

FIRST PRINCIPLES STUDY OF STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF La DOPED PEROVSKITE PZT USING DENSITY FUNCTIONAL THEORY

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ABSTRACT

Ferroelectric lanthanum doped PbZrTiO₃ (PLaZT) were investigated via first principles study. The structural, electronic and optical properties of PLaZT in tetragonal structure (P4mm space group) have been performed in the framework of density functional theory (DFT), using the method with generalized gradient approximation (GGA) and local density approximation (LDA). We observe that the structural properties of PLaZT are approximately close to the experimental data. The electronic part was covered with the energy band gap and density of states (DOS). For the optical part the refractive index, dielectric constant and absorption also was calculated. Our calculated results can be seen as a prediction for future investigations.

Keywords: Density Functional Theory; Electronic properties; First Principles; Optical properties; Structural;

INTRODUCTION

Ferroelectric materials (ABO₃ type perovskite) is one of the interesting material that has been investigated widely in recent year due to the technological interest arises. This

type of materials may be prepared with very high values of dielectric, piezoelectric, electrostrictive and electro-optical constants in wide temperature ranges, non-volatile and DRAM memories, capacitors, electro-optic modulators, optical switches and also in piezoelectric technologies [1]–[4]. The well-known perovskite ferroelectric materials are PbTiO_3 and PbZrTiO_3 (PZT) and Lanthanum doped PZT (PLZT).

In the ferroelectric systems of PLZT, the compositional changes within this quaternary especially along the morphotropic phase boundaries (MPB) and it can significantly modify the materials properties and performance under temperature variations or applied electric fields [5]. This allows such a system to be design to a variety of transducer applications. They exhibit a much larger electro-optical effect than LiNbO_3 [6] and [7], which is commonly used in commercial waveguide devices. The incorporation of lanthanum into the lattice enhanced the densification rates of the PZT ceramic, leading to pore-free homogeneous microstructures [8] and also the lanthanum radius is comparable with Pb that can substitute at A-site [3]. The contribution of La^{3+} ion in PZT enhance it domain wall mobility and the higher oxidation states of La^{3+} also contribute to the improving of spontaneous polarization, coupling factors, dielectric constant, dielectric loss tangent and increased of optical transparency in PZT materials. The results of La doping also contribute to the vacancy (V) in the A-sites of perovskite structure, thus the chemical formula of PLZT is given by formula:



PLZT one of the important parameters in electro-optical and piezoelectric material is the greater value of the band gap which is up to 3.00 eV and can be accomplished by introducing impurities in PZT ceramics. Then this investigation was continued by analyzing the effect of A-site substitution on PZT by introduced the element of La to become PbLaZT . This new compound PLZT has been analyzed and validated with available experimental data. Therefore, La impurities with its band gap and other optical properties were calculated to revealed the effect of La in PZT system.

EXPERIMENTAL

Computational Method

The supercell $1 \times 1 \times 2$ (tetragonal, $P4mm$, 99 space group) of PLZT (figure 1) were simulated using density functional theory (DFT) as implemented in Cambridge Serial Total Energy Package (CASTEP 6.1) [9]. The exchange correlation energy function for this compound was calculated within local density approximation (LDA) [10] and generalized gradient approximation (GGA) [11]–[13]. The Pb (6s, 6p), La (5d, 6s), Ti (3d, 4s), Zr (4d, 5s) and O (2s, 2p) electrons were treated as valence electron of the compound. The composition of atom for Pb and La was setup with 92% and 8% respectively. The geometric optimization was performed under the convergence of energy change per atom $< 1 \times 10^{-5}$, residual force $< 0.03 \text{ eV/\AA}$, stress $< 0.05 \text{ GPa}$ and displacement of atoms $< 0.0001 \text{ \AA}$. The calculation of electronic band gap, density of states and optical properties of tetragonal PLZT were performed via validated functional approximation of GGA-PBESol with plane wave cut-off energy 350 eV (after

convergence test) and the 6x6x6 k-point of Brillouin Zone.

