

1. Introduction

The Cu-based chalcopyrite-type (CCP) materials are well-known semiconductors with energy band gap ranging from 1 to 3 eV [1,2]. The band gap range of these materials includes almost all the frequencies of the solar spectrum. Similarly, the semiconducting nature of these materials attracts the present researcher, as these materials find promising applications in solar cells, detectors, nonlinear optical devices and many more. The important application of the chalcopyrite-type compounds includes the energy conversion and serve as photovoltaic and thermoelectric energy converters. Most of the previous studies on CCP systems have concentrated more on the optical properties, which has laid the path for highly efficient photovoltaic and solar energy applications. For example, Cu(In,Ga)Se2 based system is a remarkable solar cell material with an energy conversion efficiency of 20.3% [3–5]. Apart from the photovoltaic and solar energy cell applications, the CCP also possess good thermoelectric (TE) properties. In particular, CuGaTe2 showed a dimensionless figure of merit of $ZT = 1.4$ from experiment [6] and theoretical studies [7,8] reported $ZT$ to be 1.69 at a maximum temperature of 950 K, which is in comparison with the state-of-the-art Bi$_2$Te$_3$ [9] and PbTe-based [10] alloys. Other doping studies are also initiated in order to improve the performance of the CuGaTe2 [11,12]. This motivates the present study of analysing the iso-structural compounds CuAlS$_2$, CuAlSe$_2$, CuAlTe$_2$, CuGaS$_2$ and CuGaSe$_2$ to explore their thermoelectric properties.
properties and we intend to explore the iso-structural compounds CuAlS$_2$, CuAlSe$_2$, CuAlTe$_2$, CuGaS$_2$ and CuGaSe$_2$, which might also show good TE properties. To understand the TE properties of these compounds we have performed a systematic first principle calculations based on the density functional theory. The rest of the paper is organised as follows: Section 2 describes the methodology, and section 3 presents the results and discussions. Conclusions are given in section 4.

### 2. Methodology

Total energy calculations based on first principle density functional theory (DFT) were performed using the full-potential linear augmented plane wave (FP-LAPW) method as implemented in WIEN2k [31]. The total energies are obtained by solving the Kohn–Sham equations self-consistently within the Generalised Gradient Approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [32] and the electronic band structures are calculated using the optimised parameters. The self-consistent calculations included spin-orbit coupling. As it is well known that the calculations using standard local-density (LDA) or Generalised Gradient Approximation (GGA) schemes for the exchange-correlation potential underestimate the band gaps of semiconductors, we have used the Tran-Blaha modified Becke-Johnson [33] potential (TB-mBJ) [34]. We have used plane waves with a cutoff of $R_{MT}$ $K_{max}$ = 7, where $R_{MT}$ is the smallest of all atomic sphere radii, and $K_{max}$ is the plane wave cut-off. The maximum value for the wave function expansion inside the atomic spheres was restricted to $l_{max} = 10$. For k-space integrations, a $20 \times 20 \times 20$ k-mesh was used for CuXCh$_2$ in the Monkhorst-Pack scheme [35], resulting in 641 k-points in the irreducible part of the Brillouin zones for all the compounds, respectively. The crystal structure of CuXCh$_2$ is tetragonal with space group $I\overline{4}2d$ (no. 122). All the calculations were performed with an energy convergence criterion of $10^{-6}$ Ry per formula unit.

The carrier concentration (p for holes and n for electrons) and temperature ($T$) dependent thermoelectric properties like thermopower ($S$), electrical conductivity ($\sigma/\tau$) were computed using BOLTZTRAP [36] code, within the Rigid Band Approximation (RBA) [37–39] and the constant scattering time ($\tau$) approximation (CSTA). According to RBA approximation, doping a system does not alter its band structure but varies only the chemical potential, and it is a good approximation for doped semiconductors to calculate the transport properties theoretically when doping level is not very high [38–42]. However certain dopant can drastically modify the nature of electronic structure near the gap giving rise to resonant states [43,44] in which case, RBA can fail [45]. According to CSTA, the scattering time of the electron is taken to be independent of energy and depends only on concentration and temperature. The detailed explanation about the CSTA can be found elsewhere [18,29,46]. It is evident that CSTA has been quite successful in the past in predicting the thermoelectric properties of many materials [17,27–29,47].

| CuAlS$_2$ | CuAlSe$_2$ | CuAlTe$_2$ | CuGaS$_2$ | CuGaSe$_2$ |
|-----------|-------------|-------------|-------------|-------------|
| a(Å)      | Present     | Exp.        | Present     | Exp.        |
|           | 5.36        | 5.68        | 6.09        | 5.38        | 5.67        |
| c(Å)      | Present     | Exp.        | Present     | Exp.        |
|           | 10.56       | 11.17       | 12.08       | 10.17       | 10.71       |
| u (Internal parameter of Ch) | Present | Exp. |
|           | 0.26        | 0.25        | 0.24        | 0.25        | 0.24        |
|           | 0.275       | 0.269       | 0.25$^b$    | 0.275       | 0.250       |

$^a$ Ref. [49].
$^b$ Ref. [48].

