Optical Properties and Electronic Band Structure of Topological Insulators on $A_2{}^5B_3{}^6$ compound based

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Abstract—**We have performed a first principles study of structural, electronic, and optical properties of rhombohedral Sb_2Te_3 and Bi_2Te_3 compounds using the density functional theory within the local density approximation. The lattice parameters, bulk modulus, and its pressure derivatives of these compounds have been obtained. The linear photon-energy dependent dielectric functions and some optical properties such as the energy-loss function, the effective number of valance electrons and the effective optical dielectric constant are calculated and presented in the study**

Keywords-ab initio calculation; electronic structure; optical properties

I. INTRODUCTION

Sb_2Te_3 and Bi_2Te_3, the members of compounds with the general formula $A_2^V B_3^{VI}$ (A =Bi, Sb and B =S, Se, Te), are narrow-bandgap semiconductors with rhombohedral layered crystal structure. Sb_2T_3 and Bi_2Te_3 are well-known topological insulators [1-7], extraordinary thermoelectric materials at ambient temperature [8] and the possible topological superconductors [9] with surface states consisting of a single Dirac cone at the Γ. All of these have made A_2B_3 compounds as the subject of intensive investigation both in fundamental and applied research. These compounds possess the rhombohedral crystal structure with five atoms per unit cell belonging to the space group $D_{3d}^5(R\bar{3}m)$. Sb_2T_3 and Bi_2Te_3 can be used for many different applications such as power generation and cooling devices [10]. Thermoelectric power generators and cooler have many advantages over conventional refrigerators and power generators such as long life, no moving parts, no green house gases, no noise, low maintenance and high reliability [11-13].

In the past, some detailed works [6, 7, 14, 15] have been carried out on the structural and electronic properties of these compounds. Zhang et al [6] study in detail the topological nature and the surface states of this family of compounds using the fully self-consistent ab initio calculations in the framework of density functional theory. Zhang et al [7] focus on layered, stoichiometric crystals Sb_2T_3, Sb_2Se_3, Bi_2Te_3 and Bi_2S_3 using ab initio calculations in the framework of the Perdew-Burke-Ernzerhof type generalized gradient approximation of the density functional theory. Wang et al [14] calculated the electronic structures of Sb_2T_3 and Bi_2Te_3 crystals using the first-principles full potential linearized augmented plane-wave method. Yavorsky et al [15] performed calculations of the electronic structures of Sb_2T_3 and Bi_2Te_3 compounds by means of the screened Korringa-Kohn-Rostoker (KKR) Green's function method in the atomic sphere approximation (ASA) within local density approximation of the density functional theory.

As far as we know, no ab initio general potential calculations of the density of state and charge and the optical properties of the Sb_2Te_3 and Bi_2Te_3 have been reported in detail. In the present work, we have investigated the structural, electronic, and photon energy-dependent optical properties of the Sb_2S_3 and Sb_2Se_3 crystals. The method of calculation is given in Section 2; the results are discussed in Section 3. Finally, the summary and conclusion are given in Section 4.

II. METHOD OF CALCULATION

Our calculations have been performed using the density functional formalism and local density approximation (LDA) [16] through the Ceperley and Alder functional [17] as parameterized by Perdew and Zunger [18] for the exchange-correlation energy in the SIESTA code [19, 20]. This code calculates the total energies and atomic forces using a linear combination of atomic orbitals as the basis set. The basis set is based on the finite range pseudoatomic orbitals (PAOs) of the Sankey_Niklewsky type [21], generalized to include multiple-zeta decays.

The interactions between electrons and core ions are simulated with separable Troullier-Martins [22] norm-conserving pseudopotentials. We have generated atomic pseudopotentials separately for atoms, Sb, Bi and Te by using the $5s^25p^3$, $6s^26p^3$ and $5s^25p^4$ configurations, respectively. The cut-off radii for present atomic pseudopotentials are taken as s: 3.82 au, p: 1.71 au, 2.92 au for the d and f channels of Bi, s:3.62 au, p:2.40 au, 2.78 au for the d and f channels of Te and 2.35 for the s, p, d and f channels of Sb.

Siesta calculates the self-consistent potential on a grid in real space. The fineness of this grid is determined in terms of an energy cut-off E_c in analogy to the energy cut-off when the basis set involves plane waves. Here by using a double-zeta plus polarization (DZP) orbitals basis and the cut-off energies between 100 and 500 Ry with various basis sets, we found an optimal value of around 425 Ry for Sb_2Te_3 and Bi_2Te_3. For the final computations, 54 k-points for Sb_2Te_3 and

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Bi_2Te_3 were enough to obtain the converged total energies ΔE to about 1meV/atoms.