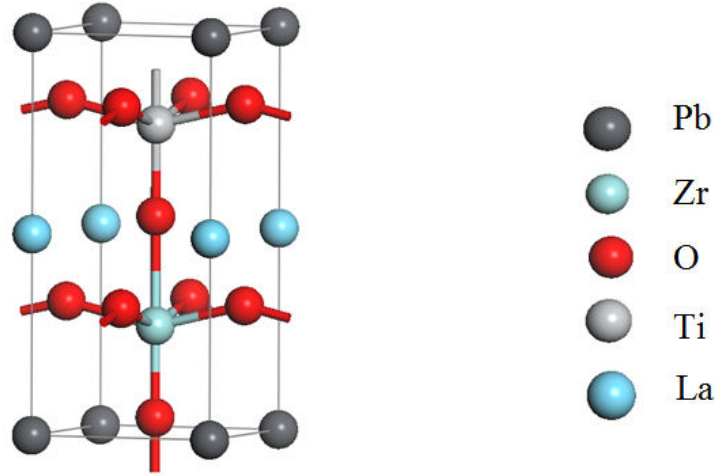


Figure 1: The crystal structure of PLZT with tetragonal 1x1x2 structure (P4mm phase)

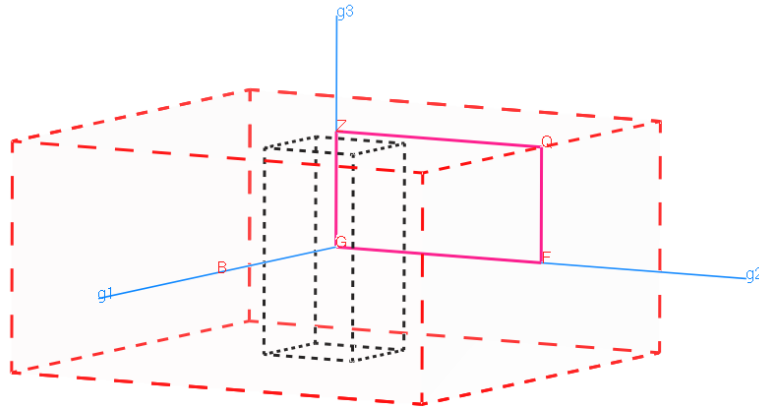


Figure 2: The high symmetry of Brillouin Zone of PLZT with tetragonal 1x1x2 structure (P4mm)

RESULTS AND DISCUSSION

(a) Structural properties of PLaZT

In order to proceed the further investigation of the effect of La in PZT ceramic, the value of unit cell lattice parameter, volume and total energy of tetragonal (P4mm space group) of PLZT after optimized from the geometry optimization calculation are listed in Table 1. Structural optimizations of PLZT tetragonal using different exchange correlations LDA-CAPZ, GGA-PBE, and GGA-PBESol as shown in Table 1. The result of PLZT obtained by using LDA-CAPZ in this work was overestimated, compared with GGA-PBE and GGA-PBESol. This result obtained by CASTEP computer code was in the good agreement by a recent study of annealed PLZT. In addition, our calculation on

the lattice parameter of tetragonal PLZT from lattice a and b shows that functional GGA-PBE and GGA-PBEsol is more accurate with percentage difference is -1.48% and -1.5% compared with LDA-CAPZ which is 2.37%. The optimized structure of PLZT show that the GGA-PBE and GGA-PBEsol are closed to the experimental value of PLZT from XRD data. The accurateness of the lattice calculation and its atomic position is significant factor of the material stability and the other calculation in perovskite oxide. The less percentage different between calculated lattice with the experiment lattice very important before proceed to other properties calculation such as electronic and optical properties. Therefore, we should ensure that the structural calculation used is acceptable, although there is the lack study of PLZT using first principles method. The present work also shows that the tetragonality of PLZT also were compared with different functional. LDA-CAPZ, GGA-PBE and GGA-PBEsol show that almost same of tetragonality value which is ~ 1.042 . The tetragonality of material very important in analyzing the spontaneous polarization.

Table 1: Calculated structural parameter (lattice constant (a and c in Å), atomic distance, volume (V in Å³) and total energy (E in eV) of tetragonal PLZT 1x1x2 with P4mm space group

	Functionals			Experiment [14]
	LDA	GGA PBE	GGA PBEsol	
Lattice Parameter (Å)				
<i>a</i>	3.960 (-2.37%)	3.996 (-1.48%)	3.995 (-1.50%)	4.056
<i>c</i>	4.125 (1.25%)	4.165 (2.23%)	4.165 (2.23%)	4.074
<i>c/a</i>	1.042 (3.78%)	1.042 (3.78%)	1.043 (3.88%)	1.004
Atomic Distance (Å)				
Ti-O	1.8765	1.8843	1.8842	
Zr-O	2.0370	2.0473	2.0476	
La-O	2.5996	2.6302	2.6294	
Pb-O	2.6787	2.7143	2.8404	
O-O	2.7102	2.7270	2.9196	
Volume (Å ³)	64.696 (-3.47%)	66.495 (-0.78%)	66.497 (-0.78%)	67.02
Total Energy (eV)	-8047.9	-8026.6	-8026.6	

