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Optoelectronic Analysis of $CdGa_2X_4$ (X= S, Se): A Promising Material for Solar Cells

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Abstract. In this paper, the optoelectronic nature of the $CdGa_2X_4$ (X = S, Se) solar cell materials are examined using full potential linear augmented plane wave (FP-LAPW) method as embodied in WIEN2K code. In present computation, we have used most suitable modified Backe-Johnson (mBJ) potential under the framework of density functional theory (DFT). The calculated electronic properties like energy band structure and density of states spectra show that these materials exhibit a direct band gap (Γ–Γ) result of 3.22 eV and 2.36 eV for $CdGa_2S_4$ and $CdGa_2Se_4$ compounds, respectively. Absorption spectra for $CdGa_2X_4$ (X = S, Se) compounds have been studied and it has been found that above the band gap, absorption are taking place and it covers wide visible spectrum energy range. On the basis of calculated band gap, density of states and absorption coefficient spectra, it is found that these compounds can be suitably applicable in optoelectronic devices such as solar cell. The evaluated properties pose well agreement with available experimental data.

Introduction

The anti-environmental impacts of conventional energy sources have redirected the scientist's debate towards high efficient solar cells which are a leading green energy source. In all accessible materials the ternary AB_2C_4 (A = Cd, Zn; B = Al, Ga, In; X = S, Se, Te) compounds are one of the emerging optoelectronic applicable materials match to ternary $A^{II}B_2^{III}C_4^{VI}$ chalcopyrite family. Regarding previous study of these materials, Syrub et al. [1] have investigated the reflectivity spectra of $CdGa_2S_4$, $CdGa_2Se_4$ and $CdAl_2S_4$ for E||c and E⊥c at 77K. Cabrara et al. [2] have reported the pressure dependent vibrational and electronic properties of $CdGa_2S_4$ and $CdGa_2Se_4$ using ab initio calculations. $CdGa_2Se_4$ thin films were prepared and characterized by Salem et al. [3] to study their band gaps, optical constants, dielectric constants and refractive index. El-Nahass et al. [4] have prepared $CdGa_2Se_4$ powder through reacting process of CdS and Ga_2S_3. Chemical vapor transport methodology is adopted by Bodnar et al. [5] to develop single crystal of $CdGa_2S_4$. Rud et al. [6] have implemented the chemical vapor deposition technique to generate single crystal of $CdGa_2S_4$. Vaipolin et al. [7] have reported photosensitive structure based single crystal of $CdGa_2Se_4$. Solution-melt method has been utilized by Sosovska et al. [8] for creation of $CdGa_2Se_4$ crystal. The investigation of electronic structure of $CdGa_2Se_4$ is reported by Lavrentyev et al. [9] using argument plane wave + local orbital and X-ray photoelectron spectroscopy techniques. High pressure optical absorption coefficient and Raman scattering measurements for $CdGa_2Se_4$ have been studied by Gomis et al. [10]. Thermal evaporation technology is implemented for the preparation of $CdGa_2S_4$ thin film by El-Nahass et al. [11]. The elastic, electronic and optical properties of $CdGa_2X_4$ (X=S, Se) compounds have been reported by Ma et al. [12] using first principle method. Mustafaeva et al. [13] have grown the single crystals of $CdGa_2S_4$ and have studied their X-ray properties. Light polarization and temperature effect on photo-luminiscence specta of $CdGa_2S_4$ was studied by Georgobiani et al. [14]. Reshak et al. [15] make use of FP-LAPW methodology to study the susceptibilities of $CdGa_2X_4$ (X=S, Se).

Theoretical Methodology

For investigation of ground state electronic and optical properties of solids we make use of Kohn Sham version of density functional theory (DFT) approach which is a power full tool to carry out theoretical investigation of physical and chemical nature of matter accurately. The Kohn and Sham find out the method of obtaining ground state electron density that only depends upon three spatial variables and for this they solve a set of single electron wave function via self-constant approach. The exchange and correlation effects, that take care about all quantum mechanical interactions between electrons, have been incorporated using most suitable mBJ exchange potential because it can eliminates the band gap underestimation problem as seen in the case of local density approximation (LDA) and generalized gradient approximation (GGA) [17]. In the present problem lattice constants taken by $CdGa_2S_4$ compound are $a = b = 5.54$ Å, $c = 10.94$ Å, whereas for $CdGa_2Se_4$ respective constants are $a = b = 5.72$ Å, $c = 11.4$ Å. The lattice positions occupied by $CdGa_2S_4$ and $CdGa_2Se_4$ are (Cd = 0, 0, 0; Ga = 0, 0, 0.5; Ga = 0, 0.5, 0.75; S = 0.270, 0.248, 0.133) and (Cd = 0, 0, 0; Ga = 0, 0, 0.5; Ga = 0, 0.5, 0.75; Se = 0.264, 0.249, 0.133) respectively. The Muffin Tin (MT) radius selected for both the chalcopyrite's $CdGa_2S_4$ and $CdGa_2Se_4$ consists of 9 a.u. and the self-consistence calculations were performed with 144 *k* points. The wave function inside the sphere was expended up to l_{max}=10 whereas the Fourier expansion of the charge density was used up to G_{max}= 12 a.u. Entire energy of crystal was converged to 10^{-5} mRy that ensure appropriate accuracy in convergence.

