

# Oxygen-vacancy defects in $\text{PbTiO}_3$ and $\text{BaTiO}_3$ crystals: a quantum chemical study

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## ABSTRACT

We study effects produced by an O vacancy and F center in cubic and tetragonal lead titanate ( $\text{PbTiO}_3$ ) crystals as well as barium titanate ( $\text{BaTiO}_3$ ) (001) surface. Displacements and charges of defect-surrounding atoms, lattice distortion and relaxation energies are carefully analyzed. It is found that the predominant cause of atomic movements in  $\text{PbTiO}_3$  around an O vacancy is the Coulomb interaction while in the case of F center also changes in the chemical bonding within the atomic planes should be taken into consideration in order to explain atomic movements. We also observe a phenomenon known as bi-stability of the fundamental state, which occurs due to the rotation of some cationic planes. The obtained vibronic energy barriers for bi-stability are found to be around 1.0 eV. In the case of the  $\text{BaTiO}_3$  crystal the computed average atomic movements around the O vacancies are around 0.12 Å and 0.15 Å for the cubic and tetragonal lattices, respectively. In the case of F center we observe somewhat smaller lattice distortion. In the latter case, however, we find a considerable redistribution of electronic charge leading to a polarization of the defect-surrounding lattice, especially if the F centre is situated within the Ti-O<sub>2</sub> plane. In general, there is a reduction of the ferroelectric dipole moment for the tetragonal phase of the crystal due to the F center presence on  $\text{BaTiO}_3$  (001) surface.

**Keywords:** Lead titanate, Barium titanate, Surface, O vacancy, F center

## 1. INTRODUCTION

Since the discovery of ferroelectricity in the 1940s, the scientific research of the perovskite-type titanates such as  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$  crystals has been augmented immensely. Due to their unusual properties, the titanates promote new scientific investigations and also alternative high-tech applications in all branches of the engineering. Lead titanate ( $\text{PbTiO}_3$ ) crystals are characterized by a nonvolatile, reversible polarization field that has been successfully used in radiation hard memories,<sup>1</sup> surface acoustic wave and micro-mechanical devices, ferroelectric field devices as well as ultrasonic and sonar listening devices.<sup>2-4</sup> Barium titanate ( $\text{BaTiO}_3$ ) has a high dielectric constant at ambient temperature and also shows piezoelectric properties. Its typical applications are in piezoelectric transducers, thermistors and actuators. In addition, this titanate has large electro-optic coefficients and high photorefractive sensitivity, therefore can be used as an optical sensor.<sup>1</sup>

It is well understood that point defects play an important role in ferroelectric and piezoelectric properties of advanced perovskites. It has been found that the O vacancies can not be avoided and the F centers are very common in titanates. Therefore, it is important to study these point defects.

In the present work the  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$  crystals are studied using the Hartree-Fock method developed for crystals and the periodic Large Unit Cell (LUC) model. It is important to note that within our method, no *a priori* assumption is made upon the pattern of the electronic density distribution in the vicinity of defect under study since it is attained in the Self-Consistent-Field (SCF) manner. This leads to reliable information about the defect influence upon the electronic band structure. The present method has been already applied to study oxygen vacancies and F centers in different oxides. Some examples include calculation of the ground and excited states of F-type centers in corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) crystals,<sup>5,6</sup> F centers in  $\text{SrTiO}_3$  bulk<sup>7</sup> and on different surfaces of the same material.<sup>8,9</sup>

## 2. METHOD

In the present work we use a quantum-chemical method modified for crystal calculation, which is based on the Molecular Orbital (MO) theory and a periodic supercell model based on the LUC approach.<sup>10</sup> The exploited CLUSTERD and SYM-SYM computer codes<sup>10,11</sup> calculate both the electronic band structure and the total energy of a perfect crystal via MO as a

