

## ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF QUATERNARY CHALCOGENIDES $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ AND $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ BY FIRST-PRINCIPLES CALCULATIONS

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In this work, by performing first principles calculations within generalized gradient approximation (GGA) based on Density Functional Theory (DFT), the band structure and optical-related properties of quaternary metal chalcogenides  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  are presented. The energy gap is found to be direct of 0.177 and 0.011 eV for the two materials, respectively. The differences of the complex dielectric functions, the absorption spectra and the reflectivity coefficients of  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  are discussed. It follows that the electronic configurations of monovalent X (X = Ag, Cu) cations are responsible for the different electronic and optical properties of  $\text{XIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ .

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### 1. Introduction

Recently, a number of ternary and quaternary semiconductors of type I-III-IV<sub>2</sub> (I = Cu, Ag; III = Al, Ga, In; IV = S, Se, Te) crystallized in the chalcopyrite structure have attracted considerable interest of researchers due to their optoelectronic properties appropriate for designing nonlinear optical devices and solar cells [1-4], especially  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS) was expected to be useful in solar cell applications because it has large absorption coefficients at the band gap energy [5-9], and  $\text{AgIn}_{1-x}\text{Ga}_x\text{Se}_2$  was used as materials for laser-frequency doublers for the mid-IR spectral region owing to the nonlinear properties [10-13]. A typical representative of this family,  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  has been widely studied. In experiments, the various interesting properties including the structure character [14-18], electronic structures [16-20], and optical constants [17, 18, 20, 21] have been investigated. The corresponding theoretical work, such as electronic structures and optical constants [22, 23], also has been followed. However, the experimental studies on the precise material characterizations of the  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  crystals concern the structure properties [12, 24], electronic and optical properties [25, 26] are still rather limited, and no theoretical work has been reported in comparison with other chalcopyrite semiconductors.

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In this paper, our motivation is to discuss the effect of monovalent cations on the electronic behaviors of  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  quaternary chalcopyrite crystals, we carry out this task by calculating the structural, electronic, and optical properties of these chalcopyrite compounds on the first principles basis.

## 2. Computational methods

The calculations are performed in the framework of density function theory. Advanced plane wave expansion technology is applied to optimize the lattice constants and calculate the electronic and optical properties of  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  using the CASTEP computer code [27]. The effects of exchange–correlation interaction are treated with the generalized gradient approximation (GGA) of Perdrew-Burke-Ernzerh [28], known as PBE-GGA. The Vanderbilt-type ultrasoft pseudopotentials (USP) [29] are employed to describe the electron–ion interactions. A plane-wave cutoff energy of 400.00 eV in USP was employed throughout the calculation. For the Brillouin-zone sampling, the electronic structures used  $4 \times 4 \times 2$   $k$ -points grid generated according to the Monkhorst–Pack scheme. In the calculations of the optical susceptibilities, a dense mesh of uniformly distributed  $k$ -points is required. Hence, we have used  $8 \times 8 \times 4$  meshes to calculate the complex dielectric functions of  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ . The calculations assured a very high level convergence with respect to all parameters: the total energy difference within  $1.0 \times 10^{-6}$  eV/atom, the maximum Hellmann–Feynman force within 0.01 eV/Å, the maximum stress within 0.02 GPa and the maximum atom displacement within  $1.0 \times 10^{-4}$  Å.

## 3. Results and discussions

### 3.1 Structure properties

The crystal structures of  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  belong to I-III-IV<sub>2</sub> chalcopyrites with the space group  $I\bar{4}2d$ , which are analogous to the widely studied zinc blend structure. The ions positions can be generated using the following minimum set of  $(x, y, z)$  coordinates expressed in units of the  $a$  and  $c$  constants:

Group II:  $(0, 0, 0), (0, 1/2, 1/4),$

Group IV:  $(0, 0, 1/2), (0, 1/2, 3/4),$

Group V:  $(u, 1/4, 1/8), (-u, 3/4, 1/8), (3/4, u, 7/8), (1/4, -u, 7/8).$

Here,  $a$  is the lattice constant in the  $x$  or  $y$  direction,  $c$  is the lattice constant in the  $z$  direction,  $u$  is the positional parameter of the Se atoms in the unit cell. The difference between  $u$  and 0.25 represents the magnitude of the anions displaced from the ideal tetrahedral site.

