Structural and electronic properties in cubic and tetragonal BaTiO₃ crystal due to La impurity

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Abstract

The effects in BaTiO₃ due to the La-doping have been studied by means of advanced quantum-chemical method based on the Hartree-Fock theory. A supercell consisting of 135 atoms has been used throughout the work. First, the effects in cubic phase of the material have been investigated after minimisation of the total energy of the crystal. The obtained relaxation energy was found to be equal to 0.94 eV. The extra electron due to the La atom was found to be situated in a local energy level within the band-gap. In tetragonal phase the relaxation energy was obtained to be equal to 0.52 eV and again the extra electron is confined in the local energy level within the band gap.

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1. Introduction

With no doubts $BaTiO_3$ is one of the most studied ferroelectric materials. Actually, the discovery of the ferroelectricity [1] was done independently in various countries during the World War II just in $BaTiO_3$ crystal. The reason of numerous investigations in $BaTiO_3$ crystal is its remarkable properties. This ceramic material shows piezoelectric properties and has chemical and mechanical stability in a wide temperature range, which facilitates its fabrication in bulk polycrystals and both epitaxial and polycrystalline thin films [2]. All of these properties make this material very useful in different applications such as dynamic random-access memories, piezoelectric transducers, thermistors and actuators [2]. In addition, this titanate has large electro-optic coefficients and high photorefractive sensitivity, which allows this crystal to be used as an optical sensor [3].

Despite to the fact that many studies have been done so far on this ferroelectric material our knowledge of its fundamental properties are not satisfactory. Most of the studies carried out up to now are experimental. There are only few theoretical investigations (see [4] and Refs. therein) made up to date. This could be partially explained by difficulties in using computer modelling to reproduce the unusual physical properties of this ceramic material.

In this work we study the effects on different properties of $BaTiO_3$ due to the La-doping in both cubic and tetragonal phases. For this purpose we utilise quantum-chemical computations. Semi-empirical intermediate neglect of differential overlap (INDO) method modified for crystal calculations and the periodic large unit cell (LUC) model as it is implemented into the CLUSTERD computer code [5] are our tools. Due to its semi-empirical character the computer program is not cumbersome and time consuming in the treatment of electronic and spatial structures of complex systems, in

particular, with a partially covalent chemical bonding. Up to now the method has been successfully employed to investigate several perfect and defective oxides and materials with a simpler electronic band structure. It has important advantage of precise geometry prediction for impurity-doped crystals as it has been recently proved for a number of titanates like $BaTiO_3$ [4, 6, 7], $SrTiO_3$ [8-10] and $CaTiO_3$ [11]. The computer code was also used in studies of another akin perovskite-type crystals as $KNbO_3$ [12, 13] and WO_3 [14]. The aim of this research is to study the influence of La-doping upon the electronic band structure properties, as well as impurity effects on crystal geometry in both cubic and tetragonal phases.

2. Description of the method

A quantum chemical method developed for crystal calculations has been used. This approach is based on molecular orbital (MO) theory [15] and is developed for periodic systems, e.g., crystal computations. The method allows one to perform self-consistent-field (SCF) calculations of monocrystals containing different point defects, like in our case the La impurity, which substitutes for a Sr atom. Our investigation is done using a supercell of 135 atoms. This model is based on the so-called LUC approach, which has shown high reliability in point defect studies in a number of crystals. The use of a large size supercell (135 atoms) has the importance of making impurity-impurity interaction negligible [9].

The main idea of the LUC method has to do with the so-called $\mathbf{k}=0$ approximation. The information about the computational equations of the total energy of the LUC model is given in [16]. Here we shall only outline the basic ideas of the method. The Fock matrix elements are made self-consistent through:

$$\frac{1}{N} \sum_k P_{pq}(\bar{k}) \exp(i\bar{k} \cdot R_v)$$

$$(1)$$

Here the summation is carried out over all **k** values in the reduced Brillouin zone (RBZ) of the LUC. In this way the information regarding the density matrix $P_{pq}(\mathbf{k})$ is obtained only in the point **k**=0. Nevertheless it has been demonstrated that several **k**-points in the RBZ are included in the calculation procedure on extending the primitive unit cell [16]. Therefore, the calculation of the band structure in **k**=0 of the RBZ is equivalent to the calculation in several **k** points in the BZ of the primitive unit cell. It has been shown in many recent studies [7, 16-18] that an eigthfold-symmetric extension of the primitive unit cell proves to be sufficient to reproduce almost exactly the electronic band structure of a given crystal. In order to reduce the computational time certain semi-empirical parameters have been introduced. Owing to its semi-empirical nature and a specific parametrization scheme [19], CLUSTERD is not cumbersome and time consuming in the treatment of electronic and spatial structure of complex systems, specially the ones with mixed ionic-covalent chemical bonding like oxide crystals. The parametrization is made to reproduce the following magnitudes: width of the forbidden energy gap, widths of the upper and lower valence bands, chemical composition of valence and conduction bands and lattice constants for both cubic and tetragonal structures. The parameter sets for the $BaTiO_3$ crystal are given in Tables 1 and 2 and details of the parametrization of this crystal are described in one of our previous works [4].

