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STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF Cu_2GeS_3. A FIRST PRINCIPLES STUDY

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Abstract

In this paper, we have performed first-principles calculations on the structural and optoelectronic properties of Cu_2GeS_3 compound in the Cc and Imm2 structures. We have applied the linear augmented plane wave method for all electrons (FP-LAPW), which is based on density functional theory (DFT) by using the local density approximation (LDA) and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA). In addition, the modified Becke Johnson Tran and Blaha potential (TB-mBJ) combined with the Hubbard potential (U), which successfully corrects the band gap problem.

The structural properties such as lattice parameter, compressibility modulus and its derivative for Cu_2GeS_3-Cc are in good agreement with the available data, but for Cu_2GeS_3-Imm_2 there is no research work in the literature. The band structure results show that the Cu_2GeS_3-Cc compound has a direct gap (Γ-Γ) and that Cu_2GeS_3-Imm_2 is a metal.

The optical properties are calculated by determining the real and imaginary parts of the dielectric function ε(ω), the absorption coefficient, the reflectivity and the refractive index. These results indicate that these alloys are very useful for UV photo catalysis applications.

1. Introduction

The CGS compound (Cu_2GeS_3) is a ternary p-type semiconductor of group I_2IV VI it belongs to the copper-based chalcogen family [1] and was prepared by solid-state reaction of the component elements in vacuum-sealed quartz ampoules and characterized by a structure of a single crista using X-ray diffraction techniques. [2]. Its crystallization is in the Cc monoclinic space group with (a=6.449 Å, b=11.319 Å and c=6.428 Å) [3]. This material was expected to have a high value compared with Cu_2SnS_3 solar cells. Consequently, the Cu_2GeS_3 ternary of Cu_2-IV-VI_3 semiconductors is an attempt to prepare In- and Se-free Cu_2GeS_3 thin films. [4]

The synthesis of quaternary semiconductors Cu_2ZnSnS_4 (CZTS) and Cu_2SnGeS_3 (CTGS) is relatively more difficult than that of binary and ternary semiconductors [5]. P-type Cu-Sn-S semiconductors have also been considered as candidates for low-cost thin-film solar cell absorbers. [6]

The nanocrystal range extends from 1.46 eV to 2.33 eV for x = 0 and 1 respectively covering the ideal band gap of 1.5 eV for solar photoelectric conversion. It is well known that the crystalline system of nanoparticles can affect both their electronic and optical properties [7]. Studies on the CGS matrix and its fundamental properties, such as crystal structure and band gap, show that they are still the subject of debate. As for crystal structure, Cu_2GeS_3 is reported in polymorphic and orthorhombic crystal structures (or-CGS; SG: Imm_2) [8] and has also been reported for a high-temperature, tetragonal Cu_2SiS_3 modification (t-CGS; SG: I-4_2m). [9] cubic (c-CGS; SG: F-43 m) [10], monoclinic (m-CGS; SG: Cc) [11, 12]. The different CGS polymorphs have various band gap energies, between 1.3 and 1.6 eV [13, 14].

We investigated the monoclinic structure (m-CGS; SG: Cc) since it is the most stable structure observed when the temperature is raised to 550°C [15]. The orthorhombic structure (gold-CGS; SG: Imm2) was also examined, as it has not been the subject of previous studies: LDA, GGA, GGA + U, and the combined Hubbard U potential (TB-mBJ+U). This material was selected because the common elements Cu, Ge and S are naturally abundant in it. It is also considered environmentally friendly and relatively inexpensive, non-toxic and non-hazardous. These properties have enabled this compound to be a filter for the following applications, such as photovoltaic materials [13, 16, 17], thermoelectricity (TE) [18] and photo electrochemistry [19, 20].

The aim of this work is to determine the structural, electronic and optical properties of the ternary compound Cu_2GeS_3, using the linearized augmented plane wave method (FP-LAPW) within the framework of density functional theory (DFT) implemented in the Wien2K code. This paper is divided into three parts. The first part presents a general introduction. The

second is devoted to the different methods used to calculate the physical properties of our material. In the third section, we present the results obtained and their interpretation. Finally, we end our study with a general conclusion.

2. Computational details

In this paper, the calculations are performed with the wien2k code [21, 22], which is based on density functional theory (DFT) [23] the last is founded on the Full Linear Enhanced Level Wave (FP-LAPW) method [24]. We used the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [25] and the density locale approximation (LDA) [26] to investigate the structural and electronic properties of Cu_2GeS_3- Cc and Cu_2GeS_3-Imm2, For the electronic properties, we introduced the modified Becke-Johnson potential of Tran and Blaha (TB-mBJ) combined with the Hubbard potential (U) [27-29]. The Plane waves are limited to RMT.Kmax=8 (or RMT is the muffin tin radii for atoms and is the maximum modulus for the reciprocal lattice vector). For Cu_2GeS_3 Cc_9 the R_{mt} of Cu, Ge, and S atoms are: 2.26 u.a, 2.16 u.a and 1.85 u.a respectively and for Cu_2GeS_3 Imm2 the R_{mt} taken equal to 2.20, 2.11, 1.80 u.a for Cu, Ge, and S atoms respectively.

