

Structural and Electronic Properties of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.5, 0.375$): A Quantum-Chemical Study

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ABSTRACT: The structural and electronic properties of the PZT materials $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ and $\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$ were studied by means of a Hartree-Fock quantum-chemical method which employs a periodic large unit cell (LUC) model. The atomic relaxation observed upon introduction of the Zr impurities resulted in outward oxygen atom displacements along the $\langle 100 \rangle$ directions for the cubic phases, and varied oxygen and lead atom movements for the tetragonal structures. For these materials, the conduction bands (CB) were composed mainly of Pb-6p atomic orbitals with less important contributions of Zr-4d and Ti-3d states. The upper valence band (UVB) for the cubic phases was mostly Pb-6s in nature, with minor contribution of O-2p atomic orbitals. The tetragonal phase on the other hand was formed by Pb-6s with some contribution of admixed O-2p with Zr-4s and Ti-3s atomic orbitals. The optical band gap (ΔSCF method) was found to decrease going from the cubic to the tetragonal phase in both titanates.

Key words: PbTiO_3 ; PbZrTiO_3 ; LUC; impurity-doping; structural and electronic properties

Introduction

Since the initial study of ferroelectricity in barium titanate in the late 1940s [1], titanate derivatives have been a subject of multiple investigation in the past decades; nevertheless, there is still not a thorough understanding of their properties at the fundamental level. The electronic structure of lead titanate has been studied extensively using different theoretical methods [2-4], which indicate that the covalent interaction between Ti and O ions is important for occurrence of ferroelectricity within the crystal [5, 6]. Lead titanate doped with Zr impurity, $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, also called a PZT ceramic, is a ferroelectric oxide whose piezoelectric, dielectric and ferroelectric properties make it suitable for applications such as, high density storage medium, integrated component for random access memories, acoustic wave devices, ferroelectric, micromechanical and ultrasonic listening devices [7-10]. A number of experimental measurements have been carried out on PZT materials [11-14], but the number of theoretical studies is rather scarce [15].

In this work, we present our quantum-chemical investigations regarding lattice distortions due to Zr impurities in the PbTiO_3 cubic and tetragonal systems. A preliminary study on this material, including a new parametrization scheme for the PbTiO_3 has recently been published by our group, [16].

Method Employed

We use a periodic large unit cell (LUC) model [17] as it is implemented into the SYM-SYM computer code [18]. The calculations are carried out using a (nonrelativistic) valence basis set of lead 6s, 6p, and 5d atomic orbitals (AOs), titanium 3d, 4s, and 4p AOs, oxygen 2s and 2p AOs, and zirconium 5s, 4d and 5p AOs. The main computational equations as well as the fundamental concepts for energy calculations within the framework of the LUC model are described elsewhere [16-19].

Our method has proven to be very reliable in reproducing spatial and electronic properties, as well as studying point defects and phase transitions in a wide variety of materials such as pure crystals and complex oxides and perovskites [20-27].

The structural properties of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.25, 0.125$) have been described in detail in a previous work [16]. In the latter, it is discussed how a 40-atom LUC was used to calculate the effects of one and two Zr impurities in the cubic and tetragonal structures of lead titanate. It was found that the replacement of one and two Zr atoms for Ti atoms cause substantial displacements ($0.14 - 0.19 \text{ \AA}$) of atoms surrounding the impurities in order to reduce the total energy of the system. In the present work, we carry out the additional analysis of three and four Zr impurities within the LUC and compare these results with the ones obtained previously [16]. Additionally, we compare the electronic properties of the doped materials with those from pure PbTiO_3 .

Structural Properties of $\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$

The substitution of three Ti for Zr atoms within our 40 atom LUC was analyzed. Symmetric and non-symmetric atomic relaxations were considered for all the possible arrangements of the impurities. The configuration containing Zr atoms along the

diagonals $\langle 110 \rangle$ and $\langle 011 \rangle$ was found to be the most stable among all the possible distribution of atoms in both the cubic and tetragonal systems.

For the cubic arrangement, the calculations on geometry optimization (e.g.: energy minimization through lattice relaxation) revealed that the O atoms moved away from the Zr impurities in the entire three axis; hence, outward oxygen displacements by 0.19 \AA were observed along the $\langle 100 \rangle$ direction (Figure 1).