linear combination of atomic orbitals (AOs). The method has been found to be very useful in the treatment of electronic and spatial structure of a number of perfect and defective crystals. Up to now, it has been applied successfully to 30-35 crystals ranging from simple ionic materials to rather complicated crystals with a mixed ionic-covalent chemical bonding. The basic idea of the LUC approach is referred to the  $k=0$  approximation. The information about the computational equations of the total energy within the LUC model is given in Refs. 10 and 11. The power of the method is also based on a reliable parametrization scheme, which takes into account crystalline peculiarities with a high precision. Due to its semi-empirical character the SYM-SYM and CLUSTERD computer codes are not cumbersome and time consuming in treatment of the electronic and spatial structure of complex systems. Briefly we can state that the semi-empirical parameters are obtained by fitting the main properties of a given crystal. The details of the  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$  parametrization are given elsewhere,<sup>12,13</sup> where also parameter sets for these crystals are described. We can state that the current method has been applied successfully to study different titanates. Some examples include calculation of hole self-trapping in  $\text{BaTiO}_3$ <sup>14-16</sup> and  $\text{SrTiO}_3$ <sup>17</sup> crystals, impurity doping in  $\text{BaTiO}_3$ ,<sup>18-22</sup>  $\text{SrTiO}_3$ ,<sup>23-25</sup>  $\text{CaTiO}_3$ ,<sup>26-28</sup> and  $\text{PbTiO}_3$ <sup>12</sup> materials and another studies.

### 3. RESULTS AND DISCUSSION

#### 3.1. Study of $\text{PbTiO}_3$ crystal

There are three separate cases for studying oxygen-vacancy defects in  $\text{PbTiO}_3$  crystals: (i) defects in the cubic phase, (ii) in the dimerized Ti-O-Ti chains along the ferroelectric polarization z-axis of the tetragonal phase, and finally (iii) in the non-dimerized Ti-O-Ti chains along the x or y axes of the tetragonal phase. We have used 40-atom LUC, which corresponds to the eight-time symmetric extension ( $2 \times 2 \times 2$ ) of the primitive unit cell of  $\text{PbTiO}_3$ , to compute defects in lead titanate. The charge of the “empty” oxygen 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. 29, in which the reliability of the charged periodic model has been shown. According to Ref. 29 the Coulomb energy  $E^c$  of a periodic array is written as follows:

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

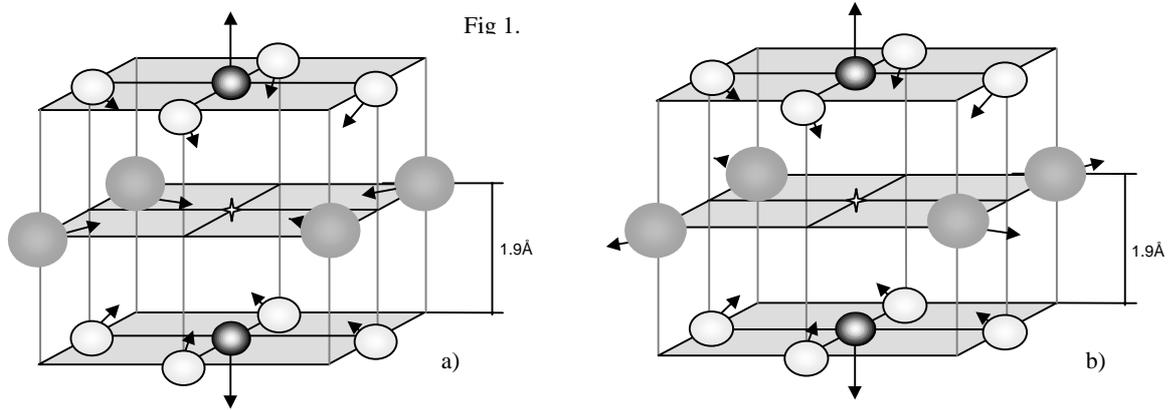
where the term  $j = i$  is omitted if  $l=0$ ,  $q_i$  is the charge on ion  $i$ ,  $\gamma$  is the Ewald parameter,  $v_0$  is the volume of the repeating 40-atom LUC, the  $\mathbf{G}$  is the reciprocal-lattice vector of the superlattice, the  $S(\mathbf{G})$  is the structure factor of the repeating unit, and  $Q$  is the net charge of the unit, which is equal to +2 in our case. The last term of equation (1) 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 (1), as a result it is not necessary to take into account the effect of the last term.