Briefly, we can state that the calculated energy bands composition for the $BaTiO_3$ crystal is in a very good accordance with the X-ray photoelectron spectra measurements [20]. In particular, as it follows from our computations, the chemical character of the lower valence band is mainly O 2s in nature while the upper valence band is predominantly O 2p in nature with a small admixture of Ti 3d AOs. The bottom

of the conduction band is mainly composed of Ti 3d states with some admixture of Ba 5s states. We observe some change in valence and conduction band compositions when study the tetragonal phase of the $BaTiO_3$ crystal. In particular, a considerable amount of Ti 3d AOs is present in the upper valence and we find also a notable contribution of O 2p states in the lower part of the conduction band. This points out to the hybridisation effect between Ti 3d and O 2p AOs, which accompanies the phase transition: cubic (paraelectric) $\rightarrow$ tetragonal (ferroelectric).

3. Results and discussion

In order to have an initial idea of how the atoms rearrange in the $BaTiO_3$ structure due to the La-impurity presence we have used a LUC of 40 atoms (see Fig 1) for both cubic and tetragonal phases. The lanthanum replaces one of the bariums located in the center of the LUC. The vicinity of defect (VOD) is thus composed of twelve oxygens and eight titaniums as it is shown in Fig 2. The performed geometry optimisation, i.e., relaxation of the lattice, for cubic phase show displacements of titaniums belonging to de VOD outward the lanthanum by 0.07 Å along the <111> directions preserving the symmetry of the system. In the case of tetragonal phase there are two possible configurations of the structure. The first one is the outward displacements of the titaniums by 0.10 Å being a bit larger along the z-axis than in the *x-y* plane. The second possible configuration shows the titaniums moving away from the defect along the <111> directions with oxygens displacing toward the lanthanum by a distance of 0.07 Å. Obviously, there is an ambiguity in the behaviour of the structure. Apparently we encounter the so-called impurity-impurity mutual perturbation problem and its influence upon the reproduction of lattice distortion. Hence a bigger LUC should be used in order to eliminate this artificial effect.

In the second step we have utilised a LUC of 135 atoms with a structure similar to the one shown in Fig 1. In this new set up the lanthanum is placed instead of one of the bariums located in the middle of the supercell. The geometry optimisation in the cubic phase is attained by the impurity-outward displacements of titaniums by a magnitude of 0.07 Å maintaining the cubic symmetry of the VOD, i.e., we have <111> equal displacements along the three crystallographic axes. Additionally we find that the impurity-closest oxygens, i.e., the ones belonging to the VOD, experience slight movements equal to 0.02 Å toward the defect. These oxygens move along the z-axis only and hereafter will be called z-oxygens. The corresponding relaxation is depicted in Fig. 3. The explanation for this awkward distortion will become clear when the situation of the extra electron is analysed. However, since the oxygens approach the impurity while the titaniums move away of the point defect, we are dealing mainly with the electrostatic forces, which means that the predominant chemical bonding in $BaTiO_3$ has ionic character. The obtained the relaxation energy is found to be equal to 0.94 eV.

In the tetragonal phase the geometry relaxation is attained by oxygens moving toward the defect by a distance of 0.06 Å. In this case the titaniums of the VOD remain motionless as it is shown in Fig 4. We explain this kind of lattice distortion by the screening effect produced by the defect-surrounding oxygens, so the titaniums of the VOD remain static. The relaxation energy obtained for this case is equal to 0.52 eV. The summary of geometry optimisation for the two phases is given in Table 3. In cubic phase there are titanium and oxygen displacements while in tetragonal phase there are oxygen displacements only. This could explain the smaller value of the relaxation energy in the tetragonal phase.

Another important point is the analysis of electronic density redistribution in the VOD region due to the La-doping. The atomic charges for both phases associated with

the atoms closest to the impurity are given in Table 4. In cubic phase, after doping, titaniums suffer an increase in their positive charge by approximately 0.15 e. On the other hand the eight z-oxygens and the remaining ones show a slight increase in their negative charge by around 0.05 e and 0.06 e, respectively. In our mind, it points out to the fact that lanthanum impurity can act as a center of a new, tetragonal phase, since this effect occurs just along the z-axis, i.e., the ferroelectric axis. In other words, we observe the occurrence of electric dipole moment along the z-axis due to the La atom insertion. In tetragonal phase, the titaniums of the VOD suffer an increase of 0.2 e in their positive charge value. The oxygens have a slight increase in their negative charge by around 0.06 e.

