

THEORETICAL STUDIES OF IMPURITY DOPED AND UNDOPED BaTiO_3 AND SrTiO_3 CRYSTALS

H. PINTO, A. STASHANS, P. SANCHEZ

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

ABSTRACT. The BaTiO_3 and SrTiO_3 crystals have many technological applications due to their unusual magnetic and dielectric properties. Using the modified for crystals INDO method which had shown reliability in a number of applications, we study self-trapped and impurity-trapped polarons in cubic lattice of both materials as well as La-doping in the SrTiO_3 crystal. The obtained results are discussed in terms of the available experimental data.

1. INTRODUCTION

Barium and strontium titanates are perovskite-type ceramics used in the design of high technology devices. The BaTiO_3 crystal possesses excellent ferroelectric and piezoelectric features that have been found increasing applications in the manufacture of micro-electronic devices. Besides, this crystal is used in optical sensors due to its large electro-optic coefficients and high photorefractive sensitivity and is a promising material for holographic storage and cheap diode lasers. The SrTiO_3 crystal has been

utilised as a grain-boundary barrier layer capacitor, oxygen gas sensor and epitaxial growth substrate of the high temperature superconductor thin films.

All relevant light-induced charge-transfer reactions in both crystals are due to the presence of polarons. In particular, the BaTiO₃ crystal exhibits a peculiar non-linear photoconductivity phenomenon [1]. Although exist some models which try to explain this phenomenon [2], the origin of the non-linear photoconductivity is not completely clear. The explanation of superconductivity in ceramic materials is not done yet as well. The SrTiO₃ crystal becomes superconducting when a little amount of electron carriers are introduced by La substitution for Sr [3] below the T_c=14K. Our investigation gives some results that are in a good accordance with the available experimental data on non-linear photoconductivity in the BaTiO₃ and superconducting properties of SrTiO₃ crystals.

2. METHOD OF CALCULATION

We have used a version of INDO method modified for crystal calculations. This method is based on Molecular Orbital (MO) theory [4] and a specific parameterisation scheme [5]. Within this method two different models have been implemented in the CLUSTERD computer code [6], namely, the large unit cell (LUC) approach [7] and the embedded molecular cluster (EMC) model [8]. In the present study, we have used 40-, 80- and 160-atom LUCs as well as 90-atom molecular cluster to study the point defects. The semi-empirical parameter sets were taken from [6, 9, 10].

In order to calculate a hole self-trapping (ST) energy, we have used the old idea of Gilbert. He considered the hole self-trapping as a hypothetical two-stage procedure: (i) localisation of a free hole in a local perfect crystal region (positive energy) and (ii) subsequent relaxation of the lattice with accompanying electronic redistribution (negative energy). A competition between the localisation energy, E_{loc}, and the relaxation energy, E_{rel}, results in the actual sign of the ST energy:

$$\Delta E_{ST} = E_{loc} - E_{rel} \quad (1)$$

The value of ΔE_{ST} leads to the final conclusion about the possibility of finding stable STHs in a given crystal. In the present work the E_{rel} was calculated as a difference between the total energies of the molecular cluster in the relaxed and unrelaxed states,

while the E_{loc} was estimated to be equal to the ‘‘centre of gravity’’ of the upper valence band [11]:

$$\epsilon^{(W)} = \int \epsilon N_j(\epsilon) d\epsilon \quad (2)$$

where $N_j(\epsilon)$ is the density of states (DOS) of the valence band j normalised to unity.

3. SELF-TRAPPED POLARONS IN THE BaTiO₃ AND SrTiO₃ CRYSTALS

In order to estimate the relaxation energy E_{rel} in the BaTiO₃ crystal, we allowed to make displacements to 18 atoms situated around the oxygen, which receives a hole. Thus obtained value of E_{rel} was found to be equal to 3.85 eV. We have computed the localisation energy using the equation (2), which gave us the value of 2.36 eV. Thus the ST energy was found to be equal to -1.49 eV. Since the value of ΔE_{ST} is essentially negative, one can expect that the self-trapping state is favoured with respect to a free delocalised hole in the valence band. Therefore, we predict the spontaneous occurrence of self-trapped polaron in the pure barium titanate cubic lattice.

To study the polaron in the SrTiO₃ crystal, we have used a molecular cluster of 90 atoms. The relaxation energy was calculated utilising the automated geometry optimisation procedure and moving 27 atoms situated around the oxygen which receives a hole. Thus computed value of E_{rel} was found to be equal to 2.90 eV while the localisation energy was estimated to be 2.85 eV. So, we obtained -0.05 eV as a value of the hole ST energy. Since the value of E_{ST} is practically equal to zero, we expect that the STH state will not occur spontaneously in this material.

