U.P.B. Sci. Bull., Series A, Vol. 79, Iss. 4, 2017 ISSN 1223-7027

A DFT STUDY OF QUATERNARY CHALCOGENIDE SEMICONDUCTORS $Cu_2ZnSnS(Se)_4$ BY TRAN-BLAHA MODIFIED BECKE-JOHNSON AND HUBBARD POTENTIALS

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The I2-II-IV-VI4 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 $Cu_2ZnSnS(Se)_4$ *(CZTS(Se)), stannite structure (SS) of Cu2ZnSnS4 and secondary phases of KS-* Cu_2ZnSnS_4 *in the DFT frame. For this purpose, we used the Wien2k code based on the density functional theory (DFT) with the modified Becke-Johnson exchange potential mBJ and the Hubbard potential U, individually or combined (TB-mBJ, and TB-mBJ+U). The results are compared with those obtained using generalized gradient approximation GGA and local density approximation LDA approximations and the available experimental ones. The obtained results using TB-mBJ and TB-mBJ+U are in good agreement with the experimental results which are different from results obtained using GGA approximation and similar published ones using LDA approximation. Some electronic states appear above the Fermi level when we use GGA approximation. These states increase when we use TB-mBJ. This phenomenon can be recovered by using the U correction potential in combination with TB-mBJ correction potential*

Keywords: Solar-cell absorbers, DFT, TB-mBJ, $Cu_2ZnSnS(Se)_4$, Secondary phases, Electronic properties.

1. Introduction

The Conversion of sun-light to electricity in solar cells is a well developed renewable energy technology. Silicon is widely used in this domain, but regarding that this material has an indirect gap, radiative and non-radiative recombination processes, it was found that an ideal, silicon based, single junction solar cell has an upper efficiency limit[1,2]. Regarding that the sun-light, on the earth, is concentrated in the visible domain, a light absorber having a direct gap of 1.3eV to 1.5 eV, with a high absorption coefficient in the visible domain is ideal for a photovoltaic cell [1,3]. $Cu(In,Ga)Se_2$ are good light absorbers, but In and Ga are not available enough to use solar energy at a very large scale[4,5]. The multinary chalcogenides $Cu_2ZnSn(S,Se)_4$ (kesterite) have recently attracted attention as promising candidates as light absorber films in photovoltaic cells [6-9] [8,9]. The

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structural, electric, and optical properties of $Cu_2ZnSnS(Se)_4$ compounds have been experimentally explored with various methods[10,11,12].

The well known density functional theory (DFT) approach has been used to calculate structural, electronic and optical properties of $Cu_2ZnSnS(Se)_4$ compounds [13,14,19,20]. However, it is well known that unlike experimental results, the DFT approach leads to an underestimation of the gap of semiconductors and insulators when LDA and GGA approximations are used [15,16,17]. The structural and electronic properties are the starting points for the calculation of other physical properties. Therefore, an accurate calculation of electronic structure is needed to get reliable and precise calculated physical properties. In order to reach as reliable calculations as possible, Several corrections were used to compensate the underestimation of the gap, like the scissors correction [17, 18]. In addition, some sophisticated and expensive calculation methods, like Green’s function screened coulomb interaction approximation GW, were used to calculate electronic structures [16,18]. However, and despite the fact that they are expensive approaches, the calculations are still inaccurate since it was reported that the gap can be overestimated in comparison with experimental results [17]. Therefore, it would be desirable to use the popular DFT approach, to understand the electronic structures and physical properties of CZTS and similar materials. Recently, David Koller and coworkers have proposed the modified Becke-Johnson exchange potential (TB-mBJ) to be used as a correction to the potential in order to calculate accurate electronic band structures for different types of semiconductors and insulators (e.g., sp semiconductors, noble-gas solids, and transition-metal oxides). This approach has proved its validity, and it permits to get values of the gaps that are close to the experimental ones at a lower cost [16].

It is known that the I_2-II-IV-VI_4 compounds adopt one of two structures: stannite and wurtzite-stannite [9]. However; Recent experimental and theoretical studies have revealed that $Cu_2ZnSnS(Se)_4$ crystallize in the kesterite structure as their ground-state structure. An occupational disorder of the Cu and Zn cations may introduce a confusion between kesterite and stannite phases [9]. According to calculations of the assessment of photons of Shockley-Queisser, CZTS should have a theoretical yield of more than 30% [1,19,20,21]. Until now, the experimental yield is rather low compared to the theoretical limit, thus, it is worth to study the electronic and optical properties of this material and to prospect some possible reasons of this experimental limit. Among these possible reasons are the occupational disorder of the Cu and Zn positions and the formation of some secondary phases that disturb the homogeneity of the absorber film.