![Fig. 1. Calculated (a) Band structure and (b) Density of states of CuAlS$_2$. The energy zero corresponds to the VBM.](image-url)
3. Results and discussion

3.1. Band structure and density of states of CuAlCh$_2$ and CuGaCh$_2$

The structural properties obtained with optimised lattice parameters and internal positions are given in Table 1, along with the available experimental results. From Table 1, it is evident that the optimised parameters are in good agreement with the available experimental results [48,49]. The band structure of all the compounds are computed using TB-mBJ

![Fig. 2. Calculated Density of states of CuXCh$_2$. The energy zero corresponds to the VBM.](image)

![Fig. 3. Variation of thermoelectric properties of CuAlS$_2$ as a function of temperature.](image)

|               | CuAlS$_2$ | CuAlSe$_2$ | CuAlTe$_2$ | CuGaS$_2$ | CuGaSe$_2$ | CuGaTe$_2$ |
|---------------|-----------|------------|------------|-----------|------------|------------|
| VBM           | 2.24      | 1.11       | 0.44       | 0.89      | 0.56       | 0.40       |
| Γ-N$_{II}$    | 3.84      | 1.69       | 0.63       | 1.29      | 0.46       | 0.46       |
| Γ-Z           | 1.03      | 0.53       | 0.26       | 0.37      | 0.25       | 0.16       |
| CBM           |           |            |            |           |            |            |
| Γ-N           | 0.42      | 0.21       | 0.36       | 0.26      | 0.15       | 0.16       |
| Γ-Z           | 0.83      | 0.20       | 1.98       | 0.25      | 0.15       | 0.15       |

Table 3: Calculated effective mass of Cu-based chalcopyrites in some selected directions of the Brillouin zone in the units of electron rest mass ($m_0$).
exchange correlation functional. The overall profile of the calculated band structures of all the investigated compounds are very similar to each other, and the band structure of CuAlS₂ along the high symmetry directions in the tetragonal Brillouin zone alone is shown in Fig. 1(a). The band structure of CuAlS₂ reveals a direct band gap at the centre of the Brillouin zone \( \Gamma \), which is the same in all the compounds of the present study. The calculated band gaps are tabulated in Table 2 and it is evident that there exist a difference between the calculated and experimental band gaps. But it is to be noted that our band gaps are slightly lower compared with the band gaps of ref. [54] which are also calculated using TB-mBJ functional. The possible reason for this might be due to the inclusion of spin-orbit coupling in the present work. The band found just below the valence band maxima (VBM) arises from the Cu-\( d \) and chalcogen-\( p \) states, and below this lies a band of chalcogen-\( p \) and Al-(Ga)-\( d \) character. The conduction band minima (CBM) is mostly the mixer of chalcogen-\( p \) states with Al-(Ga)-\( p \) states. From Fig. 1(a), the vicinity of VBM is composed of nearly degenerate bands (we call them as upper VBM(I) and lower VBM(II)) with different energies along the high symmetry direction \( \Gamma-N \), while they are degenerate along \( \Gamma-Z \). The inset of Fig. 1(a) show the upper and lower VBM. In the case of CBM there are no such degenerate bands. To explore further about the carriers at VBM and CBM, we have calculated the effective mass of the bands along \( \Gamma-N \) and \( \Gamma-Z \) directions and are shown in Table 3. We note a significant difference in the mass of the carriers of the upper and lower VBM in all the investigated compounds. The difference in the effective mass of VBM(I) and VBM(II) along \( \Gamma-N \) is because of the variation in the dispersion of the bands at the VBM and will serve as mixer of light and heavy bands, which will often be favourable for thermoelectric performance. In the case of the CBM, we find the bands with low effective mass, which might favour high electrical conductivity. The effective mass of the carriers in VBM along both \( \Gamma-N \) and \( \Gamma-Z \) directions is found to decrease from \( S \) to \( Te \) in the case of CuAlCl₂, and also in the case of CuGaCl₂ (see Table 3). This nature is because of the increase in the dispersion of the bands from \( S \) to \( Te \), which can be seen clearly in the density of states. But in case of CBM along both \( \Gamma-N \) and \( \Gamma-Z \) directions the trend is different, the effective mass of the carriers is found to decrease from \( S \) to \( Se \) (in both Al and Ga- compounds) then increase from \( Se \) to \( Te \) in CuAlCl₂.