##### 3.1.1. Defects in cubic phase

Oxygen vacancy is a lattice imperfection where one oxygen ion has been removed. The vacancy-neighboring atoms note this perturbation and start to adjust to their new equilibrium positions. It was found that the principal force causing their displacements is the Coulomb electrostatic interaction. The movements are found to be totally symmetric for the cubic symmetry of the crystal. The eight adjacent oxygen atoms move symmetrically towards the defect by about 0.14 Å along the  $\langle 110 \rangle$  directions (Fig. 1). During this relaxation the vacancy-closest oxygens become less negative (see Table 1a). The two Ti atoms move away from the defect by about 0.17 Å. The four vacancy-closest Pb atoms move towards the vacancy by about 0.07 Å. Due to their large size Pb atoms tend to fill the empty space created by the oxygen removing and as a result their motion are towards the vacancy. The relaxation energy computed as the difference between the initial and optimal configurations is found to be equal to 11.5 eV.

In order to study F center, two electrons were added to the system containing an O vacancy. No *a priori* assumptions have been made on possible localization or delocalization of these electrons. Since the system is neutral, the principal cause of the atomic movements is a relocation of the charge. As it follows from Table 1 the electrons are well localized between the two vacancy-closest Ti atoms. The atomic movements are again symmetric (Fig. 1b). The eight O atoms move towards the

**Fig 1.** a) A schematic diagram of the closest atoms to the O vacancy in the cubic PbTiO<sub>3</sub> crystal. The defect is located in the center of the cell. b) The same schematic diagram of the closest atoms to the F-center in the cubic PbTiO<sub>3</sub> crystal.



defect by around 0.05 Å. The two Ti atoms move outwards from the defect by about 0.17 Å. The Pb atoms move outward from the defect by 0.05 Å. This implies that the two electrons really are localized within the vacancy region and this causes some overlap between these two electrons and the outer shell electrons of Pb atoms thus leading to the outward movements of Pb atoms. The relaxation energy is found to be equal to 9.81 eV. This is somewhat 1.69 eV less than in the case of the O vacancy and can be explained by smaller lattice relaxation. The  $\Delta$ SCF calculated absorption energy between the fundamental and excited states of the F center is found to be equal to 2.36 eV.

**Table 1.** Charges on atoms (in e) in the cubic PbTiO<sub>3</sub> lattice for the cases of the perfect crystal, O vacancy and F center as well as displacements of the defect-neighboring atoms (in Å). The atomic numeration corresponds to the ones in Fig. 1.

Atom	Oxygen vacancy			F-center		
	Charge		Displacement	Charge		Displacement
	Perfect crystal	With vacancy		Perfect crystal	With F-center	
Ti(1)	2.48	2.38	0.17	2.48	1.87	0.17
Ti(2)	2.48	2.38	0.17	2.48	1.87	0.17
O(3)	-1.39	-1.38	0.14	-1.39	-1.38	0.05
O(4)	-1.39	-1.38	0.14	-1.39	-1.39	0.05
O(5)	-1.39	-1.38	0.14	-1.39	-1.39	0.05
O(6)	-1.39	-1.38	0.14	-1.39	-1.38	0.05
O(7)	-1.39	-1.38	0.14	-1.39	-1.38	0.05
O(8)	-1.39	-1.38	0.14	-1.39	-1.39	0.05
O(9)	-1.39	-1.38	0.14	-1.39	-1.39	0.05
O(10)	-1.39	-1.38	0.14	-1.39	-1.38	0.05
Pb(11)	1.70	1.71	0.07	1.70	1.66	0.05
Pb(12)	1.70	1.71	0.07	1.70	1.66	0.05
Pb(13)	1.70	1.71	0.07	1.70	1.66	0.05
Pb(14)	1.70	1.71	0.07	1.70	1.66	0.05

