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Electronic Band Structure of Copper Zinc Tin Sulphide (Cu_2ZnSnS_4).

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Abstract: *Cu_2ZnSnS_4 (CZTS), made entirely of abundant materials, has attracted a great interest due to its potential applications in sustainable thin-film solar cell devices. The electronic band structure of kesterite Cu_2ZnSnS_4 compound has been calculated using the pseudo-potential method. Projector augmented waves (PAW) within the density functional theory (DFT) was used in all calculations using local density approximation (LDA) for one calculation and inclusion of potential correlation term, U to LDA (i.e LDA + U) in another calculation. The results predicted Cu_2ZnSnS_4 to be a p-type semiconductor with bandgap value for (1) LDA as 0.039 eV and (2) LDA + U as 1.83 eV. This bandgap value of 1.83 eV is in agreement with experimental results and it confirmed the material as a good absorber layer for solar cells. The density of states (DOS) showed that the conduction band was mainly contributions from Sn-5p and Zn-4s orbitals. It is recommended that the orbital independent term, U be added to LDA during calculations because it improves the bandgap value.*

Keyword: *Cu_2ZnSnS_4, band structure, band gap, density of states.*

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I. Introduction

Power generation through photovoltaics (PV) has been growing every year over the last decade by means of solar cells. Solar cells are classified into first-generation, second-generation and third-generation. The first-generation solar cells are based on silicon wafers. Silicon is still used extensively in solar cell devices, even though it has many limitations, such as silicon not being an efficient material because of its indirect bandgap which leads to low efficiency of absorption of solar radiations in visible and near infrared [1]. Although, it is expensive but its extensive use can be attributed to the fact that silicon technology was among the first at the time of development of PV devices [2]. The second-generation solar cells are less material intensive and avoid the use of silicon wafers. They have lower manufacturing costs. These include devices based on amorphous-silicon, CdTe, $CuInS_2$ and Cu(ln,Ga)(S,Se). However, these solar cells have several shortcomings based on their potential environmental hazard issues and scarcity [3]. Recently research trends are moving toward finding alternatives based on earth-abundant and non-toxic elements for fabricating solar cells. These are the third-generation solar cells. All solar cells are based on semiconductors and they convert radiation into electricity. Cheaper and potentially more cost-effective materials are formed by replacing In (III) with Zn (II) and Ga (III) with Sn (IV) in Cu_2InGaS_4 (CIGS) to give Cu_2ZnSnS_4 (CZTS), because In and Ga are expensive and rare metals. This interesting I_2-II-IV-VI_4 group semiconductor has great potential with a useful bandgap of 1.4 – 1.5 eV, a large absorption coefficient of over $10^4 cm^{-1}$ and is devoid of notably toxic or expensive elements [4].

CZTS is a heavy-fermion quartenary compound characterized by kesterite or stannite structure. It belongs to the family of semiconductor chalcogenide composition containing only non-toxic and earth-abundant elements, and hence it is widely used in developing environmental sustainable processes and devices such as solar cells and optoelectronics [5]. The crystallographic structure of kesterite Cu_2ZnSnS_4 is shown in figure 1.

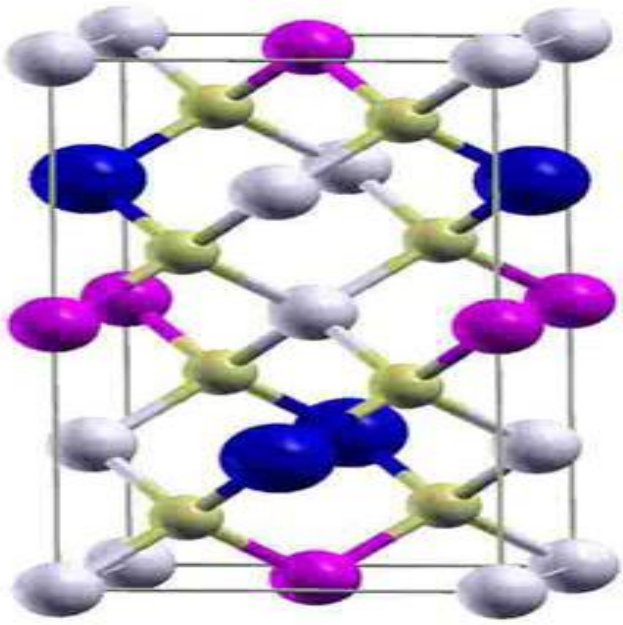

Fig 1. Crystallographic structure of kesterite Cu_2ZnSnS_4 (Cu-blue,Zn-Grey, S-Purple, S-yellow).

