KARYA ILHAM PUBLISHING
CONNECTING MINDS, BRIDGING IDEAS, INSPIRING READERS

Journal of Advanced Research in Computing and Applications

Journal homepage:
https://karyailham.com.my/index.php/arca/index
ISSN: 2462-1927


# First-principles Study on Structural, Electronic and Optical Properties of Cu2ZnSnS4 as Absorber Layer for Thin Film Solar Cell

Nafisha Balqis Khairuddin[1], Nur Ain Nabilah Mohamad Nor[1], Fatin Nabilah Sazman[1], Nurzaihani Batrisyia Said[1], Nur Amirah Syafiqah Amirul[1], Muhammad Aman Haikal Razali[1], Muhammad Nor Syazwan Saimin[1], Nur Hamizah Mohamad Zaki[1,2], Oskar Hasdinor Hassan[2,3], Mohamad Fariz Mohamad Taib[1,2,*]

[1] Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[2] Ionic Material and Devices (iMADE), Institute of Science (IOS), Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[3] Faculty of Art and Design, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

**ARTICLE INFO**

***Article history:***
Received 10 February 2026
Received in revised form 30 May 2026
Accepted 2 June 2026
Available online 14 August 2026

***Keywords:***
CZTS; Kesterite; CASTEP; optical properties

**ABSTRACT**

The quaternary compound Cu2ZnSnS4 (CZTS) has gained attention as a potential "next generation" photovoltaic material. CZTS has a high absorption coefficient (>104 cm-1) and an optimal direct bandgap energy of 1.4-1.6 eV, making it an ideal option for thin-film solar cell applications. The purpose of this study is to analyze the structural, electronic, and optical properties of CZTS in its kesterite and stannite phases using first-principles density functional theory (DFT) computations within the Cambridge Serial Total Energy Package (CASTEP) computational framework. The results revealed that the kesterite phase exhibits slightly better structural stability for solar energy conversion compared to the stannite phase. Furthermore, the calculations use Hubbard U = 7 eV for copper (Cu) and Zinc (Zn), U = 3 eV for Tin (Sn) and U = 9 eV for Sulphur (S) to fix the strongly localized 3d and 5p orbitals. It improves the accuracy of electronic structure predictions by increasing the bandgap value to 1.5 eV, as opposed to the 0.98 eV predicted by standard density functional approaches. This advancement overcomes the limitations of these methods in accurately describing electron-electron interactions in transition metal compounds. Additionally, optical absorption estimates reveal a high absorption coefficient in the visible spectrum, which is crucial for effective solar energy capture. These findings highlight the potential of CZTS, particularly the kesterite phase, as a remarkably effective and environmentally friendly material for thin-film solar cells. This study provides vital insights into the structural, electronic, and optical properties of CZTS, offering the basis for optimizing its design and fabrication, and opening the way for the development of sustainable and high-performance solar solutions.

* *Corresponding author.*
*E-mail address: mfariz@uitm.edu.my*

## 1. Introduction

Technology, economic stability, social dynamics, and living standards in developed, emerging, and underdeveloped nations depend on energy use. As population growth intensifies, energy consumption is surging. There are three primary categories of energy: fossil fuels, fissile energy, and renewable energy [1,2]. Fossil fuels, valued at $1.5 trillion, continue to dominate the global energy landscape; yet their finite supply and significant greenhouse gas emissions provide substantial environmental challenges [3,4]. The search for alternative energy sources is motivated by the difficulties that occur from traditional fossil fuels, such as global warming and rising prices, which contribute to more than 30 gigatonnes of $CO_2$ yearly, setting up dangers to ecosystems. Renewable energy is the sole solution to global energy concerns due to its abundant, sustainable, and replicable nature [1-3,5,6]. On the contrary, the global energy industry is likely to rely on fossil fuels for at least the next few decades. However, non-renewable energy sources, such as fossil fuels, are not practicable for the future since they contribute to environmental degradation [1,7].

By 2040, photovoltaics is expected to be the most often used renewable energy source since they provide power with less effect on the surroundings [6, 8]. In the semiconductor industry, band gap investigations are indispensable since they affect device efficiency. Approximately 90% of solar cells are constructed of silicon, with their cost-effectiveness resulting from lower material usage and better energy conversion efficiency. CdTe thin films for solar cells were initially introduced in the 1960s but concerns regarding cadmium toxicity and the availability of tellurium must be addressed prior to large-scale manufacture [9–12]. Low thermal expansion and great power conversion efficiency abound in solar cells absorber material such as copper indium gallium selenide (CIGS), cadmium telluride (CdTe), and amorphous silicon (a-Si). Thin film solar cells including CIS and CIGS have been widely used in solar cell applications in the following generations. Still, unfortunately, some materials have uncommon components, which could limit their availability [9-11,13].

Copper zinc tin sulphide, $Cu_2ZnSnS_4$ (CZTS) has emerged as a viable alternative to CIGS owing to its non-toxic, inexpensive, and plentiful components. CZTS possesses an adjustable direct bandgap (1.0–1.5 eV) and a high absorption coefficient (~$10^4$ $cm^{-1}$), making it ideal for solar applications, achieving up to 80% effective absorption and demonstrating strong carrier mobility (0.1–35 $cm^2V^{-1}s^{-1}$) [9–11,14–16]. Its tetragonal crystalline structure in the kesterite (KS) and stannite (ST) phases makes it an attractive substitute for silicon-based solar cells. These properties establish CZTS as an exceptionally efficient and eco-friendly material for modern solar technology [1,13,15,17]. Density Functional Theory (DFT) is a crucial technique for analysing and refining the properties of CZTS, notably in solar cell applications. This work implements DFT to thoroughly examine the structural, electronic, and optical properties of CZTS. This study enhances the comprehension of CZTS using first-principles calculations, offering critical insights for optimising its design and production, thus establishing a basis for advancing sustainable and high-performance photovoltaic technologies. This highlights the promise of CZTS as a sustainable and effective substitute for next-generation thin-film solar cells.