We used the experimental lattice parameters as a starting point for geometry optimization. The calculated lattice parameters  $a$  and  $c$ , along with the internal parameter  $u$  are compared to experimental data reported in the literature in Table 1. The lattice parameters are found to be 5.693, 11.431 Å and 6.058, 11.624 Å for  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  alloys, respectively. The lattice constant increases when the Cu ions be replaced by Ag ions for  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  alloy, it can be reasonable explained by the bigger radius of Ag ions compare to Cu ions.

Table 1. Calculated lattice parameters( $\text{\AA}$ )of  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  as compared to experimental data.

	$\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$				$\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$			
	Present		experiment		Present		experiment	
$a$	6.058	6.030 <sup>a</sup>	6.047 <sup>c</sup>	6.043 <sup>d</sup>	5.693	5.67 <sup>e</sup>	5.6924 <sup>g</sup>	5.72 <sup>h</sup>
$c$	11.624	11.26 <sup>a</sup>	11.275 <sup>c</sup>	11.30 <sup>d</sup>	11.431	11.32 <sup>e</sup>		11.30 <sup>h</sup>
$u$	0.2663	0.2737 <sup>b</sup>	0.2852 <sup>c</sup>		0.2316	0.24 <sup>f</sup>	0.2438 <sup>g</sup>	

a Ref. [12]. b Ref. [11]. c Ref. [24]. d Ref. [26]. e Ref. [15]. f Ref. [14]. g Ref. [17]. h Ref. [18].

### 3.2. Electronic properties

We have predicted the band structure for  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  along the high symmetry directions in the first Brillouin zone and corresponding projected density of states(PDOS) from the calculated equilibrium lattice constants. The bands and PDOS graphs are given in Fig. 1 and Fig. 2, respectively. For the two alloys, the calculated band structures are similar to each other. Both the two mixed crystals have a direct band gap at the  $\Gamma$  point, and the obtained band gap values are 0.011 eV and 0.177 eV for  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ , respectively. The band gaps are smaller than the experimental values[23, 26], this error is caused by the discontinuity of exchange-correlation energy [30]. From the band structure graph, it exists an energy gap about 0.93 eV in the upper valence band for  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  alloy while  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  does not, this energy gap may cause strong optical absorption naturally.

The partial density of states(PDOS) plays vital role to explain the physical properties of semiconductor. The PDOS for Ag- $s/p/d$  or Cu- $s/p/d$ , Ga- $s/p/d$ , In- $s/p/d$ , Se- $s/p$  for  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  are shown in Fig. 2, which signify the origin of valence band and conduction band lies in local atomic states of constituent atoms. The Fermi energy is set to zero. The conduction bands for the two alloys are mainly derived from In- $s/p$  and Ga- $s/p$  states and sufficient contribution from Se- $s/p$  states. The valence bands region of  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  lies between -15.45 eV to Fermi energy level ( $E_F$ ). The low-energy set of valence band ranging from -15.45 to -12.81 eV is mainly due to  $d$  orbitals of In and Ga atoms with an admixture of Se- $s$  states, and the  $d$  orbitals of In and Ga atoms are highly localized. In the energy ranging from -5 to 0 eV, the  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  alloy exists continuous upper valence bands mostly formed by Ag- $d$  states and  $p$  states of In, Ga, and Se atoms, while the  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  alloy possesses an energy gap in the region from -2.06 to -2.99 eV, this difference is mainly due to the Cu- $d$  states and the  $p$  state of In, Ga, and Se atoms don't exist in this energy range.