The reciprocal spatial integration is performed with a k-mesh of 10×9×10 , which gives 250 K-points for Cu_2GeS_3-Cc and 10×10×10 , with 170 K-points for Cu_2GeS_3- Imm2 in the irreducible Brillouin zone, which is sufficient to converge the total energy.The electronic configuration of Cu, Ge, are: [Ar] $3d^{10}$ $4s^1$, [Ar] $3d^{10}$ $4s^2$ $4p^2$ and [Ne] $3s^2 3p^4$ respectively.

3. Results and discussions

3.1. Structural properties

The equilibrium parameters were calculated by minimization of total energy relative to the cell parameters and atomic positions by the Birch-Murnaghan equation[30], to obtain the structural properties for the two types structures (Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2) Fig.1(a,b), The structure Imm2 of compound Cu_2GeS_3 is a type of orthorhombic crystal system with the space group Imm2 (No. 44) 1. This structure is composed of CuS_4 and GeS_4 tetrahedra that share corners with each other. The lattice parameters are a = 3.16 Å, b = 3.16 Å, and c = 5.31 Å. The unit cell contains 8 atoms of each element. Here is a diagram of the structure:
Cu(0,0,0)(0.5,0.5,0)(0.5,0,0.5)(0,0.5,0.5)Ge(0.25,0.25,0.25)(0.75,0.75,0.25)(0.75,0.25,0.75)(0.25,0.75,0.75)S(0.25,0.25,0.75)(0.75,0.75,0.75)(0.75,0.25,0.25)(0.25,0.75,0.25).

The crystal structure of Cu_2GeS_3 with a = 6.439 Å, b = 11.316 Å and c = 6.416 Å, β = 108.37° is monoclinic space group Cc.

$$E(V) = E_0 + \left[\frac{B_0 V}{B'(B'-1)}\right].\left[B'\left(1-\frac{V_0}{V}\right) + \left(\frac{V_0}{V}\right)^{B'} - 1\right] \quad (1)$$

V_0 is the static equilibrium volume, E_0 total energy of equilibrium state, B is the modulus of compressibility and B' its derivative witch given by:

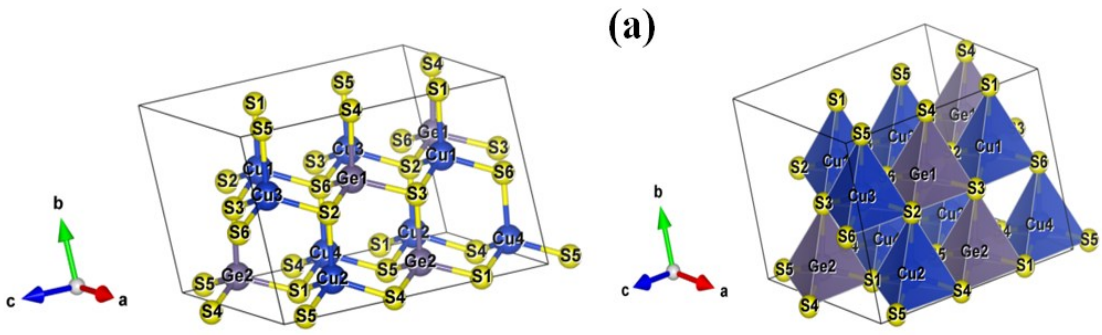
$$\acute{B}_0 = \frac{\partial B}{\partial P} \quad (2)$$

The modulus of compressibility B_0 is determined by:

$$B_0 = V_0 \frac{\partial^2 E}{\partial V^2} \quad (3)$$

Fig.2 (a, b, c and d) shows the variation of total energy as a function of system volume for two types of structure Cu_2SnS_3 (Cc, Imm2). The results obtained, lattices constants (a_0, b_0, c_0) in (Å),and β (DEG), bulk modulus B (GPa) and its derivative B', the equilibrium lattice volume V_o (bohr)^3 and the minimum total energy E(Ry) are shown in Table1.

When we calculated lattice constants (a_0, b_0, c_0) and β, we noted that the results obtained using GGA are well consistent with the experience and these lattice parameters are in good agreement with the reported values (ICSD #85138) from those recorded when using LDA.



