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The Electronic Band Structure and Dielectric Response Function of $ZnGa_2S_4$ and $ZnGa_2Se_4$

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ABSTRACT

$ZnGa_2S_4$ and $ZnGa_2Se_4$ have the vacancy defect stannite structure, belonging to the II-III$_2$-VI$_4$ family of compounds. These materials have been investigated via density functional theory (DFT). The electronic band structure, total and partial density and of states were computed using the LDA+U technique while the dielectric function calculations were performed using norm-conserving pseudopotentials. The band structure calculation showed the materials have indirect band gap of 2.65 eV and 1.82 eV for $ZnGa_2S_4$ and $ZnGa_2Se_4$ respectively. It was found that the top valence sub band for both compound have comparable energy width 0f 5.9 eV and 6.0 eV for$ZnGa_2S_4$ and $ZnGa_2Se_4$ respectively. The partial density of states calculations showed the top valence band for $ZnGa_2Se_4$ to be predominantly of Se-4p states, while the bottom of the conduction band is dominated by Ga-4s state. For $ZnGa_2S_4$, the top of the valence sub band is made up of mostly S-3p states, and the conduction band minimum is mainly of Ga-3d and Ga-4s states. The calculated The calculated $\varepsilon_1(0)$ for $ZnGa_2S_4$ and $ZnGa_2Se_4$ is 19 and 9 respectively.

Introduction

The series II-III$_2$-VI$_4$ is a family of compounds belonging to the space group $P\bar{4}2_1m$ or $I\bar{4}2m$ with vacancy defect. $ZnGa_2S_4$ and $ZnGa_2Se_4$ and $ZnGa_2Se_4$ are members of this series of materials having applications in optoelectronic devices [1,2], and degradation of pollutants [3]. $ZnGa_2S_4$ and $ZnGa_2Se_4$ have attracted the attention of researchers both experimentally and theoretically. Turowski et al [4], reported on the reflectivity of $ZnGa_2Se_4$. Lowe–Ma and Vanderah[5], investigated the structure of $ZnGa_2S_4$, and reported a defect stannite structure with space group 142m having lattice parameters a =5.2744 and c =10.407 Doping of these compounds have been reported in the literature. $ZnGa_2S_4$ was doped with Eu and F [6]. The turning of the absorption region of $ZnGa_2S_4$ from ultraviolet region to the visible region by substituting copper (Cu) and Gallium (Ga) in the Zinc (Zn) site was investigated by kaya and Kudo [2].

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The effect of doping $ZnGa_2S_4$ by silicon was studied by Gaur et al.,[7], they reported a reduction in the value of the band gap for enhanced solar absorption. Eifler et al.,[8], reported on the vibrational properties of $ZnGa_2Se_4$ and $ZnGa_2S_4$. Using powder diffraction data for $ZnGa_2S_4$, Lowe-Ma [9] reported a tetragonal structure having lattice parameters. a =5.2779Å and c =10.4179Å. Karimova et al.,[10] prepared samples of $ZnGa_2S_4$ from its elemental constituents. Their x-ray diffraction studies showed the samples belong to the space group $I\bar{4}$, the reported lattice parameters are a =5.287Å and c=10.428Å. Asadullayeva et al.,[11], using the gas transport reaction, synthesized samples of $ZnGa_2Se_4$,. The samples were analyzed via ellipsometry, and x-ray diffraction. They reported on optical properties and a band gap of 2.81 eV. Gomis et al [12], reported on the effect of pressure on the optical absorption of $ZnGa_2Se_4$. Theoretical investigations for $ZnGa_2S_4$, and $ZnGa_2Se_4$, has also been reported in the literature. Xiao-Shu et al [13], used the pseudopotential method and reported a direct band gap for $ZnGa_2S_4$, and $ZnGa_2Se_4$, with band gap value of 2.86.eV and 1.94 eV respectively, while Jiang and Lambrecht [14] reported a band gap of 2.29 eV and 1.4 eV for $ZnGa_2S_4$ and $ZnGa_2Se_4$ respectively using the muffin-tin orbital (LMTO) method. In this work, the DFT+U technique will be used to investigate the electronic and optical properties of $ZnGa_2S_4$ and $ZnGa_2Se_4$.

