

Electronic structure and optical properties of chalcopyrite CuYZ_2 (Y=Al, Ga, In; Z=S, Se): an ab initio study

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The electronic and optical properties of CuYZ_2 (Y=Al, Ga, In; Z=S, Se) compounds are calculated by using highly accurate first principal technique. Our calculated band gaps of these compounds are in excellent agreement with the experimental results. Electronic structure and charge density calculations show that these compounds have a direct band gap (Γ - Γ) with a predominantly covalent bonding. Refractivity and reflectivity spectra of these ternary chalcopyrites are discussed and compared with the available experimental spectra. On the basis of direct and wide bandgap the materials are very suitable for optoelectronic devices in the visible and ultraviolet regions of the electromagnetic spectrum.

(Received March 26, 2013; accepted January 22, 2014)

Keywords: DFT, Chalcopyrite, Bandgap, Refraction

1. Introduction

Semiconductor materials are the backbone of optoelectric industry [1-7]. Since few decades the ternary $\text{X}^{\text{I}}\text{Y}^{\text{III}}\text{Z}_2^{\text{VI}}$ type compounds which crystallize in chalcopyrite structure (space group $\text{I4}\bar{2}\text{d}$) have gained a considerable attention [8-11]. These compounds are widely used in solar cells, light emitting diodes, nonlinear optics, optical frequency conversion in all solid state based tunable laser systems, tunable frequency conversion in mid-infrared based optical parametric oscillators, and also have significant advantages for compact devices [12-15]. These compounds are also good candidates for spintronic applications when doped with transition elements [16]. CuGaS_2 compound is the most promising one for solid state lightning and high efficient solar cell because of its direct band gap in desirable energy range. $\text{Cu}(\text{Ga}, \text{In})\text{Se}_2$ emerges as a technology that could replace the current silicon panel [17].

Hahn et al. [18] reported for the first time on the ternary chalcopyrite compounds. The possibility of semiconductivity in these compounds was reported by Goodman et al., [19]. Efficient solar cell fabrication based on these compounds was presented by Tuttle et al., [20]. Lazewski et al. [21] calculated the electronic, dynamical and elastic properties of these compounds using ab-initio pseudopotential calculations. Alonso and co-workers calculated the complex dielectric tensor components of these compounds [22] and compared their results with those of Jaffe and co-authors [9]. Xue et al., [23] reported about the dielectric properties of I-III-VI₂ compounds.

Rashkeev et al., reported about the second harmonic optical response of $\text{Cu}(\text{Ga}, \text{In})(\text{S}, \text{Se})_2$ compounds [24]. Reshak et al., present the band structure and density of states for $\text{CuAl}(\text{S}, \text{Se})_2$ compounds [25] but the reported energy-gap was found much smaller than the experimental ones. Ahuja and co-workers calculated the optical properties of CuGaS_2 compound using the FP-LMTO method [8]. Therefore, we think that it is timely to perform first-principles calculations on the electronic and optical properties, using the state of the art full-potential augmented plane wave plus local orbitals approach (FP-APW+lo) based on the density functional theory (DFT) [26, 27].

The rest of the paper has been divided in three parts. In Section 2, we briefly describe the computational techniques used in this study. The most relevant results obtained for the electronic and optical properties for CuYZ_2 (Y=Al, Ga, In; Z=S, Se) compounds are presented and discussed in Section 3. Finally, in section 4 we summarize the main conclusions of our work.

