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**Density Functional Theory Investigation of Electronic Structure and  
 Phonon Dispersions of New Perovskite ZrTi (PbO<sub>3</sub>)<sub>2</sub> Materials**

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**ABSTRACT**

Using Density functional theory (DFT) within the local-density approximation (LDA), the electronic structure as well as phonon dispersion relations of the new Perovskite ZrTi (PbO<sub>3</sub>)<sub>2</sub> Materials at T = 0 have been studied. The result shows that Perovskite ZrTi (PbO<sub>3</sub>)<sub>2</sub> has a stable cubic  $Pm\bar{3}m$  phase, from the electronic properties studies it has been found that the material is direct band gap with the gap of about 1.8 eV, the soft dispersions at the phonon branch spreading from the X to R points of the cubic Brillouin zone is also observed. This soft branch persists up to high pressures.

**Keywords:** Density functional theory (DFT), Quantum ESPRESSO, Local-density approximation (LDA), Electronic structure and Phonon dispersions

**1.0 INTRODUCTION**

Piezoelectric Perovskite compounds are found to be excellent materials for the manufacture of many materials such as ceramic resonators (Rosen, Hiremath, & Newnham, 1992), heaters (Bartley, & Cartwright, 2000), cooking stoves and cigarette lighters (Powers, Moffett, & Nussbaum, 2000), these materials are found to be producing a spark and share many similar features with ferroelectric materials. They have been also found as good materials in applications of quartz watches, medical instruments as well as in Sound Navigation Ranging (SONAR) devices (Butler, & Tito, 2000; Kara, Ramesh, Stevens, & Bowen, 2003). Given that predicting new Perovskite piezoelectric compounds has been an increasable research aims but within theorist and experimentalist, major important properties that more concern in the applications of these materials in Naval SONAR is the potential difference across its two faces during compression and changes in dimension when electric field is applied (Berlincourt, 1981; Bartley, & Cartwright, 2000). Many Piezoelectric Perovskite compounds such as PbTiO<sub>3</sub> and BaTiO<sub>3</sub> have proven to be a good

material with the above mentioned nature; they have stable simple cubic phases at high temperature with so called paraelectric phase which normally transforms to a ferroelectric tetragonal phase at temperature of around 763 K and 403 K, respectively (Meyer, Padilla, & Vanderbilt, 1999; Bartley, & Cartwright, 2000; Kholkin, Pertsev, & Goltsev, 2008). It has been also observed that tetragonal PbTiO<sub>3</sub> has a large strain that exhibit ferroelectric nature even at high temperatures (Waghmare, & Rabe, 1997), on the other hand other Piezoelectric Perovskite compound found to have smaller strain but exhibits successive phase transitions from cubic to tetragonal, orthorhombic and rhombohedral structures with decreasing temperature.

It has been reported from different research work, that the phonon dispersion relations have clarify the present of soft phonon mode across the ferroelectric to paraelectric of many Piezoelectric Perovskite compounds (Taib, et al, 2014; Železný, et al, 2015). The phonon dispersion relations data are however not available both from theory and experiment for some lower symmetry ferroelectric phases. Even in the high symmetry paraelectric

cubic phase, the investigations of dispersion relations rely only on the acoustic and low frequency optic phonon branches obtain. Up till now, the complete phonon dispersion relations are reported only for the cubic phases of  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$  using first principles calculations within the density functional theory (DFT) (Taib, et al, 2014; Železný, et al, 2015).

Recently we have reported the theoretical predictions of new piezoelectric Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$  compound and study both structural and piezoelectric properties within DFT and DFPT (Adeyemi, et al, 2019). But knowing how significant important is the phonon dispersions relations is for these family of compounds has made necessarily important to study the complete phonon dispersion relations of this newly modelled compound ( $\text{ZrTi}(\text{PbO}_3)_2$ ). This is because a careful understanding of the phonon dispersion relations in the piezoelectric ferroelectric phases is essential for a microscopic understanding of their electromechanical properties and for resolving the controversies about the origin of diffuse scattering (Huang, Yuan, Shao, & Yan, 2017) in perovskite ferroelectrics and have formed the focus of this work.

## 2.0 COMPUTATIONAL DETAILS

In order to investigate our new piezoelectric Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$  electronic properties, a plane wave periodic first-principle calculations based on Density Functional Theory (DFT) as implemented in Quantum ESPRESSO (QE) package (Giannozzi, et al, 2009) were carried out. In this work, we have used the exchange-correlation generated with a Scalar-Relativistic parameterized by A. Del castro such that Zr (4s, 4p, 4d), Pb (5d, 6s, 6p), Ti (3s, 3p, 3d, 4s), and (O 2s and 2p) orbitals were treated as valence orbitals, these type of pseudo has been assumed be an excellent choice on the description of both structural and electronic properties of these piezoelectric Perovskite materials.