In this paper, we propose to investigate the electronic and optical properties of both of the $Cu_2ZnSnS(Se)_4$ and some of its secondary phases. For this purpose, we used the full potential linearized augmented plane wave (FP-

LAPW) method with the TB-mBJ correction potential alone or combined with the U potential. The studied materials are the Cu_2ZnSnS_4 in its KS and SS and some secondary phases that are Cu_2SnS_3-Cc, Cu_2SnS_3-Cmc21 and Cu_2SnS_3-Imm2. This study will allow us to prospect some possible causes of the yield limitation.

2. Method

In this paper, we use a periodic calculation with the WIEN2k code [22]. In the WIEN2k program, the full potential linearized augmented plane-wave and the full potential linearized augmented plane-wave (FP-LAPW) method are based on DFT. We used Tran and Blaha's modified Becke–Johnson (TB-mBJ) exchange potential [16] within the density functional theory to investigate the electronic structures and optical properties of KS-$Cu_2ZnSnS(Se)_4$, SS-Cu_2ZnSnS_4, Cu_2SnS_3-Cc, Cu_2SnS_3-Cmc21 and Cu2SnS3-Imm2. We, also, used TB-mBJ exchange potential combined with the Hubbard potential (U) for all cited systems. The used U value is 4eV [23]. The values 3 and 5 eV for U were also explored. The separation energy of the valence from the core states is -6.0 Ry. We expanded the basis function up to RMT*KMAX = 8, where KMAX is the maximum modulus for the reciprocal lattice vector and RMT is the muffin tin radii for atoms. The number of k-points in the whole Brillouin zone was chosen as 1000 for all systems. The iteration process was repeated until the calculated total energy of the crystal converged to less than 10^{-4} Ry.

3. Results and discussions

3.1. Structural and Electronic properties:

The knowledge of the energy band structures of materials provides valuable information on their potential utility in manufacturing electronic devices [24]. These electronic structures are tightly related to the crystallographic structures of materials. The GGA approximation was used to do structural studies of the systems KS-$Cu_2ZnSnS(Se)_4$, SS-Cu_2ZnSnS_4, Cu_2SnS_3-Cc, Cu_2SnS_3-Cmc21 and Cu_2SnS_3-Imm2 that are shown in Figure1. The space group for each compound and RMT for each atom is shown in Table1. These studies have given the equilibrium lattice parameters that are summarized in Table1. The equilibrium lattice parameters are calculated using the Murnagan equation [25]. The obtained results are in good agreement with other experimental and theoretical studies as detailed in Table1. Using the structural study, we were able to calculate the electronic band structures of all the materials and systems mentioned above. The electronic band structures, along some high symmetry lines in the Brillouin zone, of the systems KS-Cu_2ZnSnS_4 and Cu_2SnS_3-Cc using GGA approximation and TB-mBJ+U potential are shown in Figure2a and Figure2b respectively. The Fermi level is taken as origin of energies. We noticed that all the studied materials in this paper show a direct band gap at the Γ point. The obtained band gap energies, E_g, using GGA approximation are given in Table2 and compared to some available data.

Table 1

Structural properties: structure phase, space groupe, RMT, equilibrium lattice parametes of all studied systems KS-$Cu_2ZnSnS(Se)_4$, SS-Cu2ZnSnS4, Cu2SnS3-Cc, Cu2SnS3-Cmc21 and Cu2SnS3-Imm2.

