Atomic and electronic structure of perfect and defective PbZrO₃ perovskite: Hybrid DFT calculations of cubic and orthorhombic phases

S. Piskunov a,b,*, A. Gopeyenko a, E.A. Kotomin a,c, Yu.F. Zhukovskii a,b, D.E. Ellis b

a Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str., Riga LV-1063, Latvia
b Department of Physics and Astronomy, Materials Research Center, Northwestern University, Evanston, IL 60208-3108, USA
c European Commission Joint Research Center, Institute for Transuranium Elements, D-76125 Karlsruhe, Germany

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Abstract

The structural and electronic properties of pure cubic and low-temperature orthorhombic PbZrO₃ (antiferroelectric phase), as well as cubic PbZrO₃ containing single F-centers (neutral oxygen vacancies) have been simulated by means of ab initio hybrid density functional calculations. We observed a substantial increase of the Pb–O bond covalency in ideal orthorhombic PbZrO₃ with respect to its cubic phase. Relatively large displacement of four Pb atoms nearest to the F-center (0.25 Å towards the defect) could affect the PbZrO₃ ferroelectric properties. An O vacancy in the bulk PbZrO₃ attracts 0.7 e, and the remaining electron density from the missing O²⁻ is localized mostly on four nearest Pb atoms. This leads to appearance of an energy level in the middle of the band gap of cubic PbZrO₃, unlike the shallow F-level found in SrTiO₃.

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1. Introduction

Lead zirconate PbZrO₃ (PZ) due to its antiferroelectric behavior, is technologically important for applications involving actuators and high energy storage devices [1–6]. PZ is also a parent compound of PbZr₁₋ₓTiₓO₃ (PZT) solid solutions, which are of high scientific and technological interest for their ferroelectricity and piezoelectricity observed over a wide range of compositions. A field-induced ferroelectric phase transition is found feasible in PZ thin films due to a small free energy difference between the ferroelectric and the antiferroelectric phases [7,8].

Recently, antiferroelectric PZ thin film heterostructures have been found to be radiation resistant and suggested as a promising candidate for application in radiation environments [9], including diagnostic materials and bolometers for thermonuclear reactors.

The unusual dielectric behavior of PZ has been discovered more than 50 years ago (see an excellent review in Refs. [10,11]), however, the material remains under extensive study. Recent experimental reports on the PZ crystal-line structure can be found in Refs. [12,13, and references therein]. In these studies, the symmetry of antiferroelectric PZ was determined to be Pbam (orthorhombic), in agreement with previous observations. This relatively low temperature (T_c ≈ 505 K) structure is characterized by antiparallel displacement of Pb atoms in the a–b-plane with subsequent rotation of ZrO₆ octahedra; the positions of Zr atoms remain largely unchanged. Above T_C PZ becomes...
cubic paraelectric. Crystalline structures calculated in our study (details given below) are schematically shown in Fig. 1.

The electronic properties of ideal PZ cubic and orthorhombic phases have been calculated by Singh using the local density approximation (LDA) within the density functional theory (DFT) and linearized augmented plane-wave (LAPW) method [14]. The author reported a substantial hybridization between O 2p and Zr 4d as well as O 2p and outermost Pb 6s and 6p states in the cubic phase. Using the experimentally determined cation coordinates and the calculated oxygen coordinates of orthorhombic PZ, Singh found a very small energy difference (0.02 eV) between the antiferroelectric (Pbam – orthorhombic centrosymmetric space group) and ferroelectric (Pba2 – orthorhombic noncentrosymmetric space group allowing ferroelectric polarization) structures. The cation positions were held rigid. Recently, Johannes and Singh [15] reexamined the structure of an antiferroelectric PZ using the same LDA-LAPW approach, but allowing all atomic coordinates to relax. In that study authors report a very good agreement of calculated coordinates with those experimentally observed in Ref. [12]. Since LDA is known to underestimate lattice constants of solids, Johannes and Singh used the experimental lattice constants while varying

atomic intracellular coordinates. The energy difference between paraelectric cubic and antiferroelectric orthorhombic (ground state) phases was calculated to be 0.27 eV. Accurate full-potential LDA-LAPW calculations were also performed by Leung and Wright [16], in order to show the influence of pressure on the phase transformation in PZ. In agreement with Ref. [14] they found that ferroelectric and antiferroelectric phases of PZ are very close in energy. A comparative ab initio study on the atomic and electronic structure of PZ (orthorhombic phase), PbTiO$_3$ (tetragonal phase), and PbZr$_{0.5}$Ti$_{0.5}$O$_3$ (monoclinic phase) was also performed by Rodriguez et al. [17].

