Electronic, Optic and Dynamic Properties of Rhombohedral BiTeBr

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Abstract. Electronic, optic and thermodynamic properties of rhombohedral BiTeBr crystal were investigated under the local density approximation (LDA) using the density functional theory. No spin-orbit interaction (SOI) were taken into account during calculations and band gap of 0.946 eV was found as which is different from experimental results but in good agreement with previous theoretical studies without SOI. For this new type ferroelectric BiTeBr from ground states features lattice parameters, electronic total density of states (TDOS), partial density of states (PDOS) and electronic band structure, from optical properties dielectric function, refraction index, extinction, reflection and absorption coefficients, number of effective valence electrons, volume and surface loss functions, among thermodynamic properties change in Helmholtz free energy, internal energy, entropy and constant volume specific heat as a function of temperature were studied.

1. Introduction

There exist many studies on structural, electronic, elastic, dynamic, thermodynamic and optic properties of crystalline structures [1-9]. Ferroelectric crystals are being used in industrial fields extensively due to their dielectric, piezoelectric and pyroelectric properties and especially semiconductors which inherently owns ferroelectric features are being utilized in memory materials, sound sonar detectors, convertors, etc [10, 17]. Among ferroelectric materials BaTiO\textsubscript{3} is the first invented one, then SbSI group of A\textsuperscript{V}B\textsuperscript{VI}C\textsuperscript{VII} semiconductors which are extremely sensitive in photoconductivity were found and studied [18]. The need for multi-functional, cheaper materials of high efficiency, caused an increase in interest for new types of ferroelectrics [19-26]. Among the type new ferroelectric semiconducting materials of A\textsuperscript{V}B\textsuperscript{VI}C\textsuperscript{VII} bismuth tellurohalids (BiTeCl, BiTeBr, BiTel) are of high importance because they own potential of being a part of spintronic studies because of giant Rashba split, as memory materials and they are topological insulators (insulating in the bulk and conducting at the surface), surfaces can be of n or p type semiconductor depending on the outermost layer of surface after the cut[27, 28].
Thus we investigated structural properties of rhombohedral BiTeBr crystal using density functional theory under the local density approximation.

Shevelkov et al [29] found crystalline structure of bismuth tellurobromide as rhombohedral of point group -\(3\text{m}\) and space group 156 (P-\(3\text{m}1\)) and with lattice parameters of \(a=8.062\) and \(c=12.259\) Bohr and unit cell volume of \(V_0=689.996\) (Bohr\(^3\)) given Figure 1. We firstly optimized structure of BiTeBr by total energy optimization with respect to cutoff kinetic energy of plane waves (\(E_{\text{cut}}\)) and number grids for \(k\) points (\(n_{gkpt}\)), then by atomic optimization for lattice parameters, unit cell volume and reduced coordinates and finally by a two steps volume optimization for lattice parameters and unit cell volume with and without optimized reduced coordinates. We found 40 Ha for \(E_{\text{cut}}\), 12x21x12 for \(n_{gkpt}\), 186 \(k\) points and best results we found in volume optimization with optimized reduced coordinates as 634.223 (Bohr\(^3\)). Nearest calculated value of volume to the experimental one is of the step of volume optimization by reduced coordinates found in atomic optimization as 634.223 (Bohr\(^3\)). So, remaining calculations were done by using results of this step where we optimized lattice parameters as 7.809 and 12.006 Bohr.

![Figure 1. Crystal structure of double layer bismuth tellurochloride [43].](image)

2. Computational Method

Electronic, optic and thermodynamic properties of rhombohedral BiTeBr crystal were investigated via ABINIT [31] under density functional theory. Calculations were performed within LDA by the FHI98PP self-consistent pseudopotentials [32] with the Ceperley-Alder-Perdew-Wang scheme which considers the exchange-correlation effects [33, 34].

Conjugate gradient minimization method [35] was utilized to solve Kohn-Sham equations [36] and plane augmented waves were used as basis set for electronic wave functions. True valance electrons were chosen as 6s\(^2\)6p\(^3\) for Bi, 5s\(^2\)5p\(^4\) for Te and 4s\(^2\)4p\(^5\) for Br. Structural optimizations were done to a good convergence at 40 Hartree of cutoff energy and 186 \(k\) points using 12x12x12 Monkhorst-Pack mesh grid [37] in BiTeBr crystal, but for better results higher values of were used in electronical and optical calculations.
3. Electronic Properties

This step was performed without SOI by pseudo potential method within LDA based on density functional theory (DFT). A grid of 24x24x24 was chosen and producing 1872 k points were found for best convergence. BiTeBr crystal has 9 valence bands and additional 9 conduction bands were used for calculations of electronic band structure where Fermi level was set to zero and as it is seen in figure 2 BiTeBr crystal has a direct band gap at high symmetry point of A with a value of 0.946 eV which is near to and better than those calculations done without SOI (1.1 eV) [38] but deviates from experiment because of not considering SOI and Rashba split.

