

A DFT Study of the Electronic and Optical Properties of Kesterite Phase of $\text{Cu}_2\text{ZnGeS}_4$ using GGA, TB-mBJ, and U Exchange Correlation Potentials

M. MESBAHI, F. SERDOUK* AND M.L. BENKHEDIR

Laboratoire de Physique Appliquée et Théorique, LPAT, Université Larbi Tébessi, Tébessa, Algeria

The $\text{I}_2\text{-II-IV-VI}_4$ series of quaternary chalcogenides semiconductors have drawn wide interest for their potential application as solar-cell absorbers. In this paper, we present a study of electronic and optical properties of the equilibrium kesterite structure (KS) of $\text{Cu}_2\text{ZnGeS}_4$ (CZGS) calculated by means of the full potential linearized augmented plane wave method. For this purpose, we used the Wien2k code based on the density functional theory with the generalized gradient approximation (GGA), modified Becke–Johnson exchange potential (mBJ) and the Hubbard potential U. The TB-mBJ is used alone or combined with U (TB-mBJ, and TB-mBJ+U). The results are compared with other theoretical results and the available experimental ones. The obtained results show that the top of the valence band is mainly composed by the Cu d orbital while the bottom of the conduction band is a mixture of Ge s and S p states. It was found that KS-CZGS has a direct band gap of 0.3, 1.8 and 2.0 eV using GGA, GGA+TB-mBJ and GGA+TB-mBJ+U, respectively. It is observed that states exist above the Fermi level (0 eV) with a width of 0.3 and 0.2 eV when we use GGA and GGA+TB-mBJ, while these states come down under the Fermi level when using GGA+TB-mBJ+U. The optical properties are calculated and an almost isotropic behavior is found in contrast to the reported properties of the stannite phase. This behavior can be linked to the charge density and the structure.

DOI: [10.12693/APhysPolA.134.358](https://doi.org/10.12693/APhysPolA.134.358)

PACS/topics: solar-cell absorbers, DFT, TB-mBJ, $\text{Cu}_2\text{ZnGeS}(\text{Se})_4$, electronic properties

1. Introduction

It is well accepted that the solution for the increasing demand for energy and pollution problem is the renewable energies [1, 2]. The solar energy is an unlimited resource of energy. Converting solar energy to electric energy via highly efficient and low cost photovoltaic cells is gaining attention of scientists [3]. The light absorber layer is a principal part of the solar cell. The indium and gallium based materials like copper indium sulfide and copper indium gallium di-selenide are suitable materials for light absorber layer application [4, 5]. However, indium and Gallium are not abundant in earth [4]. The $\text{I}_2\text{-II-IV-VI}_4$ materials are promising to be used as light absorbers in solar cells [6, 7]. This family of materials has the advantages that their constituents are abundant and nontoxic materials. Solar cells based on $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) have achieved an efficiency of 11% [8, 9].

$\text{Cu}_2\text{ZnGeS}_4$ (CZGS) belongs to the $\text{I}_2\text{-II-IV-VI}_4$ materials family. It crystalizes in the stannite or kesterite phases and it has an experimental band gap of about 2 eV [10]. CZGS is an indium and gallium free material and can be considered as an alternative candidate in solar cells fabrication [11, 12]. Using the variable angle spectroscopic ellipsometry, Leon et al. have prospected optical properties of CZGS in the photon energy domain 1.4-4.7 eV. Nisha Kidan et al. have recently studied, in

the frame of DFT theory using GGA and TB-mBJ, the electronic and optical properties of CZGS in its stannite phase [13]. They found an optical gap of 1.21 eV using GGA+mBJ potential, which is a bit far from the experimental one. They compared their theoretical results with the experimental ones reported in [10]. Chen et al. have studied theoretically the structural and electronic properties of Wurtzite-derived polytypes of kesterite and stannite CZGS using the VASP code [14]. However, the electronic and optical properties of CZGS in the kesterite phase have not been studied, thus it would be interesting to theoretically prospect the electronic and optical properties of CZGS in its kesterite phase.

In this paper we report DFT calculations of the electronic and optical properties of CZGS in its kesterite phase using the FP-LAPW method. The calculations were done using GGA approximation and TB-mBJ and U exchange correlation potentials. The band band structure, total and partial density of electronic states and optical properties are presented. Our calculated results are compared with the experimental data of Leon [10] and the calculated ones of Nisha for CZGS in its kesterite phase [13].

