Electronic and optical properties of $CuInTe_2$

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Abstract. The electronic and optical properties of a ternary chalcopyrite compound $CuInTe_2$ with diamond like structure have been studied. The calculations are carried out using the density functional theory (DFT) based full potential-linearized augmented plane wave (FP-LAPW) method within the framework of GGA and modified Becke Johnson (mBJ) potential approach. The presence of direct energy band gap of 0.8 eV suggests the sample material can be a good material for solar cell application. The study of the optical response of the material against the incident photon energy radiation indicates the material can be an effective candidate for the optoelectronic devices.

1. Introduction

Chalcopyrite compounds form a very large and versatile group of materials formed by some members of the I-III-VI_2 family of the periodic table. These materials are distinguished by their tunable direct band gap semiconducting nature, with optimal range of energy band gap for terrestrial solar conversion [1]. With different combinations of the different members of Group I, III and VI of periodic table the band gaps of these materials vary from infrared to ultraviolet spectral range, which make them promising candidate for solar-cells applications [2,3], light-emitting diodes [4,5], nonlinear optics [6], and optical frequency conversion applications in all solid state based tunable laser systems. With further modification by partial substitution of cations or anions, some of the chalcopyrite candidates possess nonlinear optical properties, which also make them promising candidate for optical device and technology [7]. $CuInTe_2$ is also a candidate compound of ternary chalcopyrite (I-III-VI_2), characterized by their direct band gap semiconducting nature and analogs of the II-VI zinc blende compounds. The energy band gap (1.06 eV) close to the optimum value for solar energy conversion makes $CuInTe_2$ an interesting candidate for material research [8] and suitable for the fabrication of solar cells.

The several experimental and theoretical studies have been performed to understand the physical properties of this ternary Chalcopyrite. $CuInTe_2$ was synthesized by Hahn *et al*. [9] for the first time and after that several researcher conducted the theoretical and experimental calculations to investigate the electronic [10], physical [11,12] and optical [13] properties. Lateron, Jaffe and Zunger [14] used the potential variation mixed basis (PVMB) approach to study the chemical trends of the Cu-based ternary chalcopyrite semiconductors. Ahuja *et al*. [15] have used the full-potential linear muffin-tin orbital (FP-LMTO) method to investigate the optical properties of $CuGaS_2$. The series of compounds $CuXS_2$ (X = Al, Ga, In) and $CuAlX_2$(X = S, Se, Te) including $CuGaS_2$ are also investigated to study their electronic and optical properties [16]. Similarly, $CuGaS_2$ and $AgGaS_2$ were studied to explore their structural, electronic and optical properties using the FP-LAPW method by Laksari *et al*. [17].

Following this study, Reshak and Auluck [18] also studied the electronic properties of $CuAlX_2$(X = S, Se, Te) using FP-LAPW method. Recently, Xian-Zhou *et al*. [19] have studied the electronic structure and optical properties of $CuInTe_2$. However their pseudopotential based study suggests the presence of zero energy band gap for this material, which is against its experimental value of 1.06 eV [20]. Similarly, the previous local density approximation (LDA) based study [21] is also not able to predict the precise value of the energy band gap of $CuInTe_2$ (0.18 eV).

The accurate knowledge of the energy band gap and the optical functions of these materials play a significant role to understand their application as mentioned earlier. In this work, we first analyze the electronic properties of $CuInTe_2$ to predict the precise value of energy band gap, based on first-principle calculations. Another concern of this work is to understand the origin of interband transition above the band gap and the optical response of the material for the energy radiation of infrared to ultraviolet range.

2. Computational details

Ternary $CuInTe_2$ crystallizes in tetragonal structure with space group of I-42d (No. 122). The calculations presented here are performed using a semi-relativistic version of the FP-LAPW method implemented in the Wien2k code [22] within the framework of DFT. The exchange-correlation effects are treated by the Perdew– Berke–Ernzerhof generalized gradient approximation (PBE-GGA) [23]. The energy eigen values are converged expanding the wave function in the interstitial region and the plane wave cut-off was set to $R_{MT} \times K_{max} = 7$, Where R_{MT} is the smallest atomic muffin-tin (MT) sphere radius and K_{max} is the maximum value of the wave vector in the plane wave expansion. Non-spherical contributions to the charge density and potential within the MT spheres are considered up to $l_{max} = 6$, while charge density and the potential are expanded as a Fourier series with wave vectors up to $G_{max}=12$ $(a.u.)^{-1}$. The different MT sphere radii (R_{MT}) used were 2.43 a.u., 2.9 a.u. and 2.43 a.u. for Cu, In and Te, respectively. The self-consistent potentials are calculated on a 17 × 17 × 17 *k*-mesh in the Brillouin zone (BZ) and the convergence criterion is set to 10^{-4} Ry. The experimental lattice constant of a= 6.195 Å and c = 12.418 Å [24] are used to calculate the results presented here.