Optical properties of solar cell thin films such as bandgap energy of about 1.5 eV and a large absorption coefficient in the order of 10^4cm^{-1} for Cu_2ZnSnS_4 could be fabricated under Cu-poor and Zn-rich conditions in the CuS-ZnS-SnS system [6]. Fabricated Cu_2ZnSnS_4 thin films by co-sputtering Cu, ZnS and SnS compounds and sulfurizing it in $H_2S$to investigate the effect of annealing time on the composition microstructure and band gap. The optical bandgap varied from 1.67 – 1.51 eV with increase in the sulfurization time which showed that the presence of impurities can alter the band gap [7]. Cu_2ZnSnS_4 thin films were prepared using sol-gel spin-coated deposition. The Cu_2ZnSnS_4 having texture surface structure with thickness 3µm at 320^0c was obtained. The optical energy gap was about 1.5 eV and the average optical absorption co-efficient was $2.4x10^4cm^{-1}$. The high absorption band of the film covers most of the solar irradiation spectrum, thus making Cu_2ZnSnS_4 thin films potential material for solar cells [8]. A two-step process consisting of co-sputtering and subsequent sulphurization by heating at 520^0C in sulphur atmosphere to fabricate Cu_2ZnSnS_4 thin films. It was discovered to be a semiconductor with a direct bandgap of about 1.5 eV and absorption co-efficient of 10^4cm^{-1}, and for this reason, a potential thin film material for solar cells. The demonstrated efficiency of up to 6.8% makes it a good absorber layer [9]. Thin films from Cu_2ZnSnS_4 nanocrystals were deposited in Mo-coated quart-substrates using drop-casting at temperatures as low as 400^0C. It was reported that a high absorption co-efficient of the order of 10^4cm^{-1}, with energy bandgap of≈1.5 eV and conversion efficiency greater than 10% were obtained [10]. Cu_2ZnSnS_4 thin films were formed by thermal annealing layers of Cu, Zn,Sn and S on glass substrate at different substrate temperatures (between 370^0C and 390^0C) and revealed that the films have the dominant structure of kesterite with possible inclusions of stannite, giving their respective absorption co-efficients as $353cm^{-1}$ and $332.7cm^{-1}$.The energybandgap obtained was about 1.3eV which is smaller than the values expected from pure kesterite structure[1].

First principles calculations of defect formation in in-free photovoltaic Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ semiconductors using plane-wave pseudo-potential method. Cu_2ZnSnS_4 – based solar cells with high efficiency of 6.7% were fabricated under Cu-poor, Zn-rich and S(Se)-rich conditions. These were more difficult in $Cu_2ZnSnSe_4$ [11]. Many works have been done fabricating Cu_2ZnSnS_4 using various physical and chemical deposition methods. But to date, there is sparse report in literature on the theoretical calculations of any of the phases of Cu_2ZnSnS_4 thin film properties. This study is therefore aimed at calculating the electronic band structure of Cu_2ZnSnS_4 to predict the correct bandgap and other physical properties that have been observed experimentally using the pseudo-potential method.

