First principles calculations of structural, electronic and optical properties of AgAlTe₂ compound.

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ABSTRACT

We have conducted a first-principles study on the structural, electronic and optical properties of AgAlTe₂ chalcopyrite compound using the full-potential linearized augmented plane wave (FP-LAPW) method based on the density functional theory. Generalized gradient approximation as proposed by Wu-Cohen (WC-GGA) was used for treatment of exchange-correlation effect in calculations. Additionally, the Tran-Blaha modified Becke–Johnson (mBJ) potential was also employed for electronic properties due to that it gives very accurate band gap of solids. The optimized equilibrium structural parameters (a, c, and u) are in reasonable agreement with theoretical and experimental data. The calculated band structure reveals a direct band gap (Γ-Γ) for the interested compound. Furthermore, optical properties such as complex dielectric function, refractive index and reflectivity spectra of the titled compound were studied and analysed for incident electromagnetic waves in an energy range up to 15 eV. Several calculated results have been compared with available experimental and other theoretical data.

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1. INTRODUCTION

I-III-VI₂ chalcopyrite compounds (I = Cu or Ag; III = Al, Ga, or In; VI = S, Se, or Te) are attractive candidates for photocathodes in photoelectrochemical (PEC) systems because of their high optical absorption coefficients, selectable band gaps as well as some unique electrical and optical properties **[1-5]**. They have attracted considerable attention due to their potential use in optoelectronic and nonlinear optical devices. These kinds of materials have fascinating electronic and optical properties as well as wide transparency band in visible and infrared regions **[6]**. The valance band structure of such compounds is quite favourable for thermoelectric application, and several of them are promising thermoelectric materials **[7].** The silver based Ag-III-VI₂ compounds crystallize in chalcopyrite structure phase with space group No. 122 (I$\overline{4}$2d), which is typically formed by two zinc-blende unit cells with nearly the same arrangement of anions while different cation sites. In solar cell applications, chalcopyrites are predicted to be very efficient and to have a life-time in outer space fifty times as long as that of Si-based solar cells **[8]**. Wide band gap chalcopyrites such as AgAlX₂ (X = S, Se, Te) are difficult to use as single junction solar cells, however, it has been shown recently that the efficiency of a solar cell could be increased by making a tandem (multi-junction) solar cell **[9]**. Moreover, with their low cost, high flexibility and low weight, these materials could make a good alternative to Si-based materials in the electronics industry. Our study is focused on the AgAlTe₂ which belongs to this family of chalcopyrite compounds. In the experimental side, AgAlTe₂ has been widely investigated and was found to be direct band gap semiconductor. From the theoretical point of view, G.M. Dongho *et al* reported first principles calculations of structural, electronic and optical properties of AgAlTe₂ using

the plane wave projector augmented wave method (PAW) **[10]**. The compound AgAlTe$_2$ has been investigated as photocatalyst candidate by means of Vienna Ab-initio Simulation Package (VASP) **[11]**. Saeed Ullah *et al* **[12]** studied the structural, electronic and optical properties of this compound using full potential linearized augmented plane wave (FP-LAPW) method. In this work, the structural, electronic and optical properties of AgAlTe$_2$ compound has been investigated using the density functional theory (DFT) within the full potential linearized augmented plane wave (FP-LAPW) method. In Sect. 2, the theoretical method is introduced and the computational details are given. Results and discussion are given in Section 3. Finally, a summary of our main results is given in Sect. 4.