Material	structure	Space groupe	RMT	equilibrium lattice parameter(Å)	Equilibrium lattice reported in literature (Å)
Cu_2ZnSnS_4	KS	I-4 (N°82)	Cu :2.26 Zn :2.26 Sn :2.26 S :1.85	a=5.507 b=5.507 c=11.031	5.574[14],5.47[26] 5.47[26] 10.93 [26]
Cu_2ZnSnS_4	SS	I-42m (N°121)	Cu :2.25 Zn :2.25 Sn :2.25 S :2.14	a=5.432 b=5.432 c=10.823	5.637[14],5.46[26] 5.46[26] 10.95[14]
$Cu_2ZnSnSe_4$	KS	I-4 (N°82)	Cu :2.25 Zn :2.25 Sn :2.25 Se:2.14	a=5.680 b=5.680 c=11.359	5.941[14]
Cu_2SnS_3	monoclinic	Cc	Cu :2.30 Sn :2.29 S :2.04	a=6.709 b=6.741 c=11.620	6.71[26] 6.74[26] 11.62[26]
Cu_2SnS_3	Orth	Cmc21	Cu :2.31 Sn :2.29 S :2.05	a=11.575 b=6.691 c=6.400	11.58[26] 6.70[26] 6.40[26]
Cu_2SnS_3	Orth	Imm2	Cu :2.30 Sn :2.30 S :2.04	a=11.612 b=3.923 c=5.428	11.61[26] 3.92[26] 5.43[26]

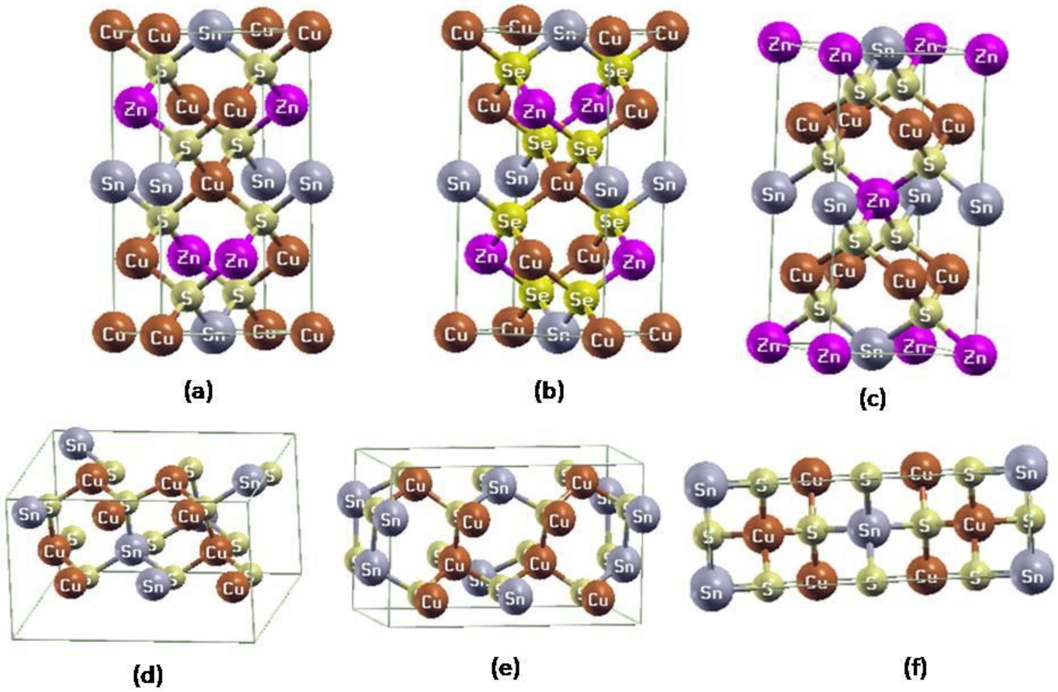


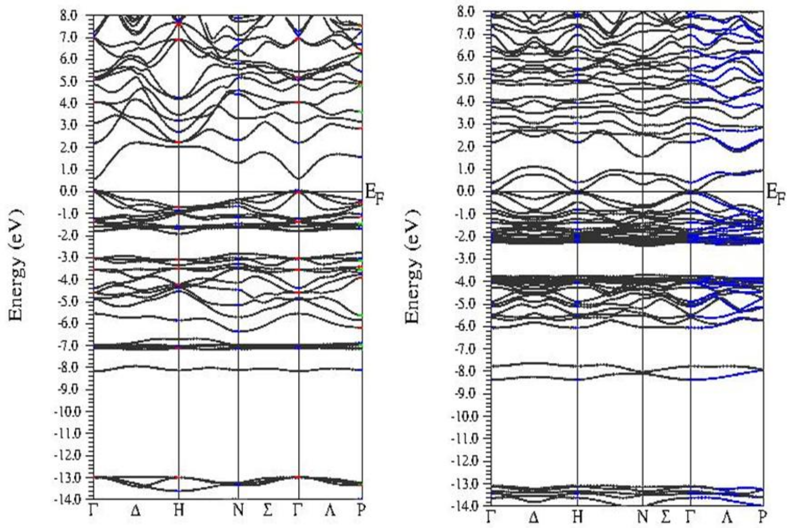
Fig.1 The crystal structures (a).KS-Cu2ZnSnS4 (b). KS-Cu2ZnSnSe4 (c).SS- Cu2ZnSnS4 (d). Cu2SnS3-Cc (e). Cu2SnS3-Cmc21 (f). Cu2SnS3-Imm2.