Computational Details

Cu_2ZnSnS_4 belongs to the kesterite structure with space group number 82. The lattice parameters a and c were taken from [11]. Table 1 shows the adopted parameters. Figure 1 shows the structure used in this work.The calculations were performed using the pseudo-potential method. Projector Augmented Waves (PAW) was usedfor the LDA+Uscheme while norm-conserving pseudoptentials wereused for the localdensity approximation (LDA) calculations. Some semi-core states were included in the PAWs. For Cu, the $3s^2$ and $3p^6$ states were included. The same was done for Zn, while the $4d^{10}$ was included for Sn. The calculations were all

based on the density functional theory (DFT) framework as implemented in the Abinit package [12, 13]. The calculations involved solving the Schrödinger wave equation using the self-consistency field theory (S-CFT) giving the eigenvalue, which is the energy of the Hamiltonian. A kinetic energy cut-off of 20 Ha was used for the generation of plane waves.For the k-points, a Monkhorst-Packgrid [14] of 6x6x1 was used for Brilliouin Zone (BZ) integration. The self-consistent ground state computation was deemed to have converged when the energy tolerance of 10^{-8} was achieved. The wave function and density were used to compute the energy bands, density of states (DOS) and partial density of states.

Table 1. Lattice Parameters of Cu_2ZnSnS_4

Cu_2ZnSnS_4	a (Å)	c (Å)	*c/a*
Theoretical	**5,465**	**10.944**	**2.00**
Experimental	**5.434**	**10.856**	**2.00**

(Source: referenced 11)

II. Results and Discussions

Figure2 displays the result of the LDA computations of electronic band structure calculation of Cu_2ZnSnS_4. The valence band maximum (VBM) and conduction band minimum (CBM) are both located at the Γ point of high symmetry, resulting in a p-type semiconductor with a direct band gap value of 0.039 eV. The compound under study is a p-type semiconductor because the valence band is closer to the Fermi level (ε_f) than the conduction band. Figure 3 shows the electronic band structure calculation of Cu_2ZnSnS_4 compound using LDA + U. The VBM and CBM are both located at the Γ point of high symmetry, resulting also in a p-type semiconductor with a direct band gap value of 1.83 eV. This result of 1.83 eV is in agreement with the experimental works of [6, 7, 9, 10]. The introduction of the U term into the calculations resulted in an upward shift of the conduction band. Figure 4 shows the total density of states (TDOS) from the LDA+U computation. The Fermi energy is 0.1 Ha and the band gap value is clearly reproduced as in the electronic band structure shown in figure 1.

