

A quantum mechanical study of La-doped $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$

Arvids Stashans*, Frank Maldonado

Grupo de Física de Cristales, Escuela de Electrónica y Telecomunicaciones, Universidad Técnica Particular de Loja, Apartado 11-01-608, Loja, Ecuador

Received 5 May 2006; received in revised form 14 November 2006; accepted 17 November 2006

Abstract

Lanthanum-modified $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT) crystals have been investigated applying a quantum-mechanical approach based on the Hartree–Fock theory. A morphotropic phase boundary (MPB), $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$, of the crystal was considered throughout the study. The obtained results show the outward atomic displacements with respect to the La impurity within the defective region and also the increase of covalent nature in the chemical bonding of the material. These outcomes are discussed and analyzed in light of the available experimental data. The occurrence of Jahn–Teller self-trapped electron polarons is predicted in the present report.

© 2006 Elsevier B.V. All rights reserved.

PACS: 61.50.Ah; 61.72.Ji; 73.20.Hb; 77.84.Dy

Keywords: PZT; Lanthanum; Morphotropic phase boundary; Electronic and structural property; Hartree–Fock method

1. Introduction

In the present times, computational physics is becoming a powerful tool in the study of different complex systems. Methods based on the quantum-mechanical approach allows one not only to simulate crystals and materials but also give the possibility to ‘see’ complex phenomena occurring at the microscopic level leading to a better understanding of the behaviour of these materials.

Perovskite-type titanates have attracted a great deal of attention from many researches since the discovery of ferroelectricity in barium titanate in the late 1940s. $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT) material is of a special interest. The PZT samples are manufactured on the base of lead titanate (PbTiO_3) and lead zirconate (PbZrO_3) crystals and nowadays are available for different high-technology applications. In particular, PZT materials have been proposed as high-density storage media and integrated components for applications in dynamic and non-volatile random access memories, and in surface acoustic wave devices, micro-mechanical devices and ferroelectric field effect devices

[1–3]. These materials also promise dramatic improvements in the resolution and range of ultrasonic and sonar listening devices [4].

It is worth to underline that the above-mentioned magnificent features of the PZT are due to the presence of different point defects therein. Lanthanum impurity currently is of considerable significance since the La-modified PZT samples are of increasing demand by both scientific and engineering communities. La incorporation into the PZT structure might improve its microstructural, electrical and electromechanical properties [5–7] and dielectric [8,9] behaviour which is important for a thermally driven (spontaneous) transformation from a relaxor to a normal ferroelectric state. Lanthanum effect on the PZT piezoelectric properties is also utilized for piezoelectric sensor manufacturing [10,11]. The ferroelectric ordering in rhombohedral and tetragonal PZT ceramics [12] due to the La-presence is of importance in highly reliable ferroelectric random access memory (FeRAM) applications [13].

The myriad of different applications, in which La-modified PZT is the key element, have fostered numerous experimental studies. Despite some important attempts to calculate the band structure of this compound by the tight-binding method [14,15] supported by corresponding

*Corresponding author. Fax: +593 72585978.

E-mail address: arvids@utpl.edu.ec (A. Stashans).

experimental measurements [16], hitherto its electronic and structural properties have not been well studied at the fundamental level. The obvious reason for this is a number of difficulties to be overcome if one dedicates himself to use a quantum-mechanical approach in study of this particular material, e.g. semi-covalent character of its chemical bonding, necessity to reproduce correctly the electrons of d-type valence atomic orbitals (AOs) and their interactions, and finally, the obligation to deal with the relativistic effects, which undoubtedly are sizeable in lead.

The huge number of experimental works and a little knowledge at the fundamental level provoked our interest in the PZT materials. In the present investigation, we limited ourselves to PZT crystals of the morphotropic phase boundary (MPB), which is believed to have some advanced piezoelectric properties [17].

2. Basic methodology

The model used to solve many-particle electron–ion problem is based on the advanced version of the Hartree–Fock theory modified for crystal calculations. The method as it is implemented in the CLUSTERD computer code [18] calculates both the electronic band structure and the total energy of a given crystal via molecular orbital (MO) as a linear combination of AOs. The method has been applied successfully so far to investigate numerous crystals ranging from simple ionic materials with cubic crystallographic lattices to rather sophisticated ones in both chemical bonding and crystalline structure.

