

Theoretical study of structural and optical properties of F-centers in tetragonal BaTiO₃

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ABSTRACT

Using the density functional theory (DFT) within the local density approximation (LDA) and a method based on the Hartree-Fock (HF) approximation, we study the structural, electronic and optical properties of F-centers (two electrons in an oxygen-vacancy) in the tetragonal lattice of the perovskite-type BaTiO₃ crystal. In this structure the F-center has two non-equivalent positions due to the two different O atoms; namely, the F-center situated in the Ti-O-Ti chains along the [001] polarization axes (V_a^0) and the F-center situated in the Ti-O-Ti chains within the x-y plane (V_b^0). Both cases are considered in our study. The obtained results point out that the crystal structure containing V_a^0 centre is energetically more stable than that of the V_b^0 center. The two electrons of the F-center are found to be localized on the two adjacent Ti ions and their ground state is composed mainly of Ti 3d_{z²} atomic orbital. Besides, we have computed the allowed optical transitions for the F-center using the so-called Δ SCF method. As a result the obtained absorption energies are found to be equal to 1.47 eV for the V_a^0 center as well as 3.07 and 4.27 eV for the V_b^0 center.

Keywords: DFT, Hartree-Fock, BaTiO₃, ferroelectric, oxygen-vacancy, F-center, structural and optical properties

1. INTRODUCTION

Perovskite-type oxides possess a variety of important physical properties. It is known that ferroelectric (FE) compounds having a perovskite-type structure, ABO₃, have a lot of important applications in the field of semiconductor devices. For instance, in the last few decades, they have been used in the manufacturing of ferroelectric random access memory (FERAM) devices. In particular, barium titanate (BaTiO₃) has a potential for replacing the static random access memory (SRAM) devices¹ due to its nonvolatile and high-speed operation. The remaining problems to be solved for the commercialization of the ferroelectric-based devices are attributed mainly to both fatigue and aging. These problems are related closely to the presence of oxygen-vacancy defects in the crystal. Therefore, such defect states are needed to be investigated in detail not only from scientific but also from technological point of view.

2. COMPUTATIONAL METHODS

The self-consistent total-energy calculations on periodic models have been performed using the density functional theory (DFT) in the local density approximation (LDA)² as it is considered in the CASTEP computer code³ and also semi-empirical INDO method in the framework of the Hartree-Fock (HF) theory as it is implemented into the CLUSTERD computer program.⁴

In order to model the tetragonal BaTiO₃ phase using the DFT, we have exploited the Vanderbilt ultrasoft-pseudopotential plane-wave technique⁵. Within this technique the semi-core Ba 5s and 5p states as well as Ti 3s and 3p states are included as valence electrons making our calculations quite accurate. To obtain the bulk properties of the crystal we have used a cutoff energy of 360 eV with 6³ Monkhorst-Pack (MP) k-points, which is necessary to take into account the ferroelectric behavior of the crystal. Thus we have obtained the cell parameters of the tetragonal phase equal to $a = 3.937$ Å and $c = 3.999$ Å, which are in a good agreement with the experimental values and other theoretical estimations.^{5,6}

On the other hand, the HF methods are more suitable than the DFT methods for studying point defects in crystals in many cases, for example, the computation of the excited states. Here we have used the advanced semi-empirical version of the HF theory developed for crystal calculations, which have already been applied successfully to study a number of titanates.

Some examples include studies of hole self-trapping in a pure⁷ and defective BaTiO₃ crystals,⁸ hole self-trapping studies in the SrTiO₃ cubic lattice,^{9,10} structural and electronic features of triplet excitons in the tetragonal BaTiO₃ crystal¹¹ and defect doping studies in the bulk of SrTiO₃,^{12,13} CaTiO₃,¹⁴ BaTiO₃,^{15,16} PbTiO₃¹⁷ crystals as well as quantum-chemical computations of defects on the SrTiO₃ surfaces.^{18,19}

3. RESULTS

3.1. Structural Properties

In our modeling we have used two supercells: 40-atoms for the DFT and 135-atoms for the HF computations. The ionic displacements for the oxygen-vacancy (charge +2) and F-center (charge 0) are presented in Table 1. It is important to notice that oxygen vacancies have two non equivalent positions within the tetragonal BaTiO₃ crystal namely: the oxygen vacancy V_a lying on the Ti-O-Ti array along the z axis or polarization axis (001) and the oxygen vacancy V_b lying on the array Ti-O-Ti along either x or y axis. The relaxation of the fourteen vacancy-nearest atoms are shown in Fig. 1 for the cases of V_a^{+2} and V_b^{+2} , where V_a and V_b denote O vacancies situated in two different crystallographic positions described above. Because of the displacements of Ba, O and Ti atoms keeps some symmetry, in Table 1 we show the average displacements in Å of the nearest Ba and O; in the other hand, displacements of the Ti atoms in the V_a defect shows non symmetrical displacements. In those cases we show the displacements of the two Ti ions. The outcome of the relaxations for the V_a^0 and V_b^0 centers keeps the same trends as for the positively charged vacancies.