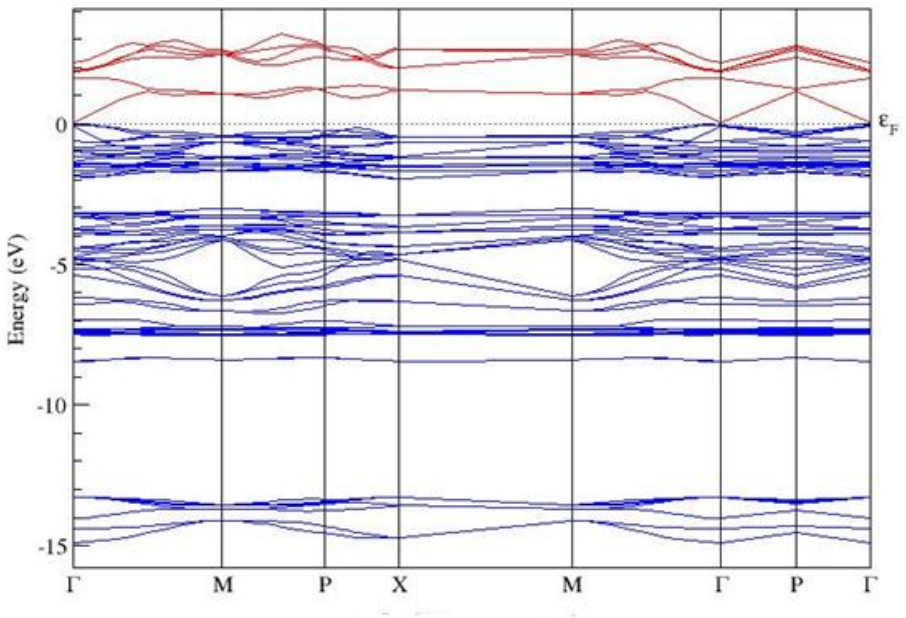

Fig 2. Electronic band structure of Cu_2ZnSnS_4compound using LDA

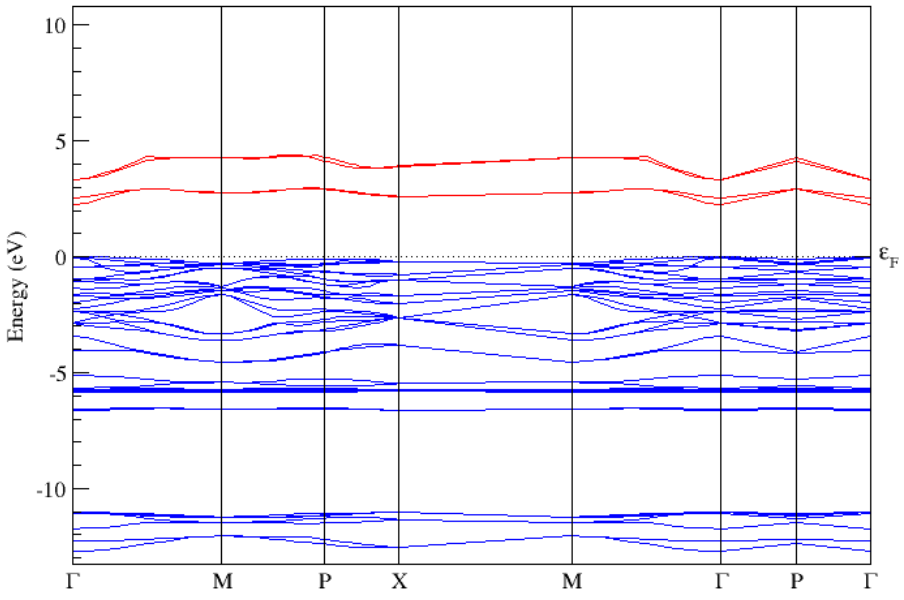

Fig 3. Electronic band structure calculation of Cu_2ZnSnS_4 compound using LDA + U.

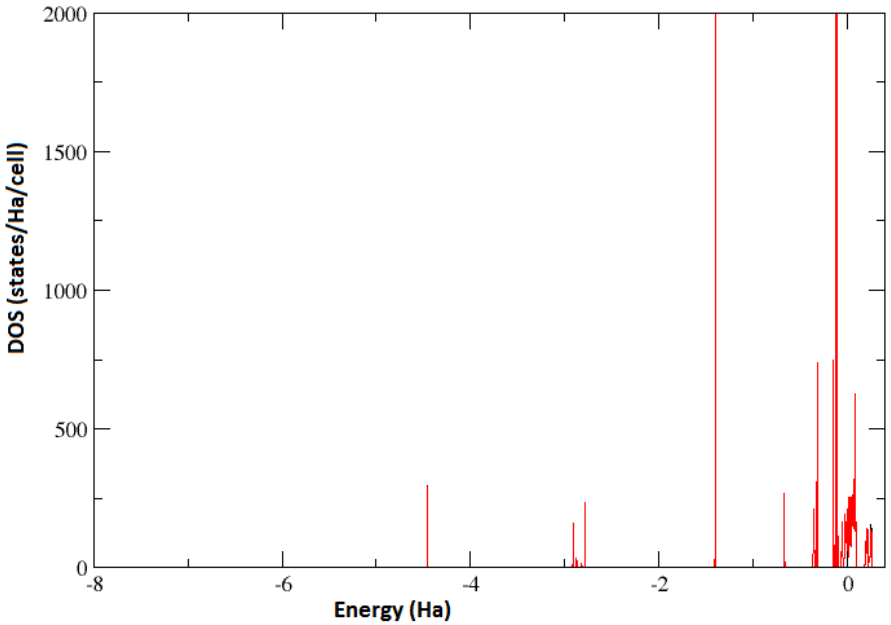

Fig. 4 Total density of states (TDOS) using LDA+U. The Fermi energy is 0.1 Ha.

