# Thermoelectric properties of CuAlCh 2 (Ch = S, Se and Te)

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# Thermoelectric Properties Of CuAl$Ch_2$ ($Ch$ = S, Se and Te)

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**Abstract.** Electronic and thermoelectric properties of ternary chalcopyrite-type CuAl$Ch_2$ (S, Se and Te) were studied using the first principles density functional calculations implemented in the full potential linear augmented plane wave (FP-LAPW) method. The thermoelectric properties are calculated by solving the Boltzmann transport equation within the constant relaxation time approximation. The calculated band gap using the Tran-Blaha modified Becke-Johnson potential (TB-mBJ), of all the compounds are in good agreement with the available experiment and other theoretical reports. Thermoelectric properties like thermopower, electrical conductivity scaled by relaxation time are calculated as a function of carrier concentrations at different temperatures. The calculated thermoelectric properties are compared with the available experiment and other theoretical calculations of similar materials.

**Keywords:** Electronic structure, Transport properties.
**PACS:** 71, 72

## INTRODUCTION

Chalcopyrite-type materials are well-known semiconductors with energy band gap ranging from 1-3 eV [1-2]. The semiconducting nature of these materials attracts the present researcher, as these materials find promising applications in solar cells, detectors, non-linear optic devices and many more. The important application of the chalcopyrite-type compounds includes the energy conversion and serve as thermoelectric and photovoltaic energy converters. Thermoelectric (TE) materials with potential applications within power generation and refrigeration have been a thrust area of research for the past few decades. The performance of a TE material is reflected in the dimensionless figure of merit, ZT, given by $ZT=S^2\sigma T/\kappa$, where S, $\sigma$, $\kappa$ and T are the thermopower, the electrical conductivity, the thermal conductivity, and the absolute temperature, respectively. $\kappa$ includes both the electronic $\kappa_e$, and the lattice contributions $\kappa_l$, i.e., $\kappa=\kappa_e + \kappa_l$. In recent years different classes of materials were explored for better TE performance. The experiment and theoretical work on the $CuGaTe_2$ has shown ZT to be more than 1.4 at a high temperature of 950 K [3-4]. The work on $CuGaTe_2$ has motivated us to investigate the TE properties of iso-structural CuAl$Ch_2$( $Ch$ = S, Se, Te).

## COMPUTATIONAL DETAILS

The electronic band structures were calculated using the full-potential linear augmented plane wave (FP-LAPW) method based on first-principles density functional theory as implemented in the WIEN2k code [5]. The calculations using standard local-density (LDA) or Generalized Gradient Approximation (GGA) schemes for the exchange-correlation potential underestimate the band gaps of semiconductors, and generally we have used the modified GGA known as the Tran-Blaha modified Becke-Johnson potential (TB-mBJ) [6-7] which is good in reproducing the experimental band gaps. A k-grid of (20x20x20) was used for $CuAlCh_2$. TE properties like thermopower ($S$), electrical conductivity scaled by relaxation time ($\sigma/\tau$) were calculated using the BOLTZTRAP code [8], within the Rigid Band Approximation (RBA) and the constant scattering time (s) approximation (CSTA).

## RESULTS AND DISCUSSION

### (a) Electronic structure properties

The electronic structure properties are initiated with the help of the experimental lattice parameters [9]. All the properties are calculated using TB-mBJ exchange