Result and Discussion

To understand the complete electronic nature of $CdGa_2S_4$ & $CdGa_2Se_4$ compounds the electronic energy bands and density of states (DOS) are calculated using mBJ exchange potential. The energy bands for $CdGa_2S_4$ are plotted in Fig. 1 whereas the corresponding DOS spectra are plotted in Fig.2. Similarly the energy band and DOS spectra for $CdGa_2Se_4$ are plotted in Fig.3 and Fig.4, respectively. From the energy bands it is clear that both $CdGa_2S_4$ and $CdGa_2Se_4$ compounds shows direct band gap result 3.22eV and 2.36 eV, respectively that lies around solar spectrum range (400-700 nm). The DOS curves inform about atomic contributions in different quantum states. Top most valence band state of $CdGa_2S_4$ (just below the fermi energy (E_F)) are originated due to major contribution of Ga-p, d, S-p and Cd-p, d states and minor contribution of Ga-s and Cd-s states. Conduction bands above the E_F are observed due to major contribution of S-p, d, Ga-s, p and Cd-s, p state with a minor contribution of S-s and Cd-d states. Similarly top most valence band state of $CdGa_2Se_4$ just below the E_F are observed due to major contribution of Ga-p, d and Cd-p, d states and minor contribution of S-p, Ga-s and Cd-d state. Conduction band state above the E_F are due to major contribution of S-p, d, Ga-s, p and Cd-s, p state and minor contribution of S-s, S-d, and Cd-d states.

