Theoretical study of oxygen-vacancy defects in ferroelectric BaTiO$_3$

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The structural, electronic and optical properties of tetragonal BaTiO$_3$ containing oxygen-vacancy defects have been investigated employing both the density-functional-theory (DFT) and Hartree-Fock (HF) based methods. The oxygen vacancy, Vo^{+2}, has two non-equivalent positions in the tetragonal lattice. It is found that the more stable vacancy is situated in the Ti-O-Ti array laying on the [001] polarization axis. Besides, the neutral charge state of oxygen-vacancy, V_o^0 (F-center), has been simulated in the present study.

1. Introduction

Perovskite-type oxides possess a variety of physical properties; so that they are considered to be a source of creating new physics .It is known that ferroelectric (FE) compounds having a perovskite-type structure, ABO$_3$, 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 has a potential for replacing the static random access memory (SRAM) devices [1]. and due to its nonvolatile and high-speed operation barium titanate has The remaining problems that are required to be solved for the commercialization of 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 have been performed using the density functional theory (DFT) in the local density approximation (LDA) [2] as it is considered in the CASTEP computer code [3] and also the Hartree-Fock (HF) method as it is implemented into the CLUSTERD computer program [4]. In order to model the tetragonal BaTiO$_3$ phase using the DFT, we have exploited the Vanderbilt ultrasoft-pseudopotential/plane-wave technique [5]. In this study the semicore Ba 5s and 5p and Ti 3s and 3p states are included as valence electrons. To obtain the bulk properties of the crystal we have used a cutoff energy of 360 eV with 6^3 Monkhorst-Pack (MP) k-points, which is necessary to take into account the ferroelectric behavior 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 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 version of the HF theory developed for crystal calculations, which have already been applied successfully to barium titanate [7-9].

3. Results
3.1 Structural Properties

In our modeling we have used two sizes of supercells: 40-atoms for the DFT and 135-atoms for the HF method. The ionic displacements for the oxygen-vacancy (charge +2) and F-center (charge 0) are presented in Table I a and b, respectively. The relaxations 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. It is found that the relaxation for the V_a^0 and V_b^0 centers keeps the same trends as for the positively charged vacancies.

Table I. a. DFT results from CASTEP[*]

Defect	Ba	Ti	O
V_a^{+2}	0.07	0.32 / 0.05	-0.173
V_a^0	0.032	0.23 / 0.04	-0.11
V_b^{+2}	0.09	0.15	-0.17
V_b^0	0.06	0.15	-0.13

Table I. b. HF results from CLUSTERD[*]

Defect	Ba	Ti	O
V_a^{+2}	0.06	0.22 / 0.20	-0.19
V_a^0	0.017	0.13	-0.12
V_b^{+2}	0.026	0.12	-0.078
V_b^0	0.057	0.03	-0.049

[*]Average ionic displacements from their initial positions in Å. The positive sign means an outward movement while the negative sign means an inward movement.

It is seen from Table I that the magnitudes of local ionic displacements are larger for the positive vacancy than the F-center. It is expected due to the Coulomb electrostatic effect, which is more influent in the former case. It is important to mention here that the results of the CLUSTED and the CASTEP are nearly in accordance with each other.
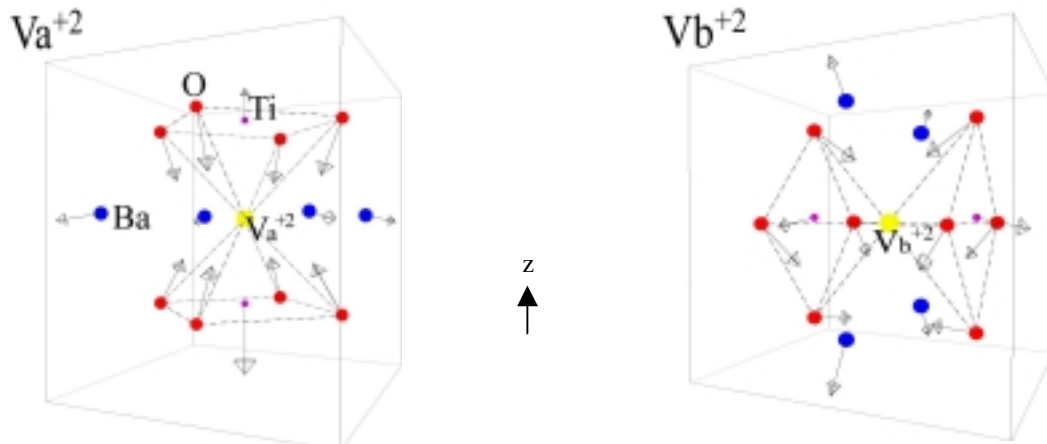

Fig. 1. Local displacements of the ions neighboring an oxygen-vacancy, V_a^{+2} and V_b^{+2}.
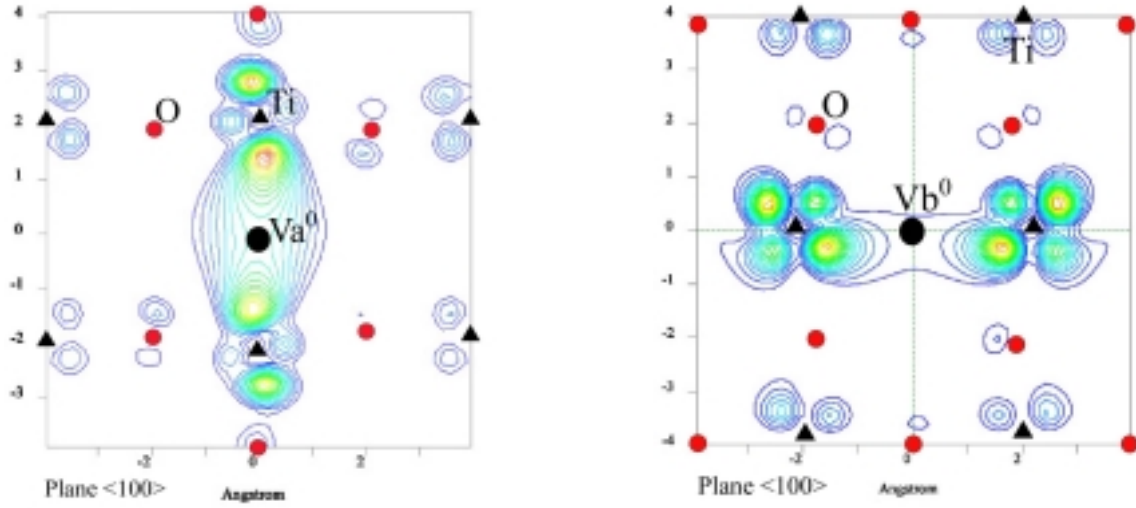
a)   b)

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

3.2 Electronic and Optical Properties

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

Table II. Difference in total energies for the vacancy and F-center in eV.

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

The absorption energies for the F center are estimated using the so-called ΔSCF method and the CLUSTERD computer code. As a result, it is found that 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 an oxygen-vacancy. Thus the allowed transitions are presented in Table III.

Table III. Calculated absorption energies for the F-centers in eV.

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

4. Conclusions

It is found from the present calculations of $BaTiO_3$ that the more stable configuration for both the positively charged vacancy and F-center is in the V_a position where the oxygen-vacancy lies in the Ti-O-Ti chain along the polarization axis. The two electrons of the F-center are localized on the two adjacent Ti ions and their ground state is composed mainly of Ti $3d_{z^2-r^2}$

AO. The Ba ions have a negligible influence on properties of the oxygen-vacancies and F-centers.

5. References

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