Computational Details

The defect stannite structure to which $ZnGa_2S_4$, and $ZnGa_2Se_4$, are members. It belongs to the I-42m space group. It has a vacancy at the 2b wyckoft site (0.0,0.0,0.5). The group II atom occupies the 2a wyckoff site, group III atom occupies the 8i site. The atomic positions for the 8i site used in the calculations and lattice parameters were adopted from [15]. There are two formula unit per unit cell, this makes it a total of fourteen atoms in one unit cell. The pseudopotential method was employed in the investigations. The abinit software code [16,17] was used in the study. The calculations carried out are the electronic band structure, density of states (total and partial) and the dielectric response (optical properties). Table 1 shows the parameter used in the calculations. The LDA+U technique was used in the electronic band structure and density of states study. The projector augmented wave (PAW) was used as the pseudopotential for the electronic band structure and density of state (DOS) calculations, while norm-conserving pseudopotential was used for the dielectric response calculations. For the ground state calculations, the tolerance on energy was 10^{-6}, a kinetic energy cutoff of 12Ha and a k-point mesh of 256 were used. The following were included as valence states: Zn-3d, Zn-4s, Ga-3d, Ga-4s, Ga-4p, S-3s, S-3p,Se-4s, and Se-4p.

Table I: parameters used in the computations

	a(Å)	c(Å)	X	Y	Z
ZnGa2S4	5.26	10.4	0.25	0.25	0.125
ZnGa2Se4	5.48	10.9	0.25	0.25	0.125

Results and Discussion

The electronic band structure of $ZnGa_2S_4$ and $ZnGa_2Se_4$ are presented in Fig. 1a and 1b respectively. The y-axis represents energy (eV) while the x-axis represents the high symmetry points in the first brillouin Zone in the Γ-X- M - P -Γ-M direction. Fig 1a shows the electronic bands structure of $ZnGa_2S_4$. The dashed line at zero indicates the Fermi energy and the band gap is indirect, having the conduction band minimum (CBM) along the Γ–point of high symmetry while the valence band maximum (VBM) is at the M-point of high symmetry. The implication of this is a semiconductor behavior for $ZnGa_2S_4$. The calculated energy band gap for $ZnGa_2S_4$ is 2.65 eV which is in good agreement with what was obtained experimentally [15]. The top valence subband has an energy width of 5.9 eV. Electronic band structure of $ZnGa_2Se_4$ is shown in Fig 1b. The plot indicates that the material is a semiconductor with an indirect band gap of 1.82 eV, which is in good agreement with

experimental value of 2.18 eV. The CBM and VBM are at Γ and M-points respectively. The energy width of the top valence subband is 6.0eV.

(a) (b)

