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# Optic, Dynamic and Thermodynamic Properties of Rhombohedral BiTeI

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**ABSTRACT**

From physical properties of BiTeI crystal in rhombohedral phaseoptic, dynamic and thermodynamic features were studied with density functional theory under the local density approximation (LDA). Spin-orbit interaction (SOI) were kept out of concern in calculations and 0.386 eV found for band gap of bismuth telluroiodide from optical-absorption edge measurements, which is similar to experimental results. As ground states properties lattice parameters, optical dielectric function, refraction index, reflection, extinction and absorption coefficients, effective number of valance electrons, loss functions for volume and surface, behavior of Helmholtz free energy, internal energy, entropy and constant volume specific heat for temperature were studied for new type ferroelectric material BiTeI.

**Keywords:** Rhombohedral, density functional theory, optic, dynamic, thermodynamic

## 1 INTRODUCTION

Many studies have been done on ground states physical properties of crystals[1-9]. Among crystals those which show ferroelectric properties are being used in industry and related areas for the fact that they can exhibit also dielectric, piezoelectric and pyroelectric aspects. Inherently ferroelectric semiconductors, especially are good for applications like memory materials, sound sonar detectors, convertors, etc [10, 17]. $BaTiO_3$ is the first invented ferroelectric crystal, then SbSI group of $A^{V}B^{VI}C^{VII}$ semiconductors were found and studied intensively owing to their extreme sensitivity for photoconductivty [18]. The need for multi-functional, cheaper materials of high efficiency, caused an increase in interest for new types of ferroelectrics [19-26]. Among new type semiconducting ferroelectrics of $A^{V}B^{VI}C^{VII}$ bismuth tellurohalids (BiTeCl, BiTeBr, BiTeI) are so important because they are good for spintronics due to giant Rashba split, they can be used as memory materials and they have topological insulating property [27, 28].

Therefore, we worked on structural, optic, dynamic and thermodynamic features of rhombohedral BiTeI crystal using density functional theory under the local density approximation.

Shevelkov et al [29] explained structure of bismuth telluroiodide as rhombohedral of point group 3m and space group 156 (P3m1) and they stated the lattice parameters as a= 8.199 and c=12.952 Bohr with unit cell volume of $V_0$= 754.195 $(Bohr)^3$ (see Figure 1).

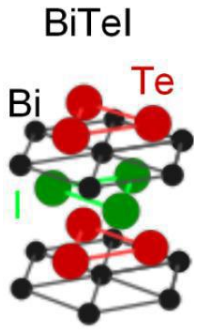



Figure 1: Crystal structure of bismuthtelluroiodide[38].

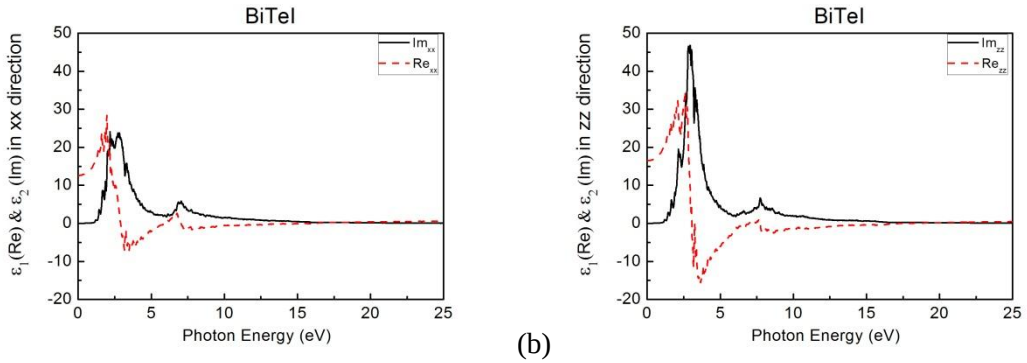
## 2 COMPUTATIONAL METHOD

Optic, dynamic and thermodynamic properties of rhombohedral BiTeI crystal were studied by ABINIT [31] with density functional theory. LDA and FHI98PP self-consistent pseudopotentials [32] were chosen for calculations with the Ceperley-Alder-Perdew-Wang scheme [33, 34].