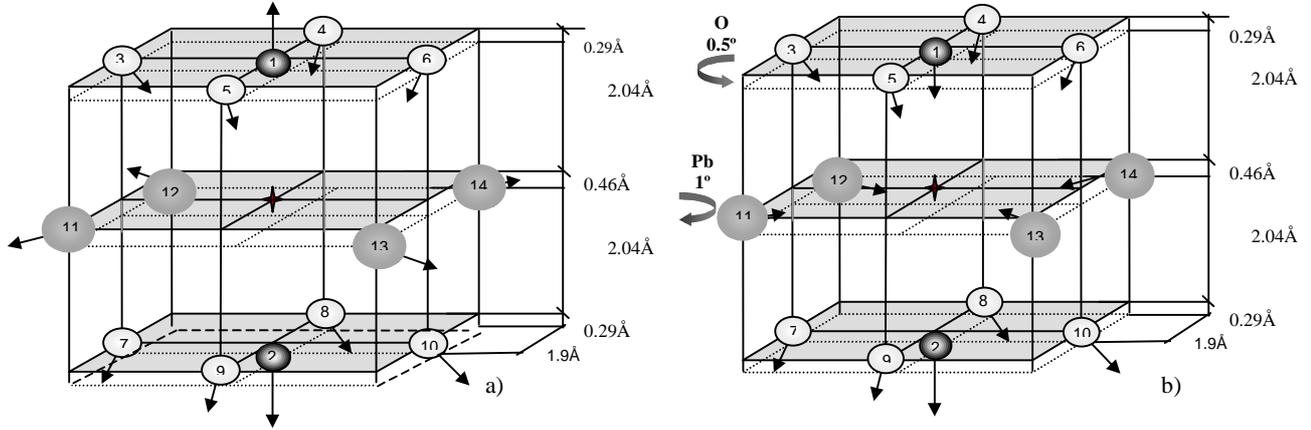
### 3.1.2. Defects in dimerized Ti-O-Ti chains

The tetragonal phase of PbTiO<sub>3</sub> crystal presents ferroelectricity and piezoelectricity due to their electric dipole moment along the z-axis. Since the lattice is elongated along the z-axis, it is normally to expect different atomic movements along this axis. In the tetragonal structure two kinds of O atoms can be distinguished. Firstly, the O atom in the dimerized Ti-O-Ti chain along the ferroelectric z-axis is going to be considered.

The defect-closest Ti atoms move outwards repelled by the positive charge of the vacancy, the Coulomb repulsion is stronger for the upper Ti atom, Ti(1), because it is closer to the defect (Fig. 2a). However, the change in atomic charges is very similar for both Ti atoms (Table 2). The O atoms in the upper plane move towards the vacancy obeying the Coulomb law. The positive Pb atoms move outwards from the vacancy repelled by its positive charge. However, their displacements are rather small due to their large size and the displacements are observed only within the xy plane. Nevertheless, as it follows from Table 2 the change in atomic charges of Pb atoms is slightly larger compared to the O atoms. The O atoms in the lower

plane move outwards from the vacancy. All the displacements are mainly along the z-axis. The calculated relaxation energy for this case is found to be equal to 5.1 eV.

**Fig. 2.** A schematic diagram of the closest atoms to the a) oxygen vacancy b) F centre. In the tetragonal  $\text{PbTiO}_3$  crystal when the vacancy is in the dimerized Ti-O-Ti chain along the ferroelectric z-axis. Due the tetragonal lattice cell the situation of atoms is as shown. The defect is located in the center of the LUC.



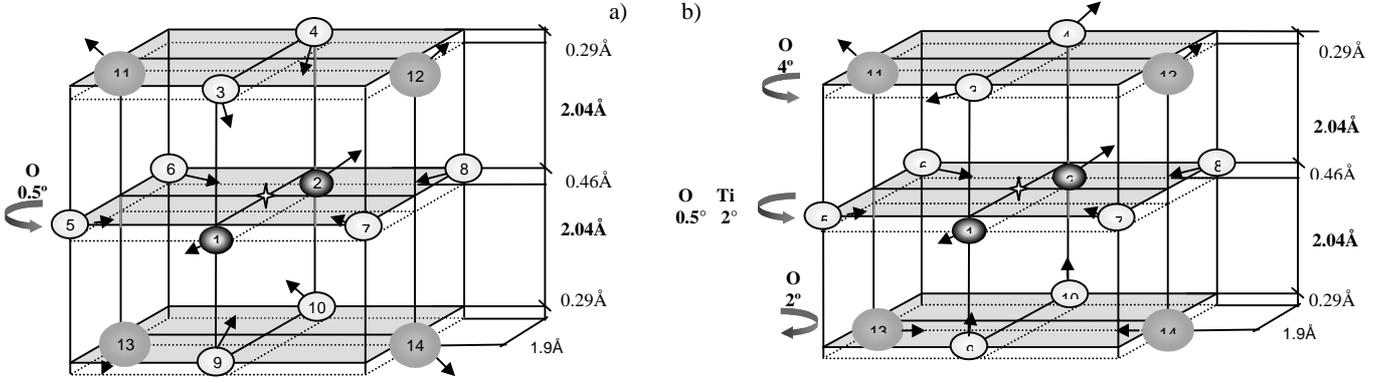
**Table 2.** Charges on atoms (in e) and atomic displacements (in Å) in the tetragonal  $\text{PbTiO}_3$  lattice with defect, O vacancy or F center, situated in the dimerized Ti-O-Ti chain along the polarization z-axis. The atomic numeration corresponds to the one given in Fig. 2.