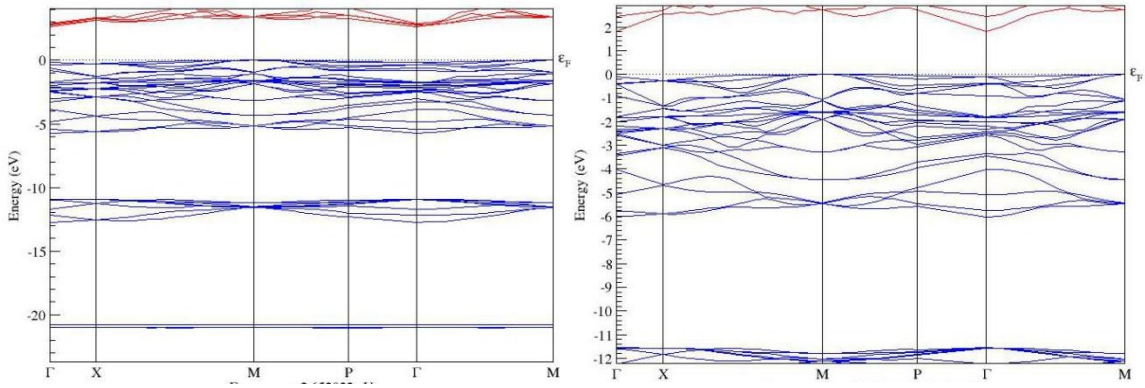

Figure 1: The Electronic band structure of (a) $ZnGa_2S_4$ (b) $ZnGa_2Se_4$

The total density of states (TDOS) for $ZnGa_2S_4$ and $ZnGa_2Se_4$ are presented in Fig 2a and 2b respectively. The plot is DOS against energy in Hartree. The feature of these graphs represents the various orbital contributions to the total density of state. Fig 2a shows the whole spectrum of the subbands of the electronic band structure of $ZnGa_2S_4$. The Fermi energy is at 0.08 Ha. The gap between 0.0Ha and 0.2Ha is the band gap of the material. The peaks and curves within -0.2Ha and the Fermi energy is the top valence subbands. There are eight (8) valence subbands separable by varying degree of intravalence band gaps. The feature at 0.2 Ha represents the state at the bottom of the conduction band. Fig 2b displays the total density of state (TDOS) $ZnGa_2Se_4$. The TDOS of $ZnGa_2S_4$ and $ZnGa_2Se_4$ are qualitatively and quantitatively similar.

(a) (b)

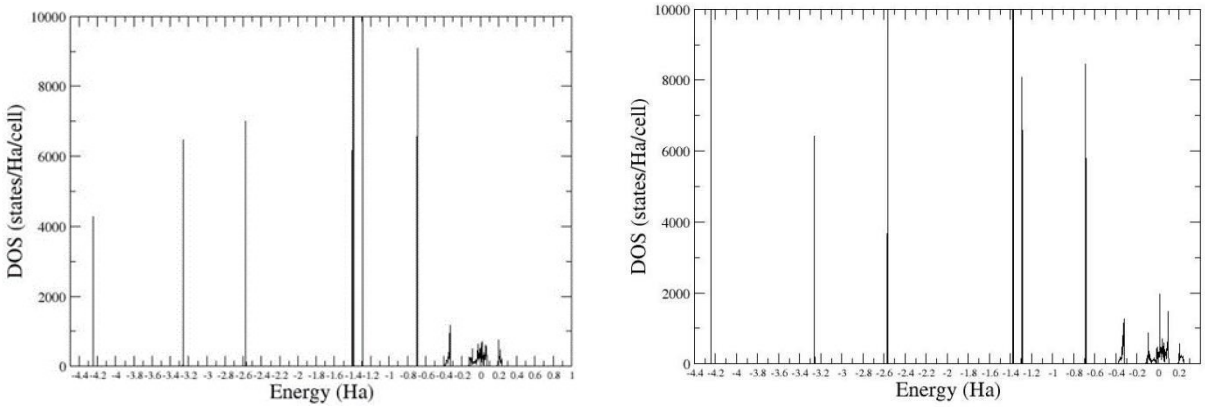

Figure 2: The total density of state of (a) $ZnGa_2S_4$ (b) $ZnGa_2Se_4$

The partial density of state (PDOS) of the various orbital contributions for $ZnGa_2Se_4$ are presented in Fig. 3 to 5. Zinc's contributionsare from the Zn-3d and Zn-4s orbitals, and they are shown in Fig 3. The feature in red are contributions from Zn-3d orbitals while those in black are from Zn-4s state. The Zn-3d states are concentrated at -0.7 Ha. There are very small portions of the Zn-3d states at about -0.4, and at the top of the valence band overlapping with the Zn-4s states. The Zn-4s state is the feature about -0.1 to 0.0 Ha and at the conduction band.