## 2. Methodology

### *2.1 Computational Method*

The first-principles approach using DFT within the generalised gradient approximation by Perdew-Burke-Ernzerhof for solids (GGA-PBEsol) exchange-correlation (XC) functional has been applied in this work. The ground state computation of the structural, electrical, and optical properties of the KS CZTS was studied by applying the DFT within XC functionals. Moreover, the Hubbard U

correlation known as (DFT + U) implemented in the Cambridge Serial Total Energy Package (CASTEP) was applied in all calculations to overcome the effect of the on-site Coulomb repulsion of the d orbital system, which affects the band gap of the electronic properties of KS CZTS [18,19]. The geometric optimization was done under the following conditions: convergence of minimal energy change per atom is at $5 \times 10^{-5}$ eV, stress is < 0.02 Gpa, maximal residual force on the atoms is < 0.01 eV/Å and displacement of atoms is < 0.0005 Å [20, 21]. In this work, the Ultrasoft pseudopotentials were applied for all the atomic species with the basis set of the valence electronic states taken as follows: 3*d*10 4*s*1, 3*d*10 4*s*2, 5*s*2 5*p*2, and 3*s*2 3*p*4 for Cu, Zn, Sn and S, respectively. The standard approximated GGA for PBEsol [22] was defined effectively for this study's most stable structures and electrical characteristics. Several U values were attempted on the 3*d* orbital electrons of Cu and Zn and 5*p* and 3*p* of Sn and S orbitals, respectively. The energy was changed from 1 eV to 10 eV for KS CZTS to fix the electronic band gaps for both structures. The calculated structural, electronic, and optical properties of this quaternary chalcogenide CZTS using PBEsol + U with the strong effective on-site Coulomb repulsion among the localized Cu 3*d*, Zn 3*d*, Sn 5*p* and S 3*p* electrons were described according to the following formalism:

$$E_{DFT+U} = E_{DFT} \frac{(U-J)}{2} \sum_{\sigma} Tr\,(\rho^{\sigma} - \rho^{\sigma}\rho^{\sigma}) \quad (1)$$

where $\rho\sigma$ indicates the spin ($\sigma$) polarized on-site density matrix and U and J are the Coulomb and exchange energy, respectively. The Hubbard U values utilized in this calculation is $U_d$ = 7 for Cu and Zn, $U_p$ = 3 for Sn, and $U_p$ = 9 eV respectively. This technique is widely used to solve the inadequacies of DFT in precisely representing the localized $d$ or $p$ electrons of materials, such as the transition metals in CZTS (Cu-Zn-Sn-S). The U parameter particularly corrects the on-site Coulomb interaction for these electrons, boosting the trustworthiness of electronic structure predictions. The chosen U values reflect the level of correction required to recreate known experimental bandgaps and other material features accurately. For CZTS, the experimentally observed bandgap is roughly 1.2-1.4 eV; the U value is changed to ensure the estimated bandgap aligns with this. Additionally, the optical properties of sodium influence on CZTS, which correlates with the thin film application, were explored in terms of the absorption coefficient $\alpha(\omega)$.

## 3. Results

### *3.1 Structural Properties*

#### *3.1.1 Crystal structures*

This section addresses the crystal structure of CZTS, which is essential in defining its material qualities and suitability for solar applications. **Figure 1** visualizes the general crystallization of CZTS in a tetragonal structure, with two prevalent variants known as the kesterite structure, which belongs to the $I\bar{4}$ space group, and the stannite structure, which is categorized under the $I\bar{4}2m$ space group. The arrangement of Cu, Zn, Sn, and S atoms inside lattice characteristics, with cation distribution affecting the material's electrical and optical properties. The structural parameters for kesterite and stannite polymorphs are tabulated in **Table 1**. As noted, the best agreement for volume (V) with the experimental values for KS CZTS was reached from GGA-PBEsol, which was underestimated by 1.90%. Meanwhile, ST CZTS, calculated using GGA-PBEsol as well, is overestimated by +1.81%. Furthermore, the computed lattice parameters for GGA-PBEsol of KS CZTS are a = b = 5.3951 Å and c = 10.7694 Å, while a = b = 5.4011 Å and c = 10.7421 Å are for GGA-PBEsol ST CZTS, respectively. Since the lattice constants are close to the experimental data, GGA-PBEsol proceeded to the following electronic and optical simulations.