2. COMPUTATIONAL DETAILS

In this work, the calculations of the structural, electronic and optical properties of AgAlTe$_2$ compound have been performed using the density functional theory **[13,14]** based FP-LAPW methodology **[15]** implemented in the WIEN 2k code **[16,17].** For the structural properties, the exchange-correlation potential was treated by the Wu-Cohen generalized gradient approximation (WC-GGA) **[18]**, whereas for determining the electronic properties, in addition to WC-GGA, modified -Becke-Johnson (mBJ) approach **[19]** was also adopted. This later is well known to reproduce results for band gap energy closer to experimental data. In the FP-LAPW, the primitive unit cell is divided into two regions (non-overlapping muffin tin spheres surrounding the atomic sites and an interstitial region). In both regions, different basis sets were used to expand wave function, potential as well as charge density. In the interstitial region, the plane wave was used as a basis set and in the region of the Muffin tin spheres, spherical harmonic multiplied with atomic-like wave functions were used. To expand the plane-wave basis set, the value of the $R_{MT}K_{max}$ equal to 8 was used (R_{MT} is the smallest muffin-tin radius in the unit cell) whereas the expansion of the wave functions in the atomic spheres, the maximum value of the l is taken as 10. The potential and the charge density were Fourier expanded up to $G_{max} = 12(Ryd)^{1/2}$. The muffin-tin radius R_{MT} was assumed to be 2.20, 2.35 and 2.15 a.u. for Ag, Ga and Te, respectively. Mesh of 35 special k-points was used in the irreducible wedge of the Brillouin zone for the total energy calculation. Both the plane wave cut-off and the number of k-points were varied to ensure total energy convergence.

.3. RESULTS AND DISCUSSION

3.1. Structural properties

As first step in this study, the structural properties of AgAlTe$_2$ compound in the chalcopyrite crystal structure were calculated with the help of WC-GGA. In the chalcopyrite structure, the Ag, Ga and Te atoms occupy the Wyckoff positions (0, 0, 0), (0, 0, 0, 5) and (u, 0, 25, 0, 125), respectively. Thus, the cell energy depends on three geometrical parameters: E = E(a, c, u). We have calculated the energy at different volumes, keeping c/a constant. The c/a ratio is optimized by calculating c/a vs. energy, keeping the volume fixed at its minimal value. The parameter u is minimized by calculating the internal forces acting on the atoms within the unit cell until the forces become negligible by using the MINI program included in the WIEN2K code. The computed total energy-volume data are fitted to the Murnaghan's equation of state **[20]** to determine the ground state properties such as the lattice constant (a), the c/a ratio, the internal structural parameter (u), the bulk modulus (B) and its pressure derivative (B'). The results of our calculations are illustrated and compared with other experimental and theoretical predictions in Table 1. From this Table, the lattice parameters are slightly lower than the experimental ones, whereas they are

Table 1. Equilibrium lattice parameter *a* (Å), c/a ratio, internal parameter u, bulk modulus B (GPa), and its pressure derivative B' of AgAlTe$_2$ compound.

a	c/a	u	B	B'
6.226[a]	1.995[a]	0.25[a]	49.76[a]	4.9[a]
6.296[b]	1.879[b]	0.26[b]		
6.22[c]	1.974[c]	0.26[c]	44.35[c]	5.0[c]
6.288[d]	1.898[d]			
6.427[e]	1.919[e]			

[a] this work, [b]Ref [21] Exp, [c]Ref [22], [d]Ref [23] Exp, [e]Ref [24]

in good agreement with theoretical results **[22]**. For the bulk modulus, it is in reasonable agreement with the available theoretical value **[22]**. On the other hand, the internal parameter u is in nice agreement with the available data **[21,22]**.

3.2. Electronic properties

The study of electronic properties allows interpretation of experimental results and provides important information about the material, which can be used for development of devices based on these materials. In this section, we are interested in the calculation of energy band structure relating to the AgAlTe$_2$ chalcopyrite compound using the optimized lattice parameters. The band structure was calculated along the high symmetry directions in the first Brillouin zone using both WC-GGA and mBJ
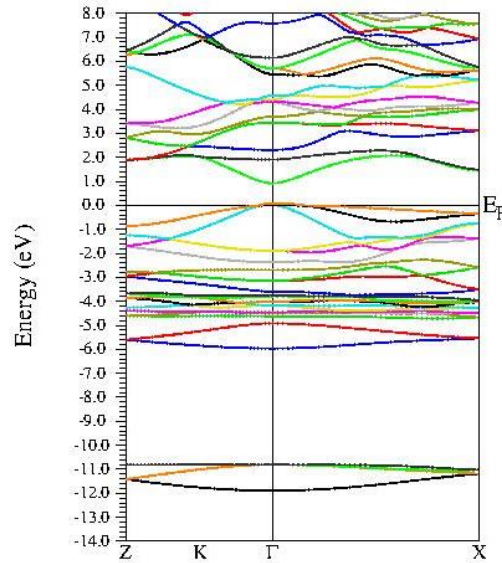