In various ABO$_3$ perovskite structures, oxygen vacancies can be formed and their concentration can be then regulated by specific regimes of irradiation or thermal treatment, analogously to deliberate deviation of oxygen content from the ideal stoichiometry in the cubic SrTiO$_3$ phase [18]. For example, oxygen vacancies could be created in PZ under neutron and ionizing irradiation [9]. However, no theoretical simulation on PZ containing defects is known so far. In this paper, we report on the atomic and electronic structure of cubic PZ containing F-centers (oxygen vacancies containing up to two electrons); further, we compare the electronic properties of three relevant structures: pure PZ in its high temperature paraelectric cubic phase $Pm\bar{3}m$, low-temperature orthorhombic Pham structure of antiferroelectric PZ, and lastly, a cubic PZ containing an isolated F-center. For this purpose, we have performed large-scale DFT calculations using the B3PW hybrid exchange-correlation functional [19]. This method was successfully applied earlier to simulations of several regular and defective ABO$_3$ perovskites providing a more adequate description of band gaps and other parameters of the electronic structure [20–23].

2. Computational details

To perform hybrid B3PW DFT calculations, we have used the CRYSTAL computer code (see [24, and references therein], which employs Gaussian-type functions centered on atomic nuclei as the basis sets (BS) for an expansion of the crystalline orbitals. The BSs for lead and oxygen have been taken from Ref. [20]: O-8-411(1d)G, Pb-211(1d)G, while the BS for Zr: 311(31d)G are from [24]. The inner core electrons of Pb and Zr atoms were described by Hay-Wadt effective core pseudopotentials taking into account the relativistic effect [25,26]. The CRYSTAL calculations were performed using the exchange-correlation B3PW functional [19] involving a “hybrid” of non-local Fock exact exchange and exchange potentials constructed using both LDA and a non-local generalized gradient approximation (GGA), combined with the GGA correlation potential of Perdew and Wang. This functional has proved to yield remarkably accurate electronic and geometrical structures. While LDA is known to underestimate the band gap width and lattice constant for perovskites, the hybrid functionals yield more reliable results [20].
In order to simulate the isolated defect, the simple cubic unit cell was extended to a $3 \times 3 \times 3$ supercell (SC). The SC retains the cubic symmetry and contains 135 atoms with the distance between periodically repeated defects of 12.53 Å. When modeling the $F$-center, we employed a "ghost" BS [24]; i.e., although the O atom is removed, its BS is left behind. This technique facilitates the accurate description of the electron distribution within the vacancy. To retain cubic symmetry and to reduce computational time, this ghost basis set was centered on the vacancy site. The equilibrium geometry was obtained using an analytical optimization method as implemented in the CRYSTAL code [24]. The lattice constants were optimized using the ParOptimize code [27] interfaced with CRYSTAL. This routine implements conjugated gradient optimization with a numerical computation of derivatives [28]. The reciprocal space integration was performed by a sampling the Brillouin zone with the $8 \times 8 \times 8$ Pack–Monkhorst and Gilat meshes [29,30] for a cubic unit cell (Fig. 1a), $6 \times 6 \times 6$ for an orthorhombic unit cell (Fig. 1b), and $4 \times 4 \times 4$ for 135-atom cubic SC with a defect (Fig. 1c). Such a sampling provides the balanced summation in direct and reciprocal lattices.

3. Results and discussion

3.1. Defect-free lead zirconate

We present in Table 1 the atomic coordinates and lattice parameters of orthorhombic PZ (Fig. 1b) as calculated in our study and obtained in powder neutron diffraction experiments at low temperatures [12,13]. Our data are in a good agreement with these experimental observations. The energy gain due to the antiferroelectric–paraelectric phase transition was calculated to be 0.39 eV (cf. 0.27 eV obtained in LDA-LAPW calculations [15]). The calculated lattice constant of a cubic PZ (Fig. 1a), 4.177 Å, also agrees well with the experimental value of 4.1614 Å (at 520 K) [31]. Thus, the computational approach used in the present study can be established as appropriate.

