ELECTRON TRANSFER EFFECT IN $BaTiO_3$ AND $CaTiO_3$ DUE TO Nb-DOPING

Edgar Patiño*, Franklin Erazo, Arvids Stashans

Centro de Investigación en Física de la Materia Condensada, Corporación de Física Fundamental y Aplicada, Apartado 17-12-637, Quito, Ecuador

Abstract

Using an advanced quantum-chemical method, a study of Nb-doping has been carried out in the $BaTiO_3$ and $CaTiO_3$ crystals. The lattice distortion due to the impurity presence is studied in a comparative manner for the two crystals and also considering different crystallographic phases. A new phenomenon of an extra electron transfer from the local energy level within the band-gap to the conduction band is found. This effect is discussed in terms of the available experimental data on electrical conductivity augmentation in these materials.

*Corresponding author, FAX: +593-2-403656, e-mail: corp_ffa@yahoo.com

¡Error!Marcador no definido.
¡Error!Marcador no definido.

1. Introduction

There has been a remarkable increase in scientific research of perovskite-type titanates since the discovery of ferroelectricity in the $BaTiO_3$ crystal in the 1940's. The reason for the inquisitiveness regarding $BaTiO_3$ and $CaTiO_3$ is their remarkable properties and a wide range of applications in the industry and technology [1, 2]. Both crystals show cubic phase structure at high temperatures. However, the $BaTiO_3$ and $CaTiO_3$ crystals experience a phase transition into the tetragonal and orthorhombic structures, respectively at low temperatures.

For both crystals most of studies carried out so far have been experimental investigations. There are only few theoretical studies (see [3, 4] and Refs. therein) done on these materials. This could be partially explained by difficulties in using computer modeling to reproduce the unusual physical properties of these ceramic materials.

In this work we study and compare the Nb-impurity effects upon different properties of both materials. In particular, the electronic band structure properties, as well as the impurity influence on the crystal geometry in both crystals and different phases is studied and analyzed. For this aim we use an advanced quantum-chemical method developed for crystal computations.

Due to its semi-empirical character the computer program is not cumbersome and time consuming in treatment of electronic and spatial structures of complex systems, in particular, with a partially covalent chemical bonding, like oxide crystals [3]. Up to now the method has been successfully employed to investigate several perfect and defective oxides and materials with a simpler electronic band structure. The computer code has important

advantage of precise geometry prediction for impurity-doped crystals as it has been recently proved for a number of titanates like $BaTiO_3$ [3, 5], $SrTiO_3$ [6, 7] and $CaTiO_3$ [4].

2. Outline of the method

The investigation is done using a supercell model based on the so-called large unit cell (LUC) approach [8], which has very high reliability in point defect studies in crystals. The impurity atom of Nb has been located in the middle of the supercell instead of one of the Ti atoms for both $BaTiO_3$ and $CaTiO_3$ crystals.

Information regarding the computational equations used for calculation of the total energy of the LUC and main ideas of the method is given in [8]. Nevertheless it is important to point out to the $\mathbf{k}$=0 approximation. This means that the information regarding the density matrix $P_{pq}(\mathbf{k})$ is obtained only in the reciprocal lattice point $\mathbf{k}$=0. Nevertheless it has been demonstrated that several $\mathbf{k}$-points in the reduced Brillouin zone (BZ) are included in the calculation procedure on extending the primitive unit cell. Therefore, the calculation of the band structure in the $\mathbf{k}$=0 of the reduced BZ is equivalent to the calculation in several $\mathbf{k}$ points in the BZ of the primitive unit cell. It has been shown in many recent studies that an eightfold-symmetric extension of the primitive unit cell proves to be sufficient to reproduce almost exactly the electronic band structure of a given crystal [9, 10]. In order to reduce the computational time certain semi-empirical parameters have been introduced. Owing to its semi-empirical nature and a specific parameterization scheme [11], CLUSTERD is very powerful in the treatment of the electronic and spatial structure of complex systems, specially the ones with mixed ionic-covalent chemical bonding like oxide crystals. The parameter sets for the $BaTiO_3$ and $CaTiO_3$ crystals are given in Table 1. The

¡Error!Marcador no definido.
¡Error!Marcador no definido.

parametrization of these crystals is described in details in our previous works [3, 4]. Here we shall only note that the current parametrization reproduces quite well the electronic and spatial structure of both crystals as well as main characteristics of some diatomic test molecules.