Vacancy						F center					
Atom	Charge		Displacement			Atom	Charge		Displacement		
	Perfect	Defect	xv	z axis	Total		Perfe	Defect	xv	z axis	Total
Ti(1)	2.37	2.26	0.00	0.53	0.53	Ti(1)	2.37	2.31	0.00	0.04	0.04
Ti(2)	2.40	2.29	0.00	0.06	0.06	Ti(2)	2.40	2.16	0.00	0.08	0.08
O(3)	-1.32	-1.30	0.12	0.18	0.21	O(3)	-1.32	-1.33	0.19	0.38	0.43
O(4)	-1.32	-1.30	0.12	0.18	0.21	O(4)	-1.32	-1.33	0.19	0.38	0.43
O(5)	-1.32	-1.30	0.12	0.18	0.21	O(5)	-1.32	-1.33	0.19	0.38	0.43
O(6)	-1.32	-1.30	0.12	0.18	0.21	O(6)	-1.32	-1.33	0.19	0.38	0.43
O(7)	-1.38	-1.36	0.08	0.24	0.25	O(7)	-1.38	-1.36	0.08	0.18	0.20
O(8)	-1.38	-1.36	0.08	0.24	0.25	O(8)	-1.38	-1.36	0.08	0.18	0.20
O(9)	-1.38	-1.36	0.08	0.24	0.25	O(9)	-1.38	-1.36	0.08	0.18	0.20
O(10)	-1.38	-1.36	0.08	0.24	0.25	O(10)	-1.38	-1.36	0.08	0.18	0.20
Pb(11)	1.74	1.69	0.03	0.00	0.03	Pb(11)	1.74	1.64	0.06	0.00	0.06
Pb(12)	1.74	1.69	0.03	0.00	0.03	Pb(12)	1.74	1.64	0.06	0.00	0.06
Pb(13)	1.74	1.69	0.03	0.00	0.03	Pb(13)	1.74	1.64	0.06	0.00	0.06
Pb(14)	1.74	1.69	0.03	0.00	0.03	Pb(14)	1.74	1.64	0.06	0.00	0.06

In the case of F center the four superior O atoms move towards the defect by 0.43 Å with a major contribution of the z component (Fig. 2b and Table 2). It is interesting to note that we observe a slight rotation around the z-axis by about 0.5° in positive sense. Similar phenomenon was found before in other tetragonal lattices of different titanates.<sup>13-16</sup> The inferior O atoms move outwards the defect without any rotation. In our mind, the origin of the rotation of one of the O planes might be attributed to the so-called Jahn-Teller effect<sup>30</sup> known to be responsible for asymmetric lattice distortion in titanates and cuprates. The Ti atoms move as shown in Fig. 2b. It is obvious that the titaniums follow the O atoms of the same atomic plane. So, we expect the opposite titanium movements due to rather strong Ti-O bonding within each one of the planes. The four defect-closest Pb atoms move towards the defect by 0.06 Å and additionally rotate by around 1° (see Fig. 2b). Speaking of the rotation of Pb atoms we would like to note that the so-called bi-stability occurs. This means that the system possesses two equilibrium states achieved by (i) Pb rotation in positive sense, and (ii) Pb rotation in negative sense. The equilibrium states are separated by a vibronic energy barrier equal to 0.9 eV. Such a special behavior has been observed before in a number of III-V semiconductors and ionic materials,<sup>31,32</sup> but never in titanate crystals. The discovery of bi-stability in the tetragonal  $\text{PbTiO}_3$  structure containing F center points to more general nature of this phenomenon. The calculated relaxation

energy is found to be equal to 4.81 eV. Finally, we would like to state that the two added electrons are found to be rather delocalized in a large part of the LUC.

**Fig. 3.** A schematic diagram of the movements of the closest atoms to the (a) O vacancy (b) F center in the tetragonal  $\text{PbTiO}_3$  crystal when the vacancy is in the non-dimerized Ti-O-Ti chain along the y-axis. Due to the elongated tetragonal cell, the situation of atoms is as shown. The defect is located in the center of the LUC.