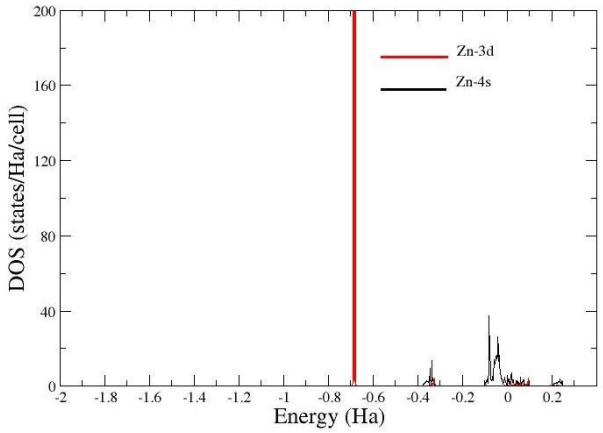

Figure 3: The partial density of state of Zn atom in $ZnGa_2Se_4$

The Gallium's Ga-4p, Ga-3d, and Ga-4sorbital contributions are shown in Fig.4, and are displayed in green, red, and black respectively. The top of the valence band has a sharp peak of Ga-3d states, while the bottom of the conduction band has sharp peak of Ga-4s state. The rear of the top valence subband has a large concentration of Ga-4s state as shown by the relatively high peak. It is also noted that the top valence subband and the bottom of the conduction band have all orbitals overlapping.

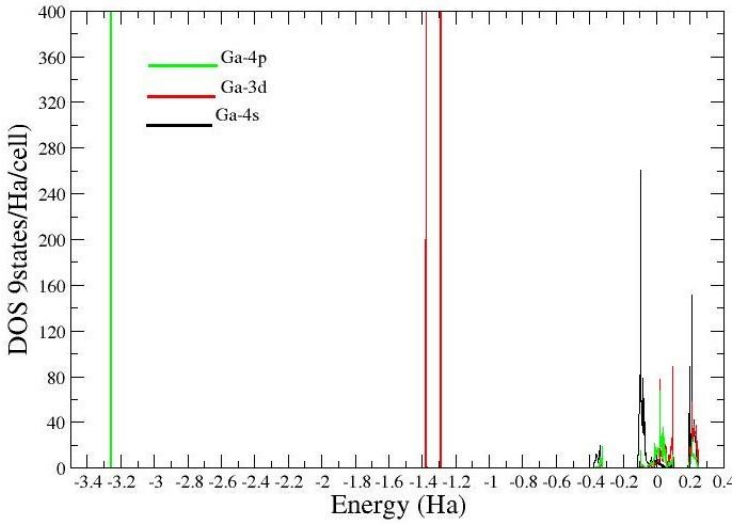

Figure 4: The partial density of state of Ga in $ZnGa_2Se_4$

The contributions of Se-4s and Se-4p are shown in Fig.5, and are depicted in black and red respectively. The graph shows that the top of the valence sub band are of Se-4p states while Se-45 is mainly between -0.3 Ha and -04Ha. The conduction band has a small portion of the Se-45 and Se-4p overlapping. So for $ZnGa_2Se_4$, the top valence band is predominantly of Se-4p states while the bottom of the conduction band is dominated by Ga-4s state.