We compare in Table 2 the Mulliken atomic charges and bond populations calculated for both PZ and PbTiO$_3$ (PT) [20] in their cubic phase (Fig. 1a). Both crystals were calculated by means of the B3PW hybrid density functional technique with the same computational parameters. The deviation of effective Mulliken charges from formal ionic charges, Pb$^{2+}$, Zr$^{4+}$, Ti$^{4+}$, and O$^{2-}$/C$_0$, is related to the partial covalency of chemical bonding in these crystals. The calculated Mulliken effective charge of Pb in PZ is slightly lower than in PT, while the Pb–O bond population in PZ is increased by more than a factor of two (despite the greater Pb–O bond length). Thus, we confirm the partly covalent nature of the Pb–O chemical bond predicted by Aoyagi et al. using maximum entropy method/Rietveld analysis of X-ray powder diffraction data [31]. These authors reported estimate of Pb$^{1.2+}$ ionic state in PZ vs. pure ionic Pb$^{2+}$ in PT. Aoyagi et al. also predicted covalency weakening for the Zr–O bond with respect to the Ti–O bond; however, our study shows similar Zr/Ti–O covalency in both PZ and PT.

Mulliken charges and bond populations for pure orthorhombic PZ (Fig. 1b) are given in Table 3. The populations of both the Pb–O and Zr–O bonds (nearest neighbor atoms Table 1

| Fractional coordinates of atoms and lattice parameters $a$, $b$, $c$ (Å) for orthorhombic structure (Pbam) of PZ calculated using the DFT-B3PW method are compared with those obtained by powder neutron diffraction of PZ at 10 K [12], and 20 K [13] |
|--------------------------------------------------|--|------------------|--|------------------|--|
| This study (0 K) | Experiment (10 K) | Experiment (20 K) |
| $x$ | $y$ | $z$ | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ |
| Pb1 | 0.6909 | 0.1234 | 0.0 | 0.6991 | 0.1228 | 0.0 | 0.697 | 0.123 | 0.0 |
| Pb2 | 0.7063 | 0.1274 | 0.5 | 0.7056 | 0.1294 | 0.5 | 0.707 | 0.125 | 0.5 |
| Zr | 0.2406 | 0.1246 | 0.25 | 0.2414 | 0.1248 | 0.2486 | 0.240 | 0.125 | 0.25 |
| O1 | 0.2797 | 0.1579 | 0.0 | 0.2756 | 0.1560 | 0.0 | 0.276 | 0.151 | 0.0 |
| O1’ | 0.3103 | 0.0934 | 0.5 | 0.3011 | 0.0956 | 0.5 | 0.298 | 0.088 | 0.5 |
| O2 | 0.0393 | 0.2646 | 0.2816 | 0.0317 | 0.2622 | 0.2798 | 0.032 | 0.262 | 0.277 |
| O3 | 0.0 | 0.5 | 0.1972 | 0.0 | 0.5 | 0.2026 | 0.0 | 0.5 | 0.200 |
| O4 | 0.0 | 0.0 | 0.2343 | 0.0 | 0.0 | 0.2293 | 0.0 | 0.0 | 0.228 |

Notation of atom sites is the same as in Ref. [12].
are considered) have increased with respect to cubic PZ, while the atomic charges remain largely unchanged. Note that these Pb–O bond lengths are shorter than those of the cubic crystal. The predicted increase of O–O repulsion is expected due to deformation of the oxygen octahedra and consequent shortening of the O–O distances. Thus, we observe a covalency increase in orthorhombic PZ as compared to the cubic phase. Additional evidence for the covalency increase emerges from the calculated electronic charge difference-density redistributions (Fig. 2, see caption for more details). Formally, solid (red) interatomic isolines in Fig. 2 correspond to the formation of covalent bonding. The increase of difference-density in the proximity of Pb atoms is clearly seen in orthorhombic PZ as compared to the cubic crystal.