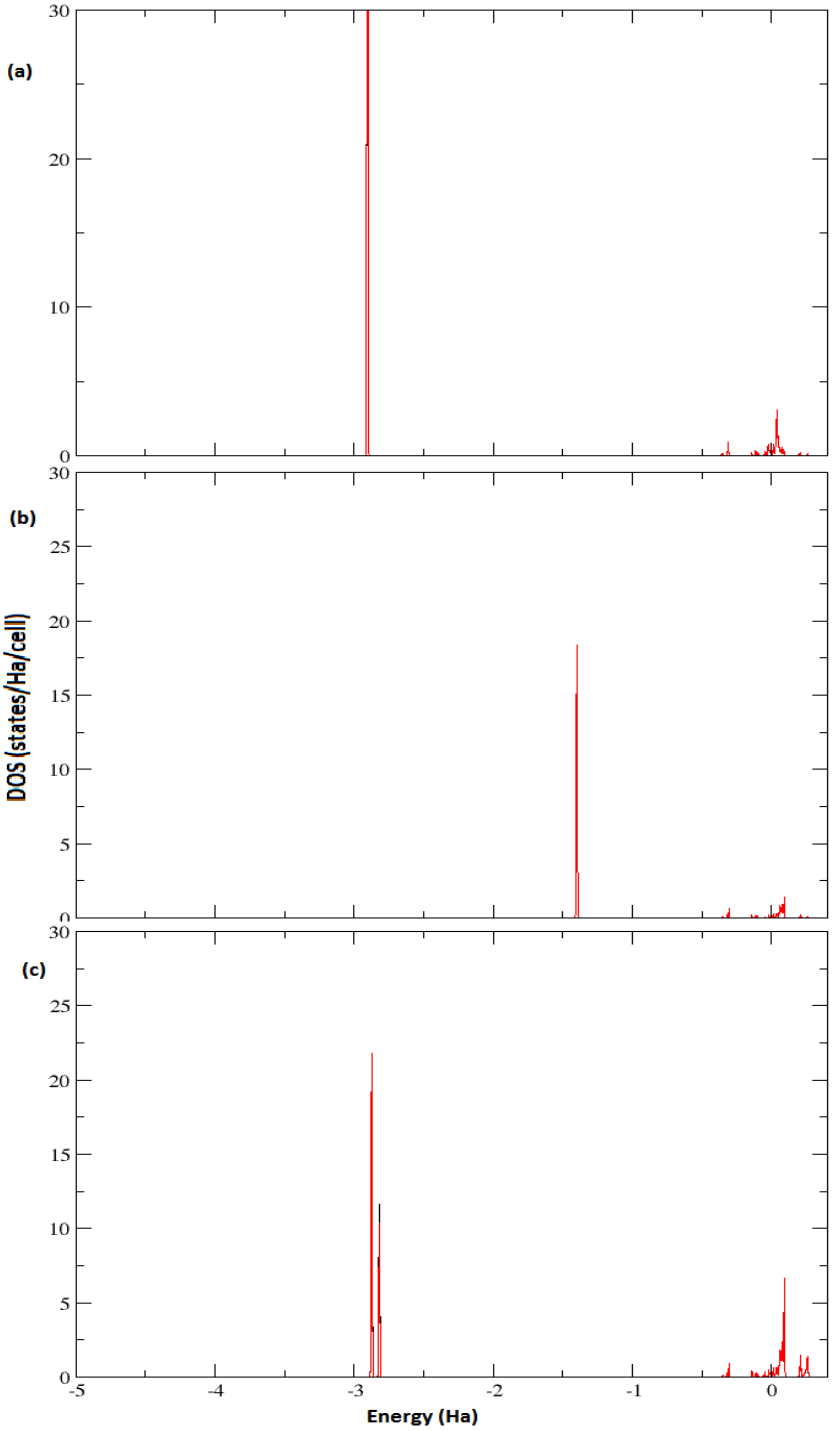

Figure 5: The orbital contribution to the density of states from the Cu atoms (a) Contributions from the Cu-s orbitals. (b) Contributions from the Cu-p orbitals. (c) Contributions from the Cu-d