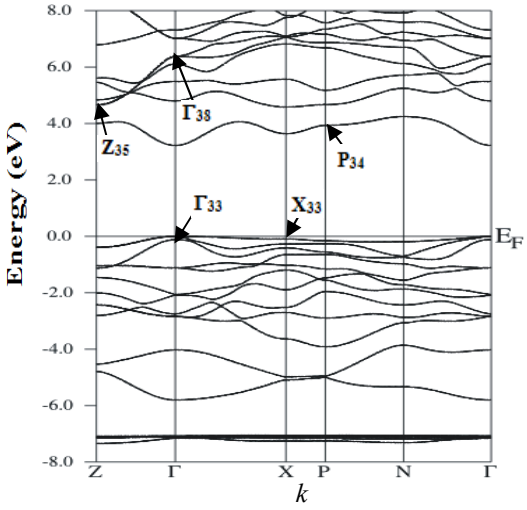

Fig. 1 Energy band spectra of $CdGa_2S_4$

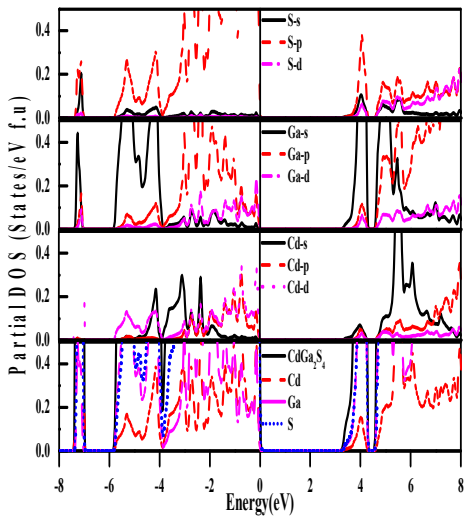

Fig. 2 Density of states of $CdGa_2S_4$

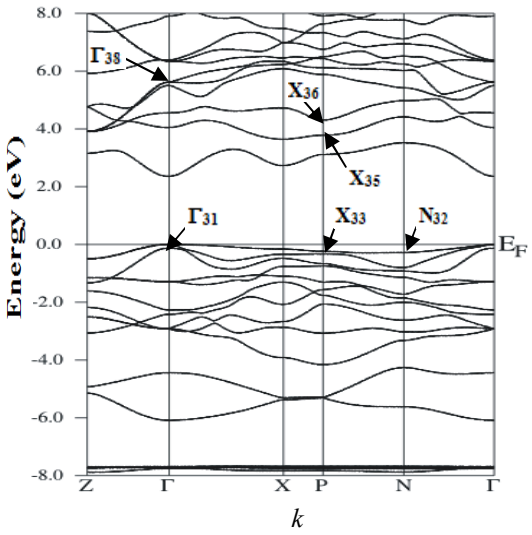

Fig. 3 Energy band spectra of $CdGa_2Se_4$

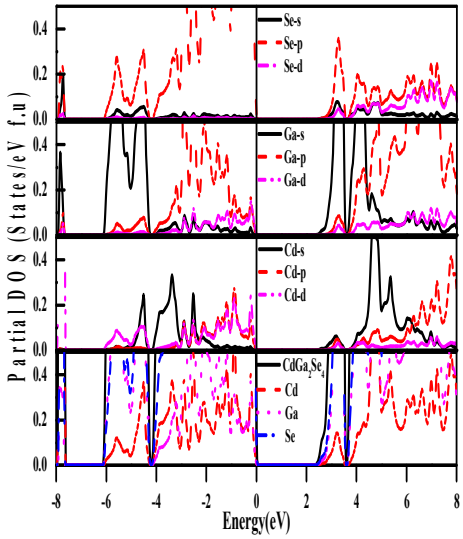

Fig. 4 Density of states of $CdGa_2Se_4$

The present and previously reported bandgap result for $CdGa_2S_4$ and $CdGa_2Se_4$ compounds are collected in Table1.

Optical nature of $CdGa_2S_4$ & $CdGa_2Se_4$ is well described by absorption coefficient spectra as indicated in Fig. 5. Calculation of absorption spectra describes energy transformation behavior from incoming electromagnetic wave towards internal energy of matter to excite an electron from valence band to conduction band. From the absorption spectra it is clear that it starts above band gap energy and increases continuously in the visible spectrum range so that maximum photons are absorbs that may be converted in to useable electricity form. We observed reasonable value of absorption spectra under the visible energy range from 3-5eV depicts the applicability of presented materials in solar cell fabrication.

Table 1 Energy band gap E_g (eV) of $CdGa_2S_4$ and $CdGa_2Se_4$

Sample	Energy gap in eV		
	Present work	Available data	
	mBJ	Theoretical	Expt.
$CdGa_2S_4$	3.22	2.19[9], 3.39[10]	3.40[10]
$CdGa_2Se_4$	2.36	1.36[9], 2.35[12], 1.35,[12] 2.50[10]	2.33-2.57[13], 2.54[10]

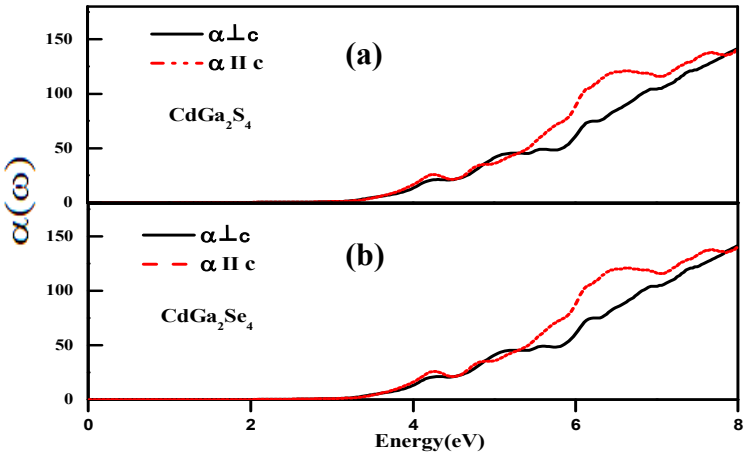

Fig. 5 Absorption spectra of (a) $CdGa_2S_4$ & (b) $CdGa_2Se_4$

Conclusion

In the present work electronic and optical nature of $CdGa_2S_4$ and $CdGa_2Se_4$ ternary compounds were calculated using mBJ exchange potential as embodied in WIEN2K (FP-LAPW) technique. Our

computations predicts a direct band gap at Γ–Γ symmetry point of first Brillouin zone for both, $CdGa_2S_4$ and $CdGa_2Se_4$, compounds that are in well agreement with available experimental results. Energy bands were analyzed through partial density of state. The nature of absorption coefficient spectra as a function of photon energy are plotted and it was found that strong absorption coefficient exists around 3 to 5 eV that reveals the applicability of these materials in optoelectronics such as solar cells.

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