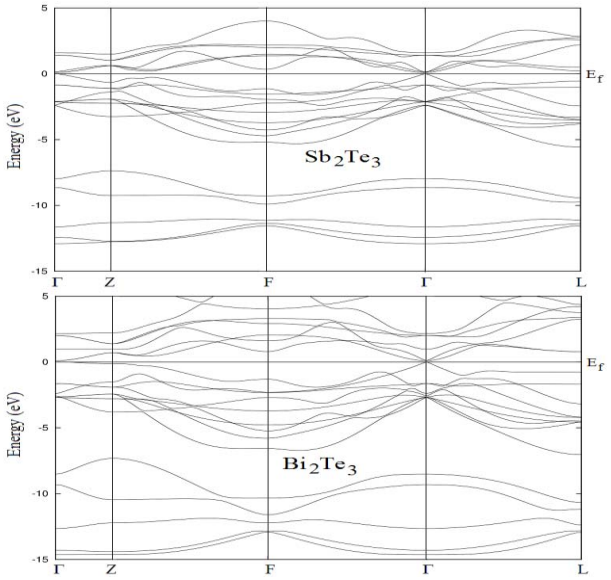

Figure 1. Energy band structure for Sb_2Te_3 and Bi_2Te_3.

III. RESULTS AND DISCUSSION

A. *Structural properties*

- Density of States and Band Structure

All physical properties are related to the total energy. For instance, the equilibrium lattice constant of a crystal is the lattice constant that minimizes the total energy. If the total energy is calculated, any physical property related to the total energy can be determined.

For Sb_2Te_3 and Bi_2Te_3, structures which are rhombohedral are considered. The equilibrium lattice parameters, the bulk modulus, and its pressure derivative have been computed minimizing the crystal's total energy calculated for the different values of lattice constant by means of Murnaghan's equation of states (eos) [23]. The lattice constants for Sb_2Te_3 and Bi_2Te_3 compounds are found to be a= 4.256 Å, b= 30.397 Å and a=4.383 Å, b=30.487 Å, respectively. The lattice parameters obtained are in a good agreement with the experimental and theoretical values [24, 14]. In all our calculations, we have used the computed lattice constants. In the present case, the calculated bulk moduli for Sb_2Te_3 and Bi_2Te_3 are 80.01 and 59.02 GPa, respectively. Unfortunately, there are no theoretical and experimental results for comparing with calculated bulk modulus.

- Charge Density

The three-dimensional valance charge density distribution of Sb_2Te_3 and Bi_2Te_3 compounds in the plane containing Sb-Te and Bi-Te bonds is illusrated in Fig. 3 and Fig. 4. Examination of the nature of chemical bonding, especially the distribution of valance charges between atoms is necessary to explain the overall shape. The overall shape of the charge distributions suggests covalent bonding of Sb-Te and Bi-Te.

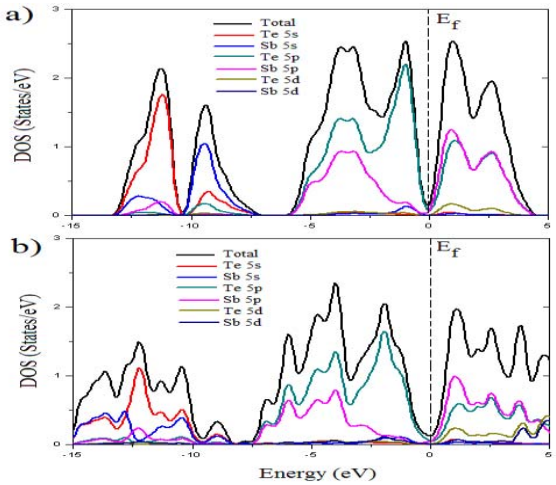

Figure 2. The total (DOS) and projected density of states for a) Sb_2Te_3 and b)Bi_2Te_3.

Ionicity is directly associated with the character of the chemical bond. It provides us a mean for explaining and classifiying the properties of V-VI compounds. The ionicity charecter is dependent on the total valance charge density by calculating the charge distribution. We have used an empirical formula [25] to obtain an estimated value of the ionicity factor for Sb_2Te_3 and Bi_2Te_3 compounds. In this approach the ionicity parameter is defined as

$$f_i = \frac{1}{2}\left(1 - \cos\left(\frac{E_{AS}}{E_{VB}}\right)\right)$$

Where E_{AS} is the anti-symmetry gap between the two lowest valance bands and the E_{VB} the total valance band width. The calculated value of the ionicity factor for Sb_2Te_3 is 0.089 for E_{AS} =1.173 eV and E_{VB} =13.192 eV , whereas The calculated value of the ionicity factor for Bi_2Te_3 is 0.089 for E_{AS} =0.631 eV and E_{VB} =14.643 eV .

