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A Study of the Electronic Band Structure of Cu_4SnS_4

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Abstract

The electronic band structure of thin film of the orthorhombic Cu_4SnS_4 using the pseudopotential method within density functional theory framework was performed. LDA+U technique and the projector augmented wave PAW was used in all the calculations. The calculated results showed that Cu_4SnS_4 is p-type semiconductor with a band gap energy value of 1.57 eV. It was also discovered that the gamma to X transition was critical in the structure of the material.

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Introduction

Ternary semiconductors are gaining ground as materials of choice in optoelectronic. Some of these materials contain toxic components examples are cadmium (Cd) and lead (Pb) based cells. A typical Pb based material is the $PbSnS_3$, which have also attracted both experimental (Paar *et al.*, 2000; Kuku and Azi, 1998; Kuku *et al.*, 2006) and theoretical investigation (Omehe *et al.*, 2013). The Cu-Sn-S system is an alternative with prospect (Wu et al, 1986).

Materials in the system includes $Cu_2Sn_3S_3$, Cu_2SnS_3, Cu_4SnS_4 and $Cu_{10}Sn_2S_{13}$. In this study, we shall investigate the electronic band structure Copper Tin Sulphide Cu_4SnS_4 (CTS). It has attracted its own fair share of experimental and theoretical studies. Cu_2SnS_3 was synthesized by Wu *et al.* (2007) and the experimental results did give the unique metallic character of hexagonal Cu_2SnS_3. Avellaneda *et al.* (2010) deposited thin films of copper sulphide (CuS, 200nm thick) over thin films of Tin Sulphide (SnS, 180nm thick) by sequential chemical deposition. The layers were heated in nitrogen atmosphere at 350°c and 400°c. The grazing incidence x-ray diffraction analysis revealed ternary composition, Cu_2SnS_3 and Cu_4SnS_4. The optical band gaps of the films are direct, 0.95eV for Cu_2SnS_3 and 1.2 eV for Cu_4SnS_4. Fernandes (2010) grew CTS ternary chalcogenide compounds by sulphurization of demagnetron sputtered metallic precursors. Cu_2SnS_3 was formed at a maximum sulphurization temperature of 350°c while Cu_4SnS_4 was obtained at a sulphurization temperature of about 400°c. The estimated band gap values were between 1.0 eV to 1.6 eV. Using the direct-coating from single metal organic precursor solution, Tiweri *et al.* (2013) deposited Cu_2SnS_3 thin films with a band gap of about 1.12 eV. Guan *et al.* (2013) deposited Cu_2SnS_3 and Cu_4SnS_4 thin films by successive ionic layer absorption and reaction method. A band gap value of 1.05 eV was obtained for tetragonal Cu_2SnS_3. Anuar *et al.* (2008) investigated the effect of varying the electrolytes concentration on the film's properties. The resulting substrate was analysed using X-ray diffraction technique. Their results show CTS to be p-type semiconductor band gap energy of 1.7 eV. In a related study (Anuar *et al.*, 2010), they studied the effect of deposition time on the crystal's properties. They reported a band gap value of about 1.6-2.1 eV. The co-evaporation method was used by Vani *et al.* (2013) to study the effect of temperature variation on the properties of CTS. The Phillips' X-ray diffractometer was used in analyzing the structural properties of the film. Band gap values of about 1.7 to 1.94 eV were observed.

The electronic structure of orthorhombic CTS was investigated by Goto *et al.* (2013) within the framework of the density functional theory (DFT) using the projector augmented wave (PAW) method. For exchange and correlation, they used the pedew-Burke-Ernzerhof parametrization (PBE). Their calculated band gap value was 0.39 which fall short of the experiment value.

In this study, we intend to investigate the electronic band structure of Cu_4SnS_4 using PAW in conjunction with the LDA+U scheme. To the best of our knowledge, this is the first time a theoretical investigation of the electronic band structure would be carried out on CTS.

Methods

Cu_4SnS_4 belongs to the orthorhombic structure with the space group Pnma (space group number 62). The lattice parameters and atomic coordinates shown in table 1 were adopted from (Goto *et al.*, 2013). The Wyckoff's atomic positions are shown in Table 1. The unit cell is made up of four formula unit, which gives a total of 36 atomic coordinates in seven (7) types. The structure of Cu_4SnS_4 used in this calculation is shown in Figure 1.

The paw for Cu contains the 3s and 3p electrons as semi core. The band structure calculations utilized the LDA+U technique within the DFT framework as implemented in the abinit package (Gonze *et al.*, 2002; Gonze *et al.* 2005).