Figure 1: Calculated band structure of AgAlTe$_2$ compound.

schemes, it is presented in Fig.1. It is noted that the maximum valence band (VBM) and the minimum conduction band (CBM) are located at the Γ point, indicating the direct band gap nature of this semiconductor compound. The obtained band gap is shown in Table 2 and compared with available data. The computed band gap with WC-GGA is underestimated compared to experiment; such an underestimation of the band gap value is typical for calculations with the GGA functional **[29]**. However, using mBJ scheme, the band gap is significantly improved and it is in reasonable agreement with the experimental one. The mBJ has proven to be a promising tool for accurate determination of the band gaps of semiconductors and insulators **[30]**.

Table 2. Calculated band gap (eV) of AgAlTe$_2$ along with available theoretical and experimental results

	Pres. work WC-GGA	Pres. work mBJ	Experiment	Other calculations
AgAlTe$_2$	0.92	2.07	2.35[a]	1.59[b], 2.27[c]

[a]Ref [25], [b]Ref [26], [c]Ref [27, 28]

3.3. Optical properties

The study of the optical properties of solids is an important tool for understanding the interaction phenomena of light radiation with matter, including the interaction of photons with the solid. The optical properties of a material are described by the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ **[31]** where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are its real and the imaginary parts, respectively. The imaginary part of the dielectric function could be calculated from the momentum matrix elements of optical transitions

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between the occupied and unoccupied electronic wave functions and the real part can be evaluated from the imaginary part $\varepsilon_2(\omega)$ using the Kramers–Kronig relations [32-34]. All the other optical properties, including the refractive index n(ω), Reflectivity, and the absorption coefficient can be calculated directly from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ [32-34]. For tetragonal crystal systems, we need two tensor components (parallel and perpendicular to *c*-axis corresponding to the electric field) namely $\varepsilon^{//}(\omega)$

and $\varepsilon^{\perp}(\omega)$ to complete the description of optical properties.

For tetragonal crystal systems, we need two tensor components (parallel and perpendicular to *c*-axis corresponding to the electric field) namely $\varepsilon^{//}(\omega)$ and $\varepsilon^{\perp}(\omega)$ to complete the description of optical properties. Fig.2 illustrates for AgAlTe$_2$ the variation of the real part of dielectric function $\varepsilon_1(\omega)$ as a function of photon energy from 0 to 15 eV. It can be seen that the optical spectrum exhibits some anisotropy with regard to the two components of the real part. $\varepsilon_1^{//}(\omega)$ and $\varepsilon_2^{\perp}(\omega)$ are positive up to 4.77 and 5.16 eV, respectively. Beyond these energies, they become negative revealing that in this spectral region, the material has a metallic behavior and the waves do not propagate [35]. Furthermore, in the ultraviolet region where $\varepsilon_1(\omega)=0$, this indicates the absence of dispersion which corresponds to maximum absorption and the reflectivity of the compound is very important. After that, $\varepsilon_1(\omega)$ slowly, increases towards zero at higher energies. The calculated static values of the dielectric function $\varepsilon_1^{//}(0)$ and $\varepsilon_1^{\perp}(0)$ are given in Table 3 and compared to other computed ones. It is well known that a smaller energy gap yields a larger $\varepsilon_1(0)$. This can be explained on the basis of the Penn model [36].