The atomic parametrization was done by one of the authors (A.S.) before and took into account of the diverse crystalline peculiarities of the PZT crystals. The details of parametrization are described elsewhere [19], however, we can briefly state that the main results obtained on pure PbTiO_3 crystals were in concordance with the other available studies [20] and reproduced some important features of the electronic band structure, e.g. density of states (DOS) and composition of the energetic bands. We also managed to reproduce the hybridization between the Ti 3p and O 2p AOs for the tetragonal phase of the crystal in accordance with the expectations [21]. In previous studies of PZT, considering different zirconium concentrations [22], some interesting tendencies were confirmed. For instance, in order to explain atomic relaxation around the newly introduced Zr impurities in the PbTiO_3 crystal, we had to consider the effect of repulsion between the overlapping electron clouds. This effect was found to be even stronger as the electrostatic Coulomb interaction in the PZT materials. The optical band gap, calculated by the ΔSCF method, was found to decrease slightly by augmenting the Zr concentration [23]. This contradicts to the other studies [15,16] done before by means of the tight-binding method and the experimental evaluation of the optical band gap width in PZT materials. This small discrepancy originating apparently from the one-electron approxima-

tion used in the Hartree–Fock theory does not influence, however, the results concerning impurity doping.

The obtained atomic parameters for the PZT crystals thus can be found in Ref. [19], while the numerical parameters of the La atom is taken from Ref. [24]. We would like to mention that the current method was applied successfully in studies of the other titanates, e.g. SrTiO_3 , BaTiO_3 and CaTiO_3 containing diverse point defects. Some examples include La-, Na- and Nb-doped SrTiO_3 [24–27], La-, Nb-, Al- and Sc-modified BaTiO_3 [28–31], La- and Nb-doped CaTiO_3 [32–34] and different electronic defects in titanates [35–40].

3. Results and discussion

The purpose of the present work is to study La-doped PZT crystals at the quantum level in order to understand better the structural and electronic properties of the material. We have used 135-atom supercell throughout the computations, which corresponds to the 27 times symmetric extension ($3 \times 3 \times 3$) of the PZT primitive unit cell. The Zr/Ti ratio was kept constant at 0.53/0.47 according to the MPB condition. The La impurity concentration was taken as 3.7 and 7.4 mol%, i.e., one- or two-La atoms were substituted for the A-site Pb atoms. This particular impurity concentration was chosen due to the numerous experimental works carried out within the same concentration range. It is worth to say that we have performed the optimization of the PZT lattice parameters just for the MPB of this material, $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$. As a result the obtained values were found to be equal to $a = 4.142 \text{ \AA}$ and $c = 4.295 \text{ \AA}$. These values are considerably larger as the corresponding numbers for the PbTiO_3 crystal, $a = 3.904 \text{ \AA}$ and $c = 4.150 \text{ \AA}$ [41].

3.1. Structural properties of La-doped PZT

One of the Pb atoms in the central part of supercell was replaced by a La atom leading to the atomic displacements shown in Fig. 1. In order to obtain the final atomic configuration corresponding to the minimum of the system's total energy, various types of atomic relaxation were considered, e.g. energy minimization through radial movements of atoms, asymmetric displacements and also automated lattice optimisation. As a result, we encountered the following lattice rearrangement leading to the lowest total energy configuration. The Zr and Ti atoms located in the planes above and below regarding the La-containing (001) atomic plane move outwards the impurity by approximately 0.21 \AA . The O atoms of the upper plane displace themselves outwards from the impurity by approximately 0.23 \AA whereas the O atoms of the lower atomic plane also tend to move away from the defect by about 0.31 \AA . Finally, the four defect-closest O atoms belonging to the same (001) plane as the La atom move outwards the impurity by about 0.28 \AA and additionally rotate around the $\langle 001 \rangle$ axis by approximately 1° as it is