Table 1: Lattice parameters and Wyckoff's atomic positions

a = 1.3608 nm, b = 0.7690 nm and c = 0.6482 nm

Atom	*x*	*Y*	*z*
Cu1	0.3341	0.9894	0.1182
Cu2	0.3375	0.25	0.5669
Cu3	0.4286	0.25	0.9017
Sn	0.083	0.25	0.1144
S1	0.1761	0.9964	0.2586
S2	0.0824	0.25	0.7288
S3	0.4094	0.25	0.2514

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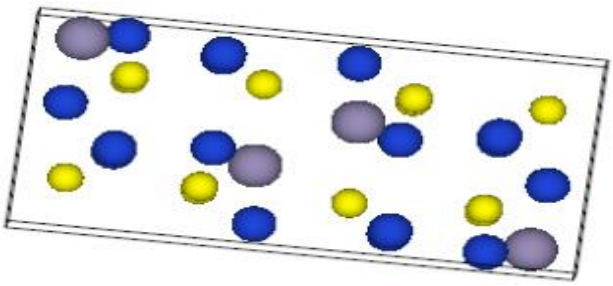

Figure 1: The structure of CTS used in this work. The blue balls represent Cu, the yellow balls represent S and the gray balls represent Sn.

A kinetic energy cutoff of 20 Ha was used for the generation of plane waves. For the k-points, a Monkhorst-Pack (1976) grid of 6x6x1 was used for Brillouin zone integration.

Results

Figures 2, 3 and 4 displays the electronic band structure of CTL within the energy range of -85 to 3 eV along lines of high symmetry in the Brillouin zone. Figure 5 shows the total density of states (TDOS) with its Fermi energy level at 0.1 Ha while figures 6 to 12 display the partial density of states (PDOS) for CTS.