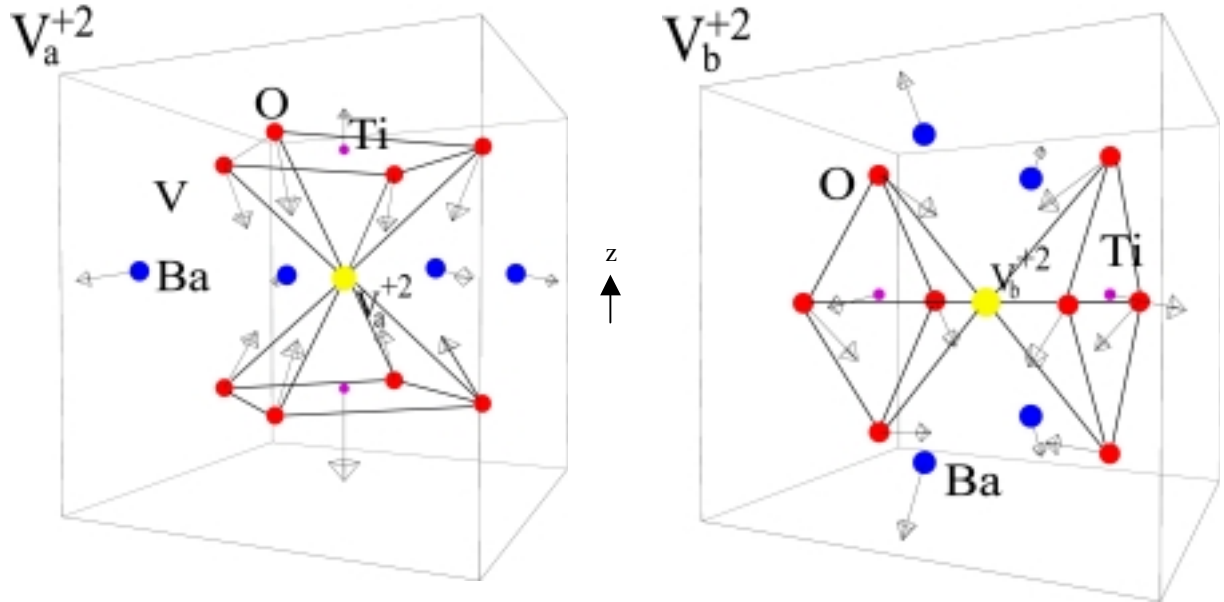


Fig. 1. Local displacements of the ions neighboring to an oxygen-vacancy, V_a^{+2} and V_b^{+2} , respectively.

Table 1. (a) DFT results from CASTEP* (b) HF results from CLUSTERD*

Defect	Ba	Ti	O	Defect	Ba	Ti	O
V_a^{+2}	0.07	0.32 / 0.05	-0.173	V_a^{+2}	0.06	0.22 / 0.20	-0.19
V_a^0	0.032	0.23 / 0.04	-0.11	V_a^0	0.017	0.13	-0.12
V_b^{+2}	0.09	0.15	-0.17	V_b^{+2}	0.026	0.12	-0.078
V_b^0	0.06	0.15	-0.13	V_b^0	0.057	0.03	-0.049

* Average ionic displacements (in Å from) are given. The “-“ sign means an inward movement while a positive value means outward movement.

As it is seen from Table 1, the magnitudes of local ionic displacements are larger for the positive vacancy than those for the F-center. This is expected due to the Coulomb electrostatic effect, which is more influent in the former case. The asymmetric displacements founded in the V_a defect might be related to local change of polarization along the z axis.

It is important to mention here that the results obtained by the CLUSTERD and the CASTEP codes are in accordance with each other.

3.2. Electronic and Optical Properties

When the vacancy captures two extra electrons (F-centre), the electron localization occur in a manner as it is shown in Fig. 2. The two Ti ions neighboring the oxygen-vacancy share these two electrons. The total energy difference between the two possible geometric configurations is given in Table 2. It is important to underline that both methods predict *the same* lowest energy configurations. It is evident from Table 2 that these lowest energy or equilibrium configurations are V_a^{+2} and V_a^0 for the vacancy and the F-center, respectively.