As it is seen in table 2, it is clear that the calculated band gap values are smaller than the experimental values. It is also well known that in the electronic band structure calculations within DFT, both LDA and GGA approximations usually underestimate the energy band gap [16]. To remediate this gap underestimation, we used the TB-mBJ potential correction for all studied systems that are mentioned in table2. The obtained new gap values are closer to the experimental ones as it can be seen in table2. However, a closer look to the electronic band structures, shows that the maximum of valence band is above the Fermi level. This can be attributed to the fact that the 3d orbitals of Cu, that form most of the top of the valence band, as it will be shown below, are not well localized. This observation can be seen in the band structure of other materials ($AgGaS_2$) calculated using PBE-GGA [27]. To overcome this problem, we propose to use a combination of TB-mBJ and U potential correction. The zoom in Fig. 3 shows the states above the Fermi level in CZTS using GGA, TB-mBJ and TB-mBJ+U, as example. The detailed obtained results are shown in table2.

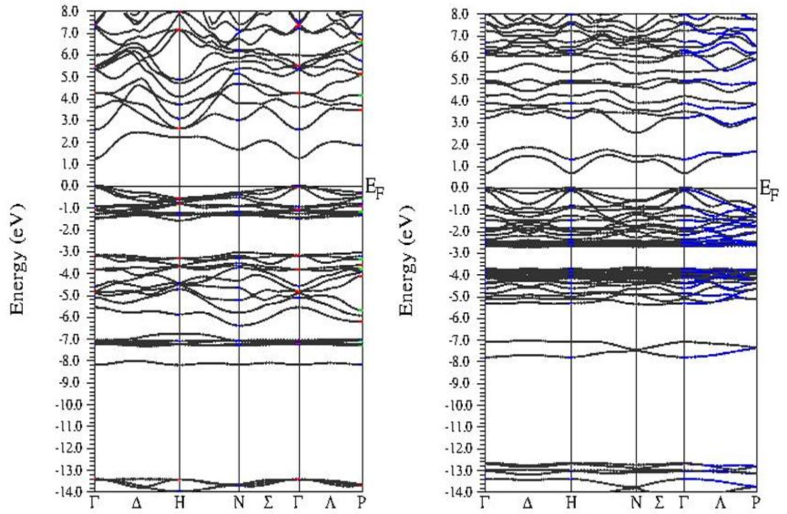
Table 2.

Energy gap of all studied systems using GGA aprroximation, TB-mBJ and TB-mBJ+U potential correction

	Eg (eV) GGA	Eg (eV) TB-mBJ	Eg (eV) TB-mBJ+U	Other calculed values	expérimental
Cu_2ZnSnS_4-KS	0.6	1.30	1.30	0.56[26],1.18[14],	1.30[29],1.50[30]
Cu_2ZnSnS_4-SS	-	0.2	0.8	0.50[26],1.17[14]	1.0[14]
$Cu_2ZnSnSe_4$	0.4	1.02	1.00	1.23[14]	
Cu_2SnS_3- Cc	-	-	0.7	0.09[26], 0.95[26] 0.84[28]	-
Cu_2SnS_3-Cmc21	-		0.8	0.11[26], 1.35[26]	-
Cu_2SnS_3-Imm2	-	-	0.6	-	-