2. Computational details

Present calculations were performed by the full potential linearized augmented plane wave plus local orbital (FP-LAPW+lo) method based on DFT [26, 27] as implemented in wien2K package [28]. The exchange-correlation potential was treated using the Engel-Vosko GGA scheme [29]. Different computational parameters, $R_{\text{MT}} * K_{\text{max}}$ (where R_{MT} is the minimum muffin-tin radii and

K_{\max} gives the magnitude of largest K vector in the plane wave basis), G_{\max} (The potential and the charge density Fourier expansion parameter), l (The valence wave functions inside the atomic muffin-tin-spheres expansion parameter) and K-points (in the irreducible wedge of the first Brillouin zone (IBZ)) that has been explored within the tetrahedron method [30] are given in Table 1. The self-consistent calculations are considered to be converged when the total energy of the system is stable within 0.001

Ry. The electronic and optical properties are calculated using the experimental lattice parameters given in Table 1. All compounds crystallize in chalcopyrite structure (S.G: I4 \square 2d) at ambient conditions. In the crystal structure the Mg atom occupies (0, 0, 0), (0, 1/2, 1/4) sites, the Y cations occupies (0, 0, 1/2), (0, 1/2, 3/4) sites, and Z atom occupies (u, 1/4, 1/8), (-u, 3/4, 1/8), (3/4, u, 7/8), (1/4, u, 7/8) sites.

Table 1. Used lattice constants, R_{MT} , $R_{MT-K_{\max}}$, l -max, and K-points.

Compound	Lattice constant(exp) \AA a[l,m]	u(exp) c[l,m]		Rmt	R_{mt} K-max	L-max	K-points
CuAlS ₂	5.32	10.43	.275 ^p	Al=2, Cu=2, S=2	7	10	99
CuAlSe ₂	5.61	10.92	.269 ^p	Al=2, Cu=2, Se=2	7	10	99
CuGaS ₂	5.35	10.46	.2539 ^o	Ga=2, Cu=2, S=2	7	10	99
CuGaSe ₂	5.61	11.0	.220 ⁿ	Ga=2, Cu=2, Se=2	7	10	99
CuInS ₂	5.52	11.08	.2295 ^o	In=2, Cu=2, S=2	7	10	99
CuInSe ₂	5.78	11.55	.250 ⁿ	In=2, Cu=2, Se=2	7	10	99

l=[24], m=[33], n=[18], o=[37], p=[25]

3. Results and discussion

a) Electronic Properties:

In this subsection we present the electronic band structure, density of states and charge density computed through GGA and EV-GGA schemes for both sets of ternary chalcopyrites CuYS₂ and CuYSe₂ (Y=Al, Ga, In). It can be seen from the band structure profiles (Fig. 1) that all the ternary compounds show a direct band gap (Γ - Γ) and the fundamental band gap decreases for both CuYS₂ and CuYSe₂ on changing the cation Y from Al to In. This can be understand in connection to the density of states (Fig. 2(a, b)). The Y-s states strongly contribute in the conduction band minima for both sets of chalcopyrites and they have no contribution in the valence band. So changing the cation 'Y' from Al to In, the conduction band minima shifts to lower energy and there is no change in the valence band, leading to decrease the band gap values.

Table 2 lists the calculated fundamental band gap values for the herein studied compounds. Results from earlier experimental and theoretical works are also quoted for comparison. It is quite clear from this table that the previous calculated band gap values are lower than the measured ones. This may be attributed to the well known fact that both LDA and GGA usually underestimate the band gaps in comparison with the experiment [31].

Furthermore it is also noticeable that the EV-GGA calculated band gaps show a significant improvement over the results based on GGA compared to the experimental values, i.e. the previous calculated band gap values of

CuInSe₂ was found to be -0.2[35] and 0.26[36] which are lower than the experimental band gap value (1.0 eV) [37]. Our computed band gap of CuInSe₂ compound is found to be 0.8 eV with GGA and 1.062 eV with EV-GGA, which are in excellent agreement with the experimental results. The same trend is seen for the other compounds. The underestimation of the band gap with the GGA is mainly due to the fact that it is not sufficiently flexible for accurately reproduce both exchange-correlation energy and its density derivative. It can also be seen from the Fig. 2(a, b) that the upper valence band for both sets of chalcopyrites is formed by the hybridization of Cu-d and Z-p states. The localized Cu/d-electrons which lie higher in energy hybridize with Y-p states. Since both LDA and GGA are not accurate for description of dual behavior, i.e. intrinsic localization and covalent hybridization of Cu-d electrons. So we propose EV-GGA as a better scheme to treat the strongly localized d- electrons and for accurate description of the exchange correlation effects in case of pd- hybridization.