2. Method of simulation

In this paper, we use a periodic calculation with the WIEN2k code [15]. In the WIEN2k program, the full potential linearized augmented plane-wave and the full potential linearized augmented plane-wave plus local-orbitals (FP-LAPW-LO) method are based on DFT. The generalized gradient approximation of Perdew-Burke-Ernzerhof 96 PBE-GGA was used to include the treat-

*corresponding author; e-mail: iserdouk@yahoo.fr

ment of the exchange-correlation energy [16]. The separation energy of the valence from the core states is -6.5 Ry. $\text{KS-Cu}_2\text{ZnGeS}_4$ has a lattice constant equal to ($a=5.354 \text{ \AA}$, $c=10.641$). We have adopted for the muffin-tin radii the values 2.27 for Cu and Zn, 2.2 and 1.86 for Ge and S respectively to achieve energy eigenvalue convergence, we expanded the basis function up to $\text{RMT}^*\text{KMAX} = 8$ (where KMAX is the maximum modulus for the reciprocal lattice vector). The number of k-points in the whole Brillouin zone was chosen as 1000. We, also, used the TB-mBJ potential correction alone or combined with U potential. The used value for U in this study is 2eV. The iteration process was repeated until the calculated total energy of the crystal converges to less than 10^{-4} Ry.

3. Results and discussion

The band structures of $\text{KS-Cu}_2\text{ZnGeS}_4$ calculated along high symmetry points in Brillouin zone using ex-

change correlation potentials: (a) GGA (b) GGA+mBJ (c) GGA+mBJ+U are presented in Figures 1a, 1b and 1c. The band gap is 0.3 eV, 1.8 eV and 2.0 eV when using GGA, GGA+mBJ and GGA+mBJ+U respectively. The Hubbard potential was set to 2 eV and applied to the orbital d of Cu that participates in the formation of the top of the valence band as it will be seen later. The choice of $U = 2 \text{ eV}$ is set after a test using $U = 2, 3$ and 4 eV [17,18]. The band gap of 2 eV calculated using GGA+TB-mBJ+U is very close to the experimental values [10]. It is worthful to notice the existence of states with a width of 0.3 eV and 0.2 eV above the Fermi level when calculation is done using GGA and GGA+ TB-mBJ respectively. These states come down to Fermi level when we use the combination GGA+TB-mBJ+U. This is probably due to the effect of U that localizes the orbital d of Copper Cu that forms the top of the valence band [19]. The three calculated band structures show that $\text{Cu}_2\text{ZnGeS}_4$ has a direct gap at gamma point.

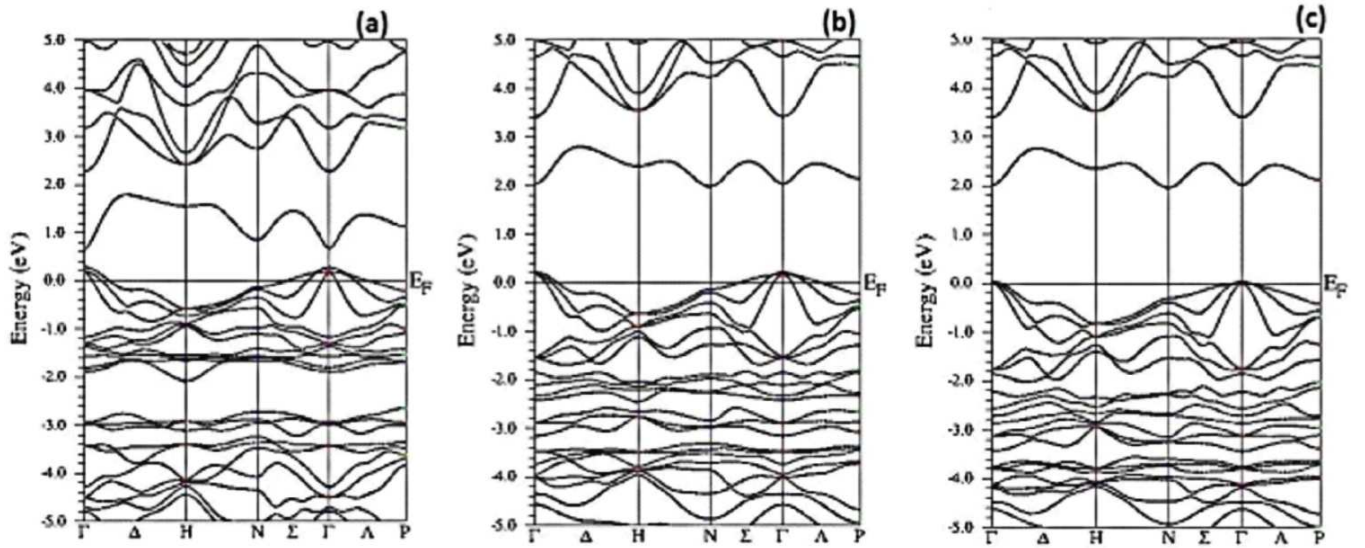


Fig. 1. Band structure of $\text{Cu}_2\text{ZnGeS}_4$ using exchange correlation potentials: (a) GGA (b) GGA+mBJ (c) GGA+mBJ+U.