3. A lattice distortion due to the Nb impurity

In order to study the relaxation of the crystalline structure we utilize a LUC of 135 and 80 atoms for $BaTiO_3$ and $CaTiO_3$, respectively. In this set up the niobium is placed instead of one of the titaniums located in the middle of the supercell. So, this substitution gives us one extra electron in the system, which means the donor type impurity doping.

In the cubic phase of $BaTiO_3$ the geometry optimization is attained by the impurity-outward displacements of the eight niobium-neighboring bariums by a distance of 0.09 Å keeping the cubic symmetry, i.e. we have <111> equal displacements along all three crystallographic axes. Neighboring oxygens move along <100> directions towards the niobium impurity by 0.02 Å. The amount of the energy, liberated by the system during relaxation, i.e., the relaxation energy, is found to be equal to 1.69 eV.

In the case of $CaTiO_3$ the eight niobium-closest calcium atoms move outwards the impurity along the directions <111> by a distance of 0.03 Å. The six impurity-neighboring oxygens approach the impurity by 0.23 Å along the <100> directions. The relaxation energy found is equal to 3.83 eV. Here we also have absolutely symmetric atomic displacements. The obtained higher relaxation energy for the $CaTiO_3$ crystal compared to the $BaTiO_3$ crystal can be explained by the fact that the cubic phase of $CaTiO_3$ is rather unstable.

¡Error!Marcador no definido.
¡Error!Marcador no definido.

The geometry relaxation for the tetragonal phase of the $BaTiO_3$ is as follows. The bariums move outwards the niobium by a distance of 0.09 Å. However, these displacements are practically only in the x-y plane while the motion along the z axis is practically negligible. Oxygens move towards the impurity by a distance of 0.01 Å but just along one axis (x or y). The relaxation energy obtained for this phase is equal to 5.44 eV.

In the orthorhombic phase of $CaTiO_3$, the six niobium closest calciums move outwards the impurity by 0.18 Å. These displacements are along <011> and <111> directions. The six defect-nearest oxygens move towards the impurity by 0.06 Å along the directions <111>. Finally, three niobium-closest titaniums also move outwards the impurity by 0.07 Å, along <110> and <001> directions. The total relaxation energy is found to be equal to 15.04 eV.

The lattice relaxation in both phases for $BaTiO_3$ and $CaTiO_3$ occurs in accordance to the Coulomb electrostatic law. The tetragonal and orthorhombic phases for $BaTiO_3$ and $CaTiO_3$, respectively are more densely packed relative to the cubic phases. Therefore, the insertion of the Nb impurity makes a larger perturbation and as a result we have larger magnitude of relaxation energy for these structures.

4. An electron transfer phenomenon

Among 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 niobium impurity? Due to the donor-impurity doping one could anticipate the occurrence of the local one-electron energy level within the band-gap. However, we observe a rather surprising transfer of this extra electron to the conduction band of the material. This effect is observed in both phases

¡Error!Marcador no definido.
¡Error!Marcador no definido.

in the case of $BaTiO_3$ and exclusively in orthorhombic phase of $CaTiO_3$. We have to note that the extra electron tends to remain in the conduction band, as it would be its natural or stable state. Actually, as it is seen from Fig.1, the meta-stable state of the electron within the band-gap has lower energy. However, the electron jumps to the conduction band, a new and final stable state of higher energy, in which the electron remains. Where the necessary energy for the electron transfer comes from? One possible answer for this question might come at glance suggesting that this energy comes from electron-phonon interaction due to the relaxation of the system. However, our computer code does not consider directly this type of interaction. Therefore, in our mind this effect might be due to some structural properties of the material or it is related to some undiscovered phenomenon in this ferroelectric material. We are still working on this question.