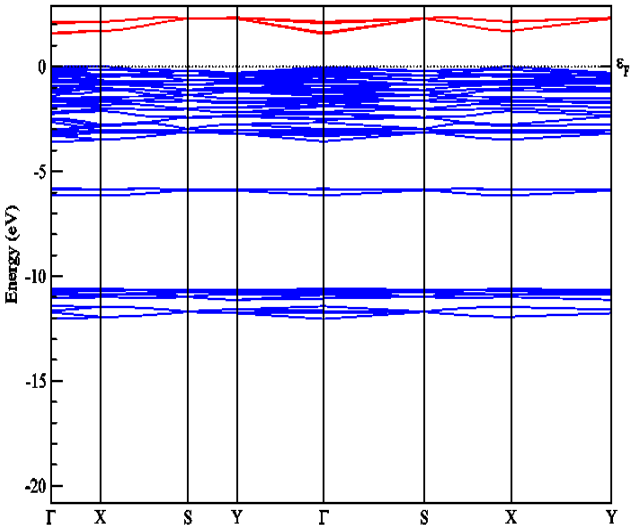

Figure 2: The electronic band structure of CTS from -20 to 3 eV

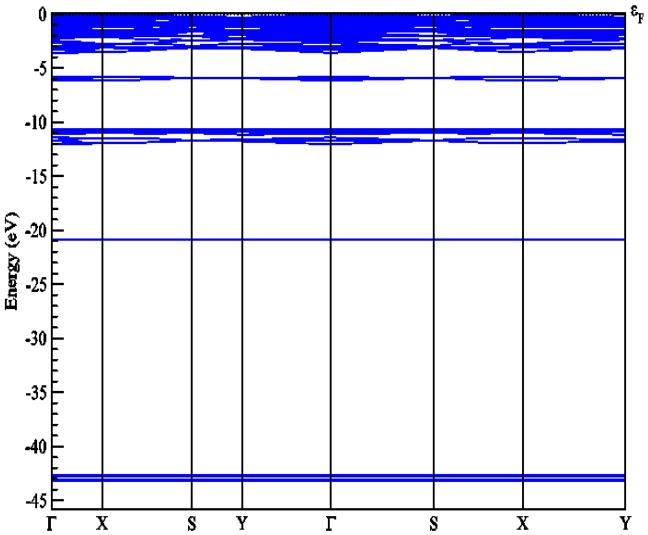

Figure 3: The electronic band structure of CTS from -45 to 0 eV

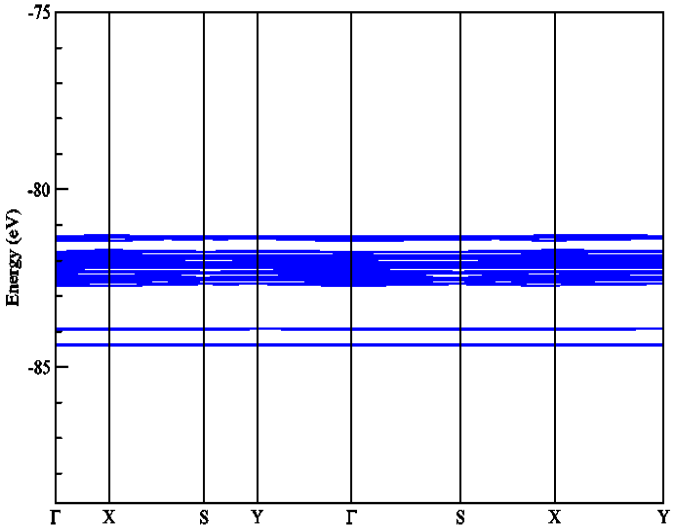

Figure 4: The electronic band structure of CTS from -85 to -75 eV

Figure 5 shows the total density of states, the band gap value is also well reproduced in the TDOS. Our calculated TDOS differ quantitatively and qualitatively from that of (Goto *et al.*, 2013).Figures 6 to 12 displays the partial density of state (PDOS) for CTS, these represent the contribution to TDOS from the various atomic species used in the computations. The Cu-3s and Cu-3p states contribution to TDOS can be seen about the energy range of -3 to -2.8 Ha. These contributions are from the three Cu types as seen from figures 6 to 8. The S-3s dominates the states about the -1.5 Ha to -0.65 Ha energy range. The states immediately below the Fermi level are mainly Cu-3d, S-3p, Sn-5s and Sn-4d orbitals. The conduction band is predominantly contributions from Sn-5s and S-3p orbitals.

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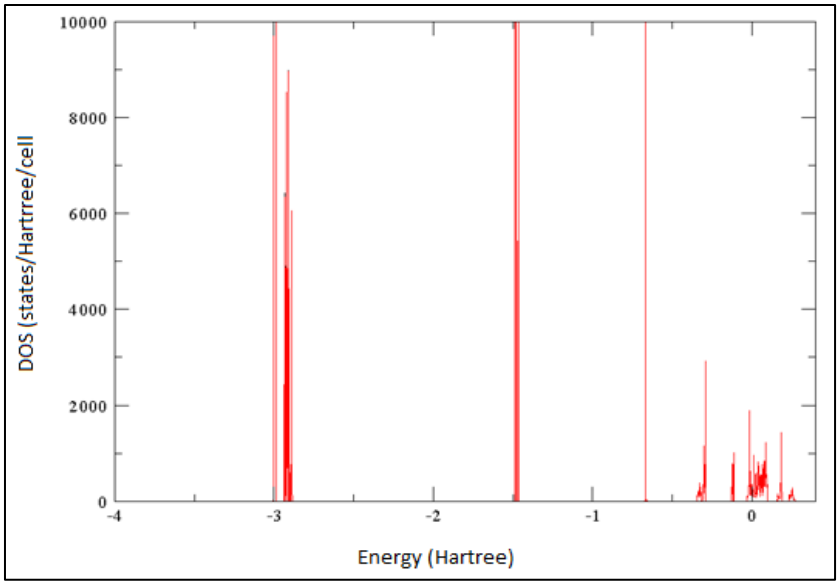

Figure 5: The total density of states for Cu_4SnS_4. The Fermi energy is 0.1 Ha.

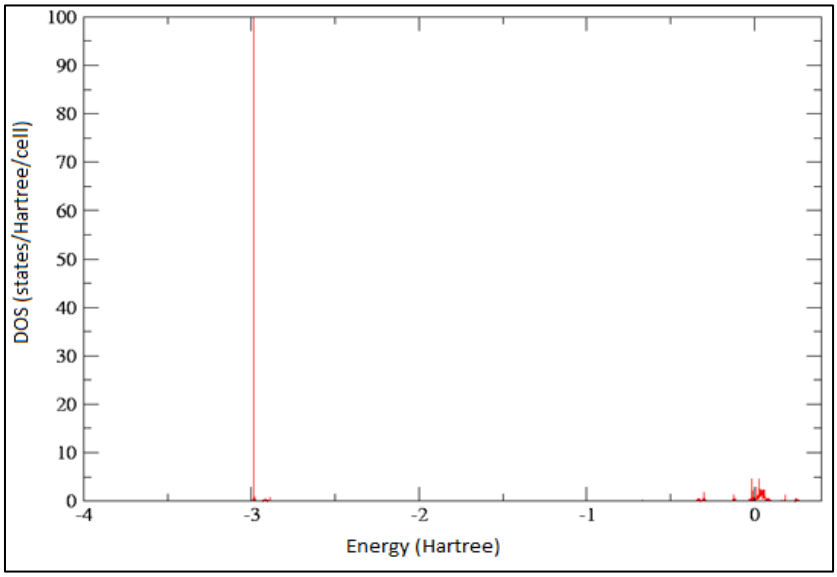

Figure 6: The partial density of states for Cu(1). The Fermi energy is 0.1 Ha.

