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A quantum mechanical study of La-doped $Pb(Zr,Ti)O_3$

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Abstract

Lanthanum-modified $Pb(Zr,Ti)O_3$ (PZT) crystals have been investigated applying a quantum-mechanical approach based on the Hartree–Fock theory. A morphotropic phase boundary (MPB), $PbZr_{0.53}Ti_{0.47}O_3$, 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.

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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. $Pb(Zr,Ti)O_3$ (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, micromechanical 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

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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 approximation 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, $PbZr_{0.53}Ti_{0.47}O_3$. As a result the obtained values were found to be equal to $a = 4.142$ Å and $c = 4.295$ Å. These values are considerably larger as the corresponding numbers for the $PbTiO_3$ crystal, $a = 3.904$ Å and $c = 4.150$ Å [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 (0 0 1) atomic plane move outwards the impurity by approximately 0.21 Å. The O atoms of the upper plane displace themselves outwards from the impurity by approximately 0.23 Å whereas the O atoms of the lower atomic plane also tend to move away from the defect by about 0.31 Å. Finally, the four defect-closest O atoms belonging to the same (0 0 1) plane as the La atom move outwards the impurity by about 0.28 Å and additionally rotate around the ⟨0 0 1⟩ axis by approximately 1° as it is