Table3. Calculated static values of optical parameters

$\varepsilon_1^{//}(0)$	$\varepsilon_1^{\perp}(0)$	$n^{//}(0)$	$n^{\perp}(0)$	$R^{//}(0)$	$R^{\perp}(0)$
9.637	9.330	3.104 3.232[a]	3.05	0.262	0.256

[a] Ref[26]

Fig.3 shows the imaginary part of the dielectric function $\varepsilon_2(\omega)$ for the photons energy up to 15 eV. It is seen that the first critical point in this figure occurs at about 0.936 eV using WC-GGA. This point denotes the threshold for direct optical transitions between the highest valence band and the lowest conduction band; known as the fundamental absorption edge, it is closely related to the obtained WC-GGA band gap value of our studied compound. Beyond this critical point, the curve increases rapidly; it is due to the fact that the number of points contributing to $\varepsilon_2(\omega)$ increases sharply, more interband transitions are observed. The main peaks in the curve occur at about 3.76 and 4.17 eV for $\varepsilon_1^{//}(\omega)$ and $\varepsilon_1^{\perp}(\omega)$, respectively. These peaks come from direct interband transitions between the different levels of the valence and the
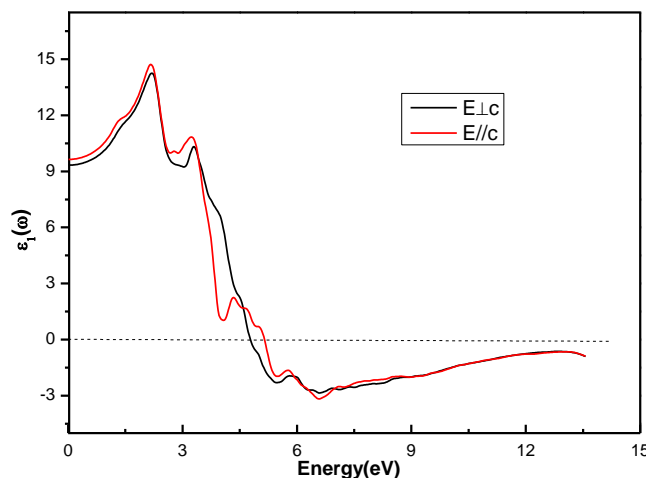

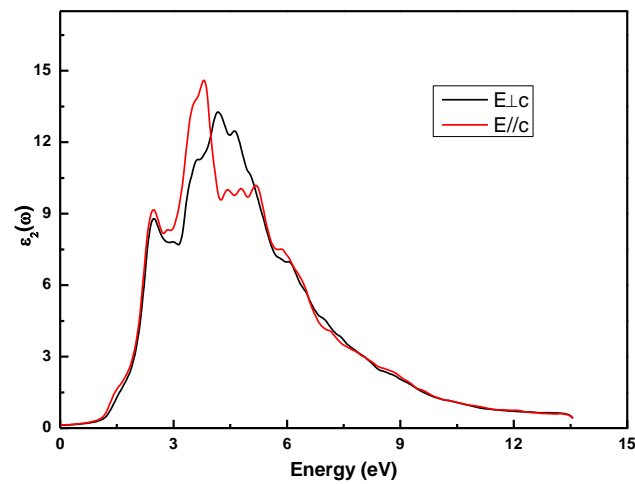**Figure 2:** Calculated real part of dielectric function versus photon energy for AgAlTe$_2$