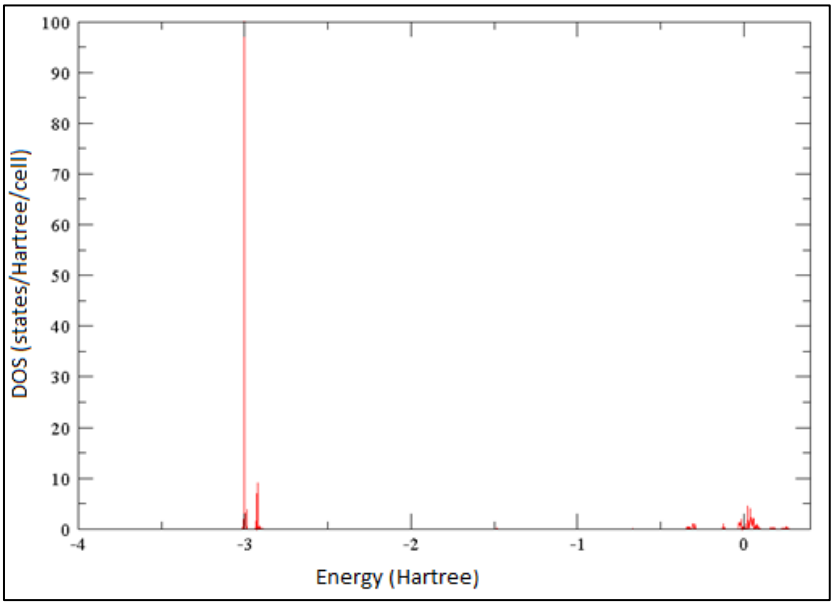

Figure 7: The partial density of states for Cu(2). The Fermi energy is 0.1 Ha.

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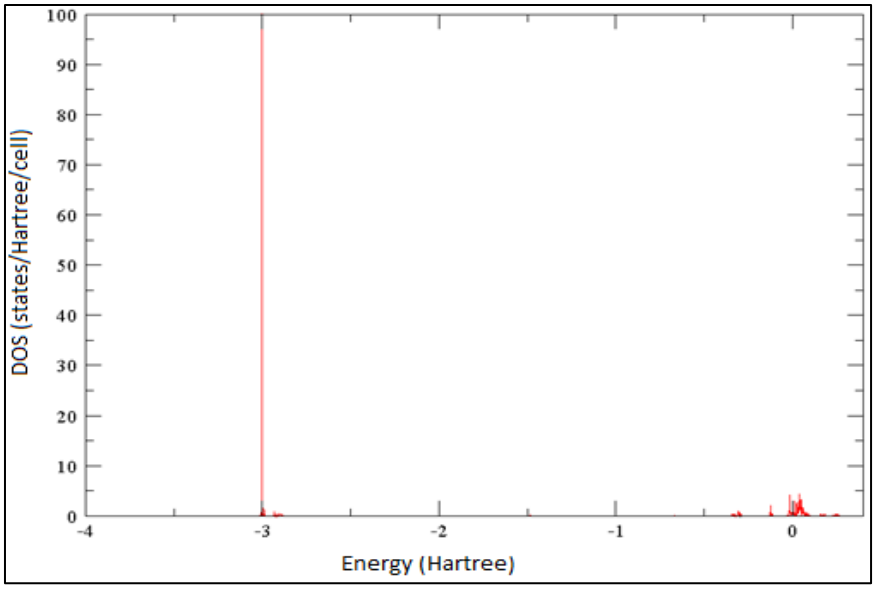

Figure 8: The partial density of states for Cu(3). The Fermi energy is 0.1 Ha.