Analysing the electronic properties of the doped crystal, the question to be answered is what happens with the extra electron imposed on the system by the lanthanum impurity? One could predict the occurrence of a local one-electron energy level within the band-gap. Indeed, in both phases the extra electron is well localised within the band-gap occupying the local energy level. The asymmetric distortion of the lattice in cubic phase could be explained by the localisation of the extra electron in the local energy level, which produces an asymmetry in the charge distribution along the z-axis, and this enables such a kind of lattice distortion. Finally, we should note that experimentally it is known that due to the La-doping in $BaTiO_3$ the conductivity remains unchanged [21]. So in our mind the electron localisation in the local energy level within the band-gap is directly related to the lack of increase in electrical conductivity in La-doped $BaTiO_3$ crystal.

4. Conclusions

Using the quantum-chemical method developed for crystal computations we study La-impurity influence upon the structural and electronic properties of BaTiO$_3$ crystal. The asymmetric lattice distortion observed in cubic phase can be justified by the localisation of the extra electron of lanthanum in the local energy level within the band-gap. This generates an asymmetry in charge distribution in the defective region with the consequent creation of electric dipole moment along the ferroelectric z-axis. This leads to the observed lattice distortion. One can also imply that the La atom in cubic phase acts as a centre of a new tetragonal phase and thus facilitates the phase transition in this material. In tetragonal phase the exclusive motion of the oxygens can be explained due to the screening effect produced by these la-surrounding oxygens upon the impurity electrostatic field, preventing in this way displacements of the titaniums entering the VOD. Localisation of the extra electron due to the La-impurity in the local energy level within the band-gap is in a good agreement with the experimental observations, which show no increase in the electrical conductivity under the La-doping.

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Table 1

Semi-empirical INDO 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
La	6s	1.0	11.3	0.40	-0.4
	6p	1.0	2.0	0.01	-0.4
	5d	1.97	11.0	0.08	-6.3

Table 2

Semi-empirical INDO two-center parameters α_{mB} (au^{-1}) optimised during the calculations, *m*th AO belongs to the atom A, where A≠B.

A	B			
	Ba	Ti	O	La
Ba	0.20	0.1	0.57	0.0
Ti	0.53	0.13	0.38	0.0
O	0.36	0.10	0.15	0.53
La	0.00	0.02	0.03	0.01

Table 3

Atomic movements (in Å) and relaxation energy in La-doped $BaTiO_3$ crystal using the LUC consisting of 135 atoms. "+" and "-" signs denote outward and inward atomic displacements with respect to the impurity, respectively.

Atom	Cubic Phase Displacements	Tetragonal Phase Displacements
Ti	+0.07	0.00
O(1)	0.00	- 0.06
O(2)	0.00	- 0.06
O(3)	0.00	- 0.06
O(4)	- 0.02	- 0.06
O(5)	- 0.02	- 0.06
O(6)	- 0.02	- 0.06
O(7)	- 0.02	- 0.06
O(8)	- 0.02	- 0.06
O(9)	- 0.02	- 0.06
O(10)	- 0.02	- 0.06
O(11)	- 0.02	- 0.06
O(12)	0.00	- 0.06

Table 4

Atomic charges (in *e*) for the VOD atoms in the cubic and tetragonal phases,

respectively.

Atom	Cubic Phase		Tetragonal Phase	
	Pure crystal	Doped crystal	Pure crystal	Doped crystal
Ti	2.13	2.28	1.90	2.10
O(1)	-1.33	-1.38	-1.26	-1.32
O(2)	-1.33	-1.38	-1.26	-1.32
O(3)	-1.33	-1.38	-1.26	-1.32
O(4)	-1.33	-1.39	-1.26	-1.32
O(5)	-1.33	-1.39	-1.26	-1.32
O(6)	-1.33	-1.39	-1.26	-1.32
O(7)	-1.33	-1.39	-1.26	-1.32
O(8)	-1.33	-1.39	-1.26	-1.32
O(9)	-1.33	-1.39	-1.26	-1.32
O(10)	-1.33	-1.39	-1.26	-1.32
O(11)	-1.33	-1.39	-1.26	-1.32
O(12)	-1.33	-1.38	-1.26	-1.32

Figure captions

Fig. 1. 40-atomic LUC of the $BaTiO_3$ crystal used to obtain the first approximation of the lattice distortion pattern.

Fig 2. Vicinity of defect (VOD) composed of eight titaniums and twelve oxygens. The lanthanum replaces one of the bariums situated in the central part of the LUC.

Fig 3. The relaxation of the structure due to the lanthanum impurity doping in cubic phase. The eight lanthanum-closest titaniums move outward while the eight z-oxygens show a slight inward displacements with respect to the defect.

 Fig 4. The relaxation of the structure due to the lanthanum impurity doping in tetragonal phase. The twelve lanthanum-closest oxygens move toward the defect while the titaniums remain motionless.

LUC of BaTiO$_3$

=Ba^{+2}

= Ti^{+4}

= O^{-2}

La

Ti

0