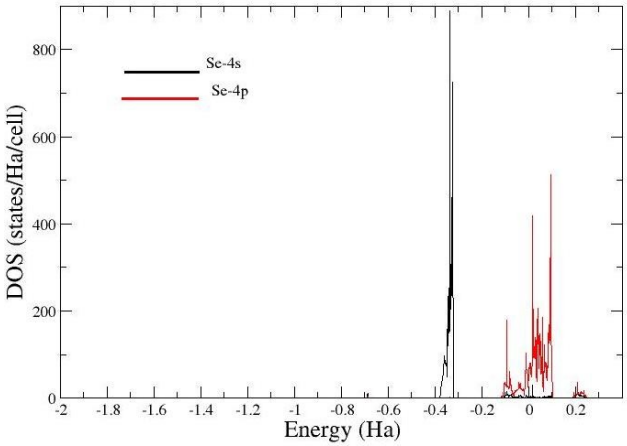

Figure 5: The partial density of state of Se in $ZnGa_2Se_4$

Figures 6,7 and 8 displays the PDOS of $ZnGa_2S_4$. Fig.6 shows Zn-3d and Zn-4s orbital contributions to TDOS. The Zn-3d orbitals are represented by red while Zn-4s is indicated by black lines and curves. Zn-3d states are concentrated at -0.7Ha while Zn-4s orbital's contribution is about -0.4Ha to 0.2 Ha. Fig.6 shows that the Zn-4s state are found mainly at the top of the valence bands and a small portion in the conduction band.

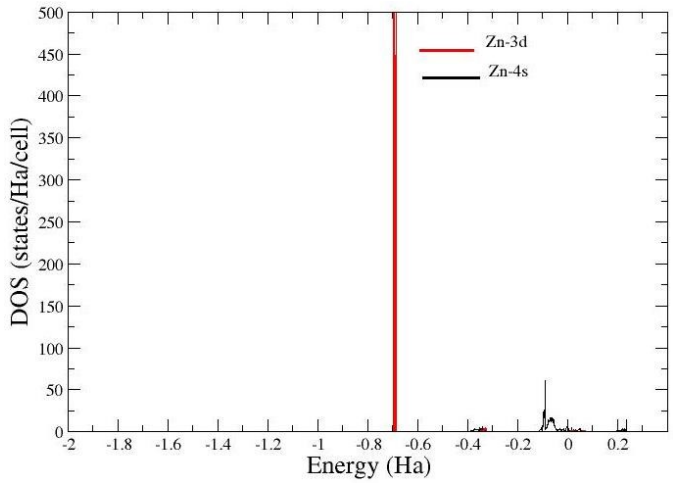

Figure 6: The partial density of state of Zn atom in $ZnGa_2S_4$

The contribution from the Gallium atom is shown in Fig. 7. The Gallium orbitals represented are Ga-4p, Ga-3d, and Ga-4s, these are marked in red, green, and black respectively. Most of the Ga-4p are located at -3.3 Ha. The Ga-3d is seen at -1.4Ha, -1.3 Ha, at the top valence subband, and at the conduction band minimum. Ga-4s state is seen at -0.1 Ha at the rear of the top valence subband and at 0.2Ha, that is, the base of the conduction band. Ga-3d has more dispersion compared to Ga-4s in the conduction band, but Ga-4s has more DOS. It is also clear that Ga-3d populated the top of the valence band as indicated by the greens at the Fermi energy. The conduction band shows an overlapping of all three states.

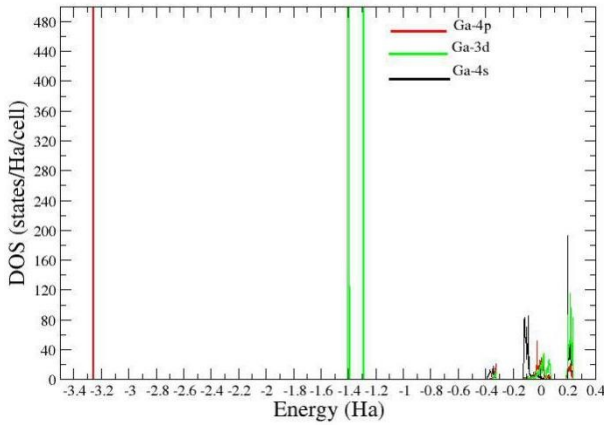

Figure 7: The partial density of state of Ga in $ZnGa_2S_4$

Sulphur's contributions are presented in Fig.8. The S-3s and S-3p orbitals are marked in black and red respectively. Most of the S-3s are found about -0.4Ha and -0.3 Ha, while S-3p is concentrated at the top level valence subband.