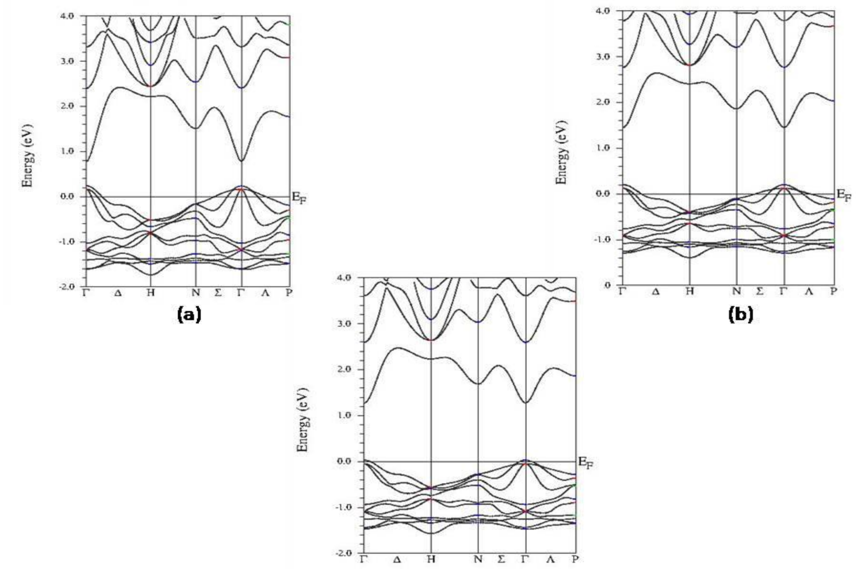


(a)



(b)

Fig. 2 Band structure of KS-Cu_2ZnSnS_4 and Cu_2SnS_3-Cc. (a) using GGA approximation. (b) using TB-mBJ+U potential



(a) **(b)** **(c)**

Fig. 3 The zoom of band structure of KS-Cu_2ZnSnS_4 using (a).GGA approximation, (b).TB-mBJ+U, (c).TB-mBJ+U potential correction.

The total and partial densities of states of two of the studied systems (Cu_2SnS_3-Cc and KS-Cu_2ZnSnS_4 are shown in Figure4. All the DOS structures, of quaternary compounds, show a deep region located between -15 eV and -13 eV formed by the orbital s and p of Sn. These systems show also a valence band between -8 eV and E_F. The Valence band has a deep region and a shallow one. The deep region is mostly formed of the orbital s and d of Zn, s of Sn and p of S(Se). On the other hand, the shallow region near the Fermi level is almost formed by the orbital d of Cu. The contribution of the orbital d of Zn in this region is very small compared to the orbital d of Cu. The bottom of the conduction band is mostly formed by the orbital s of Sn and p of S (Se).

The DOS structures of ternary compounds show a deep region located between -15 eV an -7 eV formed of s and p orbitals of Sn and s of S, the valence band between -6 eV and E_F is mostly formed by the orbital d of Cu and p of Sn and S. The bottom of the conduction band is formed by the orbital s of Sn and p of S and Sn.

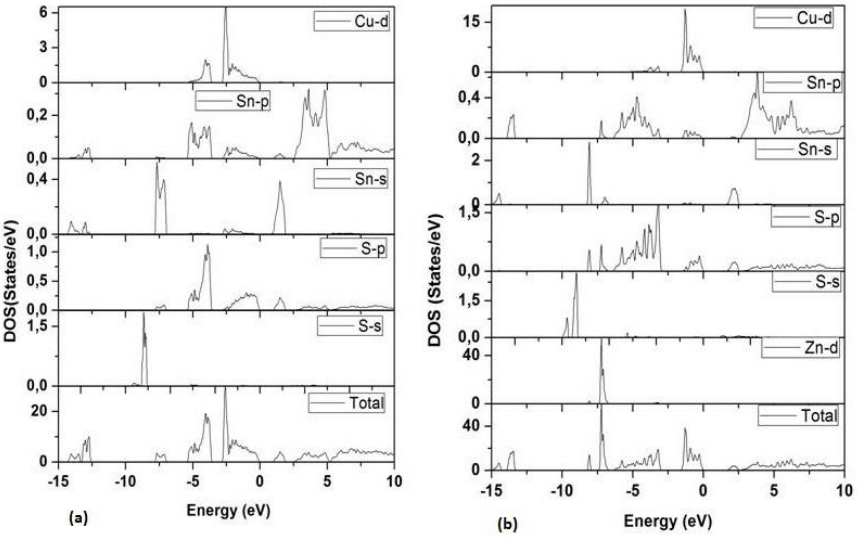


Fig.4 The total and partial density of states with TB-mBJ+U potential of (a). Cu_2SnS_3-Cc (b).KS-Cu_2ZnSnS_4.