3. Results and discussions

3.1. Electronic properties

The energy band structure and density of states are calculated and they show similar profile with their previous report. However, the energy band gap of the material is found to be close to 0.2 eV, which is lower than the experimental value with large deviation. Therefore in the present study we have included a new approach of exchange-correlation functional known as mBJ potential [25] in the calculation to find the precise values of the energy band gap. The mBJ calculated density of states (DOS) and energy bands are presented in Figures 1 and 2, respectively. The overall energy band profile matches with their previous report [19].

The energy band structure can be distinguished into three regions, namely core, valence and conduction regions, separated by well defined energy gaps. The lowest energy region, core region is primarily contributed by Te-*s* electronic state as visible from partial DOS plot. The lower valence region is Te-*p* states dominated with small contribution from In-s orbital electrons, however the region just below the Fermi energy level (E = 0 eV) is formed by Cu-*d* states. The region above Fermi energy level (E_F) is dominated by Te. Moreover the Cu-3*d* states are found to split into two sub-bands at -2 eV and -3 eV below Fermi energy level. Here the Cu-3*d* states are found to split due to tetrahedral crystal field effect, which also gives the presence of a narrow band gap at the valence region.

The energy band structure shows the presence of the highly occupied level of the valence band and the lowest level of the unoccupied conduction bands at the gamma point of the crystalline BZ giving

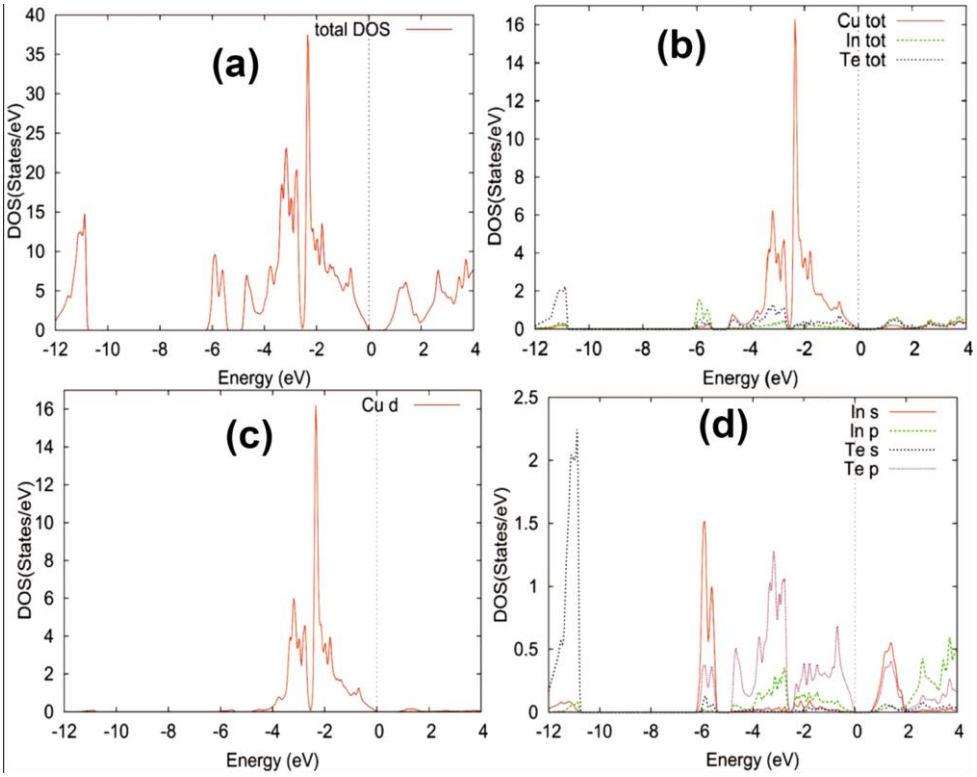

Figure 1. Total and partial density of states.