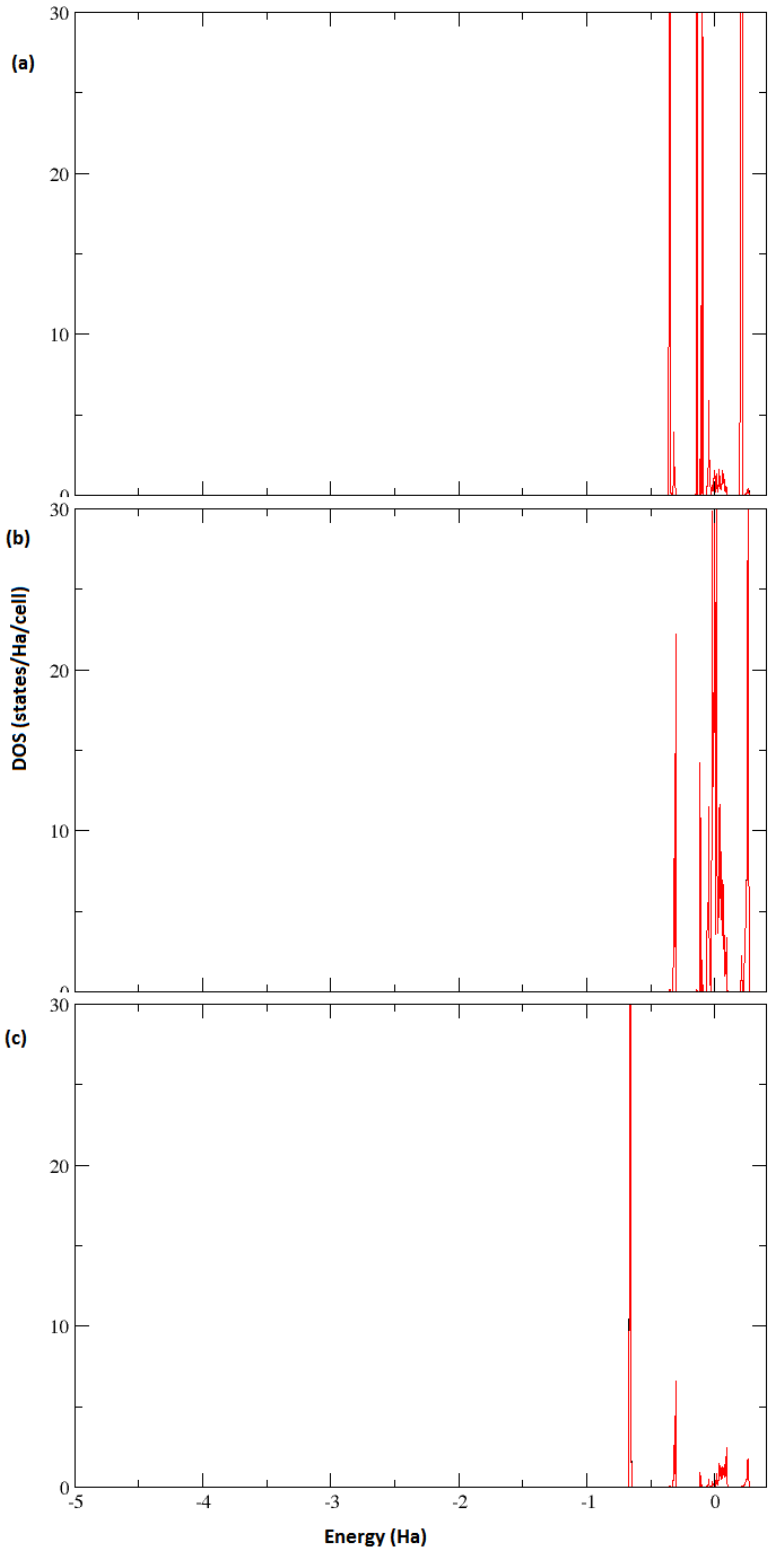

Figure 6: The orbital contributions to the density of states from the Sn atoms. (a) Contributions from the Sn-s orbitals. (b) Contributions from the Sn-p orbitals. (c) Contributions from the Sn-d

