

Structural and optical properties of F-center defects on barium titanate <001> surface

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Abstract

Structural and optical properties of F centers (two electrons trapped by an oxygen vacancy) on the BaTiO₃ <001> surface are investigated using the quantum-chemical approach. The absorption energies are calculated using the Δ SCF scheme after the performance of system's geometry optimization. The obtained results are discussed in a comparative manner for two crystallographic phases, cubic and tetragonal.

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1. Introduction

One of the most important classes of metal oxides is titanates having perovskite-type structure. Barium titanate (BaTiO_3) is of special interest due to its technological importance. It has large electro-optic coefficients and high photorefractive sensitivity [1]. The material also exhibits ferroelectric and piezoelectric properties and therefore finds increasing processibility as an active element in microelectronic devices. Additionally, BaTiO_3 is a promising material for self-pumped phase conjugation or holographic storage [2] and inexpensive diode lasers [3]. It is well understood that point defects play an important role in many applications of ceramic materials. One of the most common defects in oxide crystals is the so-called F center (two electrons in an oxygen vacancy). This defect produces changes in the crystal structure and can also contribute into the absorption spectra of the material.

In the present paper, the electronic structure of BaTiO_3 (001) surface having F center is studied using the Hartree-Fock (HF) semi-empirical CLUSTERD computer code [4]. This computer program is specially designed for periodic system, e.g., crystal calculations. Due to its semi-empirical character, the method is not cumbersome and time consuming in the treatment of the electronic and spatial structure of complex systems, especially with partially covalent chemical bonding, like oxide crystals. We have to note that, within our method, no *a priori* assumption is made upon the pattern of the electronic density distribution in the vicinity of the defect under study, i.e. it is obtained in the self-consistent-field (SCF) manner. This permits us to get reliable information about the defect influence upon the electronic band structure properties. The method allows one to calculate

with reasonable precision the excited state of the system, thus giving one the information about defect contribution to the absorption spectra of the crystal (Δ SCF method).

The method has been already applied to F center studies. Some examples include calculation of the ground and excited states of F-type centers in corundum crystals [5,6], MgO crystal [7], ferroelectric BaTiO₃ bulk [8] as well as SrTiO₃ bulk [9] and different surfaces [10,11]. In the present work we calculate absorption energies of F center in both cubic and tetragonal crystalline lattices of BaTiO₃. The analysis of F center influence upon different properties of the crystal is given in a comparative way for two structures: cubic *versus* tetragonal.

2. Computational method

The employed method of periodically repeated large unit cells (LUCs) [12] is designed for the calculation of the total energy and electronic structure of crystals. 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. 4 and 11. Here 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:

$$P_{pq}^0 = \frac{1}{N} \sum_k P_{pq}(k) \exp(i\mathbf{k}\mathbf{R}_v) \quad (1)$$

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 [4,11,12] 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 [10-12], 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 a 135-atom LUC (27-fold, 3 x 3 x 3 extension) for defect computations on BaTiO₃ (001) surface.

The method is based on a semi-empirical modification of the molecular orbital (MO) theory with a specific parametrization scheme [13]. 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 BaTiO₃ crystal has been parametrized by us before [14] 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 BaTiO₃ crystal giving encouraging results. Some examples include study of the self-trapped and impurity-trapped hole polarons [14-16], calculation of Nb- and La-doped crystal [17-19] as well as the determination H impurity influence upon the ferroelectricity in this material [20].

3. Lattice distortion due to the F centers

One of the oxygens situated in the middle of the (001) surface of the LUC was taken out of the system and two electrons were inserted. This was done for both, Ti-O₂ and Ba-O terminations. As a result we have the following lattice distortion for the defect-the nearest

atoms: approximately 0.15 Å for O atoms and 0.12 Å for the Ba atoms in tetragonal lattice, 0.10 Å for the O atoms and 0.04 Å for the Ba atoms in cubic lattice. The atomic movements obey, in general, the Coulomb electrostatic law, i.e. the O atoms move towards while the Ba atoms outwards the defect. Thus obtained relaxation energy was found to be equal to 2.94 and 1.81 eV for cubic and tetragonal phases, respectively.

The magnitude of atomic movements in the tetragonal phase are larger compared to those of the cubic phase. We explain this effect by stronger perturbation, which is executed by the same point defect in a more compact crystalline lattice.

The two inserted electrons are well localized (82% cubic phase, 75% tetragonal phase) in the O vacancy region only in the case of the Ba-O termination. In the case of the Ti-O₂ termination, the electrons are not well localized. In the latter case, the two extra electrons jump to the conduction band. Thus we observe the augmentation of number of free electrons in the conduction band which can contribute into n-type electric conductivity of this material.

4. Optical properties

The absorption energies were obtained as a difference of total energies for the SCF ground and excited states for optimized defect geometry (Δ SCF method). That is, the potential energy curves are calculated for the ground and excited states of defect; then according to the Frank-Condon principle the absorption energy is that for the vertical transition to the Δ SCF excited state for a fixed atomic configuration. Note that these Δ SCF energies do not coincide with the difference of the relevant one-electron (orbital) energies, which usually give only rough estimates for the absorption and luminescence energies.

Thus computed absorption energies were found to be equal to 1.3 eV for both, cubic and tetragonal phases when the F center finds itself situated on the Ba-O termination. The relevant one-orbital transitions corresponding to the above-mentioned energies are: $3d_{xy} \rightarrow 4p_z$ (tetragonal phase) and $3d_{xy} \rightarrow 3d_{xz}$ (cubic phase). No attempts were done to calculate absorption energies of F centers on the Ti-O₂ termination due to the delocalized nature of wave functions for this case.

5. Conclusions

We have presented the computational study of structural and optical effects produced by the F centers on the BaTiO₃ <001> surfaces. The properties are studied within the same computational method and applying the same physical model to describe the surface.

The main conclusions are as follows.

- (i) Defect produced perturbation on the tetragonal phase structure is stronger than in the case of the cubic lattice; this leads to larger lattice distortion in the latter case.
- (ii) In cubic and tetragonal phases, the atomic displacement and charge variation are stronger along the ferroelectric c-axis (<001>) compared to those along the <100> and <010> directions.
- (iii) F center wave function is well localized within the Ba-O surface termination while it is rather extended in the case of the Ti-O₂ termination. This leads us to the conclusion that electrons are not well trapped by the O vacancy. They tend to become free, conductive electrons in the latter case.

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

		B		
A		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