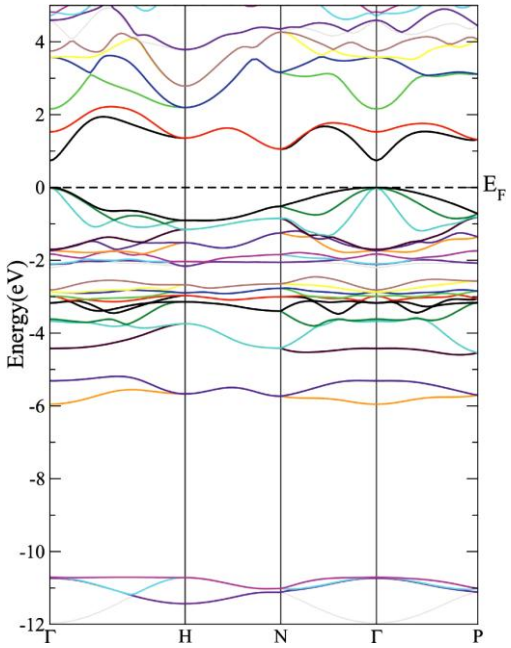

Figure 2. mBJ calculated energy band structure.

an energy band gap of 0.8 eV. The energy band gap of 0.95 eV with values from 0.88 to 1.04 eV have been reported for this compound [26]. However, Xian-Zhou *et al*. [19] have reported the vanishing

energy band gap of this material using PBE-GGA as exchange-correlation functional within the framework of ultrasoft pseudopotential method based on DFT. Rashkeev and Lambrecht [21] have estimated the energy band gap of 0.18 eV from the potential-variational mixed basis based method and LDA approach. It is known that LDA underestimate the band gap but here it is seen that LDA is giving better result than previous GGA estimated result [19]. We found that the mBJ calculated gives the better result as compared to previous LDA and GGA estimated values.

3.2. Optical properties

The understanding of the optical response of the material plays a significant role for the optoelectronic application of the material. The dielectric function, which is the most important parameter to describe the optical response of a material, is given by $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$, where, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function. The scissor shift was used as implemented in the computational code used with energy of 1.06 eV to overcome the discrepancy between the experimental and theoretical values of the energy gap. The frequency dependent dielectric function of $CuInTe_2$ is investigated in the energy range 0.0 -12.0 eV, and presented in Figure 3. In the figure (Figure 3) the dielectric functions are plotted with the incident radiation polarized with both perpendicular and parallel to the tetragonal c-axis of the crystal.

The peaks in the spectra correspond to the transition from the valence to the conduction region of the energy bands. From the energy band structure plot one can say that the peaks below 1 eV of energy are due to the optical transitions from the bands just below the E_F to the bands just above the E_F. Similarly, the optical transitions from the middle of the valence band to the conduction band are responsible for the peaks above 1 eV. In the plot one can find that $\varepsilon_1(\omega)$ shows anisotropic behavior in the whole energy range, whereas $\varepsilon_2(\omega)$ shows anisotropic behavior in the inter-mediate energies. The $\varepsilon_2(\omega)$ plot is characterized by the presence of two sharp peaks and shoulder like structure. The first critical point, which corresponds to the threshold for direct optical transitions between the highest occupied states to the lowest unoccupied states, is located at 1.8 eV. The zero frequency limits, $\varepsilon_1(0)$ is the electronic part of dielectric constant, and its value is obtained to be 7.7 and 7.3 for E||C and $E \perp C$, respectively. The obtained value of $\varepsilon_1(0)$ is lower than the previous experimental value of 9.3 [27]. The $\varepsilon_1(\omega)$ spectrum, after certain energy (5.7 eV and 6.1 eV for E||C and $E \perp C$, respectively) tends to fall below unity, which corresponds to the metallic behavior with high value of reflectivity for the incident electromagnetic radiation. So, this compound can be used as a protection from electromagnetic radiations in the specific energy limits.

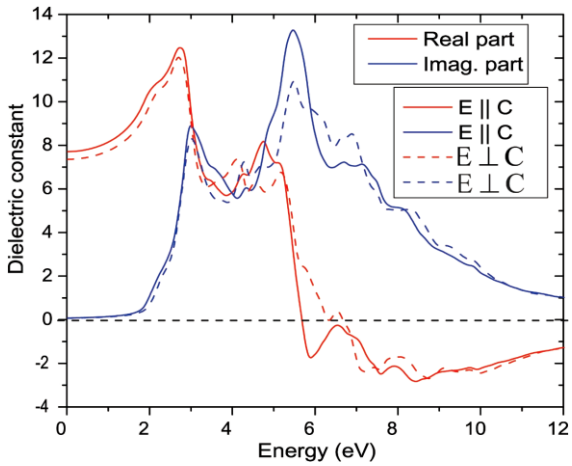

Figure 3. Real and imaginary parts of frequency dependent dielectric constant.