Table 3
Calculated effective Mulliken atomic charges, $Q$ (in e), and the bond populations, $P$ (in milli e), for pure PZ in its antiferroelectric (Pbam) phase

<table>
<thead>
<tr>
<th></th>
<th>$Q$</th>
<th>$P$</th>
<th>$d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb1</td>
<td>1.30</td>
<td>Pb1–O1</td>
<td>76</td>
</tr>
<tr>
<td>Pb2</td>
<td>1.29</td>
<td>Pb2–O1</td>
<td>76</td>
</tr>
<tr>
<td>Zr</td>
<td>2.18</td>
<td>Zr–O2</td>
<td>162</td>
</tr>
<tr>
<td>O1</td>
<td>−1.16</td>
<td>Zr–O4</td>
<td>198</td>
</tr>
<tr>
<td>O1'</td>
<td>−1.18</td>
<td>O1–O3</td>
<td>−96</td>
</tr>
<tr>
<td>O2</td>
<td>−1.15</td>
<td>O1'–O2</td>
<td>−84</td>
</tr>
<tr>
<td>O3</td>
<td>−1.21</td>
<td>O4–O3</td>
<td>−20</td>
</tr>
<tr>
<td>O4</td>
<td>−1.09</td>
<td></td>
<td></td>
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</tbody>
</table>

Bond lengths $d$ are given in Å.

The total and projected density of states (DOS) for both cubic and orthorhombic PZ are shown in Fig. 3. Our calculated DOS are in a good qualitative agreement with
those reported in a earlier first-principles LDA-LAPW study [14]. The DOS of cubic PZ (Fig. 3a) shows a valence band (VB) region which consists mainly of O 2p atomic orbitals with small contributions of Zr 4d, and Pb 6s and 6p states. The observed Zr 4d peak at the bottom of the VB indicates a stronger hybridization between O 2p and Zr 4d as compared to O 2p and Pb 6s and 6p. However, weak covalency of Pb–O bonds is confirmed by presence of a small admixture of Pb states in the VB. The bottom of the conduction band (CB) is formed by Zr 4d, Pb 6p, and O 2p states. The calculated band gap (direct gap at the X point) of cubic PZ of 3.79 eV is in essentially perfect agreement with the experimentally measured PZ band gap of 3.7 eV (see Ref. [32, and references therein]).

Band gap calculated in this study is substantially larger than the earlier LDA value (2.34 eV [14]). As noted previously, hybrid functionals generally yield more reliable band gaps than LDA.

The DOS calculated for the orthorhombic PZ (Fig. 3b) exhibits a wider VB as compared to the cubic crystal. The main difference between this DOS and that of cubic PZ is the additional small peak around −1 eV, which consists mainly of O 2p and Pb 6s orbitals. These contributions reflect the increase of the Pb–O bond hybridization, that, in particular, explains the above-mentioned covalency increase in orthorhomic PZ. The band gap in orthorhombic PZ increases as compared to the cubic phase, being shifted to the Γ point (direct gap); its calculated value is 4.26 eV.

Cohen [33] showed that different ferroelectric behavior of structurally similar BaTiO₃ and PbTiO₃ perovskites can be due to the hybridization of Pb and O states, unlike Ba–O. Therefore, our findings on the increase of Pb–O covalency due to additional hybridization of O 2p, and Pb 6s and 6p orbitals in orthorhombic PZ could provide a deeper insight for understanding of extraordinary antiferroelectric properties of lead zirconate.

3.2. Defective cubic PZ

In order to obtain an equilibrium geometry of PZ with an oxygen vacancy (see structure in Fig. 1c), all atoms belonging to first eight coordination spheres around the F-center were relaxed along directions allowed by cubic symmetry. The displacements of other atomic sites were expected to be negligible. The calculated displacements and Mulliken charges of these atoms are summarized in Table 4. The two Zr atoms nearest to the defect shift slightly outwards from the F-center, while the next four Pb atoms reveal substantial displacement (0.25 Å) towards the F-center. Deformation of oxygen octahedra (Fig. 1a) follows the displacement of Pb and Zr atoms. Note that the magnitude of displacement of Pb atoms induced by the point defect is close to that observed for Pb atoms in the transition from cubic to orthorhombic PZ (∼0.2 Å) [10] and thus, could affect its ferroelectric–antiferroelectric behavior.