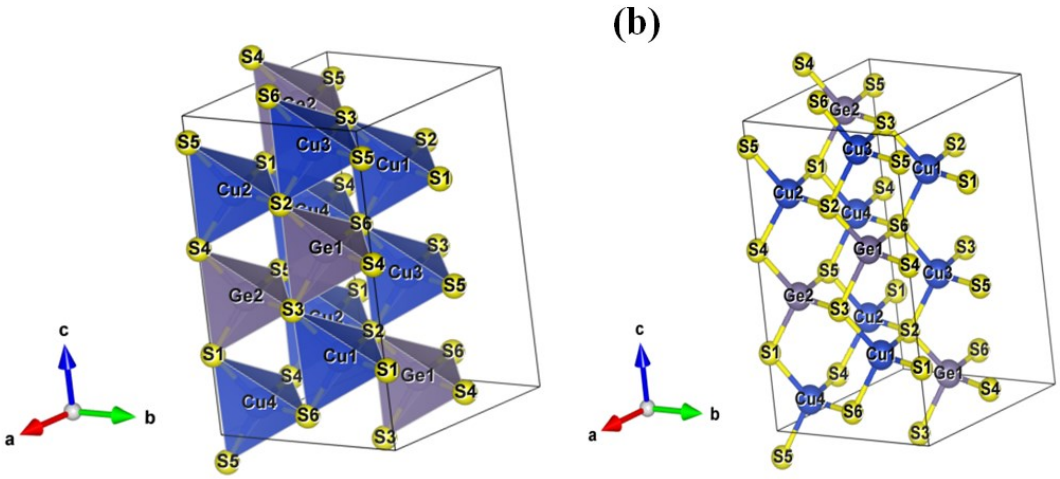


Figure 1. Crystal structure of: (a) Cu_2GeS_3-Cc and (b) Cu_2GeS_3-Imm2

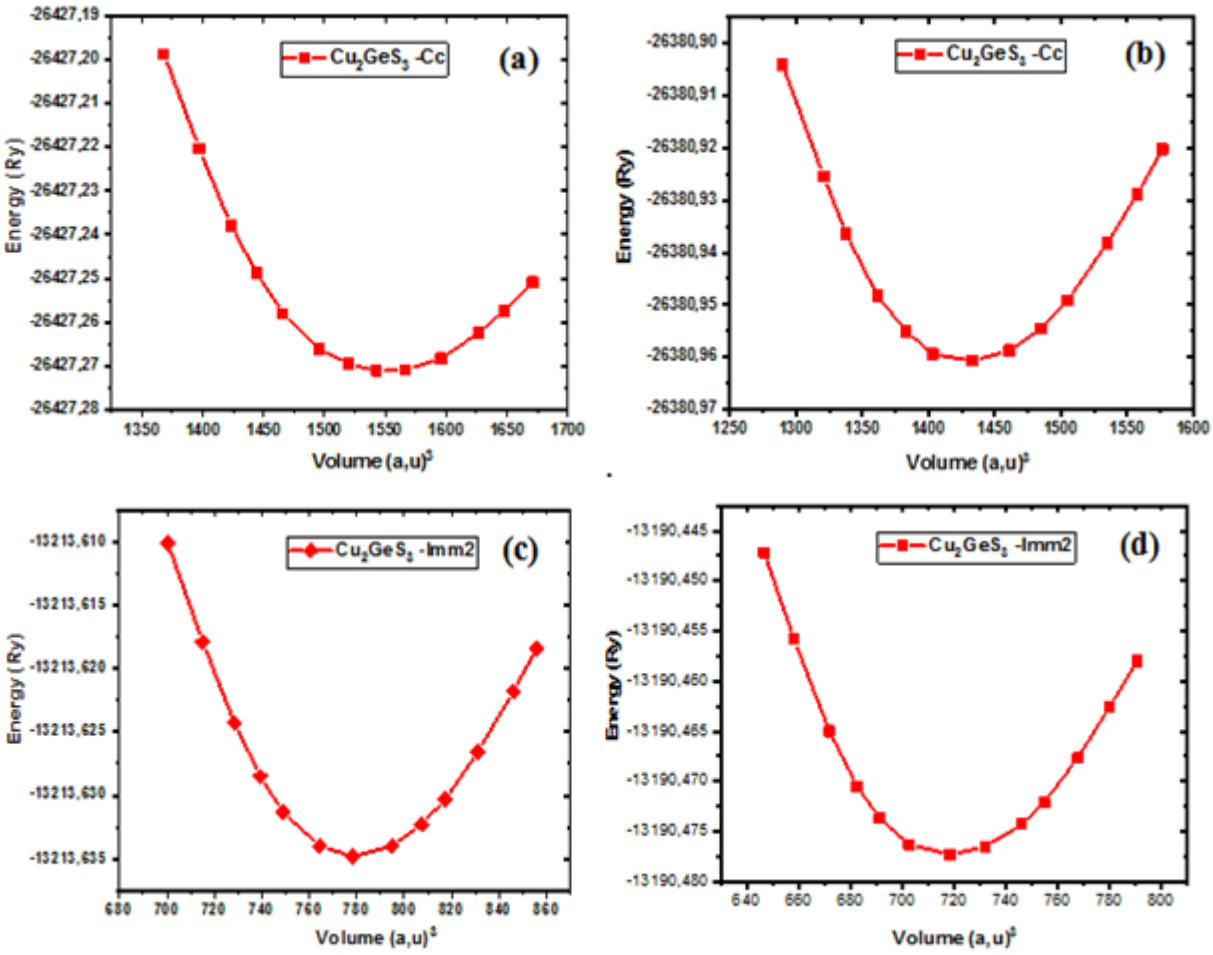


Figure 2. The volume optimization of Cu_2GeS_3-Cc using:(a)(GGA-PBE), (b)(LDA) and Cu_2GeS_3-Imm2 using:(c) (GGA-PBE), (d) (LDA)

Table 1. Calculated of: lattices constants (a_0,b_0 ,c_0), bulk modulus B (GPa) and its derivative B' and total energy E (Ry) for Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2

Cu_2GeS_3	**Total energy (Ry)**		***B***		***B'***		**a_0(Å)**		**b_0(Å)**		**c_0(Å)**		***β***	
	Cc	Imm2	Cc	Imm2	Cc	Imm2	Cc	Imm 2	Cc	Imm2	Cc	Imm2	Cc	Imm2
LDA	-26427.27	-13190.47	75.52	98.08	5.17	5.03	6.55	3.75	6.60	11.06	11.66	5.21	09.77	-
GGA	-26380.96	-13213.63	98.0	74.70	4.99	4.72	6.40	3.83	6.43	11.33	11.10	5.32	08.82	-
Theo		-	-	-	-	-	6.45[a]	-	6.42[a]	-	11.28[a]	-	08.52[a]	-
Exp		-	-	-	-	-	6.43[a]	-	6.42[a]	-	11.29[a]	-	08.36[a]	-
		-	-	-	-	-	6.44[b]	-	6.42[b]	-	11.31[b]	-	08.30[b]	-
		-	-	-	-	-	6.41[c]	-	6.43[c]	-	11.30[c]	-	08.29[c]	-

[a]Ref [11], [b]Ref [3] and ,[b]Ref [31]

3.2.1. Band structure

The calculation of band structures for our compounds studied in this section Cu_2SnS_3-Cc, Cu_2SnS_3- Imm2 are calculated according to the directions of symmetry in the first Brillouin zone (ZB), with the Fermi level fixed at 0 eV. As shown in Fig. 3 (a and b), using the GGA method we found that the CGS material is a metal, as there is an overlap at the high symmetry point Γ between the valence and conduction energy bands at the Fermi level observed by EF, with a gap of 0.30 eV for Cu_2GeS_3-Cc and 0 eV for Cu_2GeS_3-Imm2, which is contrary to the results obtained in the experimental study demonstrating that this compound is a semiconductor [3, 11].

This overlap is due to the 3d orbits of Cu, which form the top of the valence band. To resolve this situation, we have introduced the approximation of TB-mBJ + U [27] with type *d* orbital correction potential, where Ud (Cu) = 6 eV on Cu atoms [32, 33]. The results obtained are shown in Fig.3 (c, d, e and f). it's right there is a direct gap *Γ–Γ* around the Fermi level, this confirms that our material is a semi-conductor (S.C) type *p* with a half gap of (1.2 and 0.7) eV for Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2 respectively. Finally, table.2 summarizes the band gap calculated by the different approximations they used in this part.