### 3.1.3. Defects in non-dimerized Ti-O-Ti chains

This case is depicted in Fig. 3. In the case of O vacancy the two defect-closest Ti atoms move towards the vacancy by 0.15 Å changing slightly their charges by equal magnitude (Table 3). The two superior O atoms move towards the defect by about 0.03 Å having slightly larger z component. The four O atoms within the xy plane not only move towards the vacancy by 0.03 Å but also rotate by 0.5° in positive sense. The two inferior O atoms also move towards the vacancy by about 0.05 Å. Thus one can conclude that the Coulomb interaction is responsible for these movements. The four Pb atoms move outwards from the vacancy as shown in Fig. 3a. One can note larger movements of the upper Pb atoms due to the shorter initial distance between these Pb atoms and the defect. The obtained relaxation energy is equal to 5.52 eV.

**Table 3.** Charges on atoms (in e) and atomic displacements (in Å) in the tetragonal  $\text{PbTiO}_3$  lattice with defect situated in the non-dimerized Ti-O-Ti chain along the y-axis. The data are given for the perfect crystal, O vacancy and F center. The atomic numeration corresponds to the one given in Fig. 3.

Atom	O vacancy					F center				
	Charge		Displacement			Charge		Displacement		
	Perfect crystal	With vacancy	xy plane	z axis	Total displacement	Perfect crystal	With F-center	xy plane	z axis	Total displacement
Ti(1)	2.40	2.30	0.15	0.00	0.15	2.40	2.09	0.10	0.00	0.10
Ti(2)	2.40	2.30	0.15	0.00	0.15	2.40	2.09	0.10	0.00	0.10
O(3)	-1.36	-1.36	0.02	0.03	0.03	-1.36	-1.37	0.13	0.00	0.13
O(4)	-1.36	-1.36	0.02	0.03	0.03	-1.36	-1.37	0.13	0.00	0.13
O(5)	-1.38	-1.34	0.03	0.00	0.03	-1.38	-1.33	0.13	0.00	0.13
O(6)	-1.38	-1.34	0.03	0.00	0.03	-1.38	-1.36	0.13	0.00	0.13
O(7)	-1.38	-1.34	0.03	0.00	0.03	-1.38	-1.36	0.13	0.00	0.13
O(8)	-1.38	-1.34	0.03	0.00	0.03	-1.38	-1.33	0.13	0.00	0.13
O(9)	-1.33	-1.29	0.04	0.02	0.05	-1.33	-1.28	0.07	0.01	0.08
O(10)	-1.33	-1.29	0.04	0.02	0.05	-1.33	-1.28	0.07	0.01	0.08
Pb(11)	1.74	1.68	0.15	0.38	0.41	1.74	1.62	0.08	0.33	0.34
Pb(12)	1.74	1.68	0.15	0.38	0.41	1.74	1.62	0.08	0.33	0.34
Pb(13)	1.58	1.62	0.02	0.01	0.02	1.58	1.11	0.08	0.00	0.08
Pb(14)	1.58	1.62	0.02	0.01	0.02	1.58	1.11	0.08	0.00	0.08

In the case of F center we again observe the bi-stability phenomenon related to the rotation of Ti atoms by about 2° in both positive and negative sense leading to the two different equilibrium states. These states are separated by a vibronic energy barrier equal to 1.4 eV, the magnitude of titanium movements is about 0.1 Å with a considerable change in their atomic charges testifying that partially two extra electrons are localized within the defective region. The two upper O atoms move away by 0.13 Å and additionally rotate by 4°. The O atoms situated in the defective xy plane and just below it move towards the defect and experience also rotation by about 2°. The upper Pb atoms move outwards from the defect by 0.23 Å with

main contribution of the z component, while lower Pb atoms move towards the defect. These opposite displacements of Pb atoms occur because the two upper Pb atoms are closer to the defect, so their outer electronic shells have repulsion with the two F center electrons due to the electronic shells overlap. We can state that the two electrons are only partially localized within the vacancy region. The calculated relaxation energy is found to be equal to 6.29 eV.