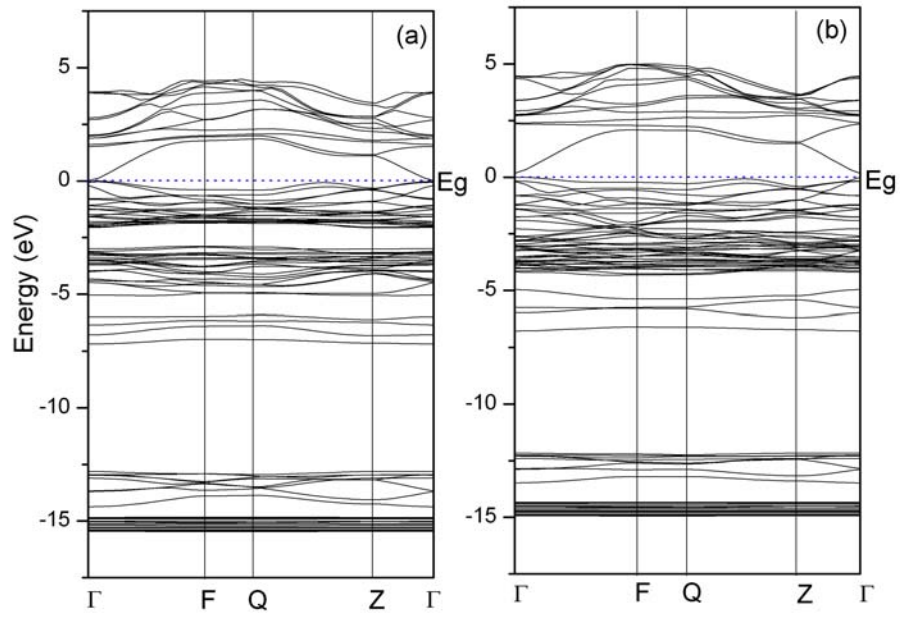


Fig. 1. Calculated band structure of  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  (a) and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  (b).

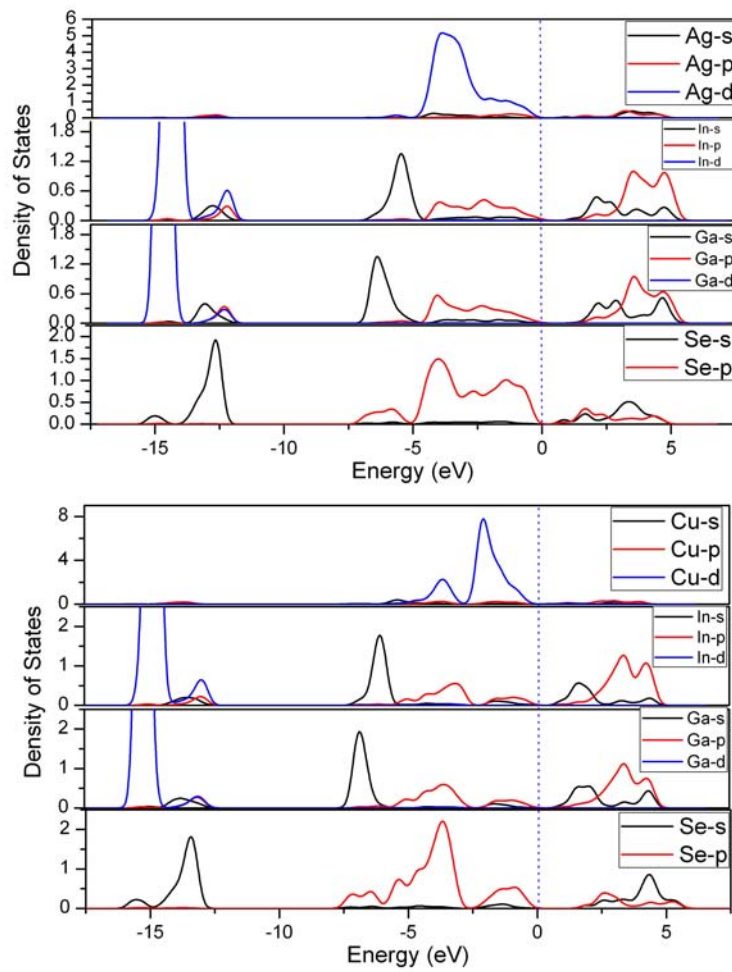


Fig. 2. Projected density of states for  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ .

### 3.3 Optical properties

We now consider the optical properties of  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ . The dielectric function  $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$  can be used to describe the linear response of the system to electromagnetic radiation, which relates to the interaction of photons with electrons. The real  $\varepsilon_1(\omega)$  and imaginary part  $\varepsilon_2(\omega)$  of the dielectric functions are calculated using the usual Kramers–Kronig relationship[31]. Other optical properties, such as reflectivity spectra  $R(\omega)$ , absorption coefficient  $\alpha(\omega)$ , can be derived from the complex dielectric function.