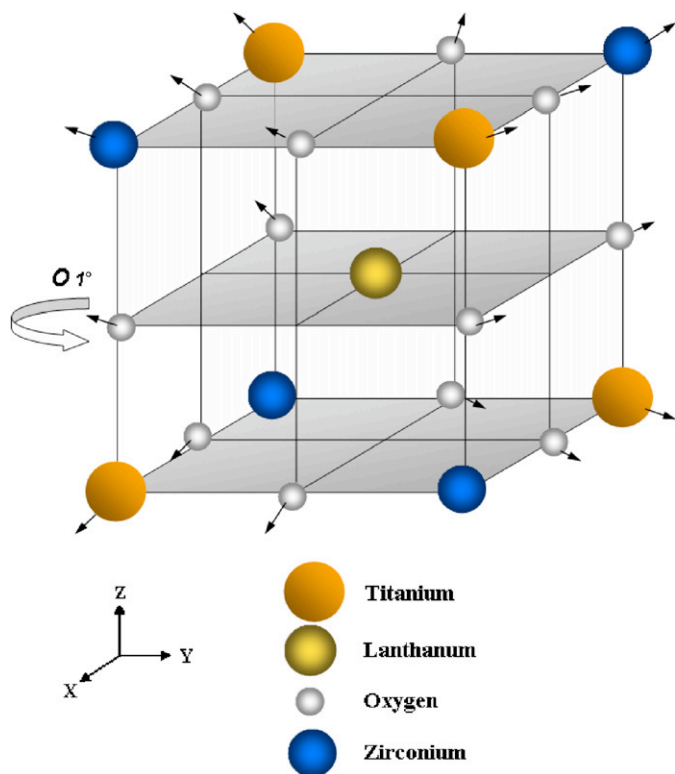


Fig. 1. A schematic diagram showing the vicinity of La atom in the PZT crystal. The outward atomic movements with respect to the impurity are indicated by pointers. The four O atoms belonging to the same (001) plane as the La impurity tends to rotate slightly due to the Jahn–Teller effect.

drawn in Fig. 1. The larger displacements of atoms in the lower O plane compared to those of the upper O atoms we explain by the fact that initially the lower plane O atoms are situated closer to the impurity and thus receive a stronger defect-produced perturbation leading to a larger magnitude of their relaxation. In general, the atomic rearrangement is radial with respect to the newly introduced impurity atom, except the already mentioned rotation of four O atoms. The latter we attribute to the Jahn–Teller effect and will discuss its consequences below.

When two Pb atoms are replaced by two La atoms we obtain 7.4 mol% impurity concentration in the PZT crystal. Nevertheless, the lattice response to the defects' presence in this case is rather similar to the one discussed for the 3.7 mol% La impurity concentration. In particular, the Zr and Ti atoms situated above the upper La atom and below the lower La atom move outwards from the defect by 0.21 Å (Fig. 2). The outward displacements of Zr and Ti atoms located in between the two La-defective (001) planes are smaller, approximately 0.17 Å, and are within the (110) plane only. Such an outcome is expected because these Zr and Ti atoms have less possibility to rearrange their positions because of the La atoms imposed by both sides of them along the $\langle 001 \rangle$ axis (see Fig. 2). The outward relaxation of the O atoms is the following: the