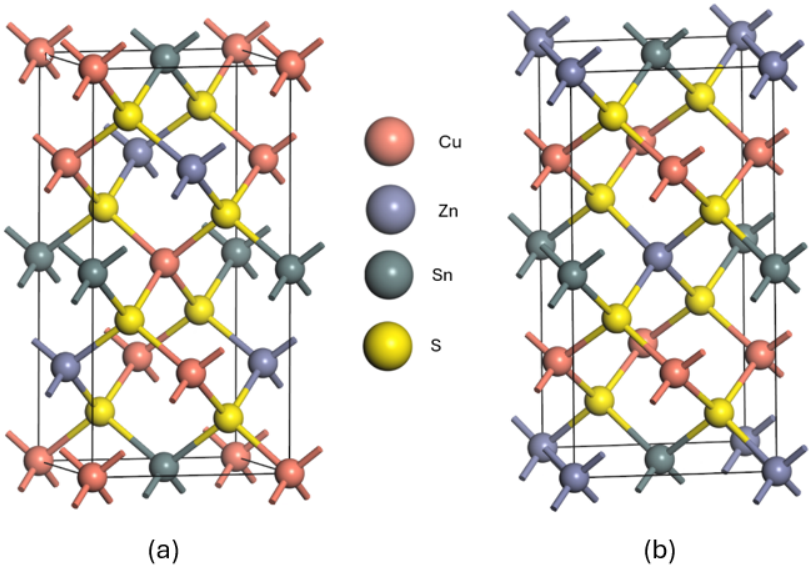



**Fig.1.** The crystal structures of unit cell quaternary chalcogenide semiconductor (a) KS CZTS and (b) ST CZTS

**Table 1**
The lattice constants, volume of both kesterite and stannite for CZTS compared to experimental data

| Structures | Method | a (Å) | b (Å) | c (Å) | V (Å$^3$) |
|---|---|---|---|---|---|
| CZTS (Kesterite) | Expt.[a] | 5.4258 | 5.4258 | 10.8537 | 319.5253916 |
| | LDA | 5.303789 (-2.25%) | 5.303789 (-2.25%) | 10.586162 (-2.46%) | 297.7906188 (-6.80%) |
| | GGA-PBE | 5.472380 (+0.86%) | 5.472380 (+0.86%) | 10.933479 (+0.74%) | 327.4242709 (+2.47%) |
| | **GGA-PBEsol** | **5.395078 (-0.57%)** | **5.395078 (-0.57%)** | **10.769424 (-0.78%)** | **313.4641880 (-1.90%)** |
| CZTS (Stannite) | Expt.[b] | 5.389 | 5.389 | 10.599 | 307.8089613 |
| | LDA | 5.305015 (-1.56%) | 5.305015 (-1.56%) | 10.581835 (-0.16%) | 297.8065311 (-3.25%) |
| | GGA-PBE | 5.472270 (+1.55%) | 5.472270 (+1.55%) | 10.927980 (+3.10%) | 327.2464364 (+6.31%) |
| | **GGA-PBEsol** | **5.401107 (+0.22%)** | **5.401107 (+0.22%)** | **10.742142 (+1.35%)** | **313.3693026 (+1.81%)** |

[a] Reference [22]
[b] Reference [23]

### *3.1.2 Phasestability of Kesterite and Stannite $Cu_2ZnSnS_4$*

Cohesive energy is an essential metric that indicates the stability and bonding strength inside a material's crystalline structure. It is defined as the energy necessary to deconstruct a crystal into its individual isolated atoms. The cohesive energy of CZTS is a crucial determinant of structural stability, directly influencing its suitability for photovoltaic applications. The cohesive energy of two CZTS

phases in tetragonal KS ($I\bar{4}$) and ST ($I\bar{4}2m$) was estimated as a function of their crystal volume per CZTS formula unit, using GGA-PBEsol XC functional to assess phase stability between these CZTS phases. The cohesive energy is defined as the disparity between an isolated atom's energy and that atom's energy in a solid state. The cohesive energy of CZTS, $E_{coh}$(CZTS), is determined using equation (4.1):

$$E_{coh}(CZTS) = \frac{E_{total}(CZTS)}{2} - 2E_{Cu} - E_{Zn} - E_{Sn} - 4E_s \quad (2)$$

Where $E_{total}$(CZTS) represents the total energy of CZTS, computed by normalizing with the CZTS formula unit, whereas $E_{Cu}$, $E_{\mathrm{Zn}}$, $E_{Sn}$, and $E_S$ represent the total energies of Cu, Zn, Sn, and S atoms, respectively. Each unit cell of the KS and ST phases contains 2 formula units. Consequently, to determine the equilibrium volume, the volume of each CZTS is divided by its respective formula unit (2) in all instances. Based on Figure 2, it can be concluded that KS CZTS is more stable as it exhibits the lowest energy of -5860.67 eV, compared to -5860.065 eV of ST CZTS.