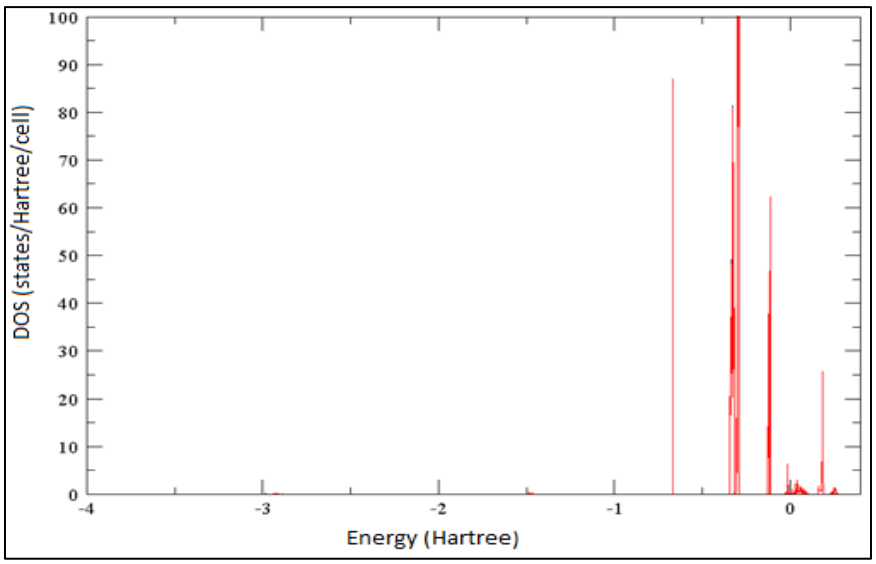

Figure 9: The partial density of states for S(1-3). The Fermi energy is 0.1 Ha.

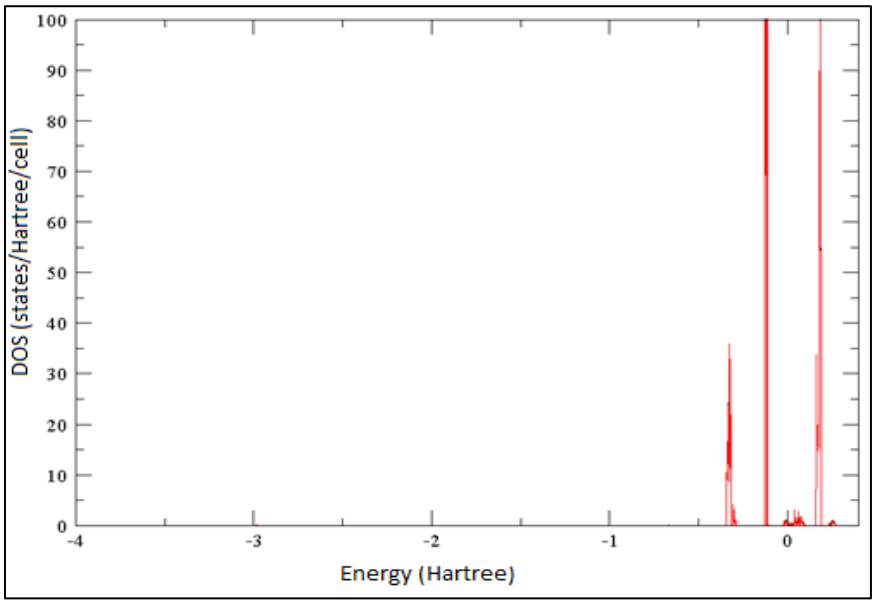

Figure 10: The partial density of states for Sn. The Fermi energy is 0.1 Ha.

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Discussion

It can be seen that, the valence band maximum (VBM) and the conduction band minimum (CBM) are located at the gamma point resulting in a direct energy gap of 1.57 eV (Figures 2 - 4). The CBM occur at both the gamma and the x-points of high symmetry. This makes it a critical transition in the structure. It may also indicate the material's versatility, that is, it can be used for applications requiring direct and indirect band gaps. The direct band gap of 1.57 eV is in agreement with the experimental results. This result is an improvement over the LDA results of 0.39 eV obtained by Goto *et al.* (2013). This is as a result of the addition of the U term to the LDA. Gunnarsson and Schonhammer (1986) showed that the discontinuity in the one-electron potential can give a large contribution to the band gap. To overcome this deficiency, an orbital dependent correction is added to the LDA potential. This induces an upward shift of the unoccupied states and a downward shift of the occupied states. The screen coulomb interaction U and the exchange parameter J used in the calculations were taken from (Marel and Sawatzky, 1988).

Conclusion

The electronic band structure of Cu_4SnS_4 (CTS) has been carried out using the LDA+U technique in conjunction with the projector augmented wave (PAW). This work was done within the framework of the density functional theory (DFT). It was observed that CTS is an n-type semiconductor with a band gap energy value of 1.57 eV.

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