(b) Band gap and density of states (DOS) of PLZT

The calculated electronic band structures along the direction G-F-Q-Z-G at the high-symmetry Brillouin zone of PLZT tetragonals are shown in Figs. 2, respectively. The highest valence band (VB), which lies at the Fermi level (E_F) at 0 eV, is dominated by the O 2p at Q point. Meanwhile, the conduction band (CB) of PLZT occurs at G point, which is primarily dominated by Ti 3d mixed at Pb and La p-state. The calculation of the electronic band gap shows that PLZT has an indirect band gap with the highest value of 2.91 eV at Q-G. However, calculation of the band gap value of PLZT in this work is higher than PLZT as reported by Baedy et al [15]. The values in present work in good agreement with other computational studies that reported values of tetragonal PLZT with 2.9 eV with GGA calculation. Therefore, the exact and approximate value of PLZT are needed to predict the experimental value of the band gap for single-phase PLZT. This band gap value is related to our absorption coefficient, which will be explained in the optical discussion.

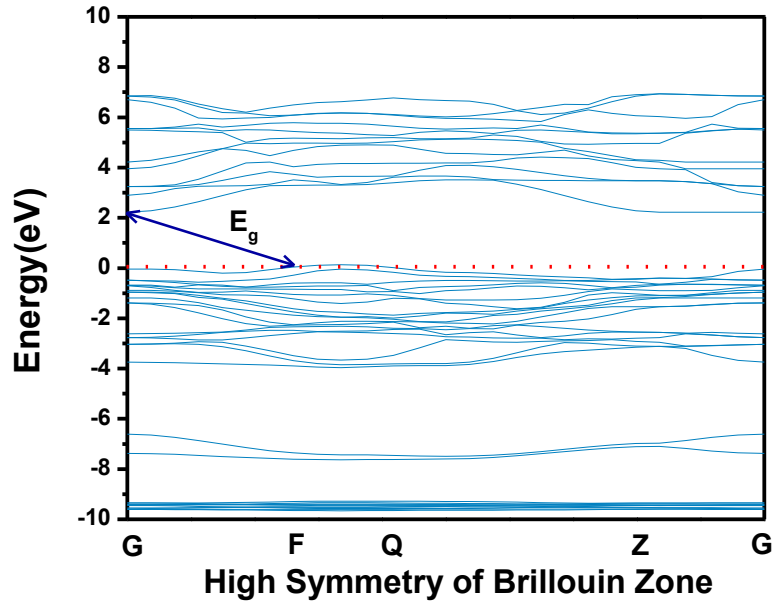


Figure 3: The calculated Band Gap of PLZT along the high-symmetry Brillouin zone.

Table 2: Calculated and experimental band structure of tetragonal PLZT

Functional	PLZT			GGA	Exp.
	LDA-CAPZ	GGA-PBE	GGA-PBEsol		
Band Gap (eV)	2.73	2.69	2.63	2.29	3.36
Band Gap Type	indirect	indirect	indirect	-	-
Direction	G-F	G-F	G-F	-	-

The total DOS for tetragonal PLZT is shown in Fig. 4 below. The PLZT reports in this work are similar with the report using first principles study. The Fermi level presented at the zero energy with dashed lines. The highest valence band of the PLZT are mainly dominated by electron O 2p and Pb 6s orbitals. and the lowest conduction band mainly originate from the Ti 3d, Zr 4d and La 6p states. The PLZT is a good ferroelectric material due to the special hybridization between special lone pair Pb 6s and O 2p at valence band as shown in Figure 5. The separation between valence band and conduction band for PLZT is 2.91 eV as mentioned in band gap structure. This is due to the different strength covalency of the Pb-O, Ti-O, La-O and Zr-O.