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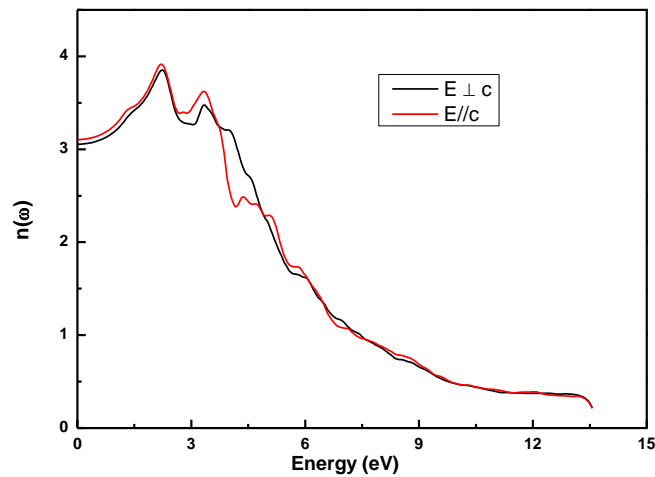**Figure 3:** Calculated imaginary part of dielectric function versus photon energy for AgAlTe$_2$.

Figure 4: Calculated refractive index versus photon energy for AgAlTe$_2$.

conduction bands. The refractive index n (ω) is an essential optical parameter related to the microscopic atomic interaction **[37]**. This parameter has indispensable impact in the investigation of optoelectronic properties. The plots of refractive index n (ω) are displayed in fig.4. From this figure n(ω) has the same isotropic behavior of ε$_1$ (ω). The calculated refractive index values are listed in Table 3. These values are closer to those obtained with the following relation $n(0) = \sqrt{\varepsilon_1(0)}$ **[38]**. The difference Δn = n$_e$-n$_o$ is called birefringence of the of the medium where n$_e$ and n$_o$ represent the refractive indices for an electric field oriented parallel and perpendicular to c-axis, respectively. It is clear that, the refractive index spectrum shows a very weak anisotropy (Δn = 0.054). Beyond the zero frequency limits, the refractive index increases with energy reaching a maximum value in the visible region and finally decreases with the further increase in energy.
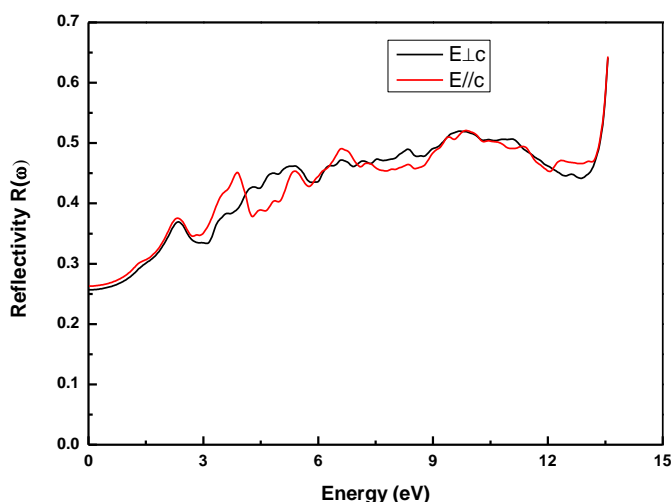
Figure 5: Calculated reflectivity versus photon energy for AgAlTe$_2$.

The reflectivity spectra of this compound starts from the zero frequency which is the static part of the reflectivity. Beyond the zero frequency limit, it increases with the increase in energy having some oscillations. The static values R(0) are given in Table 3. The compound AgAlTe$_2$ shows reflectivity over 50%, therefore the compound can be effectively used for the shielding of high frequency ultraviolet radiations.

4. CONCLUSIONS

The structural, electronic, and optical properties of AgAlTe$_2$ have been studied using FP-LAPW method. The optimized lattice parameters (a, c and u) are in reasonable agreement with available theoretical and experimental data. We have confirmed that AgAlTe$_2$ is semiconductor material. The predict band gap value using mBJ is significantly improved over the WC-GGA and it is closer to the experimental one. The real and imaginary parts of the dielectric function, the refractive index and the reflectivity were determined for energies ranging from 0 eV to 15 eV. We found that the compound shows anisotropy along both ordinary and extraordinary directions of polarization of light. Based on its direct band gap and unique optical properties, the material is very useful for the applications in photonics and optoelectronics.

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