The chemical bonding nature of the investigated compounds can be identified by the charge density plots [39, 40]. It can be seen from the charge density plots shown in Fig. 3 that the bonding nature in these chalcopyrites is significantly covalent with a small ionic character. By changing Y from Al to In the bonding gets less directional for both CuYS₂ and CuYSe₂ and when changing Z from S to Se the covalent bonding becomes stronger.

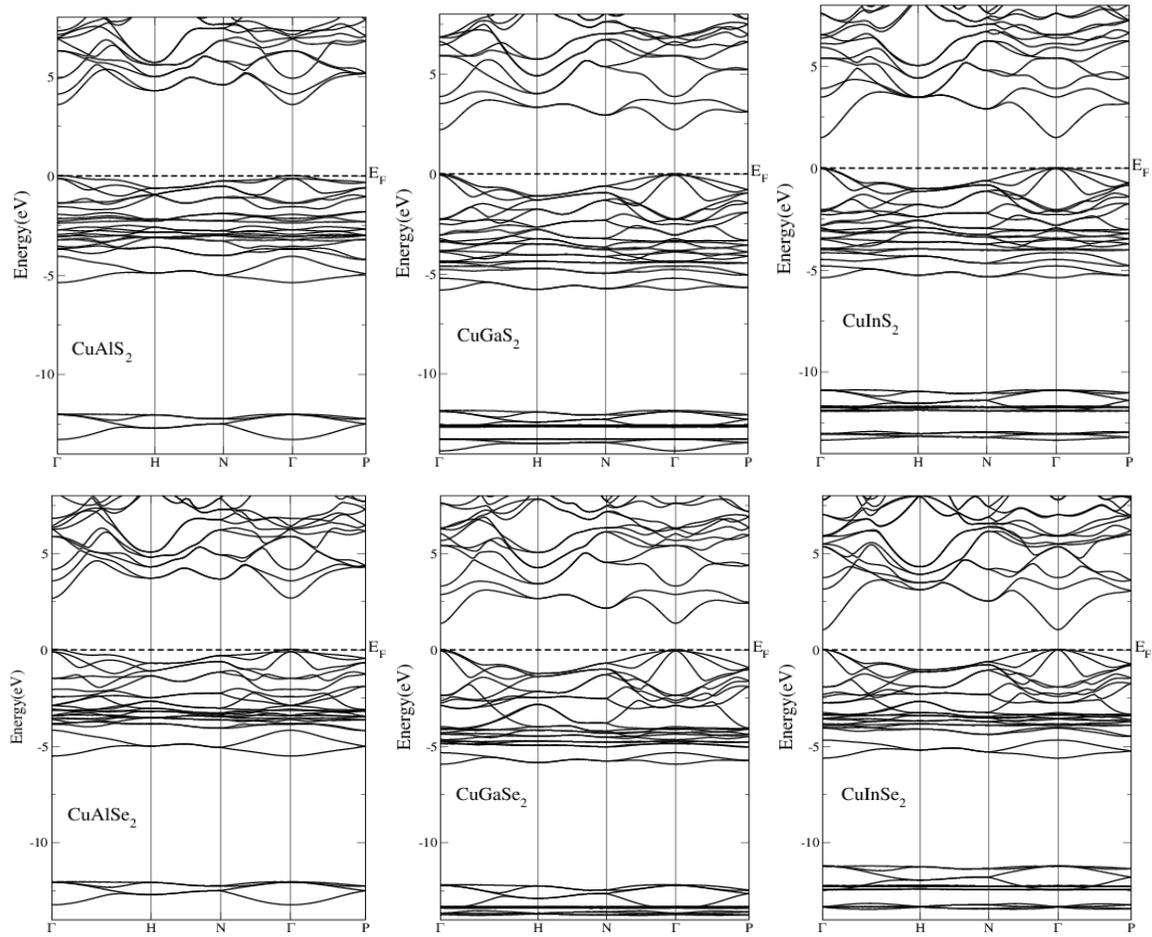


Fig. 1. EV-GGA band structures of CuYZ_2 compounds along high symmetry directions.