We have attempted to calculate the absorption energy of self-trapped polaron in the BaTiO₃ crystal using the ΔSCF method. The calculated value was equal to 0.5 eV, which is very close to the energies of 0.53 eV and 0.57 eV, observed experimentally in the light-induced absorption measurements [8] for undoped BaTiO₃ crystal. We suppose that this is not just simple coincidence but indirect prove of existence of self-trapped polarons in the BaTiO₃ crystal.

4. IMPURITY-TRAPPED HOLE POLARONS

In order to study K-bound polaron in the SrTiO₃ crystal, we have used the EMC model and the molecular cluster consisting of 90 atoms. The K atom substituted one of

the Sr atoms situated in the centre of the EMC. The result was that the polaron is localised on one of the K-nearest O atoms, denoted hereafter as O_k atom. The automated geometry relaxation has been carried out which showed 0.07 Å displacements of O_k atom towards the potassium impurity. The movements of another atoms in the defective region were smaller as 0.04 Å. The ground state of polaron in the equilibrium state was described by $2p_y$ AO. The absorption energy for the transition: $2p_y \Rightarrow 2p_x$ (or electron transition $2p_x \Rightarrow 2p_y$) was computed to be equal to 0.35 eV, where the $2p_x$ AO describes the excited state of the polaron.

We substituted one of the Ti atoms by either the Al or Sc atom in order to study Al- and Sc-bound polarons in the $BaTiO_3$ crystal. The results showed that two oxygen atoms (denoted hereafter by O_{Al}) situated at both sides of Al atom along z-direction trap the hole. The result of the automated geometry optimisation was the following: the six Al-neighbouring O atoms move towards the Al atom by 0.07 Å. For the Sc-bound polaron the results were not very different from those obtained for the Al impurity. In this case, the hole is trapped by two oxygens (denoted hereafter by O_{Sc}) located along the x-direction. The result of automated geometry relaxation was that the two O atoms situated at both sides of the Sc atoms in z-direction move about 0.028 Å towards the Sc atom. At the same time, the four Sc-nearest O atoms in the x-y plane rotate by 0.8° around the vertical z-axis, which passes through the Sc atom. It is important to note that these four atoms conserve their original distances with respect to the Sc atom.

The ground state of Al-bound polaron has the contribution of $2p_z$ AOs of two O_{Al} atoms, while in the case of Sc-bound polaron the ground state is described by the wave function composed of $2p_x$ AOs of the two O_{Sc} atoms. By means of the Δ SCF method we found the absorption energies being equal to 0.27 eV for the Al-bound polaron and 0.62 eV and 1.92 eV for the Sc-bound polaron, respectively.

5. La-DOPING IN THE CUBIC AND TETRAGONAL $SrTiO_3$ LATTICES

In order to study the effects of La-doping in $SrTiO_3$ crystal, we have used the LUC model replacing one and/or two Sr atoms by La atoms, which corresponded to the donor doping.

Our calculations showed that the extra electron in 6s AO of the La is the origin of the local energy level, which occurs within the bandgap for both, cubic and tetragonal structures. The presence of impurity atom produces lattice distortion in the La-

surrounding region. However, it has to be said that the atomic displacements are rather different for cubic and tetragonal lattices. In the cubic phase the relaxation is completely symmetric for both, Ti and O atoms. In the tetragonal phase the atomic movements along the z-axes are considerably larger as in the other directions. This might be

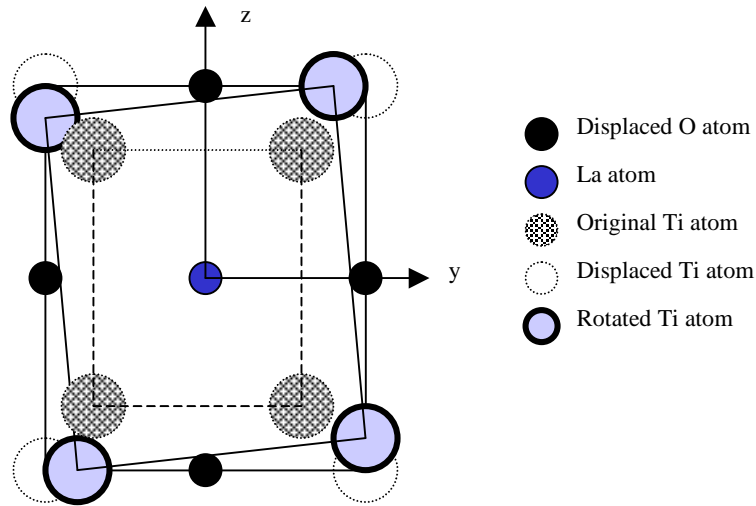


Figure 1. Atomic displacements in the tetragonal La-doped SrTiO₃ crystal.