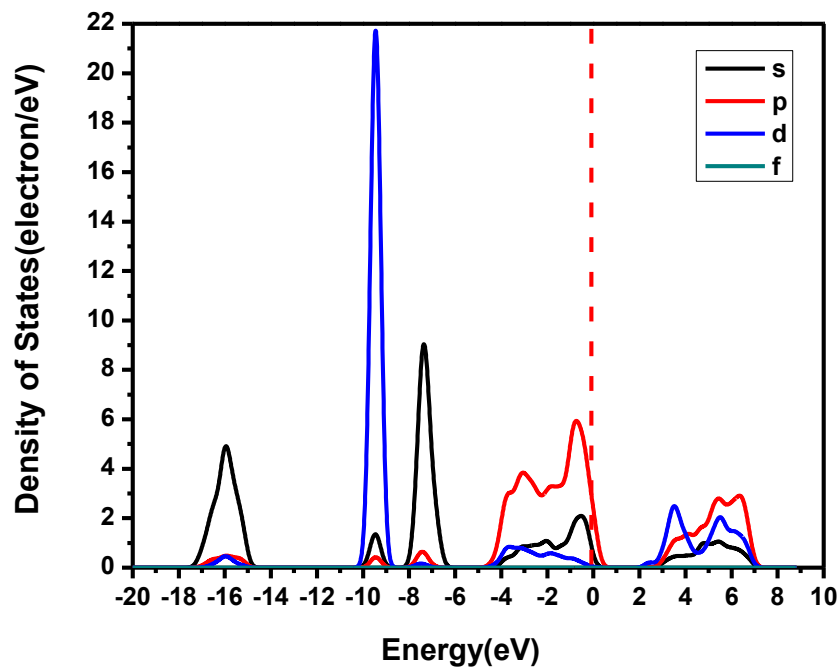


Figure 4: The total density of states (DOS) of PLZT

(c) Optical properties

The refractive indices n and the extinction coefficient k are calculated as shown in Figs. 5 respectively. The values of static refractive index n are represented as increase in photon energy. Subsequently, the value of $n(\omega)$ decreases with increase in photon energy to a minimum value at 40 eV, respectively. The intercept between refractive indices $n(\omega)$ and the extinction coefficient of compound in this work correspond to the zero value for the real part of the dielectric function. The refractive index for PLZT is 8.00 and the peak that observed from extinction coefficients correspond to the optical transition in PLZT.