Table 2. Calculated energy bandgaps along with experimental and other theoretical works.

Compounds	This work		Experimental	Others
	GGA	EV		
CuAlS ₂	2.98	3.6	3.50 ^a	2.05 ^b , 2.44 ^c , 2.7 ^d
CuGaS ₂	1.62	2.2	2.43 ^k	1.1 ^g
CuInS ₂	1.43	1.52	1.53 ^k	0.01 ^e , 0.821 ^f
CuAlSe ₂	2	2.7	2.70 ^a	1.65 ^b , 2.1 ^d
CuGaSe ₂	0.9	1.41	1.68 ^j	0.83 ^h , 0.48 ⁱ
CuInSe ₂	0.8	1.062	1.00 ^j	0.26 ^h , -0.2 ⁱ

a=[22], b=[32], c=[33], d=[25], e=[24], f=[23], g=[34], h=[35], i=[36], j=[37], k=[38]

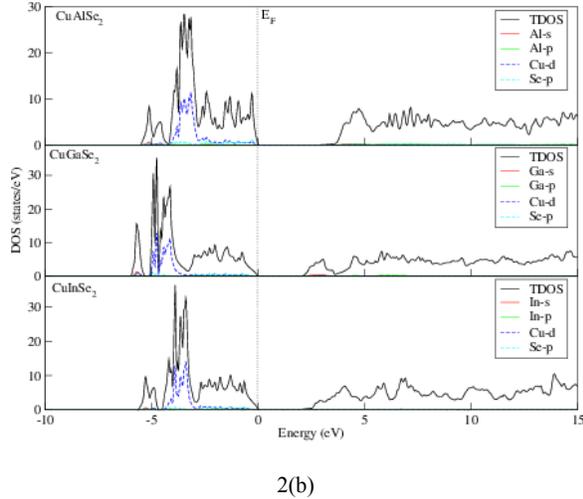
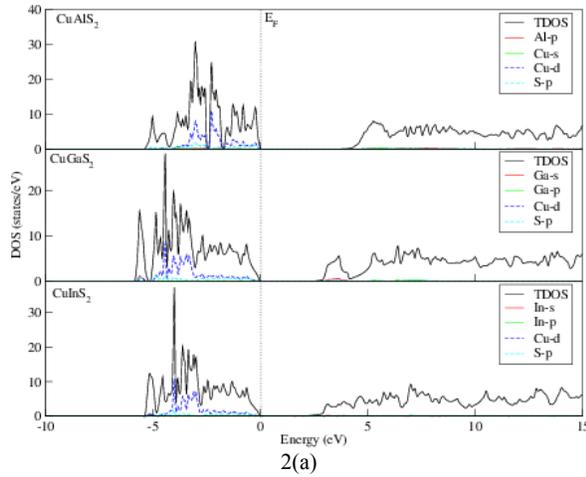


Fig. 2. EV-GGA total and partial density of states of CuYZ_2 .