explained by ferroelectricity phenomenon, which occurs in the tetragonal phase. The more interesting effect is the rotation of Ti atoms by 0.6° around the x-axes (see Fig. 1). Up to now only the asymmetric displacements of O atoms were considered [14]. Our studies point out to the importance of Ti rotations in the presence of impurity atom.

We substituted two La atoms for Sr atoms in order to study the effects of superconductivity discussed in [3]. Since in this case we have two extra electrons in the system, two states are possible: (i) singlet with both electrons occupying the same local energy level and (ii) triplet with two different local energy levels populated by one electron. For the 160-atom LUC we obtained local energy level situated at 2.5 eV and 1.5 eV above the top of the upper valence band for the singlet and triplet states, respectively. This agrees very well with the experimental data of 2.4 eV and 1.5 eV [3]. It has to be noted that the triplet state is energetically favourable compared to the singlet state by approximately 1.0 eV. If we repeat the same kind of computations in the 80-atom LUC, i.e., increasing twice the La concentration, the favourability of the triplet

state increases until 1.3 eV. This explains the experimental observation of the augmentation of intensity of 1.5 eV peak with increasing La concentration.

6. CONCLUSIONS

By means of the modified for crystals INDO method we have managed to reproduce some interesting features of impurity-doped and undoped BaTiO₃ and SrTiO₃ crystals. In particular, we predict the existence of self-trapped hole polarons in the BaTiO₃ crystal, which can contribute considerably into non-linear photoconductivity in this material. The studies of La-doped SrTiO₃ crystal explain the origin of the energy peaks within the bandgap and the effect of La concentration upon the intensity of these peaks.

7. References

1. Brost, A., Motes, R. A. and Rotgé, J. R. (1988) *J. Opt. Soc. Am. B* **5**, 1879.
2. Song, H., Dou, S. X., Chi, M., Gao, H., Zhu, Y. and Ye, P. (1998) Studies of shallow levels in undoped and rhodium-doped barium titanate *J. Opt. Soc. Am. B* **15**, 1329.
3. Suzuki, H., Bando, H., Ootuka, Y., Inoue, I. H., Yamamoto, T., Takahashi, K. and Nishihara, Y. (1996) *J. Phys. Soc. Jpn.* **65**, 1529.
4. Pople and Beveridge, D., (1970) *Approximate MO Theories*, McGraw-Hill, New York.
5. Shluger, A. (1985) application of molecular models to electronic structure calculations of defects in oxide crystals. I. Parametrization of modified INDO method *Theor. Chim. Acta*, **66**, 355
6. Stefanovich, E., Shidlovskaya, E. K., Shluger, A. L., and Zakharov, M. A. (1990) Modification of the INDO calculation scheme and parametrization for ionic crystals *Phys. Status Solidi B* **160**, 529.
7. Evarestov and Lovchikov, V. A. (1977) *Phys. Status Solidi B* **79**, 743.
8. Kantorovich, L. (1988) An embedded-molecular-cluster method for calculating the electronic structure of point defects in non-metallic crystals: I. General theory *J. Phys. C* **29**, 5041
9. Stashans, A. and Pinto, H. (1999) Hole polarons in pure BaTiO₃ studied by computer modelling *J. Phys. Condens Matter*, submitted
10. Stashans, A. (1999) *J. Phys. Chem. Solids*. Submitted
11. Kantorovich, L., Stashans, A., Kotomin, E. and Jacobs, P. W. M. (1994) Quantum chemical simulations of hole self-trapping in semi-ionic crystals *Int. J. Quant. Chem.* **52**, 1177
12. Englman, R. (1972) *Jahn-Teller Effect in Molecules and Crystals*, Wiley, New York,
13. Zhukovskii, Yu. F., Kotomin, E. A., Nieminen, R. M., and Stashans, A. (1997) Quantum-chemical simulations of free and bound hole polarons in corundum crystal *Comput. Mater. Sci.* **7**, 285
14. Cowley, R. A. (1996) *Phil. Trans. R. Soc. Lond. A* **354**, 2799