

# Density functional theory study of copper zinc tin sulphide (Cu<sub>2</sub>ZnSnS<sub>4</sub>) doped with calcium and barium

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**Abstract.** The sun is the most important source of renewable energy today. Producing energy from sunlight using cheap, abundant and non-toxic materials is considered a major challenge in the field of solar-electrical energy conversion. To harvest solar energy, a thin film solar cell composed of the Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) semiconductor is a candidate to harvest as much energy as possible. Some of its advantages include optical direct band gap and high absorption coefficient. The structural, electronic and optical properties of pure and doped CZTS structure were calculated using density functional theory (DFT) as implemented in the Cambridge Serial Total Energy Package (CASTEP) codes. An adsorption doping mechanism was used to dope the structure with alkali earth metals, Calcium (Ca) and Barium (Ba). The dopants were adsorbed on the structure rather than replacing one of the atoms. Doping using different elements is expected to yield improved the conversion efficiency of the CZTS based solar cells.

## 1. Introduction

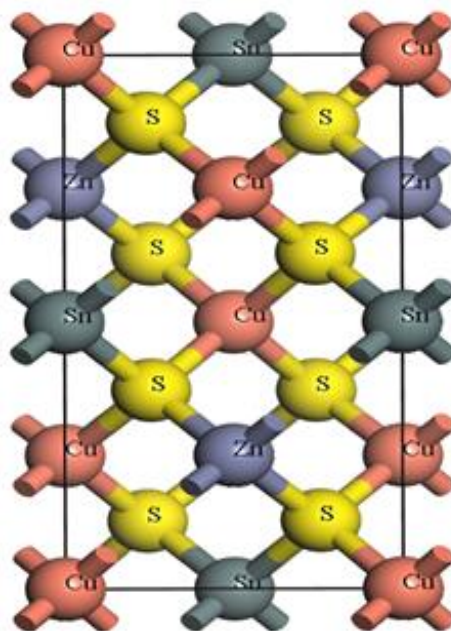
The quaternary CZTS is a promising material for thin film solar cell application [1]. It has been intensively examined as an alternative photovoltaic (PV) material due to its similarity in material properties with copper indium gallium selenide (CIGS), which has attained the conversion efficiency of 20% and its relative abundance of its constituent raw materials. Although GIGS has reached a very high efficiency amongst thin film solar cells, it contains expensive materials (Indium and Gallium) and the band gap is usually not optimal, hence there is a strong desire to discover novel, high efficiency, low cost solar cell absorber materials to replace GIGS [2]. CZTS is a compound semiconductor of (I<sub>2</sub>)(II)(IV)(VI<sub>4</sub>) with a high absorption coefficient (>10<sup>4</sup> cm<sup>-1</sup>) and a desirable bandgap (~1.45 eV) and thus considered an excellent PV material. The cost of raw materials for CZTS PV technology is much lower than that of the existing thin film PV technologies. Theoretical calculations have shown that conversion efficiency as high as 32% are possible for CZTS thin film solar cell, with a CZTS layer of several micrometres [3].

CZTS is a promising candidate for efficient solar cell materials as it inherits all the merits of CIGS while possessing other significant features such as being solely composed of abundant, non-toxic and economic elements in the earth's crust [4] [5]. CZTS film has gained much interest in recent years since its optical property is optimum for PV application. Current thin film technologies are not as effective as crystalline silicon, but they are cheaper to manufacture and have several other important

advantages including good performance in incident light, less sensitivity to temperature-related efficiency reduction and flexibility. The main advantages of CZTS is the relatively high absorption coefficient for the solar spectrum and its tuneable bandgap to make an optimum match to the solar spectrum [6]. The most basic component of a PV cell is the semiconductor. There is a reasonable number of first principle studies on doping of CZTS with different atoms. Some of the atoms used to enhance the efficiency of CZTS through doping include Cadmium (Cd) [7], Sodium (Na) [8], Chromium (Cr) [9], Oxygen (O<sub>2</sub>) [10], Antimony (Sb) [11], Potassium (K) [12], etc. Out of all the dopants that have been used generally, there is no viable improvement on the efficiency of CZTS-based photovoltaic solar cells reported so far. The doped semiconductor develops an excess of free electrons (leading to n-type material) or develops vacancies (called holes) and giving rise to a p-type material. These n-type and p-type materials combine to form a photovoltaic cell. Better understanding of the properties of CZTS is encouraged by improving efficiencies and has drawn interest in the development of these cells through experimental and theoretical means. This study seeks to investigate photovoltaic properties of CZTS material using computer modelling techniques for application in solar cells.