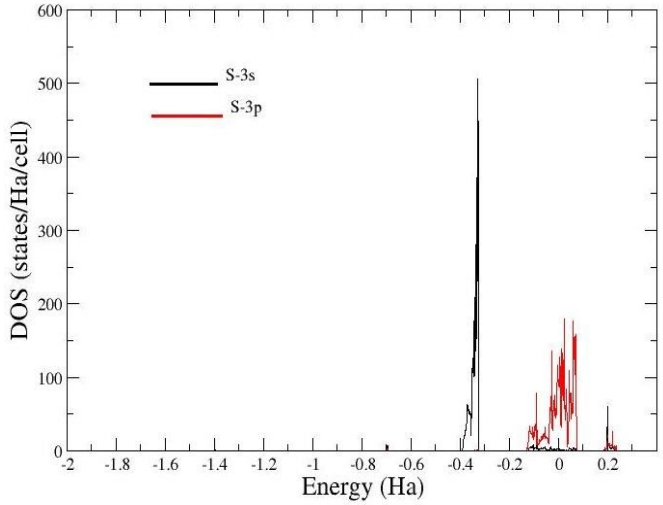

Figure 8: The partial density of state of Se in $ZnGa_2S_4$

So, for $ZnGa_2S_4$, the top of the valence band is made up of mostly the S-3p states while the conduction band is dominantly of Ga-3d and Ga-4s states.

Optical properties

The dielectric function $\varepsilon(\omega)$ is the basis from which optical properties are derived, it is a complex function given as $\varepsilon(\omega)= \varepsilon_1(\omega)+i\varepsilon_2(\omega)$; where $\varepsilon_1(\omega)$ represents the real part and $\varepsilon_2(\omega)$ the imaginary part. The plot of the dielectric function of the real and imaginary parts for $ZnGa_2Se_4$ are presented in Fig. 9a and 9b respectively. The peaks and crests indicate critical points, that is, transition points in the electronic band structure of the material. The calculation of the dielectric function is with scissors shifts, so, the onset of the first peak indicates the energy band gap. Fig. 10a show three major peaks occurring at 1.88eV, 2.13 eV and 25 eV. There are three smaller peaks at 2.88eV, 3.13 eV, and 6.0 eV. The $\varepsilon_1(0)$ is found to be 9. There is a sharp descend of $\varepsilon_1(\omega)$ between 6.0eV and 6.25 eV.The highest peak of $\varepsilon_1(\omega)$ is 26 at 1.88eV.

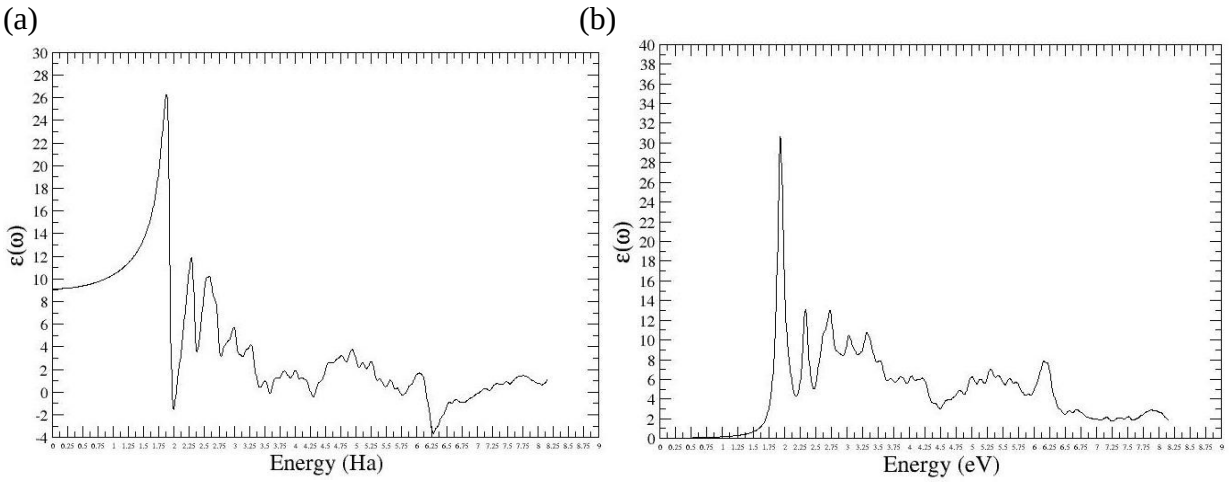

Figure 9: The plot of Ɛ(ω) in XX direction for $ZnGa_2Se_4$ (a) real part (b) imaginary part