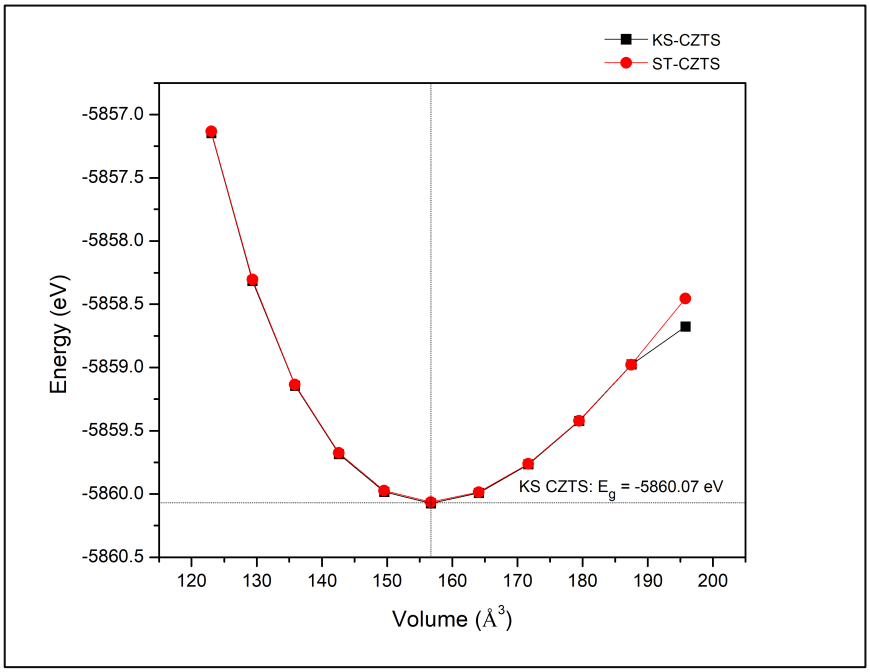



**Fig. 2.** Calculated cohesive energy versus volume (Per CZTS Formula Unit) for KS and ST Phases for CZTS from GGA-PBEsol

### *3.2 Electronic Properties*

#### *3.2.1 Band structures*

The band gap of CZTS is a crucial factor affecting its efficacy in photovoltaic applications. This study used DFT to examine the electronic structure and band gap of CZTS, employing the GGA-PBEsol exchange-correlation functional. Figure 3 illustrates the preliminary application of the Hubbard $U_d$ parameter on the $d$-orbitals of Cu 3*d* and Zn 3*d*, leading to a band gap estimation that is markedly lower than the experimental values. This difference highlights the limitations of focusing solely on the localized $d$-states in CZTS. To address this issue, the Hubbard $U_p$ parameter was implemented to consider the localization effects in the $p$-orbitals, specifically those of Sn and S, as illustrated in Figure 4. The utilization of $U_p$ values, that range from 1 eV to 10 eV, was methodically assessed for KS CZTS.

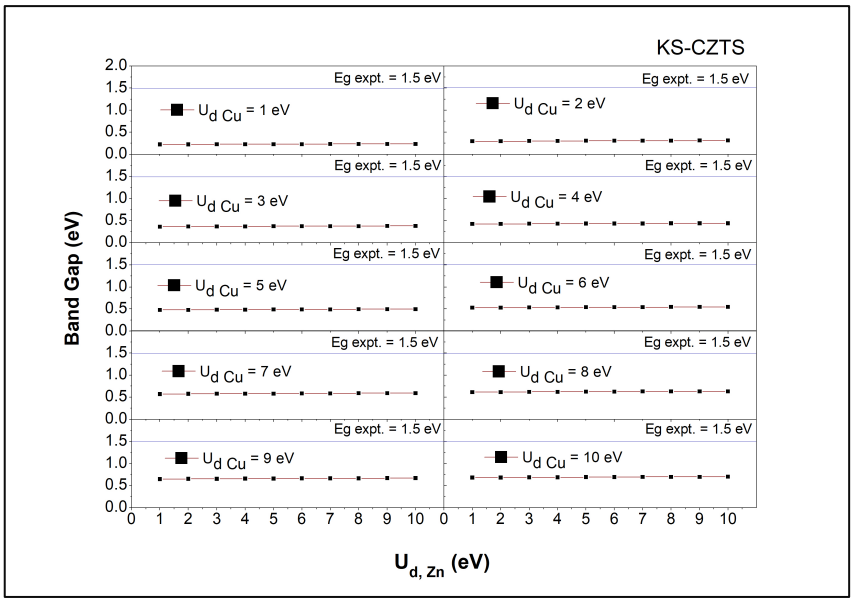



**Fig. 3.** Dependences of band gaps for KS CZTS on $U_{d,\,Cu}$ = 1 to 10 eV and $U_{d,\,Zn}$ = 1 to 10 eV. The experimental band gap represent as dashed lines