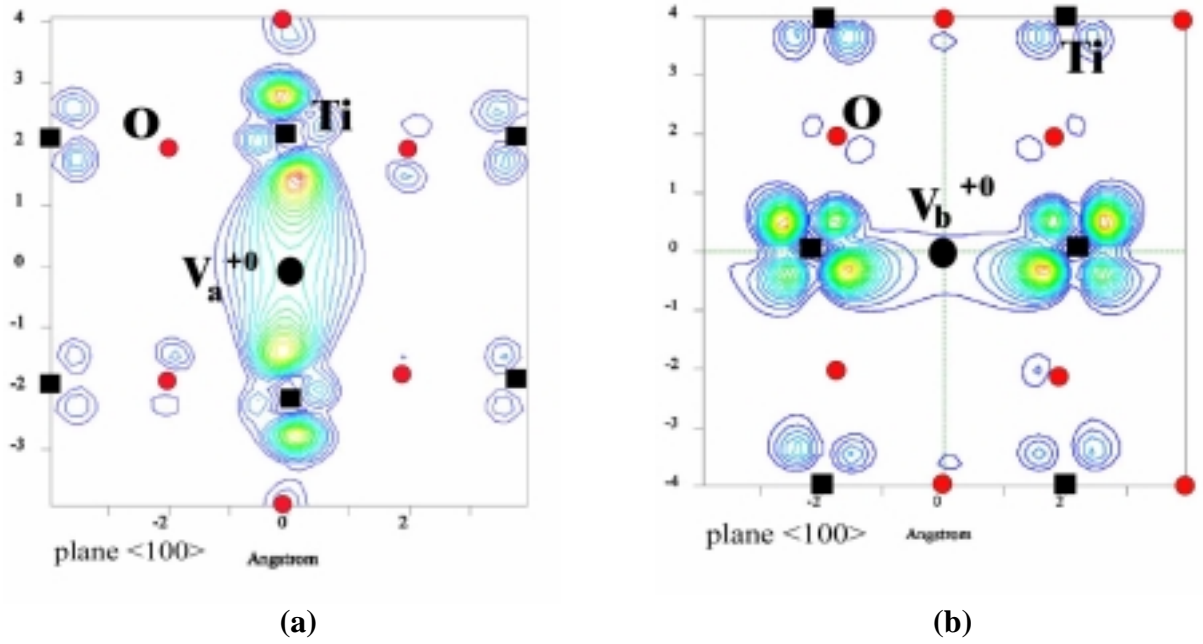


Fig. 2. Plot of the electronic density distributions around (a) V_a^0 and (b) V_b^0 centers in the tetragonal $BaTiO_3$ crystal. The contour lines are drawn by every step of $0.25 e^-$ per atom.

Table 2. Difference in total energies, ΔE , (in eV) for the oxygen-vacancy and F-center obtained by both methods.

ΔE	DFT	HF
$EV_a^{+2} - EV_b^{+2}$	-0.132	-0.452
$EV_a^0 - EV_b^0$	-0.114	-0.684

In order to obtain the excitation energies of the F-centre, we proceed in the following way: An electron from the ground state of the F-centre within the band gap was taken and put into the unoccupied excited state of the F-centre within the conduction band. Then according to Frank-Condon principle the absorption energy was obtained as a difference of total energies of the supercell for the self-consistent field (SCF) ground state and excited states with a fixed atomic configuration (Δ SCF method). After the ionic relaxation using DFT, the electronic ground state density distribution of the F-centre is plotted and it shows clearly its Ti 3d character. This result is in complete agreement with the HF theory calculation that shows the ground state of the F-center is composed mainly of the Ti $3d_{z^2-r^2}$ atomic orbitals (AO) belonging to the two Ti ions neighboring to the oxygen-vacancy. Our results show that the V_a^0 defect has only one allowed transition namely from Ti $3d_{z^2-r^2}$ to Ti $4p_z$, whereas the V_b^0 defect has two allowed transitions showed in the Table 3. Mind that here we mean Ti $3d_{z^2-r^2}$ as the linear combination 3d AO of the two nearest Ti ions surrounding the oxygen-vacancy.

Table 3. Calculated absorption energies (in eV) for the F-centers by the Δ SCF method.

F-center	Transition	Energy
V_a^0	Ti $3d_{z-r}^2 \rightarrow Ti$ $4p_z$	-1.47
V_b^0	Ti $3d_{z-r}^2 \rightarrow Ti$ $4p_x$	-3.07
	Ti $3d_{z-r}^2 \rightarrow Ti$ $4p_y$	-4.27

The magnitudes of the excitation energies obtained in the present study points out that it is more likely to excite the V_a^0 centre than V_b^0 because of their appreciable differences in energies.

4. CONCLUSIONS

The positively charged oxygen-vacancies and neutral F-centers in tetragonal $BaTiO_3$ are studied in the present work using the DFT and HF methods. It is found that the more stable configuration for both the positively charged oxygen-vacancy and F-center is in the V_a position, i.e. where the oxygen-vacancy lies in the Ti-O-Ti chain along the polarization axis. The two electrons due to the F-center are localized on the two vacancy-adjacent Ti ions and their ground state is composed mainly of Ti $3d_{z-r}^2$ AO. It is also possible to conclude that the Ba ions have a negligible influence upon different properties of $BaTiO_3$ crystal containing oxygen-vacancies and F-centers.

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