3.2. Optical properties

The optical properties can be approached by calculating the dielectric constant epsilon:

$$\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega) \tag{1}$$

Where $\varepsilon_1(\omega)$ is the real part while $\varepsilon_2(\omega)$ is the imaginary part. These parameters are given as:

$$\varepsilon_1(\omega) = 1 + (\frac{2}{\pi})\int_0^\infty \frac{\omega'\varepsilon_2(\omega')}{(\omega'^2 - \omega^2)} d\omega' \tag{2}$$

$$\varepsilon_2(\omega) = (\frac{4\pi e^2}{\omega^2 m^2})\sum_{i,j}\int \langle i|M|j\rangle^2 f_i(1-f_j)\delta(E_f - E_i - \omega)d^3k \tag{3}$$

The absorption coefficient is given by the equation:

$$\alpha(\omega) = \frac{\sqrt{2}}{c}\omega\sqrt{-\varepsilon_1(\omega) + \sqrt{\varepsilon_1^{\,2}(\omega) + \varepsilon_2^{\,2}(\omega)}} \tag{4}$$

From the real part we can estimate the static dielectric constant $\varepsilon_1(0)$that is the value of $\varepsilon_1(\omega)$at $(\omega = 0)$. $\varepsilon_1(0)$ is in good agreement with the reported values in literature for all studied systems as it can be seen in table3. Figure5 shows the real part $\varepsilon_1(\omega)$ for the systems KS-Cu_2ZnSnS_4 and Cu_2SnS_3-Cc. The $\varepsilon_1(0)$ value in GGA approximation for KS- Cu_2ZnSnS_4 , SS- Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ is a bit higher than the obtained values using the TB-mBJ+U potential correction. The latter obtained values are closer to the reported experimental values [5]. This can be attributed to the better localization of orbitals when using the TB-mBJ+U potential correction [16]. It is worth noticing that the $\varepsilon_1(0)$ of $Cu_2ZnSnS(Se)_4$ systems have almost the same value (about 8.4), that is quiet lower than the secondary phases, studied here. This fact is congruant with the lower gap of secondary phases compared to the gap of CZTS. This high value of $\varepsilon_1(0)$ in secondary phases gives a lower serial resistance for a photovoltaic cell using this material as a light absorber. However, the low gap may be the most important parameter that affects the cell yield. The existence of the secondary phases in CZTS light absorber layer introduces higher density of defects, and thus a higher probability of recombination.

Table 3.

The real part of dielectric functions at zero frequency using GGA approximation and TB-mBJ+U potential correction for KS-Cu2ZnSnS(Se)4, SS-Cu2ZnSnS4, Cu2SnS3-Cc, Cu2SnS3-Cmc21 and Cu2SnS3-Imm2.

Materials	$\varepsilon_1(\omega)$		
	GGA	TB-mBJ+U	Other results
Cu2ZnSnS4-KS	8.9	6.2	7.72[14],6.8[31],6.79[32]
Cu2ZnSnSe4-KS	10.1	7.5	11.26[14],8.6[31],8[32]
Cu2ZnSnS4-SS	10.8	6.9	7.72[14],6.5[31],6.53[32]
Cu2SnS3-Cc	25.1	8.1	-
Cu2SnS3-Cmc21	18.4	8.9	-
Cu2SnS3-Imm2	22	8.2	-

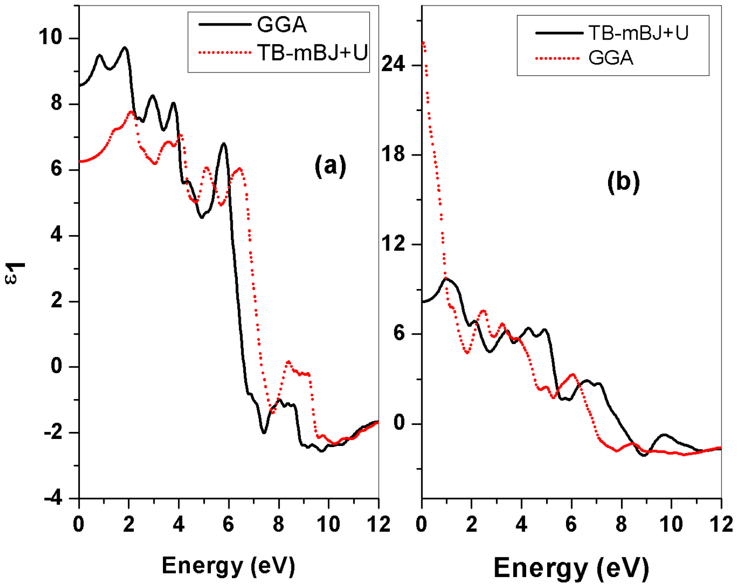


Fig. 5 The real parts of dielectric functions for (a).KS-Cu_2ZnSnS_4 (b). Cu_2SnS_3-Cc.