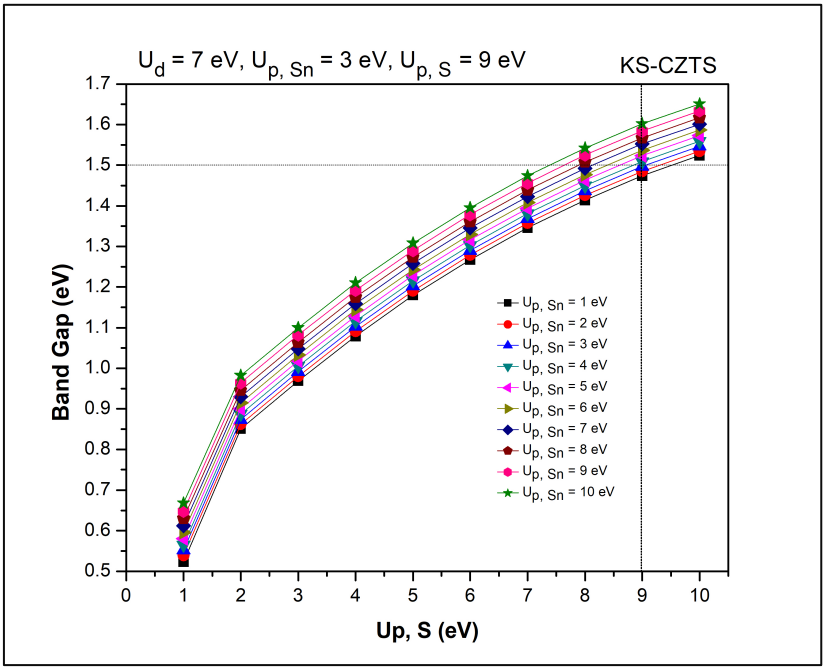
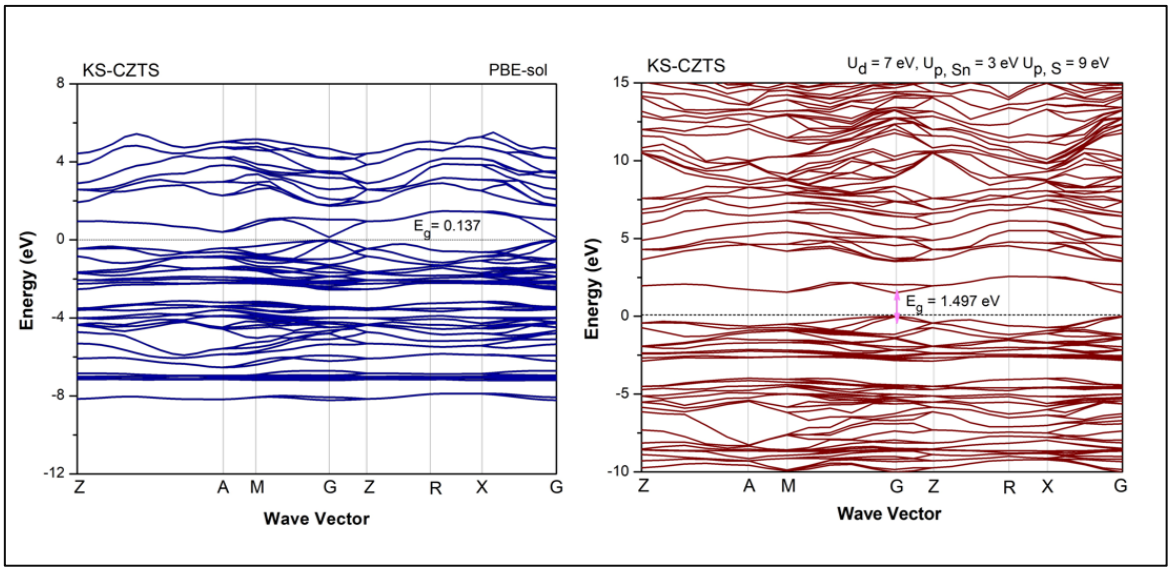



**Fig. 4.** Dependences of band gaps for KS CZTS. The experimental band gap represents dashed lines

Figure 5 (a) displays the band structures of KS CZTS, respectively, within the first Brillouin zone, characterized by the k-point trajectory along the Z-A-M-G-Z-R-X-G symmetry points derived from a conventional DFT calculation. It can be inferred that this material exhibits metallic behavior, as no discernible gaps exist between its conduction band (CB) and valence band (VB). Nonetheless, KS CZTS demonstrates a minimal gap of 0.137 eV, which does not align well with the experimental data. However, the issue of underestimated band gap values in CZTS due to the limitations of conventional DFT has been effectively addressed using the DFT + U method. By applying Hubbard U parameters, this technique corrects the electron localization in the $d$- and $p$-orbitals, leading to more accurate

band gap predictions. As shown in Figure 5 (b), the band structure of KS-CZTS computed with PBEsol + U indicates a direct band gap of 1.497 eV at the G point, coherence with experimental results ($E_g$ = 1.50 eV) when the Hubbard U parameters were set at $U_{d,\,Cu} = 7$ eV, $U_{d,\,Zn} = 7$ eV, $U_{p,\,Sn} = 3$ eV and $U_{p,\,S} = 9$ eV. This modification underscores the necessity of simultaneously addressing localized $d$- and $p$-orbitals to attain precise band gap predictions.

The direct band gap of 1.49 eV positions KS CZTS within the ideal region of 1.4–1.5 eV for photovoltaic applications, boosting its suitability for thin-film solar cells. The presence of a straight band gap is helpful as it promotes efficient absorption and carrier production, needed for obtaining high conversion efficiencies. These results show the efficiency of the DFT + U approach in providing a more accurate description of the electronic structure, further proving the potential of CZTS as a cost-effective and sustainable material for solar energy applications.




(a) (b)

**Fig. 5.** Band structure of KS CZTS at (a) U = 0 eV and (b) $U_{d,\,Cu,\,Zn}$ = 7 eV, $U_{p,\,Sn}$ = 3 eV and $U_{p,\,S}$ = 9eV. The dashed lines represent fermi level at 0 eV

### *3.2.1 Density of states*

The density of states (DOS) is an essential instrument for comprehending the electronic properties of CZTS and its applicability in solar applications. It refers to the number of electronic states accessible at each energy level for electron occupancy. Analyzing the total and partial density of states allows for identifying the contribution of individual atoms and orbitals to the electronic structure of CZTS, offering insights into its optoelectronic properties. Figures 6 and 7 illustrate the DOS of CZTS computed using the DFT and DFT+U methodologies. The valence band (VB) beneath the Fermi level (0 eV) predominantly comprises Cu 3*d*, Zn 3*d*, Sn 5*p*, and S 3*p* states. Identical orbital states were detected at the conduction band above the Fermi level. The unsaturated bonding of atoms allows these states to be viewed clearly and vividly around the Fermi level. The lowest conduction band (CB) for both DFT and DFT + U of KS CZTS is comparatively high and is attributed to the S-3*p* state. Simultaneously, the predominant contribution to the highest VB is primarily from the Cu-3*d* state, as illustrated in Figures 6 and 7, respectively. Notably, numerous minor peaks exist in the valence band of all CZTS structures, signifying an abundance of localized states, while most of these minor peaks coalesce at the Fermi level.