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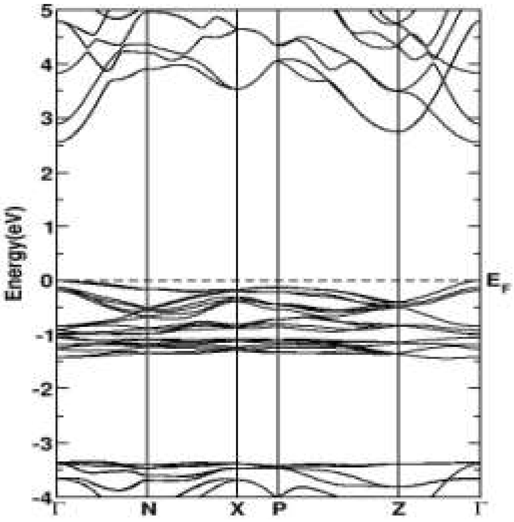
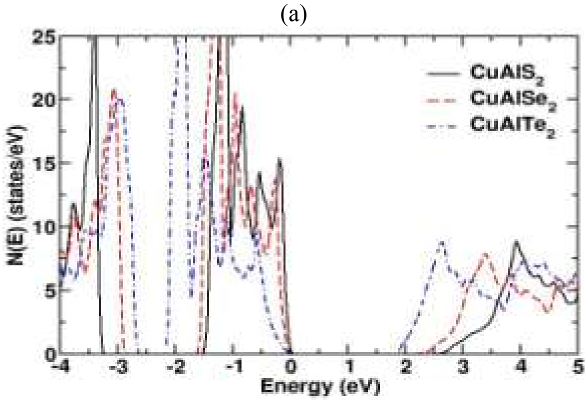
correlation functional. The scenario of the calculated band structures of all the investigated compounds are very similar to each other, so we have given only the band structure of $CuAlS_2$ in Figure 1(a). The band structure of all the investigated compounds shows direct band gap. The calculated band gaps are tabulated in TABLE 1. From the table it is evident that the calculated band gaps are in good agreement with the available experiments and other theoretical values, except for $CuAlS_2$. The nature of band gaps decreasing from S to Te is a peculiar behaviour of the chalcogen group materials [10]. From the large band gaps, it is expected that there should not be any bipolar conduction in the present compounds. The band structure in the vicinity of the valence band maxima (VBM) exhibits a combination of heavy and light bands, which is often favourable for thermoelectric performance. The heavy band found just below the VBM arises from the Cu-d and S-p states, and below this lies the light band of S-p and Al-d states. These heavy bands are responsible for the strong increase in the density of states (DOS) (see Figure 1(b)) at the vicinity of the VBM. The steep increase in the DOS at the conduction band minima (CBM) also resembles the same as that of VBM. This might show a better performance of TE properties for both electron and hole doping. The heavy bands usually contribute to a high thermopower, while the lighter bands offer an advantage of high mobility, a favourable combination often leading to an excellent TE performance of the material.

**TABLE 1.** Calculated bang gap of CuAl*Ch₂* (*Ch* = S, Se, and Te) along with the experiment and other theory

| Eg(eV) | Present | Experiment | Other theory[14] |
|---|---|---|---|
| $CuAlS_2$ | 2.562 | 3.46[11] | 2.7 |
| $CuAlSe_2$ | 2.110 | 2.65[12] | 2.1 |
| $CuAlTe_2$ | 1.863 | 2.06[13] | 1.6 |



(a)