The imaginary parts $\varepsilon_2(\omega)$ for the systems KS-Cu_2ZnSnS_4 and Cu_2SnS_3-Cc are shown in Figure6. In these curves, we can see the fundamental transition in all studied systems. We notice that the transition in $Cu_2ZnSnS(Se)_4$ systems occurs at about 1 eV (0.6 eV) in GGA approximation while it occurs at 1.4eV (1.0 eV) with TB-mBJ+U potential correction these transitions correspond to the transition from the top of the valence band to the bottom of conduction band at the Γ point in these systems. The first peak in $\varepsilon_2(\omega)$ is at 2 eV (2.2)eV using GGA and TB-mBJ+U respectively for both systems. This transition can be attributed to the transition from the top of the valence band to the maximum of the first peak in conduction band. The main peak in $\varepsilon_2(\omega)$ is at about 6 eV in both systems with GGA approximation while it is at about 7 eV in CZTS and 6.2 eV in CZTSe using mBJ+U potential correction. It is remarkable here that the effect of U is much bigger in the CZTS system in comparison to the CZTSe system. The difference in the energetic position of the main peak in $\varepsilon_2(\omega)$, when using GGA or TB-mBJ+U is about 1eV in CZTS while it is only 0.2 eV in CZTSe. The correction in the states above the valence band is also greater in CZTS compound than the CZTSe. This suggests that the U correction is much efficient when applied to the CZTS than the CZTSe compound. Regarding that all orbitals of S atom and Se atom are equivalent in the two compounds, and that the d orbital of Se is located in the conduction band the difference in the U correction effect may be attributed to the volume of Se that is greater than that of S and the difference in electronegativity between S and Se [29]. The secondary phases show a similar behavior, the fundamental absorption occurs at almost 0 eV following the calculated band structure using GGA while it shifts to about 0.6 eV for the 3 phases using TB-mBJ+U potential correction. The monoclinic phase shows an $\varepsilon_2(\omega)$ that has a shoulder at 0.2eV (1eV), a first peak at about 1eV(1.5 eV) and a main peak at about 4eV (5eV) using GGA approximation and TB-mBJ+U potential correction respectively.

The orthorhombic phases have similar imaginary epsilon part, that consists of a shoulder at about 0.3eV (1eV) , a first peak at about 0.9eV(1.5eV) , a second pick at about 1.3eV(1.8eV) using GGA and TB-mbj+U . The main pick in the Orthorhombic-Cmc21 phase is at about 4.6 eV(5eV) while it is at about 3.1eV(4eV) in the Orthorhombic-Imm2 phase using GGA and TB-mBJ+U respectively. The shoulder may be linked to the transition from the top of valence band to the bottom of conduction band at the Γ point. Other peaks can be linked to the transitions between the valance band and the conduction band as it is possible in DOS structures.

The stannite phase of Cu_2ZnSnS_4 shows an $\varepsilon_2(\omega)$ that has a shoulder at 0.8eV (1.2eV), a first peak at about 2eV(2.7 eV) and a main peak at about 4.2eV (5eV) using GGA approximation and TB-mBJ+U potential correction respectively.