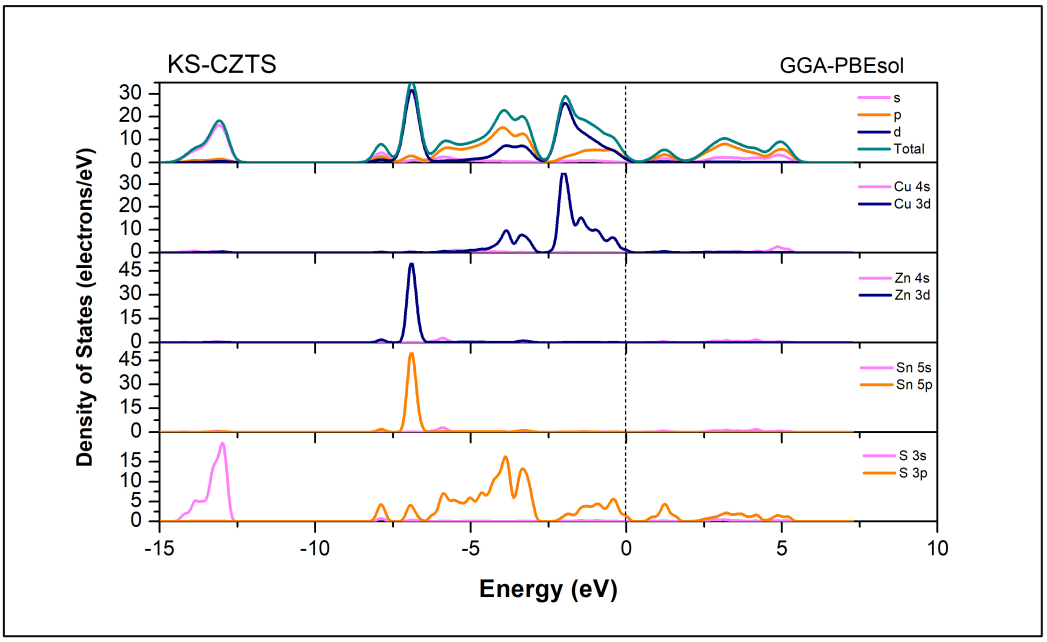



**Fig. 6.** Density of States (DOS) of KS CZTS within GGA-PBEsol

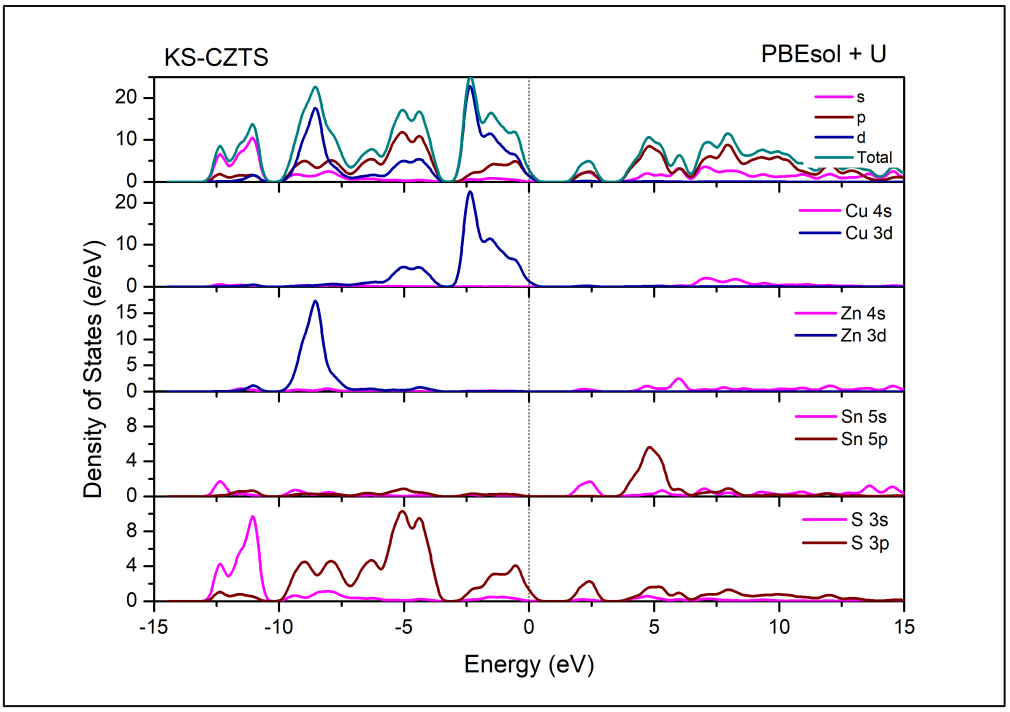



**Fig. 7.** Density of States (DOS) of KS CZTS within GGA-PBEsol+U

### *3.2 Optical Properties*

Significant attention is directed towards examining optical qualities, including the absorption coefficient, which are essential for enhancing solar energy conversion. The absorption coefficient quantifies a material's capacity to absorb sunlight and convert it into electrical energy effectively, which is crucial for the advancement of high-performance solar cells. They function as transparent conductors, selective absorbers, and the primary element of photovoltaic solar cells. This study

computed the optical characteristics of KS CZTS using DFT and DFT+U approaches. The optical computations were conducted from the first principles, utilizing an electronic transition characterized by a time-dependent perturbation of the lowest electronic state (ground state). The absorption coefficient, $\alpha(\omega)$, can ascertain the optimal power conversion efficiency (PCE) and the extent of light penetration into a material before absorption. The absorption coefficient can elucidate the linear optical response from the uppermost valence band to the lowest conduction band. Figure 8 demonstrates that KS CZTS+U possesses the highest optical absorption coefficient in the visible spectrum (~400 nm–700 nm), rendering it a promising contender for photovoltaic (PV) applications.