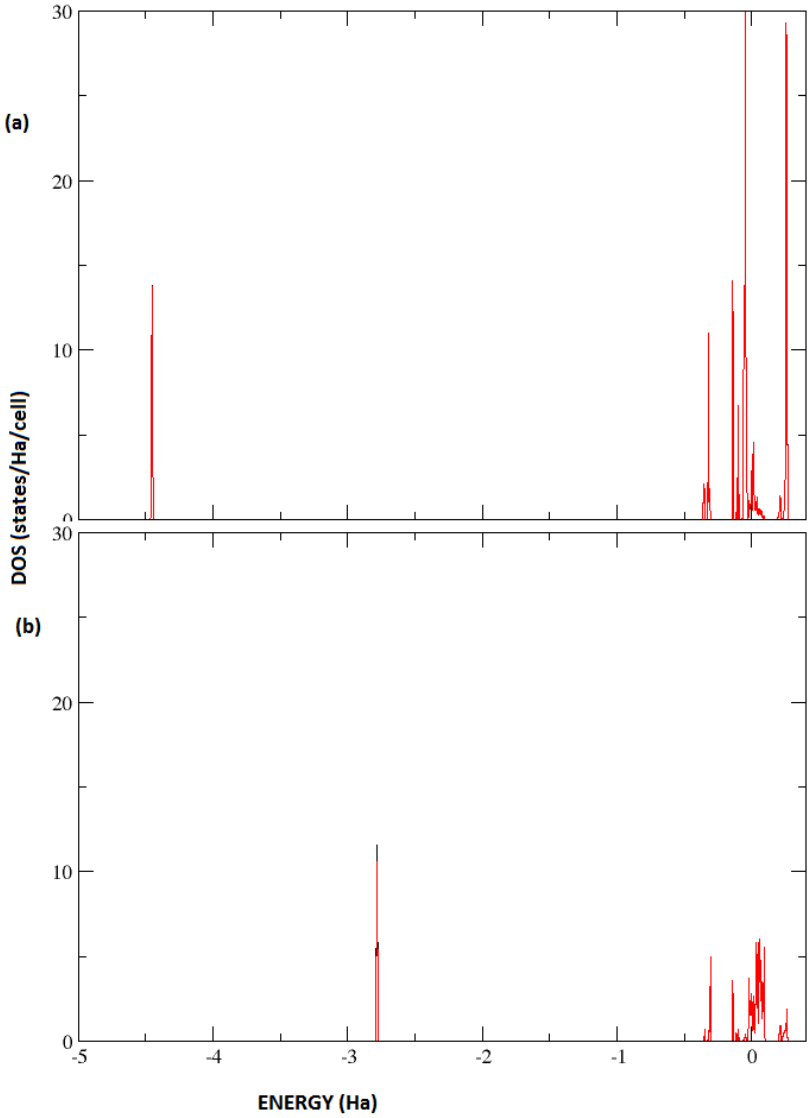

Figure7: The orbital contributions to the density of states from the Zn atoms. (a) Contributions from the Zn-s orbitals. (b) Contributions from the Zn-p orbitals.

Figure 5 shows the orbital contribution to the density of states from the Cu atoms. There are basically two peaks in figure 5a. The peak about -3 Ha represents the contribution from the Cu-3s states while the states about the Fermi level are those of Cu-4s. The states about -3 Ha are Cu-3s dominated. The states from -1 to 0 are mostly Sn-s, Sn-p and Zn-s as seen from figures 6 and 7. Contributions to the conduction band from the Cu atom is marginal with the bulk coming from the Sn-3s, Sn-5p and Zn-4s.

III. Conclusion

The band structure of $CuZnSnS_4$ has been performed using the pseudo-potential method. LDA and LDA + U techniques in conjunction with PAW within the DFT framework as implemented in the Abinit package was used in all calculations. The result from this work predicted Cu_2ZnSnS_4 as a p-type semiconductor with direct bandgap. The bandgap value of 1.83 eV (fig3) using LDA + U makes the material a good absorber layer for solar cells. This improvement over the bandgap value of 0.039 eV (fig2) using LDA only shows that addition of the correlation term, U to LDA increases the bandgap value of materials.

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