## 2. Computational method

In this work, first principle calculations were implemented in the framework of density functional theory within the generalized gradient approximation (GGA) using the PBE exchange correlation potential and utilizing the plane wave total energy pseudopotential method as implemented in CASTEP code [13]. The structure was modelled in material studio using the 3D Atomistic window in which space group representing the tetragonal structure of I - 4 was used. Lattice parameters of  $a = b = 5.430 \text{ \AA}$  and  $c = 10.890 \text{ \AA}$  were used to draw the external skeleton of the structure. Copper (Cu) atoms were placed in separate positions, 2a (0, 0, 0) and 2c (0, 0.5, 0.25). Zinc (Zn) atoms placed at position 2d (0.5, 0, 0.25), the tin (Sn) atom at position 2b (0.5, 0.5, 0) and sulphur (S) in position 8g (0.7560, 0.7566, 0.8722) respectively [14].

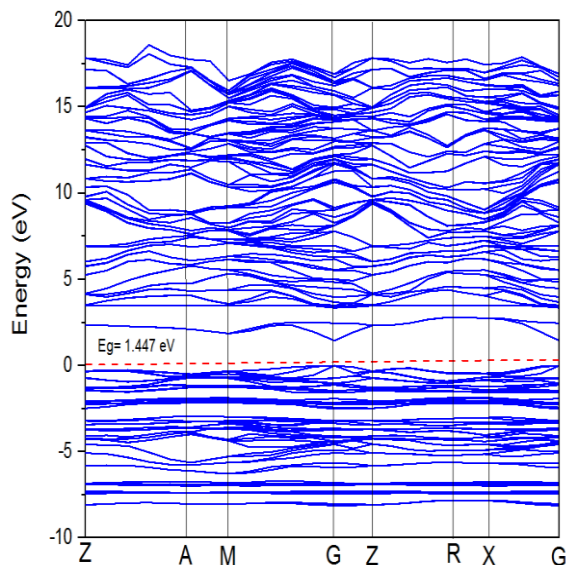


**Figure 1.** CZTS crystal structure indicating the atomic positions for Cu, Zn, Sn and S respectively

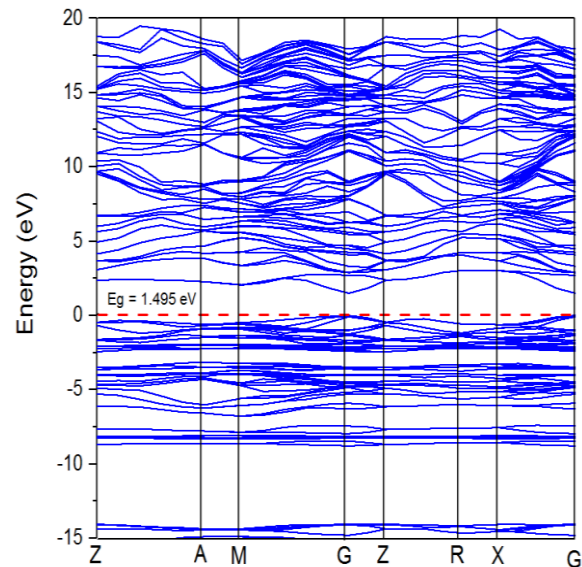
The structure was doped with three elements, the first of which was sodium (group one element) which will act as a basis to validate the study as it has been studied extensively in both experimental and theoretical studies, and hence results of the study will be monitored using sodium. The other two dopants which were used to give identity to the study were the two alkaline earth metals, calcium and barium (they exhibit low toxicity, combines with several metals, abundant, environmentally friendly and they have very high chemical reactivity).

### 3. Results and discussion

The band gap obtained for the bulk structure was found to be 1.447 eV which is not far off from the expected experimental value of 1.5 eV for CZTS kesterite structure [15]. Kesterite is a sulphide mineral with a formula  $\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4$ . The band gap is obtained accurately by making use of the scissors operator because the internal structural parameters are relaxed in the GGA functional and thus this method underestimates the band gap. The scissors operator describes the difference between the theoretical and experimental values of the band gap. It is applied to make the theoretical band gap match the experimental value. To further justify the use of scissors operator, the Heyd–Scuseria–Ernzerhof (HSE06) hybrid density functional was used to determine the band gap because of its accuracy for typical semiconductors. The hybrid HSE06 functional most certainly gives a better value for the band gap. The HSE06 includes short-range, exact Hartree-Fock exchange. It shifts the conduction band to higher energies similar to a scissor correction. The band gap obtained by using the HSE06 functional was 1.495 eV which agrees very well with the experimental value. As seen from figure 2 and 3, it is evident that CZTS has a direct band gap and thus favorable for application in the photovoltaics solar cells for improved and efficient solar technologies.