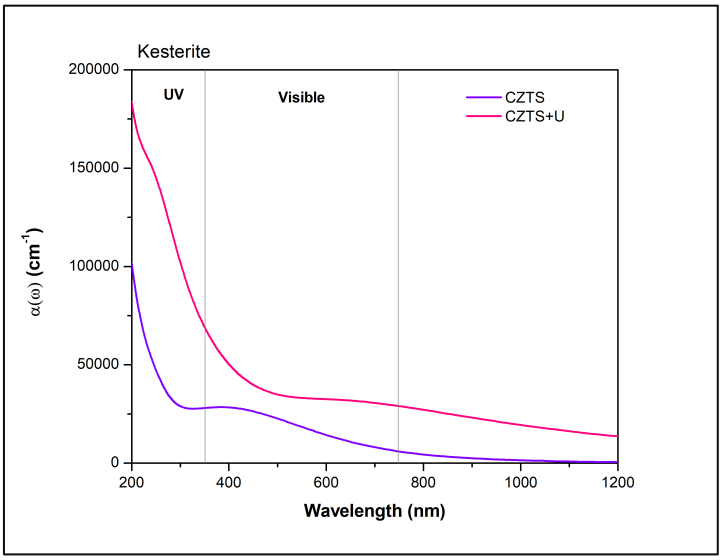



**Fig. 8.** Absorption coefficient against wavelength (nm) of KS CZTS and CZTS +U

## 4. Conclusions

In summary, this study thoroughly analyzed the structural, electronic, and optical characteristics of CZTS in its kesterite and stannite phases utilizing first-principles DFT. Significant findings reveal that KS CZTS is the more structurally stable phase, demonstrating enhanced potential for photovoltaic applications. The implementation of the Hubbard U correction successfully mitigated the shortcomings of conventional DFT methods, improving the precision of electronic structure predictions and reconciling the computed bandgap (1.50 eV) with the data from experiments. The optimal bandgap, along with a high absorption coefficient in the visible spectrum, highlights the promise of CZTS as a sustainable and efficient absorber material for thin-film solar cells.

The DOS study indicated substantial contributions from Cu 3*d*, Sn 5*s*, and S 3*p* orbitals to the valence and conduction bands, elucidating the material's electronic transitions and light absorption properties. Assessments of optical properties verified the material's significant absorption in the visible spectrum, hence affirming its photovoltaic potential.

These findings underscore the significance of sophisticated computational techniques in enhancing CZTS for solar energy applications. The results establish a basis for subsequent experimental and theoretical endeavours focused on enhancing the material's efficiency and performance, facilitating the advancement of economical, eco-friendly solar solutions.

## Acknowledgement

This work was supported by the UiTM Excellent Fund (600-RMC/FRGS 5/3 (055/2022). Most appreciate to Ionics, Materials and Devices (iMADE) Research Laboratory, Institute of Science (IOS), UiTM for the facilities provided.

**References**

[1] Yussuf, Sodiq Tolulope, K. C. Nwambaekwe, M. E. Ramoroka, and E. I. Iwuoha. "Photovoltaic efficiencies of microwave and Cu2ZnSnS4 (CZTS) superstrate solar cells." *Materials Today Sustainability* 21 (2023): 100287. https://doi.org/10.1016/j.mtsust.2022.100287

[2] Kannan, Nadarajah, and Divagar Vakeesan. "Solar energy for future world:-A review." *Renewable and sustainable energy reviews* 62 (2016): 1092-1105. https://doi.org/10.1016/j.rser.2016.05.022

[3] Demirbas, Ayhan. "Global renewable energy projections." *Energy Sources, Part B* 4, no. 2 (2009): 212-224. https://doi.org/10.1080/15567240701620499

[4] Shafiee, Shahriar, and Erkan Topal. "When will fossil fuel reserves be diminished?." *Energy policy* 37, no. 1 (2009): 181-189. https://doi.org/10.1016/j.enpol.2008.08.016

[5] Kumar, M. Suresh, Sreejith P. Madhusudanan, and Sudip K. Batabyal. "Substitution of Zn in Earth-Abundant Cu2ZnSn (S, Se) 4 based thin film solar cells–A status review." *Solar Energy Materials and Solar Cells* 185 (2018): 287-299. https://doi.org/10.1016/j.solmat.2018.05.003

[6] Khalate, S. A., R. S. Kate, and R. J. Deokate. "A review on energy economics and the recent research and development in energy and the Cu2ZnSnS4 (CZTS) solar cells: A focus towards efficiency." *Solar Energy* 169 (2018): 616-633. https://doi.org/10.1016/j.solener.2018.05.036

[7] Benda, Vítězslav, and Ladislava Černá. "PV cells and modules–State of the art, limits and trends." *Heliyon* 6, no. 12 (2020). https://doi.org/10.1016/j.heliyon.2020.e05666