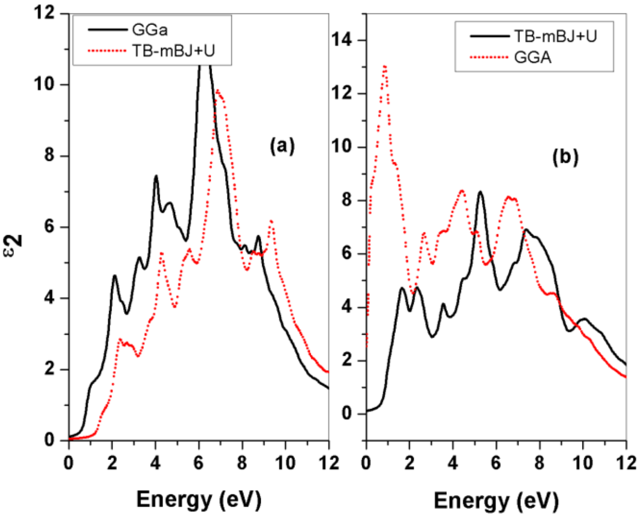


Fig. 6 The imaginary parts of dielectric functions for (a).KS-Cu_2ZnSnS_4 (b). Cu_2SnS_3-Cc.

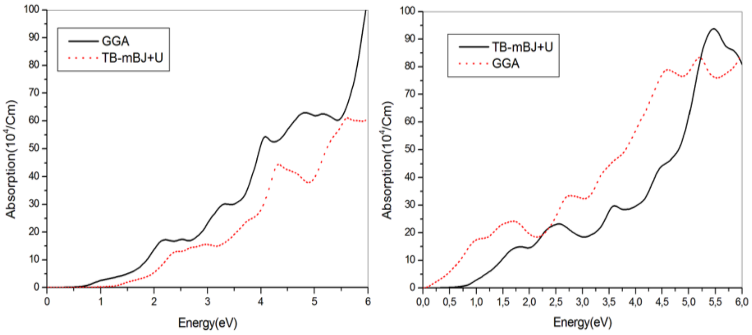
Fig.7 shows the absorption coefficient of our studied systems Cu_2ZnSnS_4-KS and Cu_2SnS_3-Cc. the absorption coefficient values at the fundamental transition ($\Gamma_V \rightarrow \Gamma_C$) for all studied systems are shown in table 4.

It is obvious that the KS phase of CZTS is the better material to be used as an absorber in a photovoltaic cell. It has a direct gap of 1.3 eV as calculated here and that is very close to the experimental values ; it has, also, an absorption coefficient more than 4x10^4 cm^{-1} at the fundamental absorption and higher in all visible light spectrum. The SS phase of CZTS shows a lower gap than the KS phase with a bit lower absorption coefficient as it can be seen in Table4. The KS phase of CZTSe has a direct gap of about 1.0 eV. This is a bit far from the ideal gap value for this application. It is important to note that the studied secondary phases, in this study, show a low gap associated with a low absorption coefficient. These remarks suggest that the “accidental” existence of SS phase or secondary phases in a prepared KS phase of CZTS can be a part of the reasons standing behind the low experimental efficiency factor of CZTS cells compared to the expected theoretical one.

Table 4.

The absorption coefficient using GGA approximation and TB-mBJ+U potential correction for systems KS-Cu2ZnSnS(Se)4, SS-Cu2ZnSnS4, Cu2SnS3-Cc, Cu2SnS3-Cmc21 and Cu2SnS3-Imm2.

Materials	$\alpha(\omega)$ (cm^{-1})		
	GGA	TB-mBJ+U	Other results
Cu2ZnSnS4-KS	10^4	4*10^4	>10^4[14]
Cu2ZnSnSe4-KS	10^4	2.5*10^4	
Cu2ZnSnS4-SS	10^4	2*10^4	
Cu2SnS3-Cc	-	10^4	
Cu2SnS3-Cmc21	-	0.1*10^4	
Cu2SnS3-Imm2	-	0.2*10^4	



(a) (b)

Fig. 7 The absorption coefficient for (a). KS-Cu2ZnSnS4 (b). Cu2SnS3-Cc.

4. Conclusions

We calculated the structural, electronic and optical properties of KS-$Cu_2ZnSnS(Se)_4$, SS-Cu_2ZnSnS_4, Cu_2SnS_3-Cc, Cu_2SnS_3-Cmc21 and Cu_2SnS_3-Imm2 using GGA approximation, TB-mBJ and TB-mBJ+U potential correction in the frame of the full potential linearized augmented plane-wave plus local-orbitals (FP-LAPW-LO) method are based on DFT. The obtained results using TB-mBJ+U were the closer to the experimental results. The U potential helped to solve the problem of the states that appear above the Fermi level when using GGA or TB-mBJ potential only. An accidental existence of SS phase or secondary phases of CZTS can partly explain the low experimental yield compared to the expected theoretical one.

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