The lattice parameters and atomic positions of our modelled compound were full-relaxed using BFGS minimization method as implemented in QE. The matrix density diagonalization for calculating the density of state (DOS) was carried

out using the grid of  $12 \times 12 \times 12$  K points in the Monkhorst-Pack reciprocal space (Evarestov, & Smirnov, 2004)

For the phonons dispersions calculations, we have obtained the dynamical matrix using Density-Functional Perturbation Theory (DFPT) (Baroni, De Gironcoli, Dal Corso, & Giannozzi, 2001) as implemented in Phonon code of the QE. In this method, one normally obtains the charge response to lattice distortions of definite wave-vector  $q$ . The key starting point is the calculated electronic structure of the undistorted supercell of the compound, obtained from a normal DFT total energy calculation. Therefore, the dynamical matrices of Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$  were evaluated for phonon wave vectors on a  $2 \times 2 \times 2$  q-point mesh. The dynamical matrices at arbitrary wave vectors were evaluated by Fourier interpolation on this mesh. By minimising the total energy as a function of the lattice parameters, the ground state of compound was obtained. Hence all our Phonon calculations were carried out on the  $2 \times 2$  supercell of Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$

## 3.0 RESULTS AND DISCUSSIONS

### 3.1 Electronic properties

#### 3.1.1 Density of state

One of the major requirements for any material to be a ferroelectric piezoelectric material for SONAR use is to be an energy band gap material. Therefore, in order to have a precise knowledge of the energy band gaps behaviour of our Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$  we calculated the density of state (DOS) as well as projected density of state (PDOS) given in Figure 1 and 2 respectively.

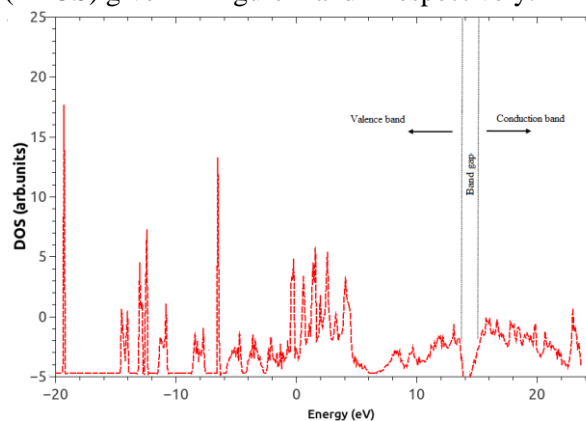


Figure 1: Calculated DFT-LDA total density of state (DOS) of cubic Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$

Our calculated total DOS which we used to describes the electron distribution in an energy spectrum of our modelled. The electronic state is divided into three different regions based on the highest peaks, the lower valence band (LVB), upper valence band, and conduction band (CB). The UVB density of the state peak is about  $-18$  eV and has a  $1.4$  eV width that is separated with a large gap of about  $9$  eV, while the LVB states which have a width of about  $5$  eV. That separated by a narrow gap of about  $0.9$  eV. For the CB we found that the material is direct band gap with the gap of about  $1.8$  eV. This large value of the band gap even as we used LDA as a functional make us to believe that Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$  is really a direct band gap material.

### 3.1.2 Projected Density of state

From figure 2 the first part of the valence band (VB) is due to the  $4s$  and  $4p$  states of Zr. The second part of the VB is completely dominated by the  $3p$  states of Ti, which is the valence band maxima, and occurred at  $-14.5$  eV. Similarly, the lowest CB is dominated by  $2s$  state of O with the little contribution from  $4p$  state of Pb. This shows that Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$  may probably have little presence of lead during the bonding formation.

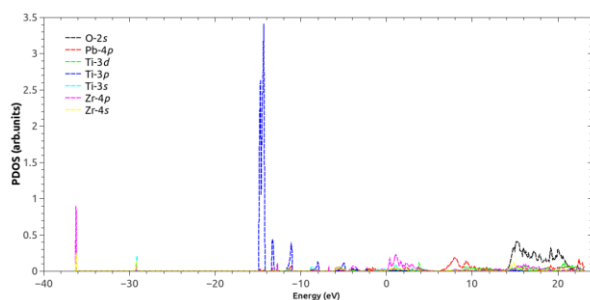


Figure 2 Calculated DFT-LDA projected density of state (PDOS) of cubic Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$

More significantly, our PDOS express a title significant hybridization of Ti  $3d$ , and Zr  $4p$  states throughout the maximum part of the valence band. This type of hybridization is between transition metals  $d$  state and another one of  $p$  state has normally found to be important in certain number of ferroelectric perovskite materials.

However, in order to have a clearer picture of our modelled material we plot a two dimensions' charge density show in Figure 3 below.