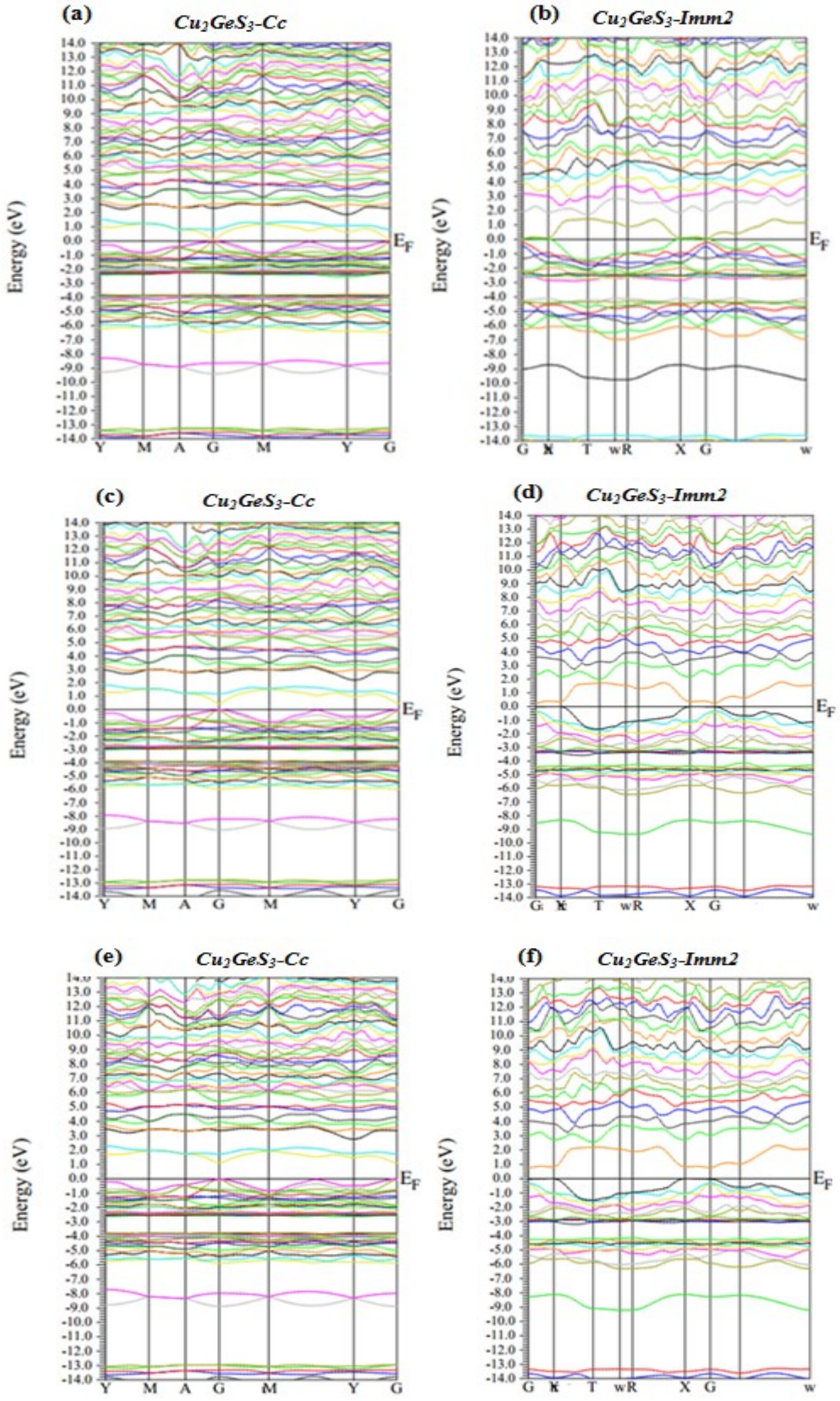


Figure 3. Band structures of Cu_2GeS_3–Cc (left panel) using: (a) PBE-GGA, (c) Hubbard, (e) TB-mBJ+U and Cu_2GeS_3–Imm2 (right panel) using: (b) PBE-GGA, (d) Hubbard, (f)TB-mBJ+U.

Table 2. The calculated band gap E_g (eV) of Cu_2GeS_3.

Compound	Energy gap E_g (eV)			
	GGA	Hubbard (U=6 eV)	TB-mbj +U	Other
Cu_2GeS_3–Cc	0.30	0.613	1.202	1.53[31] ,1.54 [34] ,1.54[35]
Cu_2GeS_3–Imm2	0	0.158	0.702	/

3.2.2. Density of state

From the above parts, we concluded that TB-mBJ+U is the best approximation that may be used to study CGS compounds, and so we investigated the density of state with this approximation to explain the contribution of different states in the band structures, the total density (TDOS) and partial densities of states (PDOS) were evaluated as shown in Fig.4(a and b), and the Fermi level F_E is set at 0 eV.

There is high similarity between (DOS) for Cu_2GeS_3-Cc and (DOS) of Cu_2GeS_3-Imm2, where (TDOS) clearly shows the existence of three regions: The first energy region between ~[-14,-8] eV is a region isolated from the others, it mainly results from a significant contribution from the s and p states of the (Ge) atom and s of (S),the second energy region between ~[-6, 0] eV is the most important region in (TDOS), it comes mainly from a significant contribution of the *4d* states of (Cu) and a small contribution of the *p* states of (S) and *p* of (Ge). We also note that the maximum of the valence band is dominated mainly by *d* states of (Cu). The third energy region between [0,14] eV is characterized by the presence of a gap (1.2, 0.7) eV for Cu_2GeS_3- Cc and Cu_2GeS_3-Imm2 respectively resulting from the important contribution of states of (Ge) and the small contribution of states *p* of atom (S). This region results from the hybridization of electrons *p* of (Ge) and *p* of (S). This *p-p* hybridization is indicative of the covalent character of Ge - S bonds.