The observed outward movement of oxygens in this phase was expected due to Coulomb considerations [16] for the Zr atoms are substantially more negative than the Ti atoms in the pure crystal (Table 1). It is noteworthy to point out that the cluster of Ti and O atoms farthest from the impurities $\langle 101 \rangle$ carry charges much different than the other atoms in the same structure and in pure PbTiO_3 , and this is directly related to the influence of the Zr atoms on the surrounding environment.

In the case of the tetragonal structure (Figure 2), the atomic relaxation pattern for the O atoms surrounding the impurities is quite similar to the above-mentioned structure; that is, the displacement of oxygens amount to 0.19 \AA in the direction $\langle 100 \rangle$ within the xy-plane, but a smaller displacement of 0.16 \AA along the z-axis was observed. This pattern is similar to that established for this same geometry when two Zr replaced Ti atoms within the LUC: $\text{PbZr}_{0.25}\text{Ti}_{0.75}\text{O}_3$ [16]. In the latter, the movements along the z-axis turned out to be shorter than the ones within the xy-plane by 0.03 \AA . The displacement for the structure containing three impurities ($\text{PbZr}_{0.375}\text{Ti}_{0.675}\text{O}_3$) is also shorter in the z-direction by 0.03 \AA . We believe the nature of this property may be due the ferroelectricity phenomenon and possibly to size differences because one of the Zr

impurities lie diagonally and above the other two within the structure and this may prevent the axial oxygens from being displaced the same length as the others based on steric grounds.

Another important feature of the tetragonal arrangement was the characteristic displacement of the Pb atoms closer to the impurities since the lowest total energy configuration indicated that each set of Pb atoms on the xy-plane moved in a similar pattern: the Pb atoms below the plane containing two Zr impurities moved along the $\langle 101 \rangle$ direction (xz-plane) by 0.06 Å. These atoms showed no displacements along the y-axis at all. The Pb atoms on the next plane (above the two Zr impurities) exhibited movements of similar magnitude (0.07 Å) in the $\langle 111 \rangle$ directions that placed each pair of Pb atoms closer to each other but away from the impurities (Figure 2). The outward movements of the Pb atoms can be explained in terms of the size difference between the Ti and Zr atoms. The bigger Zr atoms (compared to Ti) exert a larger repulsion between overlapping electron clouds from Zr and Pb atoms in the surrounding environment.

The distribution of charges proved to be quite heterogeneous; the Pb atoms above the xy-plane occupied by the two Zr impurities possessed equal charges (1.72e), but the Pb counterparts below the impurities exhibited a decrease in charge of 0.14 e (1.58 e). This is an unusual distribution of charges because the Pb atoms in the pure PbTiO_3 crystal have shown a charge of 1.66 e [16], which essentially corresponds to the average values of the two Pb sets in the $\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$ structure.

In a similar manner, the charges of the Ti atoms varied according to their positions in relation to the Zr impurities. Only the Ti atoms along the $\langle 111 \rangle$ directions

had similar charges (2.47 e), and the Ti farthest away from the Zr atoms exhibited the least positive charge (2.33 e) (Table 2).

As would be expected because of the tetragonal configuration (elongated z-axis), the O atoms located on the xy-plane surrounding the Zr impurities displayed the equal charges: -1.32 e for oxygens along $\langle 110 \rangle$ and -1.27 e for oxygens along $\langle 011 \rangle$. The distribution of charges for the O atoms located along the z-axis was similar to those for the Pb atoms around the zirconiums: the magnitude of the charges increases along the +z direction (O = -1.37 e & -1.4 e) and decreases on the -z direction (O = -1.18 e, average). This is consistent with the expected charge distribution: The more positive Pb atoms are located next to the more negative oxygen atoms (+z direction) and the opposite is observed for the less positive Pb atoms (-z direction).

Structural Properties of $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$

The $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ formula reflects a substitution of half the Ti atoms for Zr atoms within our 40 atom LUC. Among all the possible arrangements of atoms, the lowest energy configurations for both the cubic and tetragonal phases were obtained for the structures containing the Zr impurities along the diagonals; that is, two Zr atoms in the $\langle 110 \rangle$ direction and the remaining two Zr in the $\langle 011 \rangle$ direction. As it was common for the cubic phase when 1, 2 or 3 Zr impurities were present ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$; $x = 0.125, 0.25, 0.375$), the cubic structure of $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ shows the same pattern of atomic displacements for the oxygens surrounding the impurities (Figure 3): they move away from the Zr atoms along the $\langle 100 \rangle$ directions by 0.19 Å. As in other cases, this

type of outward movement supports the idea of a symmetric atomic rearrangement due to Zr doping; no other atoms move in this phase [16]. The aforementioned symmetric displacement of atoms is reflected in the charge distribution within the LUC structure: all O atoms exhibited the same charges, as did all Pb, Ti, and Zr atoms (Table 3).