### 3.2. Study of O vacancies and F centers on the BaTiO<sub>3</sub> <001> surface

In order to characterize the perfect BaTiO<sub>3</sub> <001> surface, a LUC of 40 atoms was used. In the cubic phase we obtained inward displacements of the atoms of the exterior Ba-O and Ti-O<sub>2</sub> layers. The inward atomic movements were 0.14 Å for Ba and 0.06 Å for O atoms in the case of the Ba-O layer. The inward relaxation for the Ti-O<sub>2</sub> exterior layer showed O movements of 0.23 Å and Ti movements of 0.01 Å. In the tetragonal phase some atomic movements showed somewhat different pattern. The O atoms moved inward by about 0.04 Å for the Ba-O and 0.15 Å for the Ti-O<sub>2</sub> layers, respectively. However, the cationic displacements were found to be outward, 0.11 and 0.06 Å for Ba and Ti atoms, respectively. In our mind, the displacements of Ba and Ti atoms situated in the top-most layers of the tetragonal phase might be explained by the presence of ferroelectricity. This phenomenon occurs just due to the opposite displacements of cations and anions.

#### 3.2.1. O vacancies and F centers on the exterior Ba-O layer

In order to study the O vacancy we removed one of the O ions from the upper Ba-O layer. Due this perturbation, the vacancy-nearest O atoms move towards the defect symmetrically. The positively charged Ti and Ba atoms move outwards from the O vacancy, basically due to the electrostatic Coulomb interaction. It was obtained some variations of the electronic charge distribution in the defective region, especially for the vacancy-closest Ti atom. The obtained relaxation energy is found to be equal to 3.68 eV. In the case of F centers we obtained atomic movements of a smaller magnitude than for the O vacancy. This is due to the fact that the system becomes neutral, less perturbed. The calculated relaxation energy for this case is about 2.95 eV. The two extra electrons due to the F centre are well localized on the nearest Ti atom. We also observe 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<sup>33</sup> obtained by scanning tunneling 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 center on the Ba-O upper layer in the tetragonal phase. The atomic displacements are analogous to those for the cubic structure but are slightly asymmetric. The calculated relaxation energies are found to be equal to 1.30 eV and 1.81 eV for the O vacancy and F center, respectively. The F center localizes on the same Ti atom but its wave function is more diffuse. The local energy level originated from the F center is obtained to be about 0.9 eV below the conduction band edge.

#### 3.2.2. O vacancies and F centers on the exterior Ti-O<sub>2</sub> layer

In the case of O vacancy on the Ti-O<sub>2</sub> layer for the cubic lattice all Ti and Ba atoms move outwards while the O atoms move towards the defect, obviously because of the electrostatic Coulomb interaction. The computed relaxation energy is found to be about 2.79 eV. In the case of F center we find smaller atomic movements maintaining their directions of relaxation. The displacements of Ti atoms along the <001> direction are considerably larger compared to their movements along the <100> and <010> directions. This implies symmetry reduction and a possible formation of a new phase in the defective region due to the F centers. The relaxation energy is obtained to be equal to 1.65 eV. A noticeable difference compared to the defects on the Ba-O layer is found for the localization nature of the F centers. As it follows from our output the F centre is delocalized. We also do not observe any local energy level within the band-gap. The same results are obtained in the tetragonal phase of the material. The relaxation energies are about 2.16 eV and 1.46 eV for O vacancy and F center, respectively.

## 4. CONCLUSIONS

As a result of our studies of oxygen-vacancy defects in PbTiO<sub>3</sub> crystals we can conclude that the Coulomb interaction has a predominant role in atomic movements. However, in some cases of F center one has to consider also the importance of chemical bonding within the atomic planes, especially the Ti-O interaction. We find for the first time in titanates the so-called bi-stability phenomenon, which occurs in the tetragonal phase due to the rotation of cationic planes if the F center is

present. The estimated vibronic energy barriers for the bi-stability are found to be around 1.0 eV, which are close to magnitudes obtained before in other crystals.<sup>31,32</sup>

The results obtained for the BaTiO<sub>3</sub> crystal imply the importance of (i) Coulomb interaction, (ii) the ionic chemical-bonding, and (iii) polarization-correlation effects in this material. In general, the calculated atomic movements and relaxation energies are larger for the O vacancy compared to the corresponding values obtained for the F centre. In the case of the Ti-O<sub>2</sub> layer the F center is found to be rather delocalized and the two extra electrons are found in the lower part of the conduction band of the material.

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