4. Optical Properties

4.1 Dielectric function

The dielectric function can be defined as [36]:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (4)$$

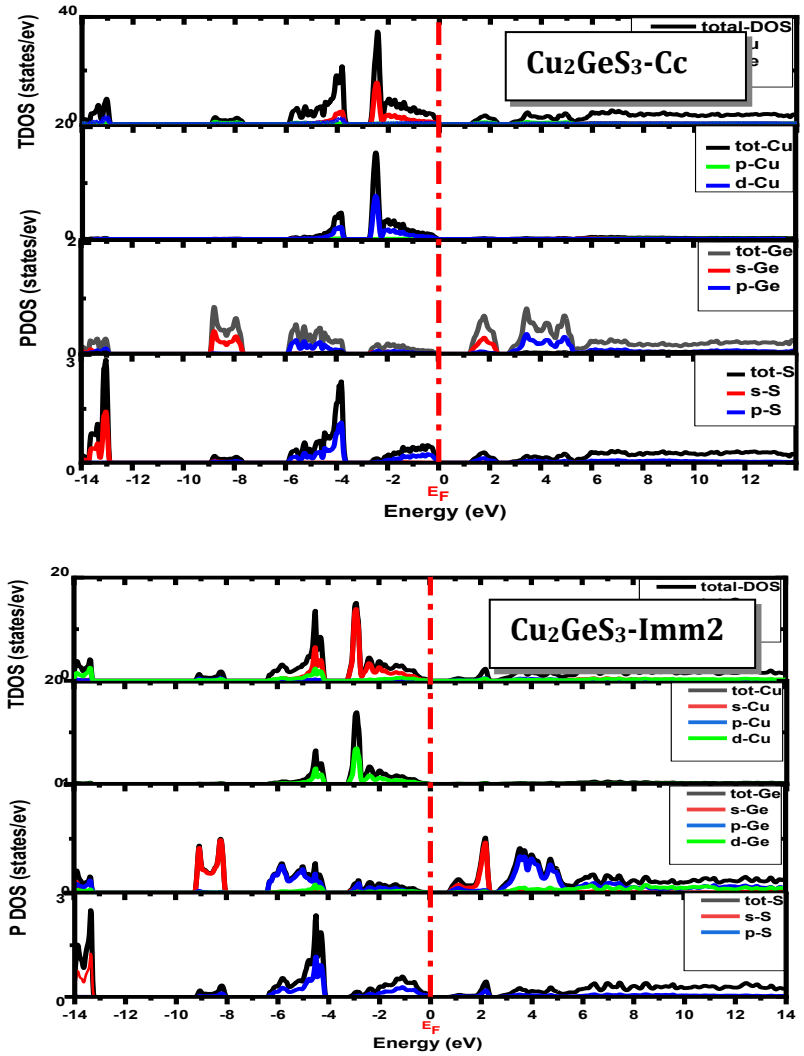


Figure 4. Total and partial densities of states (DOS) for Cu_2GeS_3usingTB-mBJ+U: (a)Cu_2GeS_3-Cc. (b)Cu_2GeS_3-Imm2

It can be applied to describe the optical properties of media for any photon energy where the imaginary part $\varepsilon_2(\omega)$ of this dielectric function depends on frequency and is directly related to the electronic band structure and can be determined by summing all possible transitions from occupied to empty states using the following expression [37]:

$$\varepsilon_2(\omega) = \frac{2\pi e^2}{\Omega\omega_0}\sum_{k,v,c}\left|\langle\psi_k^c|\vec{u}.\vec{r}|\psi_k^v\rangle\right|^2 \delta(E_k^c - E_k^v - \hbar\omega) \qquad (5)$$

where $\boldsymbol{e}$, ω and $\boldsymbol{\Omega}$ are electron charge, photon frequency of the incident photons and crystal volume respectively, $\vec{r}$ is the position vector, $\vec{u}$ is the unit vector defining the polarization of the incident electromagnetic wave, ψ_k^c and ψ_k^v are the conduction band (CB) and valence band

(VB) wave functions, respectively.

The real part of this function $\varepsilon_1(\omega)$ is derived from the imaginary part of the dielectric function by the Kramers-Kronig transformation according to the following formula [38, 39]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \omega \varepsilon_2(\omega')}{(\omega'^2 - \omega^2)} d\omega' \quad (6)$$

Pis the principal value of the integral.

The variation of $\varepsilon_1(\omega)$ as a function of energy for the compounds Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2 between 0 and 13.6 eV is shown in Fig.5.a. In general, we can see that the spectra have almost the same appearance, with small differences. We note that for all these compounds, the static dielectric constant is 3.96 for Cu_2GeS_3-Cc and 4.05 for Cu_2GeS_3-Imm2. the $\varepsilon_1(0)$ function cancels at the following energy values: 7.46 (Cu_2GeS_3-Cc) and 8.96 (Cu_2GeS_3-Imm2). It should be noted that at these energy values, dispersion is zero and, consequently, absorption is maximum.