In Figure 2 the total and partial density of states (DOS) for $\text{Cu}_2\text{ZnGeS}_4$ are presented. The presented DOS are calculated using GGA+mBJ+U exchange correlation potential. In order to understand the role of each orbital of the constituent atoms of KS-CZGS we plot the angular momentum decomposition of partial DOS. The lowest part of the DOS is between -15 eV and -12.5 eV and is mainly composed of S-s orbital. The second part of the DOS extends from -8 eV to -5 eV is constituted of Zn-d, Ge-s and a small admixture of S-p and Ge-p. the third part extends from -5 eV to 0 eV is mainly composed from Cu-d and a small admixture of Cu-p and S-p. Thus, the top of the valence band is mainly composed of Cu-d states. The bottom of the conduction band is mainly formed of Ge-s and S-p states while the higher part of the conduction band is formed of Cu-p, Ge-p and

S-p states. Our calculated DOS for kesterite phase of CZGS is similar to the calculated DOS for kesterite and wurtzitekesterite phases of CZGS using the VASP code [14]. The only difference is that the bottom of the valence bande is shifted to the higher energies by 1 eV when applying the GGA+TB-mBJ or GGA +TB-mBJ+U exchange correlation potentials.

Figure 3 (a) presents the real and imaginary parts dielectric constant ϵ in the direction parallel and perpendicular to the c axis of the crystal. The static value of $(\epsilon_1)_0$ is 5.8 which is a bit lower than 6.2 and 6.4 values of $(\epsilon_1)_0$ for stannite phase in the xx and zz directions respectively [13]. It is remarkable that the two parts of the dielectric constant are isotropic in the energy domain between 0 and 3 eV. And that they are almost isotropic in the rest of the photon energy domain. The same re-

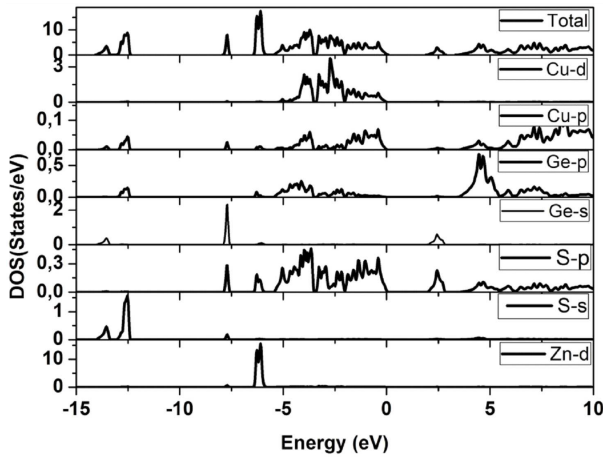


Fig. 2. Total and partial densities of states of $\text{Cu}_2\text{ZnGeS}_4$ calculated using GGA+TB-mBJ+U.

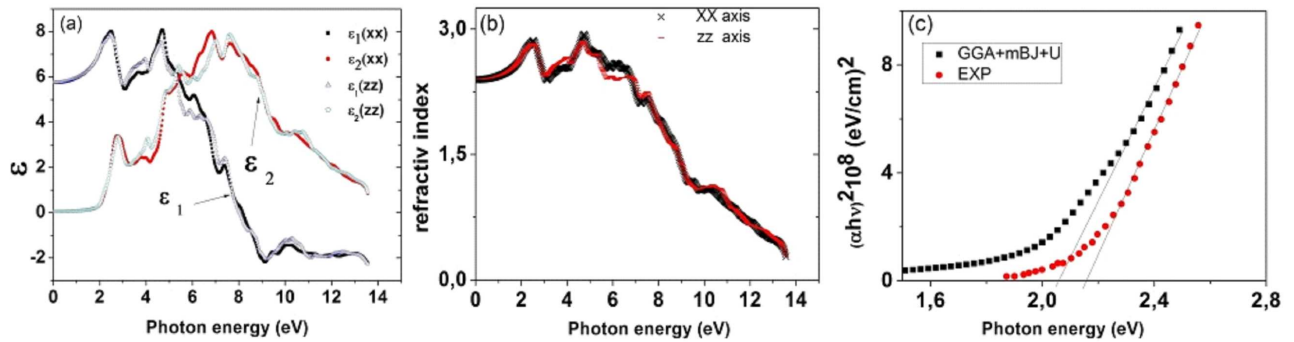


Fig. 3. (a) dielectric constants (real and imaginary parts) (b) refractive index in the direction xx and zz. No important anisotropy is observed (c) Tauc plot calculated and experimental for stannite phase CZGS [10].