For solving Kohn-Sham equations [36] conjugate gradient minimization method [35] was used and as basis set for electronic wave functions plane augmented waves were utilized. True valance electrons were taken as $6s^2 6p^3$ for Bi, $5s^2 5p^4$ for Te and finally $5s^2 5p^5$ for I. First step of optimization in our study was optimizing total energy with respect to cutoff kinetic energy of plane waves ($E_{cut}$) and number grids for k points (ngkpt). Then we made atomic optimization for lattice parameters, unit cell volume and reduced coordinates and finally volume optimization with and without optimized reduced coordinates for lattice parameters and unit cell volume. Good convergence was reached at 40 Hartree of cutoff energy and 186 k points using 12x12x12Monkhorst-Pack mesh grid [37] for structural optimizations of BiTeI crystal, but for best accuracy much more higher values of were utilized in electronical and optical calculations.

## 3 OPTIC PROPERTIES

770 k points were found for optical calculations of BiTeI by 20x20x20 M.P. mesh grid. BiTeI crystal exhibits symmetry of the point group 3m and the linear frequency dependent dielectric tensor for BiTeI crystal has two non-zero and independent components along “a” (in x axis) and along “c” (in z axis) and calculated real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of these components are given in Figure 2a and Figure 2b for two axis separately.




(a) (b)

Figure 2: Imaginary and real parts of dielectric functions of BiTeI in a) x and b) z directions.

From Figure 2 it is seen that real parts of linear dielectric functions of BiTeI, $\varepsilon_1$, reach maximum values at 1.96 and 2.56 eV of photon energies and the static dielectric constants are 12.59 and 16.56 for x and z directions, respectively.

The main peak values in the imaginary parts of linear dielectric functions, $\varepsilon_2$, in present work are at 1.43, 1.64, 2.01, 2.19,2.72, 2.86, 3.03, 6.88 and 7.06 eV for x axis and 1.41, 1.62, 2.12, 2.80, 2.98, 3.29, 6.62 and 7.74 eV for z axis, respectively. Highest peak values are in visible region.

For x direction, intervals of 0-1.98 eV, 3.48-6.80 eV, for z direction those of 0-2.06 eV, 2.34-2.62 and 3.64-7.67 eV are regions of normal dispersion where $\varepsilon_1$ increases as photon energy increases.