The variation of the imaginary part of the dielectric function with the variation of the photon energy of the compounds Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2 is plotted in Fig.5.b for radiation up to 13.6 eV. We can first note that the first critical points of the dielectric function, corresponding to the fundamental absorption thresholds, start at around at ~ 0.78 eV for Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2.

The critical point values correspond to the transition (direct optical gaps) between valence and conduction bands (Γ_v- Γ_c). The main peak, reflecting the absorption maximum, is located at 5.11 eV and 6.54 eV for Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2 compounds respectively. These spectra also show the presence of secondary peaks around the main peak. For example, in the spectrum of the compound Cu_2GeS_3-Cc, the second is the main peak, centered around the value 2.41 eV. The third peak is located at 3.65 eV, and the fourth peak is positioned at 4.61eV. For the Cu_2GeS_3-Imm2 compound, the second is the main peak, centered around 3.06 eV. The third peak is located at 4.51eV. secondary peaks due to indirect transitions. However, the $\varepsilon_2(\omega)$ spectra are apparently more restricted in the ultraviolet. Based on the dielectric spectra, we conclude that Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2 are suitable for solar energy conversion and other optoelectronic applications.

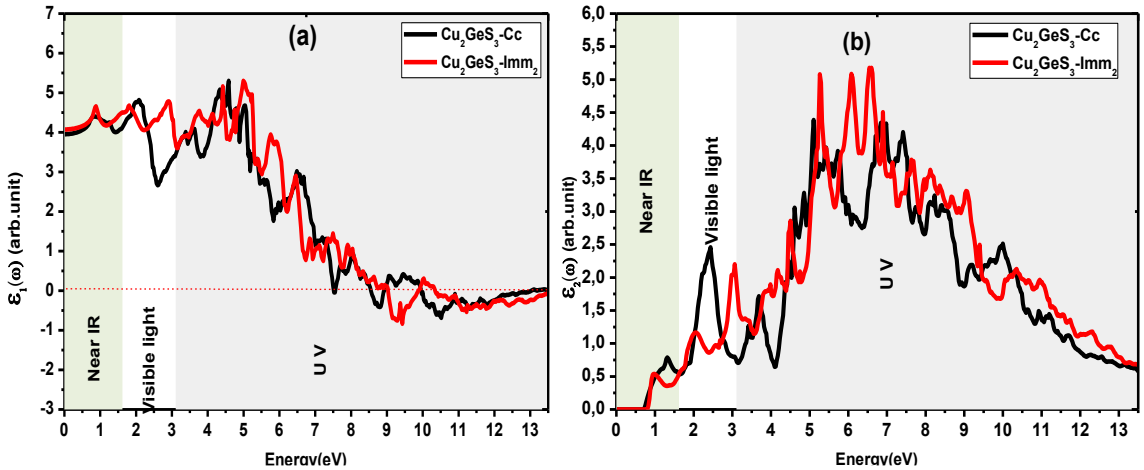


Figure 5. Dielectric function: real part (a) and imaginary part (b) of Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2 using TB-mBJ+U

4.2 Absorption coefficient, reflectivity and refraction index

The variation of the absorption coefficient as a function of photon energy up to 12 eV is shown in Fig. 6.a for the compounds Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2. We can note that the fundamental absorption thresholds start at around 1.07 for Cu_2GeS_3-Cc and 1.41 eV for Cu_2GeS_3-Imm2. The curves show a maximum at energies 5.91 and 9.67eV for Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2compounds respectively.

The evolution of reflectivity for the compounds studied is shown in Fig. 6.b. The spectra show reflectivity values in the energy range [0-13.6] eV. The curves show a maximum of 38.49% at 5.91eV for Cu_2GeS_3-Cc compounds and 33.95% at 9.51 eV for Cu_2GeS_3-Imm2. These results show that our ternary compounds are priori good candidates for use in the ultraviolet range.

The refractive index variation as a function of energy for the two compounds is shown in Fig. 6.c. The curves show a maximum at energies of 4.58 and 5.23eV for compounds (Cu_2GeS_3-Cc) and 2.03 (Cu_2GeS_3-Imm2) respectively. These peaks are mainly due to the transition of electrons from the valence band to the conduction band. The static refractive index n(0) is 1.98 (Cu_2GeS_3-Cc) and 2.03 (Cu_2GeS_3-Imm2). The refractive index starts to increase with photon energy reaching maximum values of around 1.03 eV in the infrared range for the corresponding compounds.