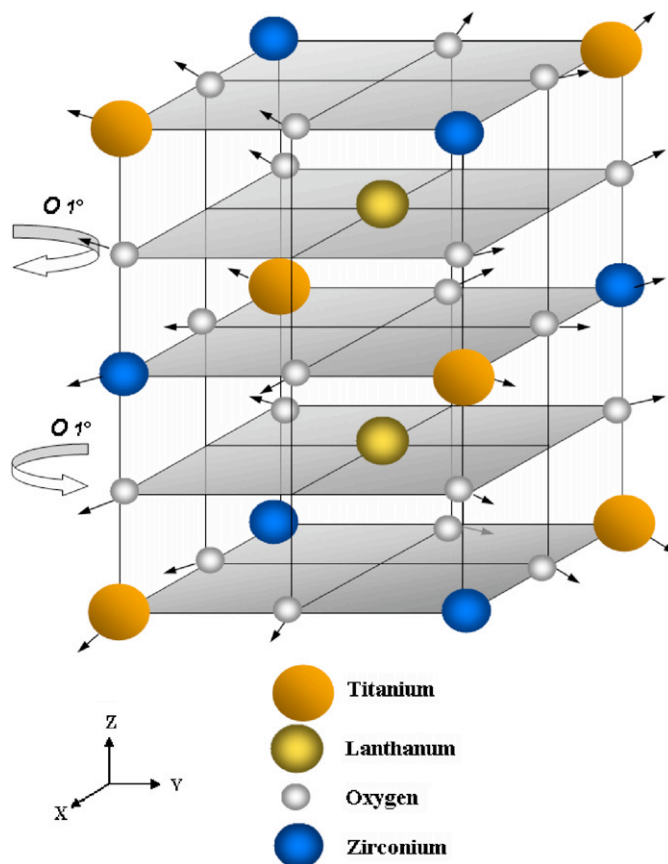


Fig. 2. A schematic diagram corresponding to the case of 7.4 mol% impurity concentration, i.e. when two La atoms replace for two of the Pb atoms in the central part of the supercell. The pointers show the atomic displacements in the defective region. The depicted rotations of the O atoms within the (001) planes are obviously associated to the Jahn–Teller effect.

four O atoms situated below the lower La impurity move by 0.31 Å, while the four O atoms in the plane just above the upper La atom displace themselves by 0.16 Å. Such a considerable difference in the magnitude of relaxation can be explained again by different initial distances of each type of oxygens regarding the corresponding La atom, producing stronger impact on the closest atoms being situated in the lower atomic plane. The O atoms contained by the (001) plane in between the two La-defective atomic layers move outwards the defects by about 0.16 Å within the (110) plane only, due to the reasons similar to those for the Zr and Ti atoms of the same atomic layer. Finally, the O atoms belonging to the two La-containing planes move outwards from the corresponding impurity by 0.25 Å (atomic plane of the lower La impurity) and 0.30 Å (plane of the upper La atom) and additionally tend to rotate by about 1° in the opposite directions around the $\langle 001 \rangle$ axis as it is depicted in Fig. 2. This rotation is apparently due to the Jahn–Teller effect producing the reduction of system's total energy by a non-symmetric atomic distortion and in this way lifting the threefold orbital degeneracy [42], which is a common matter in titanates.

3.2. Electronic properties of La-modified PZT

The outward atomic displacements discussed in the previous section imply the enlargement of chemical bond lengths between the atoms in defective region. This normally occurs if the contribution of covalent chemical bonding is to increase in a given crystal. The analysis of atomic charges confirms this hypothesis. In the case of one La impurity, the reduction of negative charge on O atoms is between $0.01e$ and $0.05e$ and is accompanied by a similar lowering of the positive charge on Ti atoms and especially on the defect-neighbouring Zr atoms. The addition of growing covalent contribution into the chemical bonding around the La impurity partially can be explained by the atomic charge of La impurity, $+1.41e$, compared to that one of the Pb atom, $+1.54e$, for which it substitutes. We also observe a local energy level within the band gap situated approximately 0.4eV above the top of the upper valence band (UVB) and being composed mainly of La $6s$ AO. In our mind, this implies the self-trapped electron (STE) formation which actually is Jahn–Teller STE polaron according to the non-symmetric atomic displacements produced within the La-impurity (001) plane.

The results obtained for the $7.4\text{mol}\%$ impurity concentration mainly confirm those for a lower La atom ratio already discussed above, however, there are some exceptions. First of all, we should mention that we observe again a tendency of increasing covalent character in the chemical bonding in the vicinity of defects. It is true for both La-containing atomic planes and for the atoms in (001) plane in between them. The observed decrease in atomic charges is between $0.01e$ and $0.07e$ for the O atoms and between $0.01e$ and $0.09e$ for the Zr and Ti atoms. The notable and interesting fact is that in the most upper atomic plane (Fig. 2), we observe an increase in the magnitude of atomic charges compared to the case of pure PZT crystal. This implies a stronger ionic contribution into the chemical bonding just for the atoms within the upper atomic plane. Such a phenomenon could be elucidated by the electron density redistribution between the two La atoms. As it follows from the charge density analysis, the lower La atom becomes less positive, $+0.76e$, whereas the upper La atom tends to be more positive, $+2.11e$. So, the stronger Coulombic nature of the upper La atom produces somewhat more ionic bonding in its nearest vicinity while the general picture does not change, i.e. the La-incorporation leads to the increase in covalent chemical bonding in the PZT crystals. The charge changes for impurity atoms are also in accordance with the outcome that the local energy level being situated 0.7eV above the UVB is predominantly composed of the $6s$ AO of the lower La atom. The electron density relocation from one to another impurity atom and a subsequent rotation of the O atoms situated in La-containing (001) planes in opposite directions (Fig. 2), proves creation of the Jahn–Teller STE polarons and also implies the system preference for the singlet state. Actually,