For the calculations of optical properties, by using the scissors operator, we have corrected our band gap values with 1.33 eV for  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and 1.4 eV for  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ , respectively. The optical functions calculated by neglecting all lattice vibrational effects and pertaining only the electronic transitions are shown in Fig. 3-Fig. 5. The average of complex dielectric functions are presented in Fig. 3. The main shape of the real parts of these complex dielectric functions of  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  are similar. The static dielectric constants  $\varepsilon_1(0)$ , calculated at the equilibrium lattice constants, are about 9.68 and 7.12, respectively. The calculated imaginary parts of the frequency-dependent linear dielectric function are different obviously. For  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  the main peaks position locate around 2.62 and 6.08 eV, respectively. For  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  the main peak position locates around 6.72 eV. These peaks correspond to the optical transitions from the valence band to the conduction band.

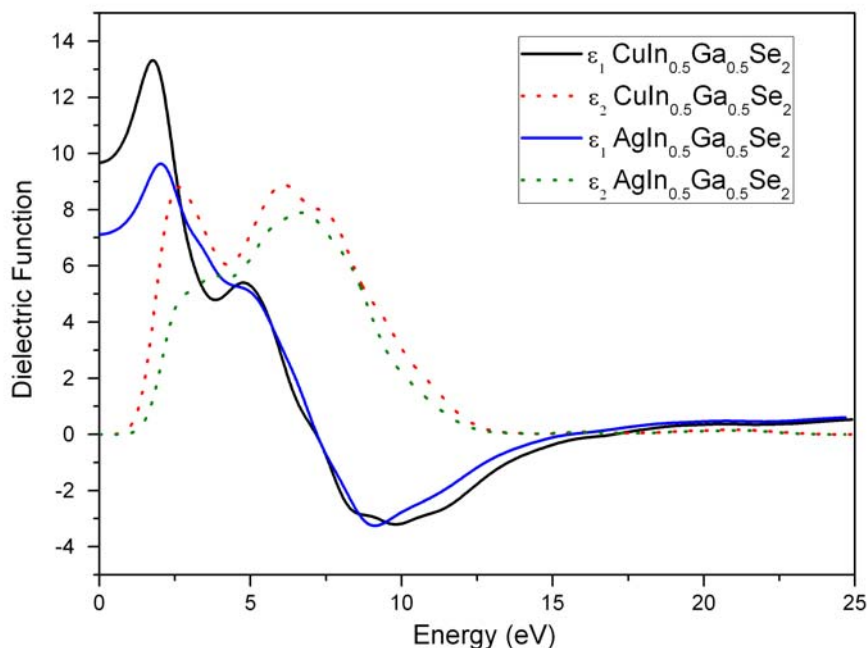


Fig.3. Dielectric functions for  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ .

The absorption spectra are shown in Fig.4. For the two interesting materials, according to the graph, it is obvious that the shape of the curves of absorption spectra are similar, and the absorption coefficients decrease rapidly in the low-energy region, which is the representative character of the semiconductor and insulator. One can see that  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  alloy has a higher absorption than  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  in the 0 -5 eV region, the main visible sunlight spectrum could be possible to be absorbed. This results are similar to the earlier measurements [32]. In Fig.5, we present the calculated optical reflectivity spectra of  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  crystal, there is a reflectivity peak for both two materials at 2.4 eV around, it is mainly caused by the

transition from Se-4*p* to Cu-3*d*. In 0-5 eV region, especially in the infrared and visible light region, we found that, the reflectivity of  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  is lower compared to  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ , the calculated reflectivity increases slowly only from 20.6% to 24.8% with the photon energy in the infrared area for  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ . So, from the absorption and reflectivity spectra, one can draw a conclusion that the transmission of  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  is higher and it is a more excellent IR material for making nonlinear optical device, while the absorption of  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  is higher and it is a more outstanding material for solar energy.