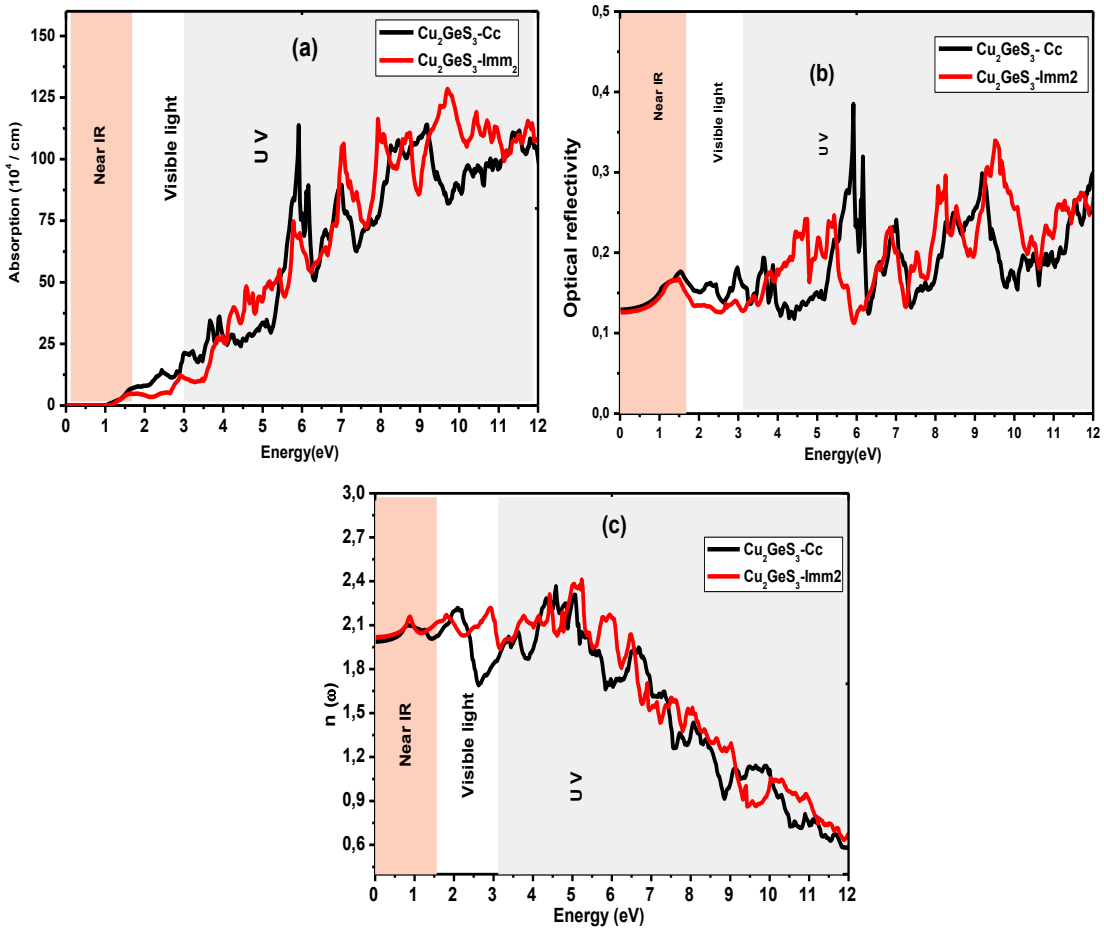


Figure 6. Absorption coefficient(a), reflectivity(b) and refraxion index(c) of Cu_2GeS_3-Cc and Cu_2GeS_3-Imm2 using TB-mBJ+U

5. Conclusion

In summary, the aims of this study are to investigate the structural, electronic and optical properties of the Cu_2GeS_3 compound in the Cc and Imm2 structures. The method used to carry out this research is the linearized augmented plane wave method (FP-LAPW) implemented in the Wien2k code within the framework of density functional theory (DFT). We used the generalized Perdew-Burke-Ernzerhof gradient approximation (GGA-(PBE) and the local density approximation (LDA) as exchange-correlation potentials, as well as the modified Becke Johnson Tran et Blaha potential (TB-mBJ) combined with the Hubbard potential (U).

The structural properties such as equilibrium lattice parameters and compressibility modulus are well described for Cu_2GeS_3-Cc by using the different approximations applied in this study (LDA and GGA- PBE). These calculated values are in good agreement with other theoretical and experimental works, but for Cu_2GeS_3-Imm2, there are no literature searches. From the calculations of partial and total densities of state and band structures, the obtained

results show that the Cu_2GeS_3-Cc compound is an indirect gap semiconductor (Γ-Γ) and that Cu_2GeS_3-Imm2 is a metal.

The optical properties of a material are very important from an optoelectronic point of view, so a qualitative dielectric function, absorption coefficient, reflectivity and refractive index are calculated to study these properties, so this compound significantly enhances photo-catalytic activity in the ultraviolet range.

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