4. Conclusions

The electronic and optical properties of $CuInTe_2$ have been studied by using the first principles calculation. The sample material shows the presence of direct band gap with magnitude of 0.2 eV. The mBJ treatment of the material shows an enhanced value of energy band gap with its value of 0.8 eV, which is close to the experimental result. The investigation of the optical response of the material for the photon energy radiation of infrared to ultraviolet range suggest the metallic nature of the material in the ultraviolet range of radiation with high value of reflectivity.

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References

[1] Shay J L and Wernick J H 1975 Ternary Chalcopyrite Semiconductors: Growth Electronic *Properties, and Applications* (Pergamon Press,Oxford)
[2] Shao L X, Chang K H, Chung T H, Tseng B H, Hwang H L 2003 *J. Phys. Chem.* **64** 1505
[3] Ramanathan K, Hasoon F S, Smith S, Young D L, Contreras M A, Johnson P K, Pudov A O, Sites J R 2003 *J. Phys. Chem. Solid.* **64** 1495
[4] Shay J L, Schiavone L M, Buehier E, Wernick J H 1972 *J. Appl. Phys.* **43** 2805
[5] Wagner S, Shay J L, Tell B, Kasper H M 1973 *Appl. Phys. Lett*. **22** 351
[6] Levine B F 1973 *Phys. Rev.* **B 7** 2600 and references therein
[7] Lin L J , Tabatabaie N, Wernick J H, Hull G W, Meagher B 1988 *J. Elec. Mater.* **17** 321
[8] Mobarak M, Shaban H T 2014 *Mater. Chem. Phys.* **147** 439
[9] Hahn H, Frank G, Klinger W, Merer A and Stroger G 1953 *Z. Anorg. Chem.* **271** 153
[10] Berger L I and Petrov V M 1970 *Neorg. Mater*. **6** 1348
[11] Range K J, Engert G and Weiss A 1969 *Solid. State. Commun*. **7** 1749
[12] Locher P R and Van Stapele R P 1970 *J. Phys. Chem. Solids.* **31** 2643
[13] Koshkin V M, Galchinetski L G, Karas V R, Nesterova T N and Skovskaya I L 1971 *Ukkr. Fiz. Zh.* **16** 1746
[14] Jaffe J E and Zunger A 1984 *Phys. Rev*. **B 29** 1882
[15] Ahuja R, Auluck S, Eriksson O, Wills J M, Johansson B 1998 *Sol. Energy Mater. Sol. Cells* **53** 357.
[16] Zhou H G, Chen H, Chen D, Li Y, Ding K N, Huang X, Zhang Y F 2011 *Acta Phys.-Chim. Sin*. **27** 2805
[17] Laksari S, Chahed A, Abbouni N, Benhelal O, Abbar B 2006 *Comput. Mater. Sci*. **38** 223
[18] Reshak A H, Auluck S 2008 *Solid State Commun*. **145** 571
[19] Xian-Zhou Z, Ke-Sheng S, Zhao-Yong J, Xiao-Fen H 2013 *Comp. Theor. Chem.***1010** 67
[20] Jaffe J E, Zunger A 1984 *Phys. Rev*. **B 29** 1882
[21] Rashkeev S N, Lambrecht W R L 2001 *Phys. Rev*. **B 63** 165212
[22] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D, Luitz J 2014 *An augmented plane wave + local orbital program for calculating crystal properties* Technische Universität, Wien
[23] Perdew J P, Wang Y 1992 *Phys. Rev*. **B 46** 12947
[24] Termsaithong P and Tubtimtae A 2015 *Matt. Lett*. **138** 41
[25] Tran F, Blaha P 2009 *Phys. Rev. Lett.* **102** 226401
[26] Kazmerski L L and Juang Y J 1977 *Journal of Vacuum Science & Technology* **14** 769
[27] Davis J G, Bridenbaugh P M, Wagner S 1978 *J. Electron. Mater.* **7** 39