we tried to simulate the triplet state for the case of two impurity doping but the obtained system's total energy was found to be considerably higher as that one for the singlet state.

3.3. La impurity influence upon the dielectric and piezoelectric properties of PZT

Our results on La-modified PZT crystal clearly demonstrate the augmentation of covalent character in the chemical bonding of material by the La impurity addition. This effect is stronger in the case of a single La impurity doping since in the case of two La atoms we observe somewhat more ionic character in the chemical bonding of some defect-surrounding atoms. On the other hand, we find a rising of the defect-induced local energy level within the band gap when the La concentration increases (0.7 Versus 0.4eV with respect to the UVB). Apparently, the rising of the local energy level is accompanied by the reduction of the dielectric constant of the material, i.e. the system becomes more metallic when the La concentration corresponds to $7.4\text{mol}\%$. This important deduction arguing that the $3.7\text{mol}\%$ La concentration gives better dielectric properties of La-doped PZT compared to the ones of $7.4\text{mol}\%$ La concentration is in a direct agreement with the experimental findings [5], where it was observed that the maximum dielectric constant in the La-modified PZT is reached when the impurity concentration is between 4 and $5\text{mol}\%$. Thus, we elucidate that the La substitution for an A-site Pb atom in the PZT crystals produces some redistribution of the electron density in the defective region. This leads to the augmentation in covalent character of the Ti–O and Zr–O chemical bonding while the La–O bonds remain essentially ionic. The increase in covalent nature, therefore, is directly related to the improvement of dielectric and piezoelectric properties of the La-doped PZT.

4. Conclusions

The quantum-chemical method based on the Hartree–Fock ideology and modified for crystals modelling is exploited in the present work to perform investigation on La-doped PZT crystals corresponding to the MPB condition. The obtained equilibrium geometry configuration points out to the defect-outward atomic displacements. The observed rotation of the O atoms belonging to the defective La-containing (001) atomic planes implies the presence of the Jahn–Teller effect in the system. This obviously leads to the occurrence of Jahn–Teller STE polarons. The analysis of calculated atomic charges shows the increase of covalent character into the Ti–O and Zr–O chemical bonding of La-modified PZT. This also makes clear experimentally demonstrated improvement of piezoelectric and dielectric properties in PZT due to the La-doping.