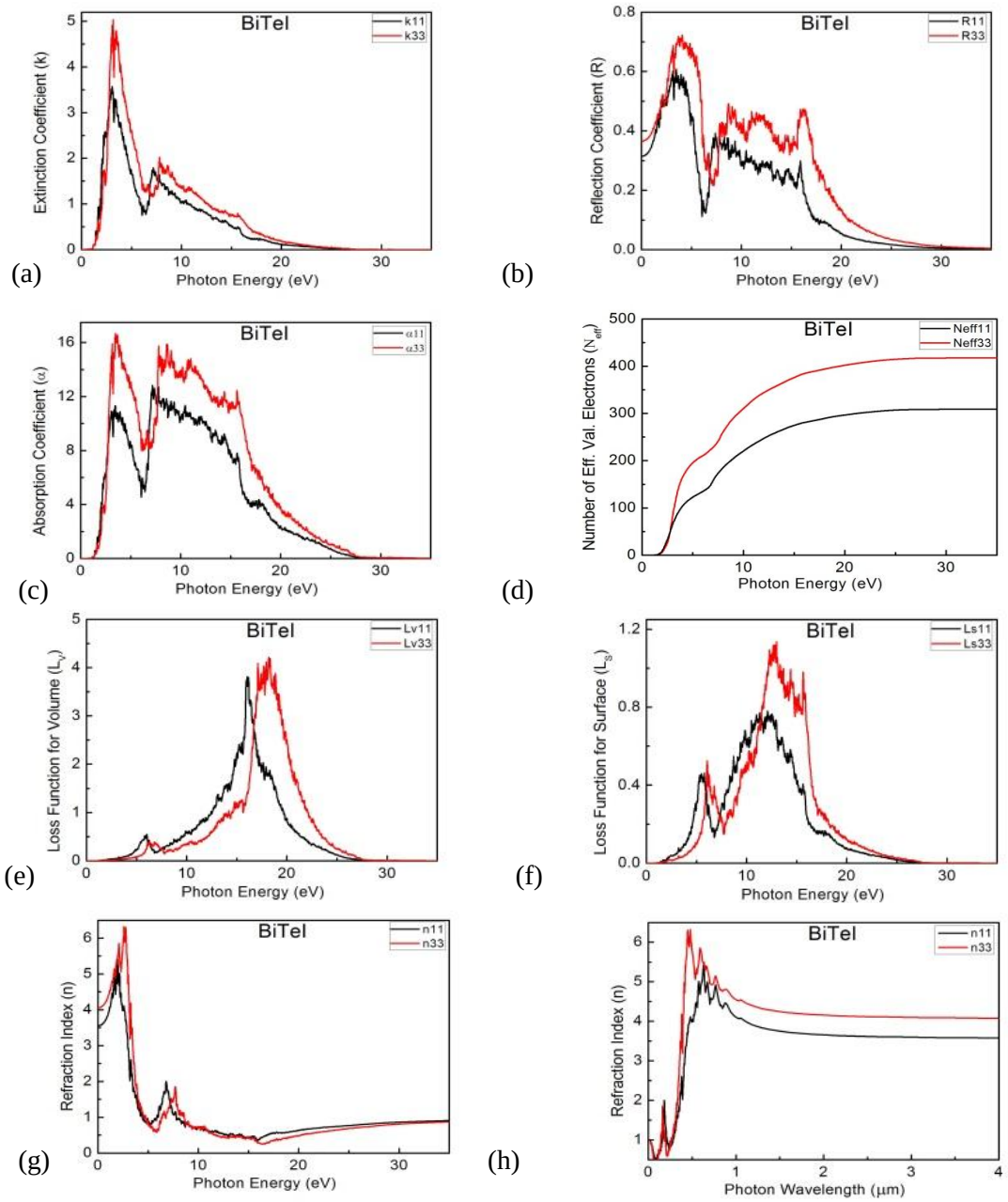



Figure 3: The calculated extinction coefficient (k), reflection (R) and absorption coefficients (α), number of effective valance electrons ($N_{eff}$), energy loss functions for volume ($L_V$) and surface ($L_S$), and refractive index (n) functions for BiTeI in 11 (x) and in 33 (z) directions

## 4 DYNAMIC PROPERTIES

There are 3 atoms per primitive unit cell of bismuth telluroiodide crystal at zero pressure. Experimental reduced coordinates of Bi, Te and I atomsare(0, 0, 0), (2/3, 1/3,0.6928) and (1/3, 2/3, 0.2510) and for calculations of electronic, optic and dynamic properties they were optimized at first.

Figure 4 below showsthe phonon band structure and phonon density of states for BiTeI.