In the tetragonal phase, the atomic relaxation is as follows (Figure 4): the oxygens closer to the Zr atoms move outward along the $\langle 100 \rangle$ directions by 0.19 Å in the xy-plane and by 0.16 Å along the z-axis. This uneven displacement of O atoms may be due to the ferroelectricity effect although atom size effects may also play an important role in determining this atom rearrangement. The asymmetric displacement of atoms along the z-direction in the tetragonal phases has also been found in our previous works regarding impurity doping studies on SrTiO₃ [21] and BaTiO₃ [22, 28]. The eight Pb atoms nearest to the Zr impurities also move symmetrically outward along the $\langle 111 \rangle$ directions by 0.07 Å. In contrast to the homogeneous atom relaxation pattern observed, the atomic charges are distributed in a characteristic pattern. The lowest four Pb atoms (in the LUC) positioned on the xy-plane possess a charge of 1.59 e, whereas the next group of Pb atoms exhibited a charge equal to 1.73 e. This configuration is also observed for the other metals, for there appears to be two types of Ti and Zr atoms based on their charges, which in turn seems to depend on their position. The uppermost Ti and Zr atoms in the LUC on the xy-plane have equal charges: Ti = 2.52 e, Zr = 1.89 e. Underneath these atoms and below the Pb group, both Ti atoms present a charge of 2.57 e, but the Zr impurities exhibit charges of 1.97 e and 1.93 e. On the same xy-plane, the oxygens surrounding the impurities along the $\langle 110 \rangle$ direction have the same charge of -1.33 e, but this is not quite the case for the oxygens surrounding the $\langle 110 \rangle$ Ti atoms, for their charges are slightly different (-1.26 e, -1.28 e). As expected in this phase, the most

dramatic difference in charges is observed along the z-axis where the axial oxygens (with respect to the impurities) present charges of -1.20 e and -1.40 e. This characteristic array of charges suggests an increased covalent interaction between Zr and O atoms compared to that of Ti and O atoms. The difference in charges among sets of atoms in each xy-plane can be explained in term of the ferroelectricity phenomenon that characterizes the tetragonal phase.

Electronic Properties of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.5, 0.375$)

The plethora of theoretical studies on PbTiO_3 indicate that the lower valence band of the cubic PbTiO_3 is composed mainly by O 2s AOs, while the upper valence band (UVB) is predominantly Pb 6s in nature with smaller contributions of O 2p orbitals. The bottom of the conduction band (CB) is Pb 6p with important contributions of Ti 3d states.

Electronic Properties of $\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$

For the cubic phase of $\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$ the calculated optical band gap using the ΔSCF method was 4.62 eV, while the value obtained using the difference between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) was 6.31 eV. The CB is composed mainly by Pb-6p orbitals with minor contributions (< 20 %) of Zr-3d and Zr-4s and also oxygen-3p atomic orbitals.

The UVB is formed by Pb-6s AOs plus some admixture with O-2p orbitals. A number of narrow subbands, whose widths range from 0.8 to 1.2 eV, appear below the HOMO: The first subband is noticeable at -5.4 eV and is comprised of Zr and Ti 3d and Ti 3p AOs. Further down in energy, at -6.8 eV from the HOMO important contributions (~ 40 %) from Ti-4s and Zr-5s states are observed. The bottom of this valence band (UVB) is formed by a small subband of Pb-5s AOs (80 %) and Pb-5s and Pb-5p orbitals.

The tetragonal phase of $\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$ exhibited a calculated optical band gap of 3.25 eV (ΔSCF method), while the value found using the difference between the HOMO and LUMO was 5.09 eV. The reduction of the band gap going from the cubic to the tetragonal structure suggests an augmented covalent bonding in the latter phase. A similar behavior was observed in our previous work [16].