**Figure 2.** Band structure for bulk CZTS calculated through the GGA-PBE functional



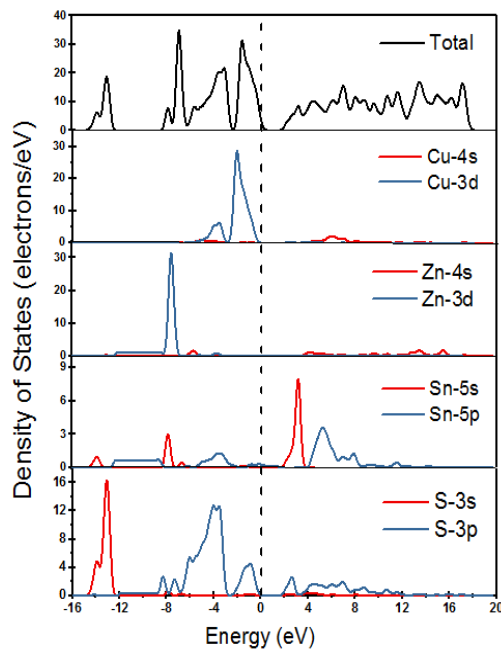
**Figure 3.** Band structure for bulk CZTS calculated through the HSE06 functional

The band gap calculated using GGA-PBE functional are obviously underestimated while the band gap calculated using HSE06 function are very comparable to other computational results as well as experimental works. It is also clear that CZTS possesses a direct band gap as it is clearly shown on the G Brillouin zone. This is because the conduction band minimum (CBM) and the valence band maximum (VBM) are located at the G point of the Brillouin zone.

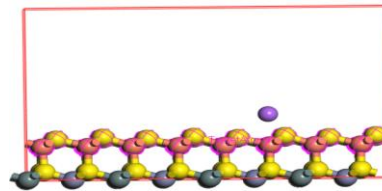
It is evident that the conduction band is made of single band due to the Sn-5s and Cu-3d states while the valence band has several bandwidths. One bandwidth is observed at energies from -2 to -3 eV

which is dominated by the Cu-3d states and another one at energies from -6 to -7 eV which is dominated by S-3p states. From -8 eV there is a huge bandwidth of about 4 eV on the valence band which is due to the S-3s state. There are a few short energy gaps on the valence band lying between -2 eV to -3 eV and -6 eV to -7 eV which are closest to the Fermi level. The conduction band has energy gap from 2 eV to 3 eV matching the energy gap in the valence band. The Cu-3s states is almost vanishing with a slight appearance in the energy range from 4 to 8 eV. It has the lowest density of states on both the valence and the conduction band. The valence atomic configurations of the CZTS structure are  $3d^{10}4s^1$  for Cu,  $3d^{10}4s^2$  for Zn,  $5s^25p^2$  for Sn and  $3s^23p^4$  for S. The total and the partial density of states considering the last two atomic orbitals are presented in Figure 4 as they are the key players in the band gap.

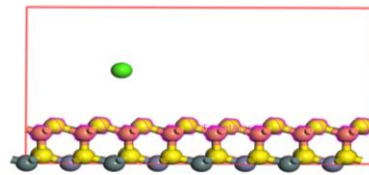
The valence band is composed mostly of the S-3p and Cu-3d states while the conduction band is composed mostly of the Sn-5s and S-3p states respectively. The conduction band is dominated by the Sn atom with its Sn-5s and Sn-5p states clearly visible, a proper Sn content could adjust all the formation energies of the Sn-related defects in an appropriate range as suggested by Xiao *et al* [16]. The s-states for Cu, Zn and S are the lowest available states on the valence and conduction bands respectively. The valence band of CZTS is mainly composed of the hybridization between Cu-3d states and S-3p states.