The Density of States (DOS) of CuAlS₂ is shown in Fig. 1(b) along with the specific contribution of the constituent atoms present in the compound. From Fig. 1(b), it is evident that the VBM is composed of Cu-\( d \) and chalcogen-\( p \) states, whereas in CBM it is composed of chalcogen-\( p \) states with Al(Ga)-\( p \) orbital as discussed earlier in the band structure. The heavy mass carriers at the VBM are responsible for the strong increase in the DOS at the VBM. However, the DOS also rises steeply above the CBM, albeit not as distinctly as around the VBM. We have also shown the DOS of all the compounds in Fig. 2, which shows that the sharp increase in the DOS near the VBM is found to decrease from \( S \) to \( Te \) in CuAlCl₂, which implies a decrease in the effective mass from \( S \) to \( Te \) in case of CuAlCh₂. A similar situation is observed for CuGaS₂ and CuGaSe₂. In case of the CBM there is a steep increase in the DOS of CuAlTe₂ compared to CuAlS₂ and CuAlSe₂ which is because of the increase in

![Fig. 4. Variation of thermoelectric properties of CuAlCh₂ (Ch = Se, Te) and CuGaCh₂ (Ch = S, Se) at 700 K.](image-url)
the effective mass of Te compared to S and Se in CuAlCh2. The combination of light and heavy bands favour better thermoelectric performance, the heavy bands usually contribute to a high thermopower while the lighter bands offer an advantage of high mobility. This will be discussed in the following section.

3.2. Thermoelectric properties of CuAlCh2 and CuGaCh2

The motivation that the mixed nature of the bands might offer a good thermoelectric performance, further lead us to calculate the thermoelectric properties of the CCP. The carrier concentration and temperature dependent TE properties of CuAlS2, CuGaS2 and CuGaSe2 are calculated using BoltzTrap code within the limit of RBA and CSTA as mentioned in section-2. The thermoelectric properties such as thermopower ($S$ in $\mu$ V/K), electrical conductivity scaled by relaxation time ($\sigma/\tau$ in ($\Omega\cdot$ms)$^{-1}$) and power factor scaled by relaxation time ($S^2\sigma/\tau$ in W/mK$^2$s) are calculated for both electron ($n_e$) and hole ($n_h$) concentrations at different temperatures. As the investigated systems are of tetragonal structure, we have also studied the effect of anisotropy in the thermoelectric properties along both $a$ and $c$-directions. The calculated thermoelectric properties of CuAlS2 as a function of both the carrier concentration (electrons on left and holes on right panel) at different temperatures are presented in Fig. 3. From these figures, it is quite evident that there is no signature of bipolar conduction which might be because of the higher band gaps ($>1$ eV) of all the compounds. We intend to look for materials with high efficiency and capable of finding application at high temperature, which lead us to compare the thermoelectric properties of all the compounds at 700 K and are shown in Fig. 4. Thermoelectric properties of CuAlS2 are shown in Fig. 3, and it is evident from the figure that the thermopower is higher in the case of holes (above +700 $\mu$ V/K) compared to electrons (above +600 $\mu$ V/K). We also found that there is small anisotropy in the thermopower values in the case of electron, while $\sigma/\tau$ is found to be more anisotropic in the case of holes compared to electrons, with the value being higher for electrons compared to holes. Although the thermopower is high for the hole carriers, the power factor of CuAlS2 is found to be little higher in case of electrons compared to holes. Similar situation is observed in other compounds also. From Fig. 4, it is clear that the thermopower of holes is found to be more compared to electrons in all the compounds and the same is also found to decrease from S to Te in the case of CuAlCh2 for holes, whereas in the case of electrons it decreases from S to Se and then increases in Te, which might be because of the heavy effective mass of the electrons in CuAlTe2. A similar trend is also seen in CuGaCh2 [7]. The anisotropy is almost similar for both electrons and holes and it is found to increase from S to Te in both CuAlCh2 and CuGaCh2. The values of $\sigma/\tau$ is found to be more along $a$-axis compared to the $c$-axis. Among the CuAlCh2 compounds the power factor of CuAlTe2 is found to be higher compared to the other two chalcogens with electrons as the charge carrier along $a$-axis. All the investigated compounds have shown good TE properties for electrons. The low effective mass for electrons have shown high
Fig. 6. Comparison of (a) thermopower (b) electrical conductivity and (c) electronic part of the thermal conductivity for CuAlTe$_2$ and CuGaTe$_2$ for holes (right) and electrons (left) at a temperature of 700 K.
electrical conductivity leading to high power factor. Hence it implies that the carriers with low effective mass may give a better performance for thermoelectric materials [56].