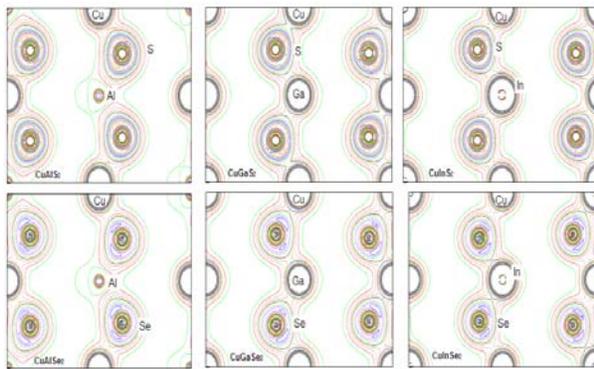


Fig. 3. EV-GGA electron density of CuYZ_2 .

Optical properties:

In this section we discuss the optical properties, namely, the refractivity and reflectivity for both CuYS_2 and CuYSe_2 ($Y=\text{Al, Ga, In}$) compounds. Since the studied compounds crystallize in chalcopyrite structure therefore

the optical spectra are plotted with the electric field polarization parallel and perpendicular to the crystallographic C-axis. Fig. 4(a, b) displays, the refractive index (n) and the extinction coefficient (k) along with the available experimental spectra [41] in the energy ranges of 0.9-5.2eV for CuInSe_2 and 1.4-5.2eV for CuGaSe_2 , CuInS_2 and CuGaS_2 , for comparison. It is clear from this figure that our spectra are in very good agreement with the experimental ones in the said energy ranges. The experimental data for CuAlSe_2 and CuAlS_2 compounds are scarce. Furthermore, one can notice that the birefringence ($\Delta n = n^{\parallel} - n^{\perp}$) is very small and positive for all the ternary chalcopyrites except that for CuInS_2 and CuInSe_2 . Both sets of ternary chalcopyrites share one common feature that the maximum value of refractive index lies between 3 eV and 7 eV and arises from the inter band transition. The extinction coefficient provides the absorption behavior of the compounds. The high absorption peaks in the visible as well as in the ultraviolet regions of the electromagnetic spectrum is clearly seen, therefore these compounds are very favorable to use for solar cells. Also the static refractive index is greater than 2, which indicates the utility of these compounds for photonic devices. Due to the positive birefringence for these compounds, they can also used for non-linear device.

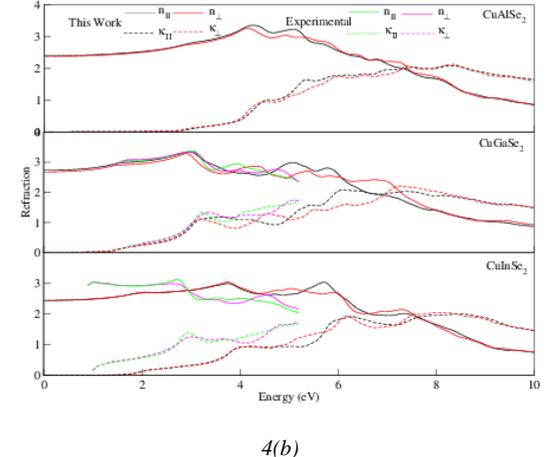
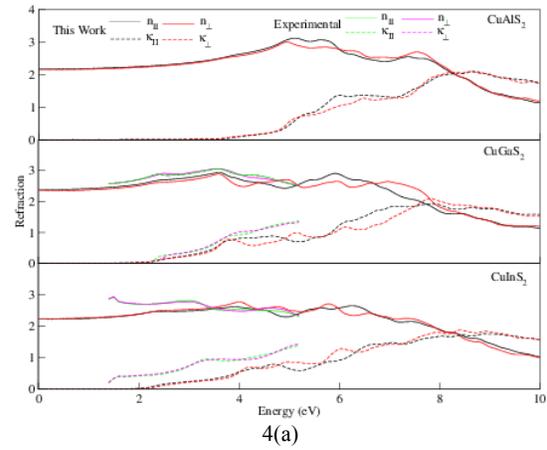


Fig. 4(a, b). EV-GGA Refractive index as a function of energy for CuYZ_2 ($Y=\text{Al, In, Ga; Z}=\text{S, Se}$).