B. *Electronic Properties*

The energy band structures calculated using LDA for Sb_2Te_3 and Bi_2Te_3 are shown in Fig. 1. As can be seen in Fig. 1, the Sb_2Te_3 and Bi_2Te_3 compounds have an direct band gap semiconductor with the value 0.093 eV and 0.099 eV , respectively. The top of the valance band and the bottom of the conduction band for both compounds positioned at the Γ point of BZ. In conclusion, our band gap values obtained are

good agreement with theoretical values and the band gaps have same character with given in Ref. [6, 7] . Band structures of Sb_2Te_3 and Bi_2Te_3 single crystals are compared, band structures of these crystals are highly resemble one another. Thus, on formation of the band structures of Sb_2Te_3 and Bi_2Te_3 the 5s 5p orbitals of Te atoms are more dominant than 5s5p and 6s6p orbitals of Sb and Bi atoms.

The total and partial densities of states of Sb_2Te_3 and Bi_2Te_3 are illustrated in Fig. 2. As you can see, from this figure, the lowest valence bands occur between about -14 and -12 eV are dominated by Sb 5s and Bi 6s states while valence

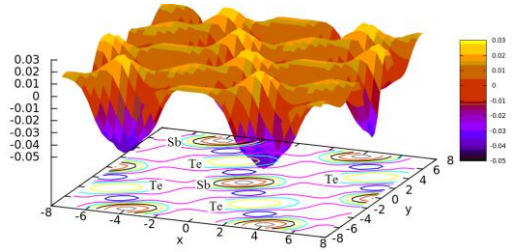

Figure 3. Charge density distribution of the valance charge of Sb_2Te_3

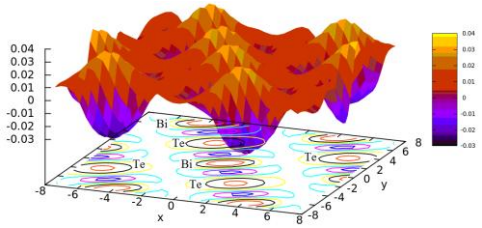

Figure 4. Charge density distribution of the valance charge of Bi_2Te_3

bands occur between about -12 and -10 eV are dominated by Te 5s states. The highest occupied valance bands are essentially dominated by Te 5p states. The 5p (6p) states of Sb (Bi) atoms are also contributing to the valance bands, but the values of densities of these states are so small compared to Te 5p states. The lowest unoccupied conduction bands just above Fermi energy level are dominated by Sb 5p and Bi 6p states. The 5p states of Te atoms are also contributing to the conduction bands, but the values of densities of these states are so small compared to Sb 5p and Bi 6p states.

C. Optical Properties

The Sb_2Te_3 and Bi_2Te_3 single crystals have an rhombohedral structure that is optically a uniaxial system. For this reason, the linear dielectric tensor of the Sb_2Te_3 and Bi_2Te_3 compounds have two independent components that are the diagonal elements of the linear dielectric tensor. We first calculated the real and imaginary parts of the x- component of the frequency-dependent linear dielectric function and these are shown in Fig. 5. The ε_1^x behaves mainly as a classical oscillator. It vanishes (from positive to negative) at about 1.27 eV , 6.98 eV , 10.24 eV and 17.32 eV (see Fig. 5) for Sb_2Te_3 compound. The ε_1^x is equal to zero at about 1.89 eV , 6.55 eV , 7.63 eV and 17.41 eV (see Fig. 5) for Bi_2Te_3 compound. The peaks of the ε_2^x correspond to the optical transitions from the valence band to the conduction band and are in agreement with the previous results. The maximum peak value of ε_2^x for Sb_2Te_3 are around 1.24 eV , whereas the maximum value of ε_2^x for Bi_2Te_3 are around 1.74 eV . Spectral dependences of dielectric functions show the similar features for both materials because the electronic configurations of Sb ([Kr],$3d^{10}$ $4s^2$ $4p^6$) and Bi([Xe], $4d^{10}$ $5s^2$ $5p^6$) are very close to each other. In general, there are various contributions to the dielectric function, but Fig. 5 show only the contribution of the electronic polarizability to the dielectric function. In the range between 0.2 eV and 3 eV , ε_1^x