The comparison of the relaxation energy for both $BaTiO_3$ and $CaTiO_3$ crystals gives us 5.44 eV and 15.04 eV, respectively. Thus these values are appreciably greater than those ones of the cubic phase. So, in our mind, the greater the energy released the greater the compactness of the structure after relaxation and we certainly believe the electron transfer effect is related to the final symmetry of the structure.

Finally, we should note that experimentally it is known that due to the Nb-doping in $BaTiO_3$ the conductivity shifts from a pure p-type semiconductor to an n-type semiconductor [12]. The increase in the electrical conductivity if niobium concentration is high enough is also well known effect in both $BaTiO_3$ and $CaTiO_3$ crystals [13, 14]. Thus the electron transfer effect observed in our work is directly related to the increase in electrical conductivity observed experimentally.

5. Conclusions

¡Error!Marcador no definido.
¡Error!Marcador no definido.

By means of the quantum-chemical method developed especially for crystal computations we study Nb-impurity influence upon structural and electronic properties of the $BaTiO_3$ and $CaTiO_3$ crystals. Our results point out to the importance of crystalline lattice compactness since the obtained lattice relaxation energy values are larger for more compact structures. The observed new effect of the extra electron transfer from the local energy level within the band-gap to the conduction band is in accordance with the experimentally observed increase in electrical conductivity for these two materials.

¡Error!Marcador no definido.
¡Error!Marcador no definido.

References

1. D. Balzar, H. Ledbetter, P. W. Stephens, E. T. Park and J. L. Routbort, Phys. Rev. B, 59 (1999), 5.

2. G. J. McCarthy, G. J., Nucl. Technol., 32 (1977), 92.

3. H. Pinto and A. Stashans, Comput. Mater. Sci., 17 (2000), 73.

4. F. Erazo and A. Stashans, Phil. Mag. B, in press (2000).

5. H. Pinto, A. Stashans and P. Sánchez, *Defects and Surface-Induced Effects in Advanced Perovskites, NATO Science Series, High Technology* (Kluwer Academic Publishers, Dortrech, 2000), Vol. 77, p. 67.

6. A. Stashans and P. Sánchez, Mater. Lett., 44 (2000), 153.

7. A. Stashans, Mater. Chem. Phys., in press (2000).

8. A. Shluger and V. Stefanovich, Phys. Rev. B, 42 (1990), 9664.

9. A. Stashans and S. Lunell, Int. J. Quant. Chem., 63 (1996), 729.

10. S. Lunell, A. Stashans, L. Ojamäe, H. Lindström and A. Hagfeldt, J. Am. Chem. Soc., 119 (1997), 7374.

11. A. Shluger, Theor. Chim. Acta, 66 (1985), 355.

12. P. Moretti, G. Godefroy and J. M. Bilbault, Ferroelectrics, 37 (1981), 721.

13. M. Maglione and M. Belkaoumi, Phys. Rev. B, 45 (1992), 2029.

14. K. Ueda, H. Yanagi, H. Hosono, and H. Kawazoe, Phys. Rev. B, 56 (1997), 12998.

¡Error!Marcador no definido.
¡Error!Marcador no definido.

Figure captions

Fig. 1. A scheme showing the extra electron transfer from the local one-electron energy

level within the band-gap (meta-stable state) to the conduction band (stable state).

Table 1. (a) The semi-empirical parameters used in the present work. (b) The two-center parameters $\alpha_{\mu B}$ (au^{-1}), the numbers in the parenthesis show the corresponding parameters for the tetragonal phase.

(a)

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
Ca	4s	1.48	14.0	0.15	-0.4
	3p	2.8	42.5	2.0	-3.0
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
Nb	5s	1.55	24.5	0.8	-0.5
	5p	1.4	2.0	0.01	-0.5
	4d	1.35	23.7	0.117	-8.0

(b)

		B			
A	Ba	Ca	Ti	O	Nb
Ba	0.20	-	0.10	0.57	0.00
Ca	-	0.15	0.55	0.18	0.10
Ti	0.53	0.07	0.13	0.10	0.03
O	0.36	0.57	0.37	0.15	0.45
Nb	0.22	0.20	0.05	0.10	0.00

¡Error!Marcador no definido.
¡Error!Marcador no definido.

Conduction Band

Band Gap

Valence Band