![Figure 2. Electronic band structure and DOS for BiTeBr with E_F adjusted to 0 eV.](image)

Some of existing experimental and theoretical results on band gap of BiTeBr are given in table 3. The difference between experimental results and calculated ones originates from two main factors as utilizing pseudo-potential method and ignoring SOI. Pseudo-potential method and inherent intractability of density functional theory can cause different estimations of band gaps up to 50 % error, mostly underestimated [39], but sometimes overestimated band gaps can be gathered in calculations [38]. Overestimation in band gap is attributed to the nature of pseudo-potentials used and large spin orbit coupling (SOC) effect of Bi atom [41], which causes Rashba splitting in real crystal and band gap decreases.

![Figure 3. High symmetry points and paths in first Brillouin zone in reciprocal space [42].](image)

| Ref. [30] (Exp.) | Ref. [38] (Teo.) | Present work (Teo) |
|------------------|------------------|--------------------|
| 0.62             | 1.1              | 0.946              |
As it is seen in figure 2 the paths of $\Gamma$-M-K-$\Gamma$ and L-H-A are non-degenerate but the $\Gamma$-A path is highly degenerate.

4. Dynamic Properties
In bismuth tellurobromide crystal, unit cell contains 3 atoms at zero pressure. In the end of crystallization of BiTeI at zero pressure, Bi atoms are located at points of (0, 0, 0), Te atoms are located at (2/3, 1/3, 0.6928) while Br atoms are at (1/3, 2/3, 0.2510) in the reduced coordinates, inside the unit cell.

Figures below show the phonon band structure and phonon density of states for BiTeBr.

![Phonon band structure and PHDOS](image)

There are 3 atoms per unit cell the crystal, 9 phonon branches totally appear. While three of them are the acoustic branches, the remaining six are optical ones. Degeneracy exists especially between high symmetry points of G-A in Brillouin zone of BiTeBr crystal. As expected, acoustic phonon dispersion curves are linear as a function of $k$ for small values of $k$.

Calculated frequency values of LO modes at the center of BZ are 2.37, 3.17 and 3.33 THz, while those of TO modes are at 3.60, 4.08 and 5.05 THz for BiTeBr.

There is a gap between the acoustic and the optic phonon branches. So, BiTeBr is a phononic crystal.

5. Optic Properties
20x20x20 M.P. mesh grid with 770 k points for optical calculations of BiTeBr crystal which is an optic crystal exhibiting symmetry of the point group -3m. Therefore the linear frequency dependent dielectric tensor for BiTeBr crystal has two non-zero and independent components in X and Z axes and calculated imaginary ($\varepsilon_1$) and real ($\varepsilon_2$) parts of these components are given in figures 5a and 5b for two axis separately.

![Imaginary and real parts of dielectric functions of BiTeBr](image)

**Figure 5.** Imaginary and real parts of dielectric functions of BiTeBr in a) X and b) Z directions.
As seen from these figures, real parts of linear dielectric functions, $\varepsilon_2$, reaches maximum values at 2.07 and 2.25 eV of photon energies for 11 (X) and 33 (Z) directions and the static dielectric constants for X and Z directions are 10.76 and 12.86, respectively.

The main peak values in the imaginary parts of linear dielectric functions, $\varepsilon_1$, (calculated in present work) are at 2.98 and 7.82 eV for X, and 3.34, 7.21 and 8.28 eV for Z directions, respectively. All of these values are at violet and near ultraviolet regions of spectrum.

For X direction, regions of 0-2 eV, 4.30-7.45 eV and above 8.60 eV, for Z direction 0-2.27 eV, 4.32-8.03 and above 9.23 eV are of normal dispersion where $\varepsilon_2$ increases as photon energy increases. Regions of transmition are 0-1.24 eV and above 17 eV, while 1.36-5.60 eV region is where reflection is strong and 5.60-17 eV is the region of absorption for Z axis while same regions for X axis are 0-1.60 eV and above 12 eV, 1.60-6.44 eV and 6.44-12 eV, respectively.

Figure 6. The calculated extinction coefficient (k), reflection (R) and absorption coefficients ($\alpha$), number of effective valance electrons ($N_{\text{eff}}$), energy loss functions for both volume and surface, and refractive index (n) functions for BiTeBr in 11 (X) and in 33 (Z) directions.
Variations of some of optical properties as a function of energy (a-g) and of wavelength (h) are given above in figure 6. There are some different results in literature compared to ours which can be due to ignoring SOI and discrepancy of DFT [40].

6. Conclusions
Electronic, optic ad dynamic properties of BiTeBr were investigated by using ABINIT [31] code within the local density approximation in the density functional theory. Calculated lattice parameters and experimental ones are in agreement and calculated thermodynamic features are found as expected. Phonon band graph is very similar to the study of Sklyadneva [44] et al.

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