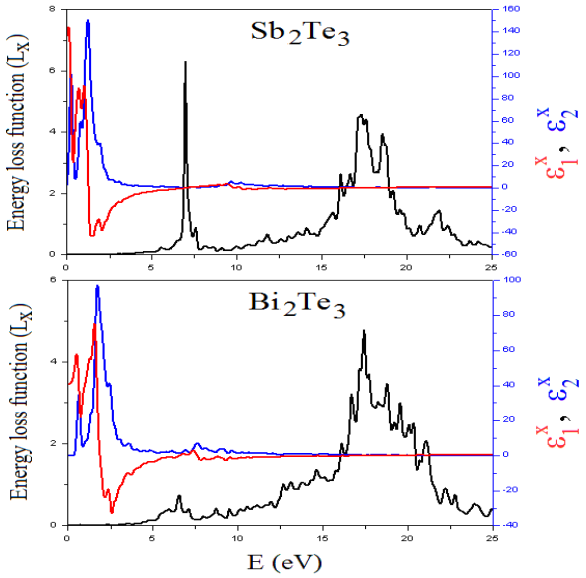

Figure 5. Energy spectra of dielectric function and energy-loss function (L) along the x for Sb_2Te_3 and Bi_2Te_3.

decrease with increasing photon-energy, which is characteristics of an anomalous dispersion. In this energy range, the transitions between occupied and unoccupied states mainly occur between Te 5p states which can be seen in the DOS displayed in Fig. 2. Furthermore as can be seen from Fig. 5, the photon –energy range up to 0.1 eV is characterized by high transparency, no absorption and a small reflectivity. The 0.1-3.0 eV photon energy range is characterized by strong absorption and appreciable reflectivity. The absorption band extending beyond 7 eV up to 10 eV is associated with the transitions from the low-lying valance subband to conduction band. Second, we see that above 8 eV , corresponding to the Sb 5s (Bi 6s) and T3 5p. Also, we remark that the region above 10 eV cannot be interpreted in term of classical oscillators. Above 10 eV ε_1 and ε_2 are dominated by linear features, increasing for ε_1 and decreasing for ε_2 .

The corresponding energy-loss functions, $L(\omega)$, are also presented in Fig. 5. In this figure, L_x correspond to the energy-loss function along the x- direction. The function $L(\omega)$ describes the energy loss of fast electrons traversing the material. The sharp maxima in the energy-loss function are associated with the existence of plasma oscillations [26]. The curves of L_x for Sb_2Te_3 and Bi_2Te_3 in Fig. 5 have a maximum near 17.32 and 17.42 eV , respectively.

Also, we calculated effective number of valence electrons N_{eff} and the effective dielectric constant ε_{eff} . The effective optical dielectric constant, ε_{eff} reaches a saturation value at about 9 eV . The photon-energy dependence of ε_{eff} can be separated into two regions. The first is characterized by a rapid rise and it extends up to 4 eV . In the second region the value of ε_{eff} rises more smoothly and slowly and tends to saturations at the energy 9 eV . This means that the greatest

contribution to ε_{eff} arises from interband transitions between 0 eV and 4 eV .

As states above, the N_{eff} is the effective number of valance electrons per unit cell at the energy $\hbar\omega_0$ (under the condition that all the interband transitions possible at this frequency ω_0 were made). In the case of Sb_2Te_3 and Bi_2Te_3 the value of N_{eff} increases with increasing photon energy and has tendency to saturate near 9 eV and 20 eV . Therefore, each of our plots of N_{eff} versus the photon energy for Sb_2Te_3 and Bi_2Te_3 can be arbitrarily divided into two part. The first is characterized by a rapid growth of N_{eff} up to ~5 eV and extend to 10 eV . The second part shows a smoother and slower growth of N_{eff} and tends to saturate at energies above 30 eV . It is therefore so difficult to choose independent criteria for the estimate of the of valance electrons per unit cell. Recognizing that the two valance subbands are separated from each other and are also separated from the low-lying states of the valance band, we can assume a tendency to saturation at energies such that the transition from the corresponding subbands are exhausted. In other words, since N_{eff} is determined only by the behavior of ε_2 and is the total oscillator strengths, the sections of the N_{eff} curves with the maximum slope, which correspond to the maxima $dN_{eff}/d\hbar\omega$, can be used to discern the appearance of new absorption mechanism with increasing energy (E=3.8 eV , 9.5 eV for Sb_2Te_3 and E=4.2 eV , 9 eV for Bi_2Te_3). The values and behavior of N_{eff} and ε_{eff} very close to each other.

IV. CONCLUSION

In present work, we have made a detailed investigation of the structural, electronic, and frequency-dependent linear optical properties of the Sb_2Te_3 and Bi2Te3 crystals using the density functional methods. The results of the structural optimization implemented using the LDA are in good agreement with the experimental and theoretical results. We have examined photon-energy dependent dielectric functions, some optical properties such as the energy-loss function, the effective number of valance electrons and the effective optical dielectric constant along the x- axe.

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