[8] Hernández-Callejo, Luis, Sara Gallardo-Saavedra, and Víctor Alonso-Gómez. "A review of photovoltaic systems: Design, operation and maintenance." *Solar Energy* 188 (2019): 426-440. https://doi.org/10.1016/j.solener.2019.06.017

[9] Tran, Thi Ha, Thi Hong Pham, Cong Doanh Sai, Trong Tam Nguyen, and Viet Tuyen Nguyen. "Study phase evolution of hydrothermally synthesized Cu2ZnSnS4 nanocrystals by Raman spectroscopy." *Nano-Structures & Nano-Objects* 18 (2019): 100273. https://doi.org/10.1016/j.nanoso.2019.100273

[10] Singh, Girish Kumar. "Solar power generation by PV (photovoltaic) technology: A review." *Energy* 53 (2013): 1-13. https://doi.org/10.1016/j.energy.2013.02.057

[11] Islam, Md Fakhrul, Nadhrah Md Yatim, and Mohd Azman Hashim. "A review of CZTS thin film solar cell technology." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 81, no. 1 (2021): 73-87. https://doi.org/10.37934/arfmts.81.1.7387

[12] Raad, N. Hakimi, E. Karimmirza, M. Yousefizad, N. Nouri, H. Sharifpour, E. Nadimi, M. Ahmadi Zeidabadi, and N. Manavizadeh. "Improving the electronic and optical properties of chalcogenide Cu2ZnSnS4 compound with transition metal dopants: A first-principles investigation." *Thin Solid Films* 766 (2023): 139653. https://doi.org/10.1016/j.tsf.2022.139653

[13] Marzougui, M., H. Hammami, H. Oueslati, R. Coq Germanicus, C. Leroux, D. Pelloquin, M. Ben Rabeh, and M. Kanzari. "Study of the beneficial effects of sodium doping Cu2ZnSnS4 material." *Optical Materials* 132 (2022): 112709. https://doi.org/10.1016/j.optmat.2022.112709

[14] Manivannan, R., and S. Noyel Victoria. "Preparation of chalcogenide thin films using electrodeposition method for solar cell applications–A review." *Solar Energy* 173 (2018): 1144-1157. https://doi.org/10.1016/j.solener.2018.08.057

[15] Rondiya, Sachin, Nitin Wadnerkar, Yogesh Jadhav, Sandesh Jadkar, Santosh Haram, and Mukul Kabir. "Structural, electronic, and optical properties of Cu2NiSnS4: a combined experimental and theoretical study toward photovoltaic applications." *Chemistry of Materials* 29, no. 7 (2017): 3133-3142. https://doi.org/10.1021/acs.chemmater.7b00149

[16] Guo, Qijie, Hugh W. Hillhouse, and Rakesh Agrawal. "Synthesis of Cu2ZnSnS4 nanocrystal ink and its use for solar cells." *Journal of the American Chemical Society* 131, no. 33 (2009): 11672-11673. https://doi.org/10.1021/ja904981r

[17] Zhao, Zong-Yan, and Xiang Zhao. "First-principles study on doping effects of sodium in kesterite Cu2ZnSnS4." *Inorganic chemistry* 53, no. 17 (2014): 9235-9241. https://doi.org/10.1021/ic5013268

[18] Nor, N. A. N. M., M. A. H. Razali, W. H. A. W. K. Annuar, N. N. Alam, F. N. Sazman, N. H. M. Zaki, A. S. Kamisan et al. "Influence of Hubbard U correction on the structural, electronic and optical properties of Kesterite Cu2XSnS4 (X= Zn, Fe)." *Physica B: Condensed Matter* 673 (2024): 415450. https://doi.org/10.1016/j.physb.2023.415450

[19] Yaakob, M. K., M. F. M. Taib, O. H. Hassan, and M. Z. A. Yahya. "Low-energy phases, electronic and optical

properties of Bi1− xLaxFeO3 solid solution: Ab-initio LDA+ U studies." *Ceramics International* 41, no. 9 (2015): 10940-10948. https://doi.org/10.1016/j.ceramint.2015.05.037

[20] Taib, M. F. M., M. K. Yaakob, F. W. Badrudin, T. I. T. Kudin, O. H. Hassan, and M. Z. A. Yahya. "First principles calculation of tetragonal (P4 mm) Pb-free ferroelectric oxide of SnTiO3." *Ferroelectrics* 459, no. 1 (2014): 134-142. https://doi.org/10.1080/00150193.2013.849178

[21] Zhang, Yi-Man, Zhan-Ju Jia, and Zong-Yan Zhao. "Secondary phases in Cu2ZnSnS4 thin film solar cell: The role of interfaces." *Physica B: Condensed Matter* 626 (2022): 413539. https://doi.org/10.1016/j.physb.2021.413539

[22] Liu, Bin, Jie Guo, Ruiting Hao, Lu Wang, Kang Gu, Shuaihui Sun, and Abuduwayiti Aierken. "Effect of Na doping on the performance and the band alignment of CZTS/CdS thin film solar cell." *Solar energy* 201 (2020): 219-226. https://doi.org/10.1016/j.solener.2020.02.088

[23] Ahmoum, H., P. Chelvanathan, M. S. Su'ait, M. Boughrara, G. Li, Ali HA Al-Waeli, K. Sopian, M. Kerouad, and N. Amin. "Impact of preheating environment on microstructural and optoelectronic properties of Cu2ZnSnS4 (CZTS) thin films deposited by spin-coating." *Superlattices and microstructures*140 (2020): 106452. https://doi.org/10.1016/j.spmi.2020.106452