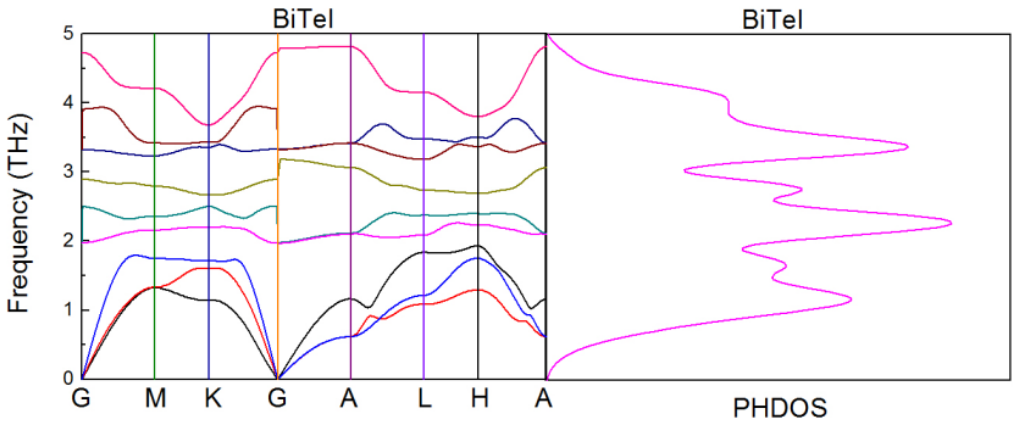



Figure 4: Phonon band structure and PHDOS for BiTeI

Since there are 3 atoms per primitive unit cell of BiTeI and 3 phonon modes for each, so totally 9 phonon branches appear in phonon spectrum. Three of them are acoustic modes and remaining are six optical branches. G-A path in Brillouin zone of BiTeI crystal is highly degenerate. Γ-M and Γ-K directions are more symmetrical compared to the other directions. Acoustic branches are linear function of *k* for small values of *k*, as expected.

Calculated frequency values of longitudinal optic (LO) modes at the center of BZ are 1.98, 2.49 and 2.90 THz, while those of transverse optic (TO) branches are at 3.33, 3.90 and 4.72 THz for BiTeI.

There is a gap between the acoustic and the optic phonon branches. As seen from figure, acoustic and optic modes do not intersect along all symmetry directions. So, BiTeI is a phononic crystal which means that it transmits only sound frequencies which are not in the band gap region.

## 5 THERMODYNAMIC PROPERTIES

Entropy (S), constant-volume specific heat ($C_V$), phonon contributions to Helmholtz free energy (F) and internal energy (E) as a function of temperature for BiTeI crystal are given in Figure 5a and Figure 5b. Contribution of phonons, that is, contribution of lattice to internal and free energies do not vanish at zero temperature and they are equal to 4265.2 J/mol at absolute zero which shows existence of zero-point oscillations.

Entropy icreases with temperature and especially above 300 K the increase is linear. Constant-volume specific heat for BiTeI crystal is calculated from phonon band structure calculations and it approaches to Dulong-Petit limit of 74.23 J/mol.K around 500 K, which is extremely close to the value of 74.826 J/mol.K, the classical limit of specific heat, for BiteI.

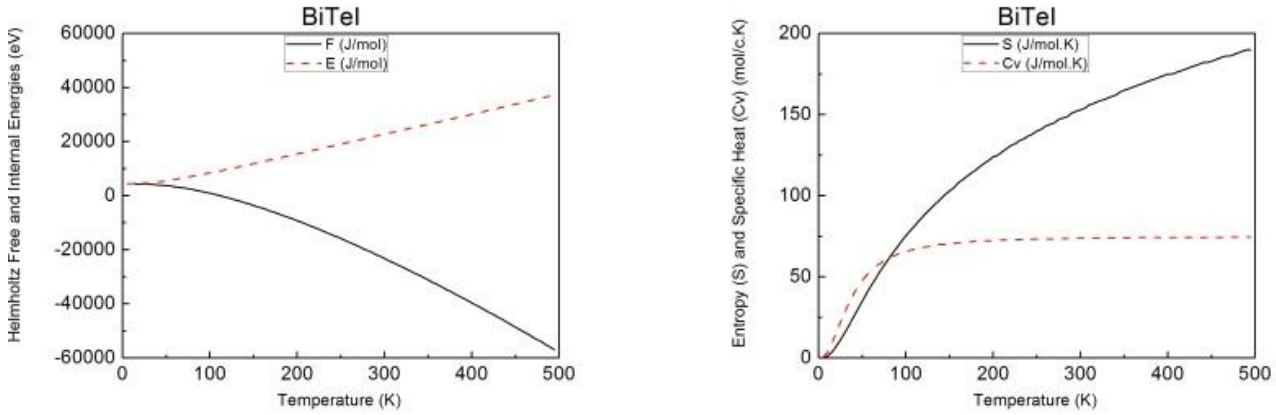



Figure 5: a) Helmholtz free energy (F) and internal energy (E), b) entropy (S) and constant volume specific heat ($C_V$) for BiTeI.

## 6 CONCLUSION

Optic, dynamic and thermodynamic properties of BiTeI were investigated by using ABINIT [31] code within the local density approximation under 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 [39] et al.

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