3.3. Comparison of CuAlTe2 with CuGaTe2

Earlier studies on CuGaTe2 have shown a good thermoelectric figure of merit $ZT = 1.4$ realised experimentally [6] and the theoretical calculations also found a $ZT$ of 1.69 [7]. Along the same line, we have calculated the thermoelectric properties of CuAlTe2 and compared with the isostructural CuGaTe2. We have calculated the thermopower and electrical conductivity scaled by relaxation time of CuAlTe2 as a function of temperature for various levels of doping. The temperature dependent thermoelectric properties of CuAlTe2 are presented in Fig. 5. As mentioned earlier, the anisotropic nature can be seen clearly from this figure along both a and c-axes, and it increases with increase in temperature and doping concentration. We found almost similar thermopower for both electron and hole doping, though a bit higher in holes. However, $\sigma/\tau$ is found to be twice for electrons compared to holes (see Fig. 5). This confirms that the electron as charge carrier is more favourable than holes for CuAlTe2. We compared the thermopower, electrical conductivity ($\sigma/\tau$) and electronic part of the thermal conductivity scaled by relaxation time ($\kappa_{\sigma}/\tau$) of CuAlTe2 and CuGaTe2 along both a- and c-directions, and the same is shown in Fig. 6. From this figure we found that the variation of $\sigma/\tau$ and $\kappa_{\sigma}/\tau$ for both the compounds along a-axis is almost similar, which might allows us to assume the relaxation time of CuAlTe2 to be almost the same as that of CuGaTe2 at 700 K, as it is well known that the electronic part of the thermal conductivity always dominate at high temperature.

Further we also compared the thermopower, electrical conductivity scaled by relaxation time and power factor of CuAlTe2 and CuGaTe2 for both electron and hole carriers at a doping concentration of $10^{19}$, $10^{20}$ cm$^{-3}$ at a temperature of 700 K.

| Table 4 | Comparison of thermopower, electrical conductivity scaled by relaxation time and power factor scaled by relaxation time of CuAlTe2 and CuGaTe2 for both electron and hole carriers.
| --- | --- | --- | --- | --- |
| Concentration (cm$^{-3}$) | 10$^{19}$ | 10$^{20}$ |
| Carriers | Direction | $n_e$ | $n_h$ | $n_e$ | $n_h$ |
| CuAlTe2 | $S$ (\mu V/K) | 398.00 | 358.61 | 360.92 | 386.13 | 281.38 | 183.72 |
| CuGaTe2 | $S$ (\mu V/K) | 1.19 | 0.33 | 1.55 | 0.49 | 5.27 | 3.75 |
| CuGaTe2 | $S/\sigma$ (W/mK) | 0.58 | 0.44 | 0.92 | 0.57 |
| CuAlTe2 | $S/\sigma$ (W/mK) | 0.088 | 0.23 | 0.88 | 0.23 |
| CuGaTe2 | $S/\sigma$ (W/mK) | 0.68 | 0.20 | 0.68 | 0.20 |
| CuAlTe2 | $S/\sigma$ (W/mK) | 0.289 | 0.11 | 0.235 | 0.09 |
| CuGaTe2 | $S/\sigma$ (W/mK) | 0.69 | 0.23 | 0.19 | 0.07 |
| CuAlTe2 | $S/\sigma$ (W/mK) | 0.7 | 0.27 | 0.69 | 0.23 |
| CuGaTe2 | $S/\sigma$ (W/mK) | 0.7 | 0.27 | 0.69 | 0.23 |

4. Conclusion

Electronic structure and transport properties of CuAlCh$_2$, CuGaS$_2$ and CuGaSe$_2$ were calculated within the density functional theory. Electronic structure properties are calculated using the TB-mBJ functional and the obtained band gaps are found to be nearly close to the experimental results and very good in comparison with the other theoretical results. The calculated effective mass of the charge carriers show a combination of mixed light and heavy bands, which would be favourable for the thermoelectric properties. All the investigated compounds are found to be very good thermoelectric materials for electron doping. Among all the compounds CuAlTe2 is found to be more promising candidate for both electron and hole doping. We compare the thermoelectric properties of CuAlTe2 with the iso-structural CuGaTe2, and the results predict almost similar TE properties of CuAlTe2 in line with CuGaTe2, which enable us to predict CuAlTe2 to be yet another promising thermoelectric material. Our study on the Cu-based chalcopyrite semi-conductors has predicted CuAlTe2 to be more promising with both electrons and holes as probable carriers which might enable device applications. We look forward for further experimental studies in this direction.

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