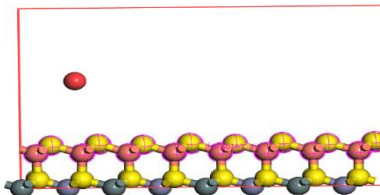
**Figure 4.** CZTS bulk structure density of states showing contribution of atomic states on the band gap



**Figure 5.** CZTS (112) sodium doped surface



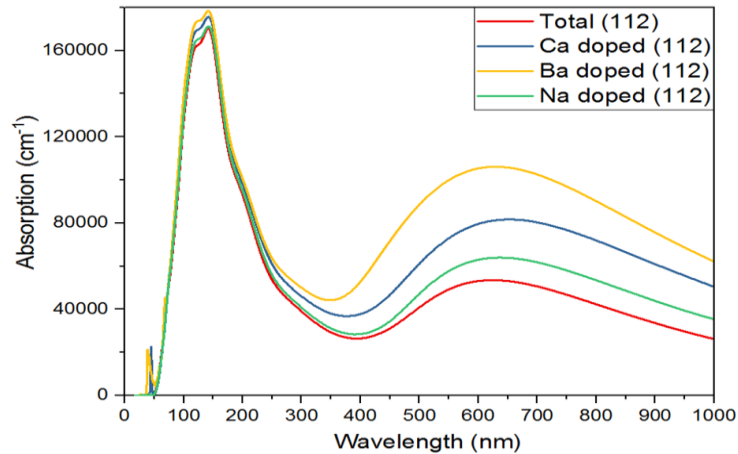
**Figure 6.** CZTS (112) barium doped surface



**Figure 7.** CZTS (112) calcium doped surface

The Zn-4s state is very low on both the valence and conduction bands and therefore there are no states available to be occupied by the dopant elements. There is a slight presence of the Sn-5s and 5p orbitals on both the valence and conduction bands as well as a strong presence of S-3s and 3p states on the valence band. The valence band is dominated by the 3d states while the conduction band is dominated by the 5s states from the Sn element. Figure 5 through Figure 7 shows the attachment of the dopants, sodium, calcium and barium on the (112) surface of CZTS. It is noticeable from the structures that the low energy regions on the surface are mostly found on the central atoms hence the dopants are

attached around the central regions. One important feature of the surface is that the energy is not uniformly distributed throughout the surface hence the presence of lowest energy regions. Absorption coefficient gives information about the solar energy conversion of material and how far light of specific frequency can penetrate the material before being absorbed. The visible region indicates more absorption activity for the spectra with barium being the highest and sodium taking the lowest compared to the total. There is an impressive improvement of absorption from the total CZTS (112) surface for Na, Ca and Ba doped surface on the visible region with the differences clearly visible.



**Figure 8.** Absorption spectra of pure and doped CZTS (112) surface

CZTS was identified as kesterite type and it is said to have a direct band gap of 1.51 eV with an optical absorption coefficient of  $1 \times 10^4 \text{ cm}^{-1}$  [17]. The highest absorption coefficient for the doped structures is for barium with  $10 \times 10^4 \text{ cm}^{-1}$ . Calcium and sodium have absorption coefficients of  $8 \times 10^4 \text{ cm}^{-1}$  and  $6 \times 10^4 \text{ cm}^{-1}$  respectively. Barium doped surface gives the highest absorption peak in the visible region followed by calcium and sodium. These peaks can be credited to the position of the elements in the periodic table and their photo electrolytic properties. Doping of CZTS with Ba can improve the absorption coefficient of CZTS-based solar cells for application in renewable energy.

#### 4. Conclusion

In this work we studied the optical and electronic properties of CZTS. The ground state conditions for the bulk structure were successfully determined and comparable. Semiconductors having band gaps of  $\sim 1.5 \text{ eV}$  are capable of creating electron-hole pairs in the visible region. Most of the solar light falls on the infrared and visible regions and has a maximum value in the visible region. The bulk CZTS (112) plane band gap is lower than the bulk CZTS structure thus indicating the flat band existence and eliminating chances of having electron traps on the band gap. It is evident that doping CZTS (112) surface with either Ca, Ba or Na reduces the band gap and could improve the efficiency of CZTS based solar cells. The material class of kesterite to which CZTS belongs has crystal structure very similar to that of chalcopyrite's and therefore similar electronic properties were expected. CZTS shows a p-type semiconducting behavior with a carrier concentration  $\sim 10^{17} \text{ cm}^{-3}$ , optical absorption coefficient  $\sim 10^4 \text{ cm}^{-1}$  and direct band gap  $\sim 1.4 \text{ eV}$ . New thin-film solar cell materials and a greater understanding of their properties are needed to meet the urgent demand for sustainable, lower cost and scalable photovoltaics. Doping of semiconductors is expected to decrease the bandgap and improve its optical response for application in renewable energy technologies. The decrease of the bandgap size can be understood from the hybrid orbital interactions. For kesterite solar cells to present a commercially viable solution it will certainly be necessary to reach 15% efficiency.