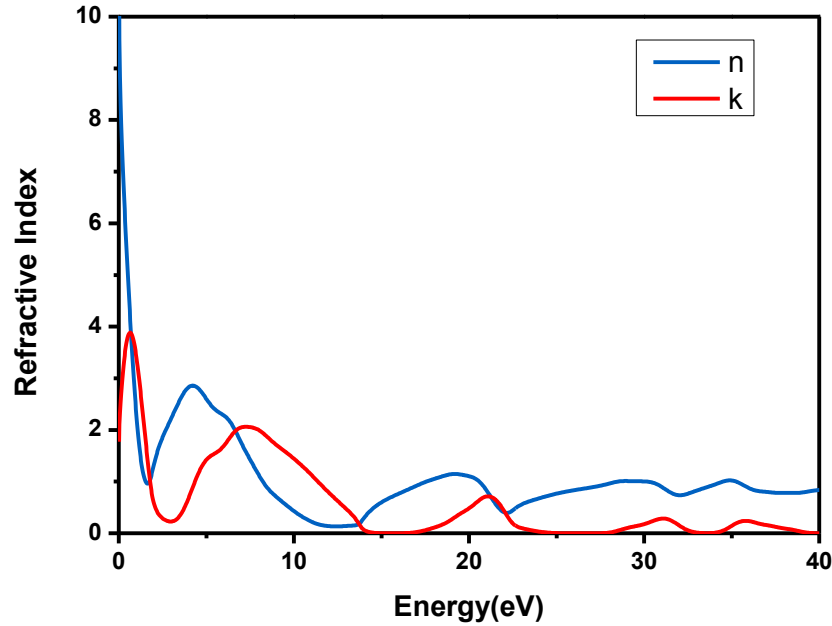


Figure 5: The calculated refractive index of PLZT

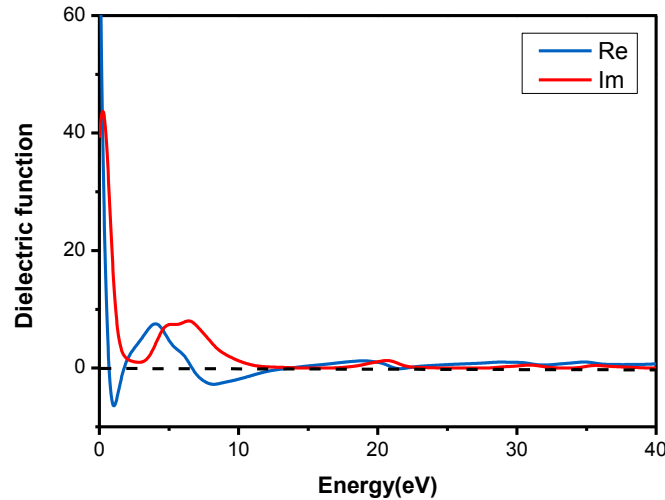


Figure 6: The calculated dielectric function of PLZT

Optical properties are closely related to the electronic band structure and phonon dispersion. Both types of interband optical transitions direct band gap and indirect band gap can be calculated from the above information. In general, the optical properties can be explained in detail through knowledge of the complex dielectric function. The graph of real and imaginary part of dielectric function against photon energy from 0 eV to 40 eV are presented in Figs. 6. The real part of dielectric function show the dielectric constant of PLZT while the imaginary part show the optical transition of PLZT. The imaginary part of PLZT present the four peaks which is at 1.0 eV, 5.1 eV, 7.0 eV and 21 eV respectively. The highest peak of imaginary part of PLZT appears due to the transition of O 2p states to Ti 3d states. At the lowest region of photon energy the value

of dielectric constant present the highest peak. The higher dielectric constant very useful for the optical application of PLZT.

The optical absorption of PLZT can be attained from the imaginary part of dielectric function. Figs 7(a) and 7(b) shows the optical absorption of PLZT against light spectrum with energy and wavelength respectively. The band gap of PLZT increasing due to the shifting of the light spectrum from high energy or short wavelength. The wavelength of PLZT is observed at the light region from 300 nm to 450 nm. This region showed that the ability of PLZT to absorb light at the wavelength with the enormous region and the absorbing light of PLZT very helpful in electro-optic devices.

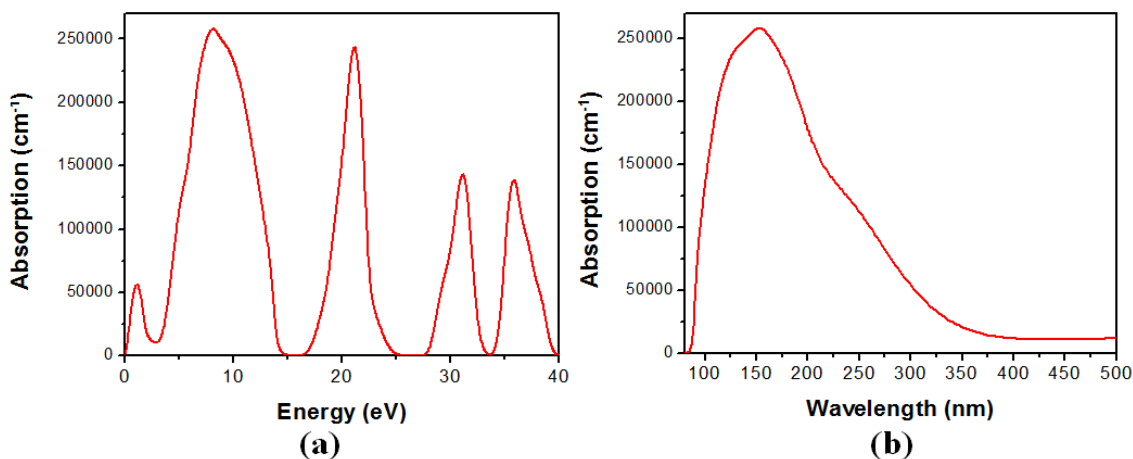


Figure 7: The calculated optical absorption of PLZT against light spectrum (a) energy and (b) wavelength

CONCLUSIONS

The calculated equilibrium structural parameters and elastic properties of the tetragonal using the LDA-CAPZ functional are in a good agreement with the results reported in the experiment PLZT. Thus, this work provided an accurate structural optimization for new tetragonals PLZT using LDA-CAPZ functional. We also successfully reported the relation between electronic and optical properties of tetragonal PLZT which will provide theoretical basis that can be used by other scholars as reference in synthesizing in order to enhance the performance of PZT.

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