References

- [1] S.L. Swartz, V.E. Woods, *Condens. Matter News* 1 (1992) 4.
- [2] G.H. Haertling, *J. Vac. Sci. Technol. A* 9 (1991) 414.
- [3] C.H. Ahm, R.H. Hammond, T.H. Geballe, M.R. Beasley, J.-M. Triscone, M. Decroux, O. Fischer, L. Antognazza, K. Char, *Appl. Phys. Lett.* 70 (1997) 1878.
- [4] R.F. Service, *Science* 275 (1997) 1878.
- [5] M. Hammer, M.J. Hoffmann, *J. Electroceramics* 2 (1998) 75.
- [6] S.R. Shannigrahi, R.N.P. Choudhary, *J. Electroceram.* 5 (2000) 201.
- [7] S. Dutta, R.N.P. Choudhary, P.K. Sinha, *Mater. Sci. Eng. B* 113 (2004) 215.
- [8] X. Dai, A. Di Giovanni, D. Viehland, *J. Appl. Phys.* 74 (1993) 3399.
- [9] P.-H. Xiang, N. Zhong, X.-L. Dong, R.-H. Liang, H. Yang, C.-D. Feng, *Mater. Lett.* 58 (2004) 2675.
- [10] S.-H. Lee, C.-B. Yoon, S.-B. Seo, H.-E. Kim, *J. Mater. Res.* 18 (2003) 1765.
- [11] J.F. Tressler, S. Alcoy, R.E. Newnham, *J. Electroceram.* 2 (1998) 257.
- [12] M. El Marssi, R. Farhi, X. Dai, A. Morell, D. Viehland, *J. Appl. Phys.* 80 (1996) 1079.
- [13] N. Inoue, T. Takeuchi, Y. Hayashi, *IEEE Trans. Electron Dev.* 49 (2002) 1572.
- [14] J. Robertson, W.L. Warren, B.A. Tuttle, *J. Appl. Phys.* 77 (1995) 3975.
- [15] W.L. Warren, J. Robertson, D. Dimos, B.A. Tuttle, G.E. Pike, D.A. Payne, *Phys. Rev. B* 53 (1996) 3080.
- [16] C.H. Peng, J.-F. Chang, S.B. Desu, *Mater. Res. Soc. Symp. Proc.* 243 (1992) 21.
- [17] L.A. Celi, *Microestructura y Propiedades de Materiales Cerámicos de PZT preparados a partir de polvo modificado superficialmente con fósforo*, Ph.D. Thesis, Instituto de Cerámica y Vidrio, Madrid, 2002.
- [18] E.V. Stefanovich, E.K. Shidlovskaya, A.L. Shluger, M.A. Zakharov, *Phys. Stat. Sol. B* 160 (1990) 529.
- [19] A. Stashans, C. Zambrano, A. Sánchez, L.M. Prócel, *Int. J. Quantum Chem.* 87 (2002) 145.
- [20] M. Kitamura, H. Chen, *Ferroelectrics* 210 (1998) 13.
- [21] R.E. Cohen, *Nature* 358 (1992) 136.
- [22] A. Sánchez, C. Zambrano, L.M. Prócel, A. Stashans, *SPIE Proc.* 5122 (2003) 310.
- [23] C. Zambrano, A. Sánchez, L.M. Prócel, A. Stashans, *Int. J. Quantum Chem.* 95 (2003) 37.
- [24] A. Stashans, P. Sánchez, *Mater. Lett.* 44 (2000) 153.
- [25] A. Stashans, *Mater. Chem. Phys.* 68 (2001) 124.
- [26] P. Sánchez, A. Stashans, *Philos. Mag. B* 81 (2001) 1963.
- [27] P. Sánchez, A. Stashans, *Phys. Stat. Sol. B* 230 (2002) 397.
- [28] H. Pinto, A. Stashans, *Comput. Mater. Sci.* 17 (2000) 73.
- [29] E. Patiño, A. Stashans, *Comput. Mater. Sci.* 22 (2001) 137.
- [30] E. Patiño, A. Stashans, *Ferroelectrics* 256 (2001) 189.
- [31] E. Patiño, A. Stashans, R. Nieminen, *Key Eng. Mater.* 206–213 (2002) 1325.
- [32] F. Erazo, A. Stashans, *Philos. Mag. B* 80 (2000) 1499.
- [33] E. Patiño, F. Erazo, A. Stashans, *Mater. Lett.* 50 (2001) 337.
- [34] F. Erazo, A. Stashans, *Int. J. Quantum Chem.* 87 (2002) 225.
- [35] A. Stashans, H. Pinto, *Int. J. Quantum Chem.* 79 (2000) 358.
- [36] A. Stashans, H. Pinto, *Radiat. Meas.* 33 (2001) 553.
- [37] A. Stashans, S. Serrano, *Surf. Sci.* 497 (2002) 285.
- [38] H. Pinto, A. Stashans, *Phys. Rev. B* 65 (2002) 134304.
- [39] A. Stashans, H. Pinto, P. Sánchez, *J. Low Temp. Phys.* 130 (2003) 415.
- [40] C. Duque, A. Stashans, *Physica B* 336 (2003) 227.
- [41] R.W.G. Wyckoff, *Crystal Structures*, Interscience, New York, 1960.
- [42] A. Stashans, *Int. J. Nanotechnol.* 1 (2004) 399.