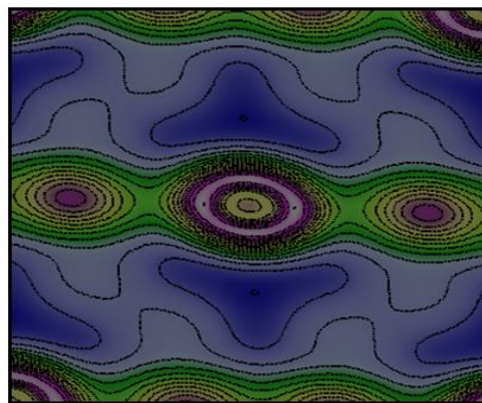
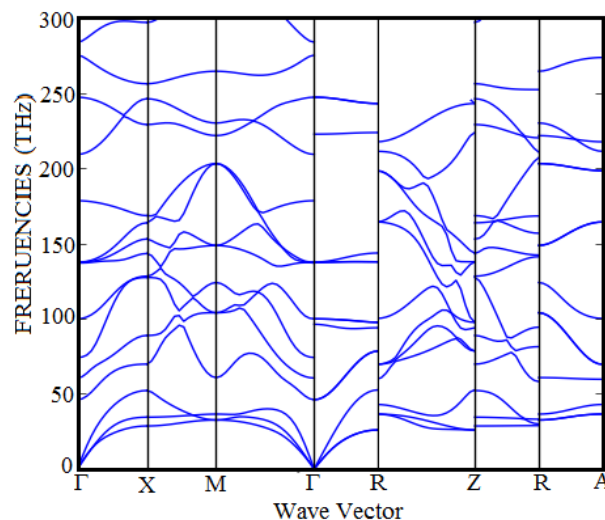


Figure 3 Two dimensions plot of charge density distribution of Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$  for the (110) planes

The charge density of  $\text{ZrTi}(\text{PbO}_3)_2$  is given in Figure 3. One can see that the Ti cations display the highest electron density in the supercell of  $\text{ZrTi}(\text{PbO}_3)_2$ . The charge density also shown that the major bonds between Ti and O are completely different from that of Pb and O, signifying the possibility of different ionic interactions in the  $\text{Pb}_2\text{O}_6$  and  $\text{TiO}_6$  octahedrons. In case of the charge density between Ti and O, we observed a separation which we may suggests that the ionic interaction is due to the electron transfer between Ti with O. Hence, expecting the B-site Ti cation and oxygen ions to be bonded by the strong ionic bond in the  $\text{TiO}_6$  octahedrons. Such strong ionic interaction gives the high energy of formation and produce the passage barrier of oxygen vacancies corresponding to the Ti cations in  $\text{ZrTi}(\text{PbO}_3)_2$ . But, in case of conjoint charge density between Pb and O one can see that the ionic interaction of Ti and O is somehow not really pure ionic bond in the  $\text{TiO}_6$  octahedron. This can be attributed to the delocalized  $4d$  orbital elections of Pb, which can be very significant in the perovskite lattice (Santos, et al, 2026).

### 3.2 Phonon Dispersion Relation

The obtained phonon dispersion curve in the cubic phase of Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$  is given in Figure 4. From the curve its clearly seen that Perovskite  $\text{ZrTi}(\text{PbO}_3)_2$  has almost thirteen (13) phonon modes (basely due to the  $3N$  freedom degrees); we assumed that 10 are optical while three of them are expected to be acoustical. Because of the high symmetry, one can see the presence of some phonon branches which are really reduced along  $\Gamma$ -R and R-Z-R high symmetry directions.



**Figure 4. Phonon dispersion curves of Perovskite ZrTi(PbO<sub>3</sub>)<sub>2</sub> in the cubic phase.**

Another important point we have observed is the phonon frequency regions which totally been positive, hence with this point we can clearly assumed Perovskite ZrTi(PbO<sub>3</sub>)<sub>2</sub> to be energetically stable. Similarly, the dispersion curves specify that the acoustic phonon frequencies can clearly be due to Zr and Pb atoms

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with much effect of Zr atoms. Because Zr atoms happen to be heavier than Pb and Ti atoms one can assume a lower vibration. Ti atoms vibrate mostly within nine optic modes in the mid frequency region as Zr atoms vibrate in the lower frequency region and N atoms vibrate in the high frequency region. Unfortunately, there is no experimental or theoretical data in the literature for comparison with Perovskite ZrTi(PbO<sub>3</sub>)<sub>2</sub> compound.

#### 4.0 CONCLUSIONS

In summary, electronic and phonon properties of Perovskite ZrTi(PbO<sub>3</sub>)<sub>2</sub> compound properties with the space group  $Pm\bar{3}m$  were investigated using the LDA approach within the density functional theory. The density of states and projected density of state indicated that Perovskite ZrTi(PbO<sub>3</sub>)<sub>2</sub> compound is band gap material with the direct gap of about 1.8 eV. The investigated phonon properties exhibits that ZrTi(PbO<sub>3</sub>)<sub>2</sub> compound is energetically stable. Our study carried out a systematic study to disclose all properties of Perovskite ZrTi(PbO<sub>3</sub>)<sub>2</sub> compound including phonon relations and presented new data for future investigations and applications.

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