

An Analytical Study of quaternary semiconductors $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ and $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ in the context of Band Structure and Optoelectronic Properties

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Abstract: In the present paper, we analyze the effect of monovalent cations on the electronic behaviors and optical related properties 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 band structure and optoelectronic properties of these chalcopyrite compounds by performing first principles calculations within generalized gradient approximation (GGA) based on Density Functional Theory (DFT).

Keywords: Chalcopyrites, Density Functional Theory, GGA, First Principal, band Structure.

I. Introduction:

Researchers have been interested in III-V multi-element alloy semiconductors for several decades. Their band gaps extend widely from infrared to ultraviolet regions and the lattice constants can be tailored by controlling their composition. They also provide the material basis for a number of well-established commercial technologies. These multi-component alloys are promising candidates for many device applications such as high speed electronic and long wavelength photonic devices. Continuing progress in III-V optoelectronics requires the synthesis of semiconductor alloys with specific structural, electronic and optical properties. The quaternary alloys lattice- matched to the given substrate provide new possibilities to realize the desired material properties and are very useful for reducing defects, dislocations and piezoelectric field. InGaAsP, GaInNAs, AlGaInN etc., quaternary alloys have been widely adopted for device applications [1–5].

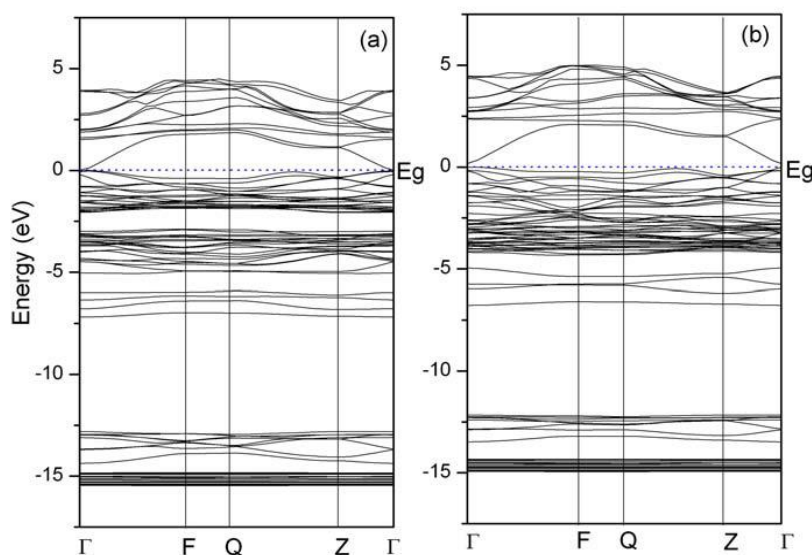


Fig. 1 Calculated band structure of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ (a) and $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ (b).

The search for new semiconductor materials with structural and electronic properties for the advancement of optoelectronic applications, such as thin-film solar cells or laser diodes, constitutes one of the central challenges in materials science. II–VI and III–V compound semiconductors have long been viewed as promising materials for the device applications in electronic and optoelectronic technologies. Many of these binary semiconductors crystallize in a cubic zinc-blende structure. Recently, a number of ternary and quaternary semiconductors of type I-III-IV₂ (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 [6-9], 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[10-14], 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 [15-18]. 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 [19-23], electronic structures [21-25], and optical constants[22, 23, 25, 26] have been investigated. The corresponding theoretical work, such as electronic structures and optical constants [27, 28], 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 [17, 29], electronic and optical properties [30, 31] are still rather limited, and no theoretical work has been reported in comparison with other chalcopyrite semiconductors. 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 $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ and $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ 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 $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ and $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ 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 $\text{XIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$.

II. Computational Method

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 $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ and $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ using the WIEN2K code [32,33]. The effects of exchange–correlation interaction are treated with the generalized gradient approximation (GGA) of Perdrew-Burke-Ernzerh [34], known as PBE-GGA. The Vanderbilt-type ultrasoft pseudopotentials (USP) [35] 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 $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$.

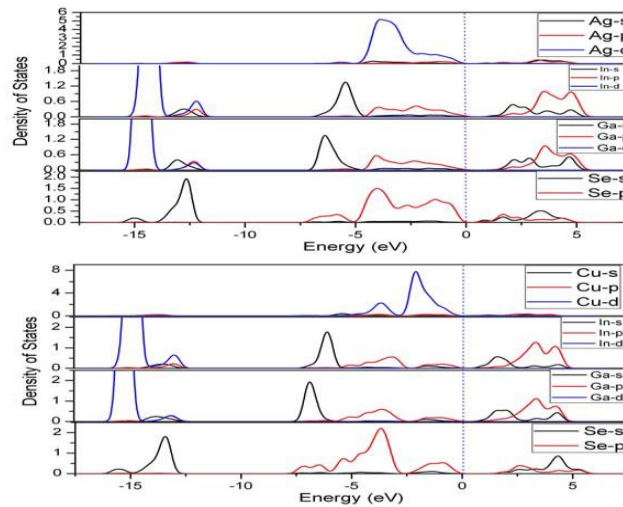


Fig. 2. Projected density of states for $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ and $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$.

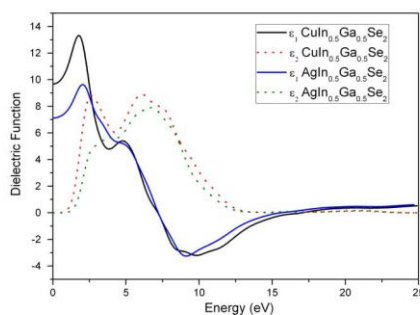


Fig.3 Dielectric functions for $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ and $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$

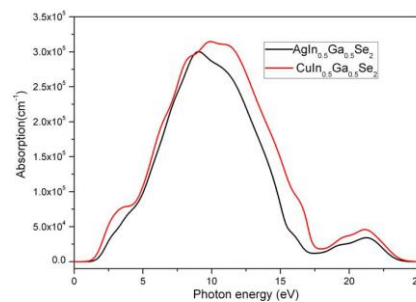


Fig.4 Absorption spectra for $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ and $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$

III. Result and Discussion:

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 Γ 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[28, 31], this error is caused by the discontinuity of exchange-correlation energy [36]. 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 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. 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 [38].

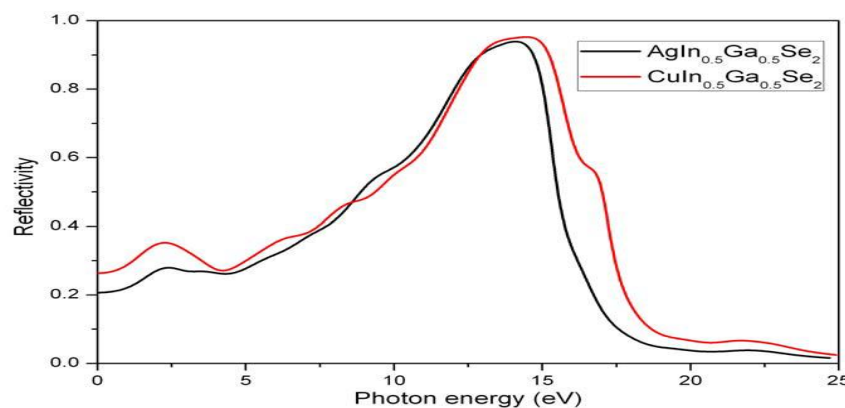


Fig.5. Reflectivity spectra of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ and $\text{AgIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$.

IV. Conclusion:

In this paper, 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 Γ 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.

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