4. Conclusion

A DFT study of electronic and optical properties of $\text{Cu}_2\text{ZnGeS}_4$ in its kesterite phase was performed using GGA, mBJ and U exchange correlation potentials alone or combined. The results are compared with available theoretical and experimental data. A direct band gap at Γ point is found, its value is 0.3, 1.8 and 2.0 eV when using GGA, GGA+mBJ and GGA+TB-mBJ+U respectively. The later value is in good agreement with experimental results. The top of the valence band is almost constituted of orbital d of Cu and is set to Fermi level by applying U potential on this orbital. The bottom of the conduction band is composed of a mixture of Ge-s and S-p states. The calculated optical constants show a small anisotropic behavior in comparison with reported calculated and experimental results for stannite phase. This could be explained by the difference of distance between pairs of atoms and density of charge in the two planes xx and zz.

References

- [1] W. Shockley, H.J. Queisser, *Appl. Phys.* **32**, 510 (1961).
- [2] M. Green, *IEEE Trans. Electron. Dev.* **31**, 671 (1984).
- [3] M.S. Dresselhaus, I.L. Thomas, *Nature* **414**, 332 (2001).
- [4] B.A. Andersson, *Prog. Photovolt. Res. Appl.* **8**, 61 (2000).
- [5] C. Wadia, A.P. Alivisatos, D.M. Kammen, *Environ. Sci. Technol.* **43**, 2072 (2009).
- [6] D.M. Berg, R. Djemour, L. Güta, G. Zoppi, S. Siebentritt, P.J. Dale, *Thin Solid Films* **520**, 6291 (2012).
- [7] A. Ghosh, R. Thangavel, M. Rajagopalan, *J. Mater. Sci.* **48**, 8259 (2013).
- [8] B. Shin, O. Gunawan, Y. Zhu, N.A. Bojarczuk, S.J. Chey, S. Guha, *Prog. Photovolt. Res. Appl.* **21**, 72 (2013).
- [9] T.K. Todorov, J. Tang, S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, D.B. Mitzi, *Energy Mater* **3**, 34 (2013).
- [10] M. Leon, S. Levchenko, R. Serna, G. Gurieva, A. Nateprov, J.M. Merino, E.J. Friedrich, U. Fillat, S. Schorr, E. Arushanov, *J. Appl. Phys.* **108**, 093502, (2010).
- [11] S. Levchenko, D. Dumcenco, Y.S. Huang, K.K. Tiong, C.H. Du, *Opt. Mater* **34**, 183 (2011).

mark for the refractive index as shown in figure 3 (b) and other optical constants calculated but not presented here as reflectivity and extinction coefficient. This behavior is different from that of stannite phase reported in [13] where a higher anisotropy is observed. Figure 3 (c) shows the Tauc plot for KS-CZGS calculated from the absorption coefficient using GGA+mBJ+U and the experimental one for a bulk crystal of stannite CZGS. The calculated Tauc plot gives an optical gap of about 2.05 which is in good agreement with experimental data [9]. Nisha et al. and Levchenko et al. reported a much higher anisotropy for stannite CZGS [13,11]. The small anisotropy could be explained by the difference of distance between pairs of atoms in the two plane xx and zz. Also, the density charge distribution could be responsible of this anisotropy. A detailed calculation is needed to answer the questions related to the difference anisotropy between the stannite and kesterite phases of CZGS.

- [12] S. Chen, X.G. Gong, A. Walsh, S.H. Wei, *Phys. Rev. B* **79**, 165211 (2009).
- [13] N. Kodan, S. Auluck, B.R. Mehta, *Journal of Alloys and Compounds* **675**, 236 (2016).
- [14] Shiyu Chen, A. Walsh, YeLuo, Ji-Hui Yang, X.G. Gong, Su-Huai Wei, *Phys. Rev B* **82**, 195203 (2010).
- [15] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, University of Technology, Vienna 2001.
- [16] J.P. Perdew, S. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [17] S.Q. Wu, Z.Z. Zhu, Y. Yang, Z.F. Hou., *Computational Materials Science* **44**, 1243 (2009).
- [18] P.M. Panchmatia, B. Sanyal, P.M. Oppeneer, *Chemical Physics* **343**, 47 (2008).
- [19] C.D. Brunetta, B. Karuppannan, K.A. Rosmus, J.A. Aitken, *Journal of Alloys and Compounds* **516**, 65 (2012).