## 5. Acknowledgments

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## 6. References

- [1] S. Shauddin, "Comparison among Various Emerging PV Cells with History, Current Status and Future Challenges," *Energy and Power*, vol. 3, no. 6, pp. 91–105, 2013.
- [2] D. B. Mitzi, O. Gunawan, T. K. Todorov, K. Wang, and S. Guha, "The path towards a high-performance solution-processed kesterite solar cell," *Sol. Energy Mater. Sol. Cells*, vol. 95, no. 6, pp. 1421–1436, 2011.
- [3] C. G. Granqvist, "Transparent conductors as solar energy materials: A panoramic review," *Sol. Energy Mater. Sol. Cells*, vol. 91, no. 17, pp. 1529–1598, 2007.
- [4] Z. Zhao and X. Zhao, "Electronic, optical, and mechanical properties of  $\text{Cu}_2\text{ZnSnS}_4$  with four crystal structures," *J. Semicond.*, vol. 36, no. 8, p. 83004, 2015.
- [5] R. J. Deokate, A. D. Adsool, N. S. Shinde, S. M. Pawar, and C. D. Lokhande, "Structural and optical properties of spray-deposited  $\text{Cu}_2\text{ZnSnS}_4$  thin films," *Energy Procedia*, vol. 54, pp. 627–633, 2014.
- [6] H. S. Min, "Optical properties of ternary thin films ( $\text{Ni}_3\text{Pb}_2\text{S}_2$ ) prepared by chemical bath deposition technique," 2017.
- [7] T. Maeda, S. Nakamura, and T. Wada, "First-Principles Study on Cd Doping in  $\text{Cu}_2\text{ZnSnS}_4$  and  $\text{Cu}_2\text{ZnSnSe}_4$ ," *Jpn. J. Appl. Phys.*, vol. 51, p. 10-11, 2012.
- [8] O. P. Singh, A. Sharma, K. S. Gour, S. Husale, and V. N. Singh, "Fast switching response of Na-doped CZTS photodetector from visible to NIR range," *Sol. Energy Mater. Sol. Cells*, vol. 157, pp. 28–34, 2016.
- [9] C. Tablero, "Electronic and photon absorber properties of cr-doped  $\text{Cu}_2\text{ZnSnS}_4$ ," *J. Phys. Chem. C*, vol. 116, no. 44, pp. 23224–23230, 2012.
- [10] C. Tablero, "Effect of the oxygen isoelectronic substitution in  $\text{Cu}_2\text{ZnSnS}_4$  and its photovoltaic application," *Thin Solid Films*, vol. 520, no. 15, pp. 5011–5013, 2012.
- [11] X. Zhang, Miaomiao Han, Zhi Zeng, and Y. Duan, "The role of Sb in solar cell material  $\text{Cu}_2\text{ZnSnS}_4$ ," pp. 1–22, 2017.
- [12] H. S. Craft, R. Collazo, Z. Sitar, and J. P. Maria, "A novel strategy to control defects and secondary phases of CZTS by surfactant Potassium," vol. 4, pp. 2105–2110, 2006.
- [13] S. J. Clark, M. D. Segall, C. J. Pickard, and P. J. Hasnip, "First principles methods using CASTEP," *Zeitschrift für Krist.*, vol. 220, no. 5, pp. 567–570, 2005.
- [14] S. R. Hall, J. T. Szymanski, and J. M. Stewart, "Kesterite,  $\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4$  and Stannite  $\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4$ , structurally similar but distinct minerals," *Can. Mineral.*, vol. 16, no. 2, pp. 131–137, 1978.
- [15] K. N. Basri, N. A. Zabidi, H. Abu Kassim, and A. N. Rosli, "Density Functional Theory (DFT) Calculation of Band Structure of Kesterite," *Adv. Mater. Res.*, vol. 1107, pp. 491–495, 2015.
- [16] W. Xiao, J. N. Wang, X. S. Zhao, and J. W. Wang, "Intrinsic defects and Na doping in CZTS: A density-functional theory study," *Sol. Energy*, vol. 116, pp. 125–132, 2015.
- [17] S. Das, K. C. Mandal, and R. N. Bhattacharya, Earth-Abundant  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  (CZTSSe) Solar Cells, vol. 4, pp. 25-74, 2016.