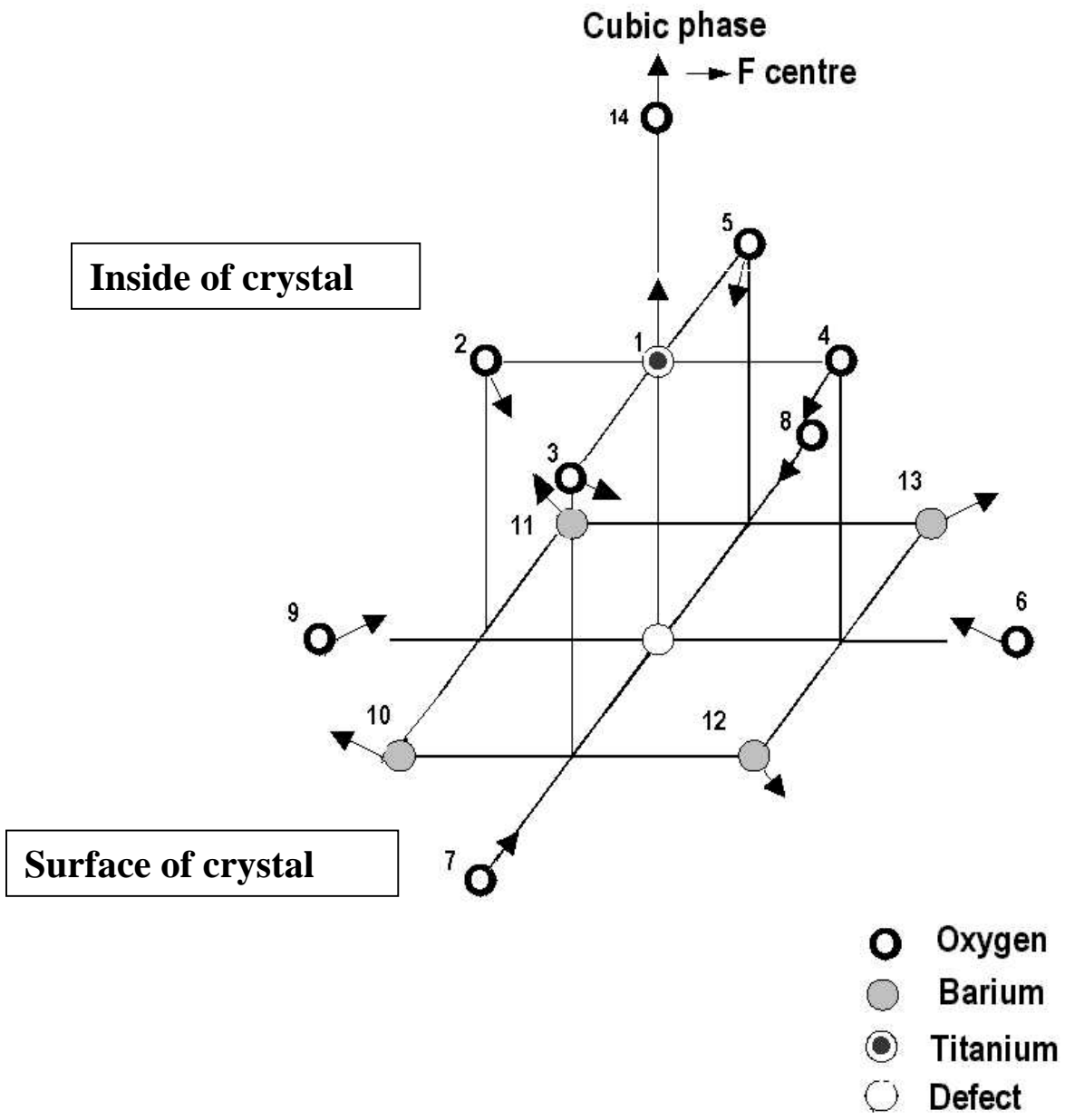
- Oxygen
- Barium
- Titanium

Inside of crystal

Ba-O Surface



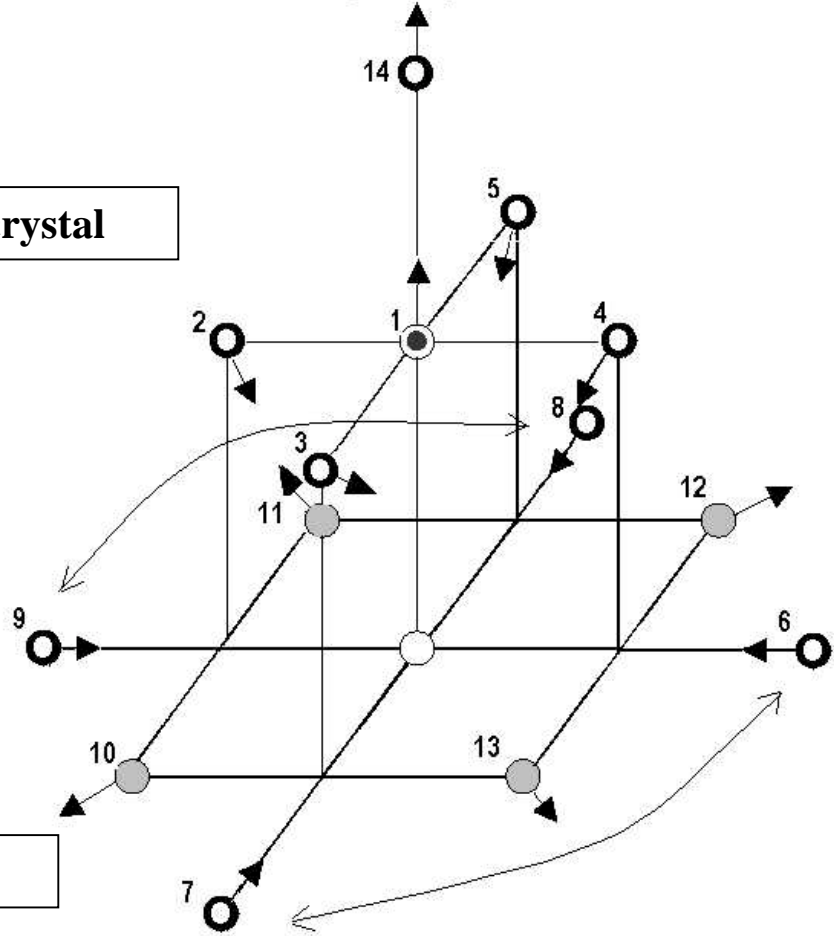
Surface of crystal



Tetragonal phase

Inside of crystal

Surface of crystal



- Oxygen
- Barium
- ⊙ Titanium
- Defect