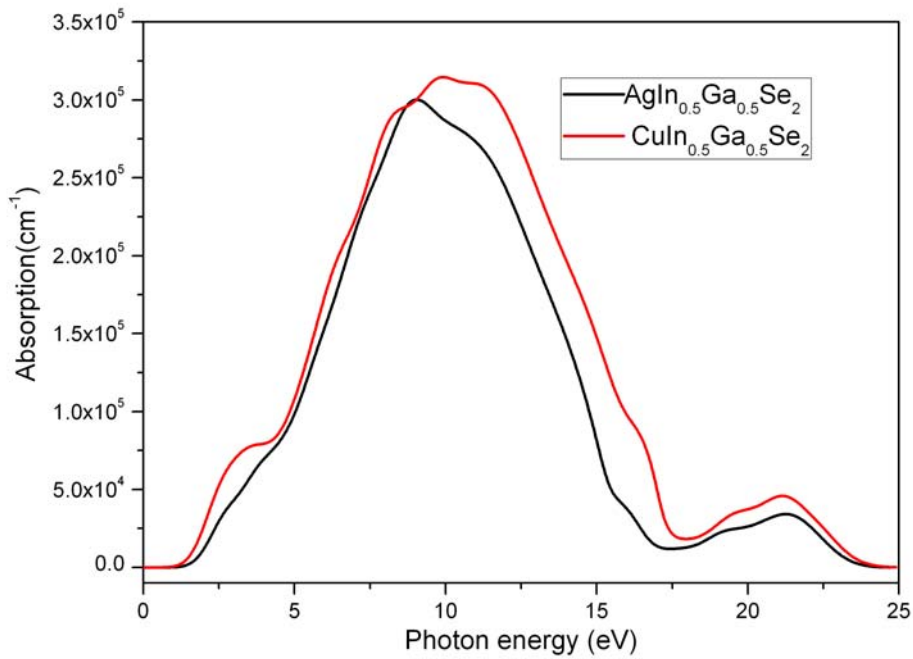


Fig.4. Absorption spectra of  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ .

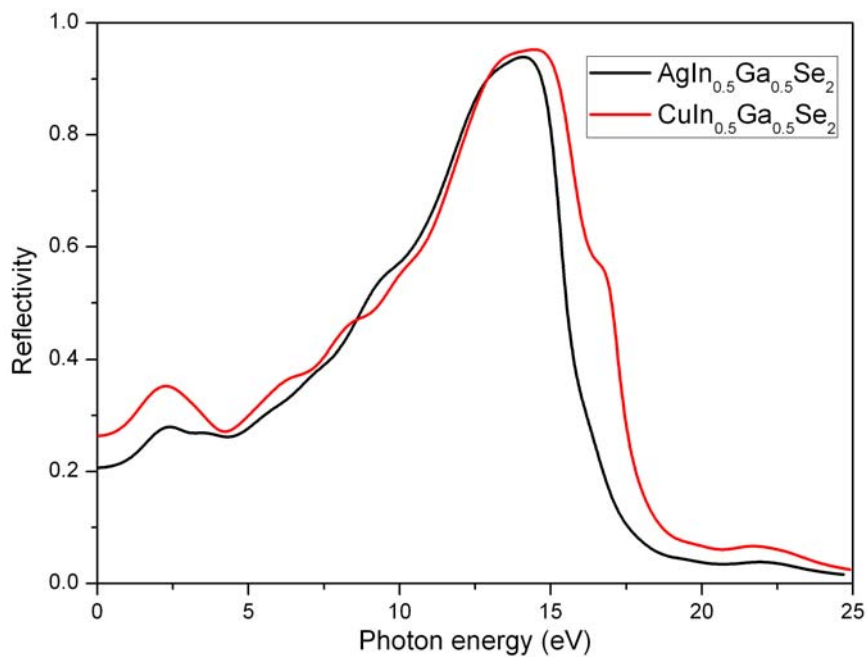


Fig.5. Reflectivity spectra of  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ .

#### 4. Conclusions

In summary, we have presented the structural, electronic and optical properties of  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  alloys using the first principles methods. The studied alloys are both characterized by direct band gap materials at the  $\Gamma$  point. Specifically, the difference of the energy band structure and the PDOS between the two interesting materials has been discussed. Also, the different electronic properties of  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  and  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  lead to their different optical properties. The investigations show that  $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  is a more excellent IR crystal material than  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  for making nonlinear optical device, while the latter is a more outstanding material for solar energy. It is hoped that the present findings may provide reliable data for producing optoelectronic devices.

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