The CB is very similar to that found for the cubic phase; hence, it is composed mainly by Pb-6p orbitals with minor contributions (< 20 %) of Zr-4s, Zr-3d and O-3p states. The UVB is also similar to that for the cubic structure: it is composed mostly of Pb-6s, but there are additional contributions from O-2p and Ti-3d and Zr-4d AOs. This points out towards 2p-3d hybridization of oxygen and titanium orbitals since this admixture behavior is known to occur during the cubic-tetragonal phase transition for titanates. Likewise, the presence of d-orbital admixture in the tetragonal phase is consistent with the appearance of more negatively charged Ti atoms as shown in Table 4 [21]. Unlike the cubic phase, only one subband is observed at 6.2 eV below the HOMO in the UVB. The latter is formed by Zr-5s, Ti-3d (26 %) and Ti-4s (40%) AOs and its width is 0.8 eV.

Electronic Properties of $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$

For the cubic phase of $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ the calculated optical band gap using the ΔSCF method was 3.54 eV, while the value obtained using the HOMO and LUMO difference was 6.42 eV. For this structure, the conduction band is made up of Pb-6p and Zr-4d AOs. Less important, but present above the LUMO in the CB are Ti-3d orbitals mixed with O-2p, Pb-6s and Zr-4s states. The UVB is formed exclusively by Pb-6s AOs. Minor contributions ($< 28\%$) of O-2p and Zr-3d orbitals are distant from the HOMO (-3 eV), while s-orbitals from Zr, Ti and Pb begin to appear at -8.2 eV.

The values calculated for the optical band gap for the tetragonal structure were 3.40 eV (ΔSCF method) and 4.87 eV (HOMO-LUMO difference). The CB was found to be formed by O-3s plus Zr-4d and Pb-6p AOs; O-2p, Ti-3d, Ti-4s and Zr-5s states were also found. The UVB was found to be quite similar to that of the pure PbTiO_3 : Pb-6s are dominant but are accompanied with an important admixture of O-2p and Ti-3d states.

Conclusions

The structural and electronic properties of $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ and $\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$ were studied using a quantum chemical method that employs a large unit cell (LUC) model implemented into the SYM-SYM computer code. The calculations were carried out using non-relativistic valence basis sets of atomic orbitals incorporated into Hartree-Fock equations. For both PZT materials, the conduction bands were found to be composed mainly of Pb-6p atomic orbitals with less important contributions of Zr-4d

and Ti-3d states. In no case the CB showed significant differences between the cubic and tetragonal phases. The upper valence band for the cubic phase of both materials was mostly Pb-6s in nature, with minor contribution of O-2p atomic orbitals. The tetragonal phase on the other hand was formed by Pb-6s with some contribution of admixed O-2p with Zr-4s and Ti-3s atomic orbitals. The optical band gap (Δ SCF method) was found to decrease going from the cubic to the tetragonal phase in both titanates. It was also observed the reduction of the band-gap augmenting the Zr impurity concentration. This implies the increase of the covalent contribution into the chemical bonding augmenting the Zr concentration.

The atomic relaxation observed upon introduction of the Zr impurities resulted in outward O atoms displacements (with respect to the Zr atoms) along the $\langle 100 \rangle$ directions for the cubic phases, whereas varied oxygen and lead atom movements were observed for the tetragonal phases. The distribution of charges and atomic relaxation patterns suggest an increase of the covalent nature in the chemical bonding in these materials.

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TABLE I**Atomic charges (e) for the cubic phase in PbTiO_3 and $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.375$)**

Atom	PbTiO_3	Atom	$\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$
Pb	1.68	Pb	1.71
Ti	2.49	Ti	2.45, 2.61, 2.67
O	-1.39	O	-1.36, -1.36, -1.42
		Zr	2.05

TABLE II**Atomic charges (e) for the tetragonal phase in PbTiO_3 and $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.375$)**

Atom	PbTiO_3	Atom	$\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$
Pb	1.66	Pb	1.72, 1.58
Ti	2.38	Ti	2.52, 2.57, 2.48, 2.33
O	-1.33, - 1.38	O	-1.33, -1.2, -1.27
		Zr	1.93, 1.96

TABLE III**Atomic charges (e) for the cubic and tetragonal phases in $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.5$)**

Atom	Cubic	Tetragonal
Pb	1.71	1.59, 1.73
Ti	2.67	2.57, 2.52
O	-1.35	-1.20, -1.26, -1.28, -1.33, -1.40
Zr	2.03	1.93, 1.89, 1.97

Figure Captions

Figure 1. Atomic movements in the $\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$ cubic structure.

Figure 2. Atomic movements in the $\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$ tetragonal structure.

Figure 3. Atomic movements in the $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ cubic structure.

Figure 4. Atomic movements in the $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ tetragonal structure.