Frequency dependent reflectivity $R(\omega)$ of CuYZ_2 ($Y=\text{Al, Ga, In; Z= S, Se}$) compounds with electric field polarization parallel $R_{\parallel}(\omega)$ and perpendicular $R_{\perp}(\omega)$ to the C-axis is depicted in Fig. 5(a, b). The reflectivity spectra of these compounds start from the zero frequency which is the static part of the reflectivity. Beyond the zero frequency limit it increases and with some oscillations it becomes maximum and then decreases and vanishes at high energy. By changing the cation from Al to In, the reflectivity peaks shift towards the lower energy. This decrease is attributed to the decrease in the band gap by changing the Y cation. The reflectivity is high in the ultraviolet region of the energy spectrum and also reasonable in the visible region. Therefore these compounds can be used as Bragg's reflectors.

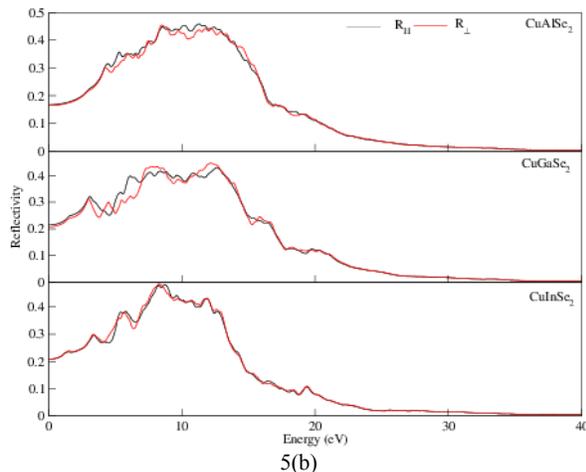
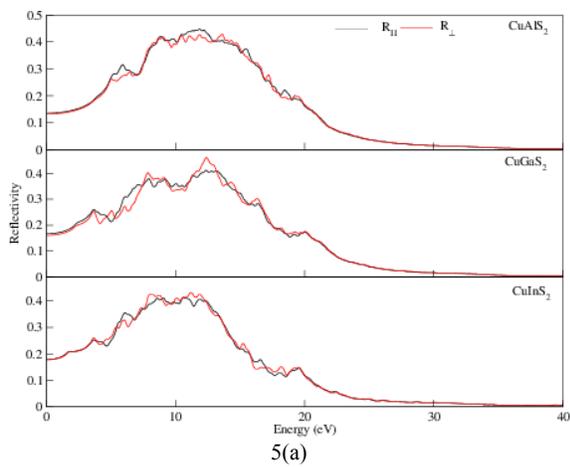


Fig. 5(a, b). EV-GGA Reflectivity as a function of energy for CuYZ_2 ($Y=\text{Al, In, Ga; Z=S, Se}$).

4. Conclusions

Highly accurate state of the art full potential linearized augmented plane wave method along with GGA and EV-GGA exchange correlation potentials have been used to

calculate the electronic and optical properties of the CuYZ_2 ($Y=\text{Al, Ga, In; Z=S, Se}$) compounds. All these compounds have a direct band gap decreasing by changing the cation from Al to In as well as anion from S to Se. The calculated band gaps are in close agreement to the experimental results as compared to the previous calculations. On the basis of our calculation EV-GGA is proposed as a better scheme for description of dual behavior, i.e. intrinsic localization and covalent hybridization of Cu-d electrons as is found in CuYZ_2 ($Y=\text{Al, Ga, In; Z=S, Se}$) compounds. Optical spectra clearly reveal the usefulness of these compounds in the solar cell technology, Bragg reflectors and non-linear optical devices.

Acknowledgements

Authors (Khenata and Bin Omran) acknowledge the financial support by the Deanship of Scientific Research at King Saud University for funding the work through the research group project N0 RPG-VPP-088.

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