The formation energy of an oxygen vacancy in perfect cubic PZ was calculated using the expression [23]:

\[
E_{\text{form}}(F) = E_{\text{tot}(F/PZ)} + E_{\text{ground state}(O)} - E_{\text{tot}(PZ)},
\]

where \(E_{\text{ground state}(O)}\) is the energy of an isolated oxygen atom in its ground state (spin-polarized), \(E_{\text{tot}(F/PZ)}\) and \(E_{\text{tot}(PZ)}\) are the energies of the defective and perfect crystal supercells, respectively. Eq. (1) yields an F-center formation energy of 7.25 eV, which is comparable to the calculated formation energy of an F-center in perfect SrTiO₃ (8.74 eV) [23].

The most remarkable aspect of the electronic density distribution shown in Table 4 concerns the F-center, which retains −0.68 e from missing oxygen anion, according to the Mulliken population analysis. The remaining Mulliken charges are largely unchanged as compared to perfect cubic PZ, except for the four Pb atoms nearest to defect. Their charges decrease from +1.3 e to +1.17 e, indicating that these neighbors captured −0.5 e from the missing oxygen. This view is confirmed by the vacancy-induced electron charge difference density plot shown in Fig. 4 which indicates a presence of trapped electron density in the vacancy site (−0.68 e). Simultaneously, one can observe a notable re-polarization of the nearest Zr and O atoms which is rather caused by strong deformation of zirconiums nearest to the F-center.

The calculated band structure and DOS for defective cubic PZ are shown in Fig. 5. The total and projected DOS are very similar to those obtained for the perfect crystal. However, the band gap is slightly increased (3.97 vs. 3.79 eV) and the defect level appears at 1.72 eV below the CB bottom, essentially in the mid-gap region. In fact, this defect level is quite flat showing small dispersion (0.14 eV) over the Brillouin zone. Thus, the interaction between the periodically repeated F-centers in the model of 135-atom SC can be rather neglected for the qualitative description of isolated defect in PZ. (The calculations of F-center in cubic SrTiO₃ where the same supercell is used...
Fig. 4. The calculated (110) cross-section of the difference electron density maps $\Delta \rho(r)$ for cubic PZ containing a single $F$-center. $\Delta \rho(r)$ is defined as the total density in the perfect PZ bulk minus the sum of electron densities of both lattice of oxygen atoms positioned in vacancy sites and defective PZ. Dashed dot (black) isolines correspond to the zero level. Dashed (blue) isolines stand for a decrease in $\Delta \rho(r)$ and solid (red) lines for an increase. Figures in brackets mean the numbers of $F$-center coordination spheres (see text). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Total and projected DOS (a), and band structure (b) for cubic PZ containing the $F$-center.

yield a shallow defect level 0.72 eV below the CB with 0.23 eV dispersion [23].) The $F$-center defect level in cubic PZ consists of Pb 6s and 6p orbitals, and a small contribution of Zr 4d states, thus confirming the charge redistribution obtained from Mulliken population analysis.

4. Summary

Using the B3PW hybrid exchange-correlation functional within DFT formalism as implemented in the CRYSTAL code using localized Gaussian basis sets, we calculated the atomic and electronic structure of defect-free lead zirconate in its high-temperature cubic and low-temperature orthorhombic structures, as well as a cubic lead zirconate superstructure containing a single $F$-center. Calculated atomic coordinates and lattice parameters for perfect lead zirconate in both phases are in good agreement with the most recent experimental observations [12,13]. The electronic charge redistribution calculated for cubic bulk lead zirconate confirms notable covalency of the Pb–O bond as proposed from analysis of X-ray powder diffraction data [31]. This covalency is considerably increased in the orthorhombic phase. Formation of an $F$-center defect in cubic lead zirconate is accompanied by substantial shift (0.25 Å) of the nearest lead atoms towards the vacancy. The $F$-center traps 0.68 e and forms a defect level in the middle of the band gap; the remaining 0.5 e from the missing anion are mainly localized on four nearest Pb atoms. The presence of point defects will affect the atomic polarization in lead zirconate and thus, influence its ferroelectric properties.
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