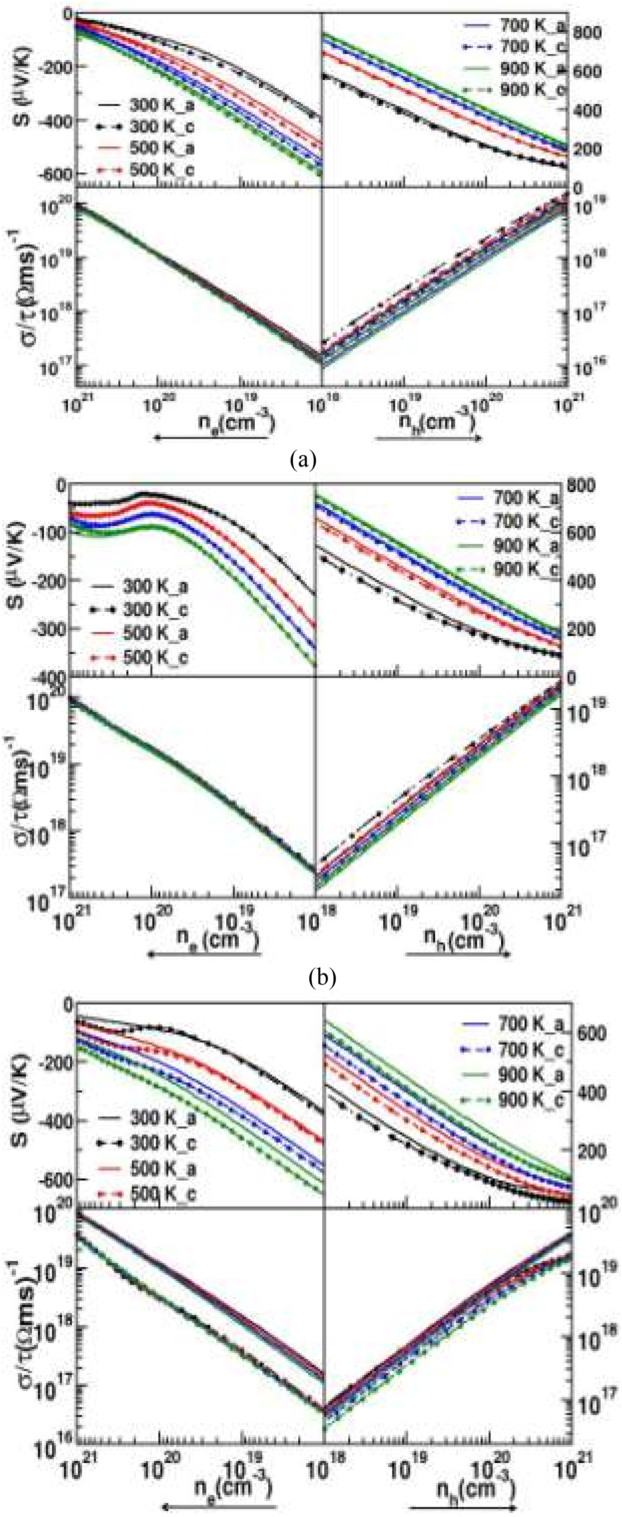


(b)

**FIGURE 1.** (a) Band structure of $CuAlS_2$ and (b) Density of states of CuAl*Ch₂*

## (b) Thermoelectric properties

TE properties of CuAl*Ch₂* are calculated using BoltzTrap code. The thermopower ($S$ in μV/K), electrical conductivity scaled by relaxation time ($\sigma/\tau$ in $\Omega^{-1}m^{-1}s^{-1}$) are calculated for both electron ($n_e$) and hole ($n_h$) doping at different temperatures. As the investigated systems are tetragonal structures, we have also studied the anisotropic nature of the thermoelectric properties in both the directions *a* and *c*. The calculated thermoelectric properties are shown in Figure 2. As these systems are shown to possess relatively larger band gaps, we do not find any signature of bipolar conduction throughout the studied temperature range. From the Figure 2, it is quite evident that all the studied compounds have high thermopower values because of the heavy bands as mentioned earlier. The anisotropic nature of thermopower is very low in the case of S and is found to increase as we move from S to Te for both the carrier concentrations. One can also observe similar situation of anisotropic nature in the case of $\sigma/\tau$ for both the concentrations, but the anisotropic nature is relatively larger in case of electrons compared to the holes. The thermopower values are found to be high for the hole doping in the case of $CuAlS_2$ and $CuAlSe_2$ compared to the electron doping, whereas for $CuAlTe_2$ it is varying almost similarly for both electron and hole doping. This is because of the symmetric nature of the DOS variation in both VBM and CBM. The variation of $\sigma/\tau$ in $CuAlS_2$ and $CuAlSe_2$ is found to be little high in the case of electron doping compared to the hole doping. We are trying to predict the value of the figure of merit from our earlier study on the iso-structural compound $CuGaTe_2$. We have taken the carrier concentration, thermal conductivity and relaxation time of $CuGaTe_2$ at a temperature of 950 K and predicted the value of the ZT for all the investigated compounds.



(a)

(b)

(c)

**FIGURE 2.** Variation of thermopower, electrical conductivity per relaxation time with respect to electron (left) and hole (right) concentrations (a) $CuAlS_2$ (b) $CuAlSe_2$ and (c) $CuAlTe_2$

It is found that the ZT of S is found to be more in the case of electron doping ZT=1.7, whereas for hole it is 0.31 in the a-axis. For Se it is found to 0.61 and 0.67 for a and c-axis, respectively for hole doping. For Te it is found to be 0.94, 0.51 for a-axis and 1.77 and 0.723 for c-axis, for hole, electron doping respectively. The estimated values of ZT of $CuAlS_2$ and $CuAlTe_2$ are almost similar to that of $CuGaTe_2$. All the investigated compounds show a promising value of ZT, among them $CuAlS_2$ and $CuAlTe_2$ are best candidates for the better thermoelectric applications with electron doping. We hope that our work will stimulate the experimentalist to explore more in this direction.

## CONCLUSIONS

The electronic structure and thermoelectric properties are calculated for the chalcopyrite-type compounds of $CuAlCh_2$. The calculated band gaps are in good agreement with that of the available experiment and other theory reports. The band structure of $CuAlCh_2$ shows the direct band gap semiconductors. The heavy and light band mixer shows the investigated compounds are good candidates for the TE applications. The calculated thermoelectric properties show the anisotropic nature to increase as we move from S to Te. Among the studied compounds it is seen that $CuAlS_2$ and $CuAlTe_2$ are the good candidates for the better thermoelectric application with electron doping.

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