The imaginary part of Ɛ(ω) for $ZnGa_2Se_4$ displayed in Fig.9b. Here, the first peak corresponds to the transition at the edge of the energy band gap. The first peak, which is the highest, corresponds to 1.88eV. other notable transitions are at 2.38eV, 2.75 eV, 3.0eV, 3.25eV, and 6.13eV. The first peak has the greatest $Ɛ_2(ω)$ of 31. The dielectric function plot for $ZnGa_2S_4$ is presented in Fig 10. The real part of Ɛ(ω) is shown in Fig. 10a, and it shows the onset of the first transition peak at about 2.75 eV. The other two peaks are at 2.88 eV and3.38eV. There is a sharp descend of Ɛ(ω) between 3.5eV and 3.75eV. The third peak at 3.38eV has two shoulder on its right and left. There are humps as the energy increases from 4.0 eV to 8.25eV. The $Ɛ_1(0)$ for $ZnGa_2S_4$ is seen to be 19. The highest Ɛ(ω) is about 86.

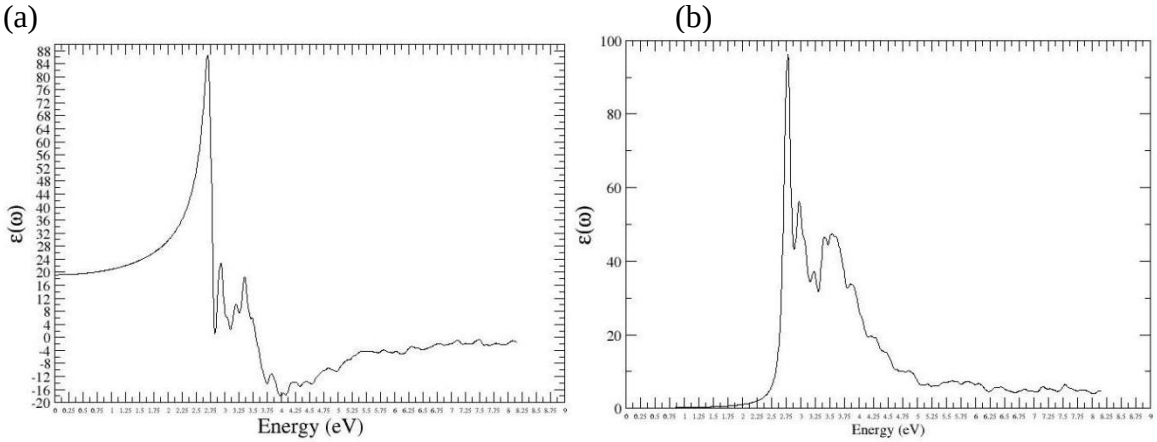

Figure 10: The plot of Ɛ(ω) in XX direction for $ZnGa_2S_4$ (a) real part (b) imaginary part

The imaginary part of Ɛ(ω) for $ZnGa_2S_4$ is shown is Fig 10b. Here, as in the real component of Ɛ(ω), the onset of transition, that is, the first peak is at 2.75eV. There is a small peak at 2.88 eV, then, Ɛ(ω) fells below 40, then there is a small peak at 3.13 eV, followed by a climb to about 50. The crest here having two humps and then a small shoulder as $Ɛ_2(ω)$ falls below 20.

Conclusion

$ZnGa_2S_4$ and $ZnGa_2Se_4$ are important materials because of their technological applications, and knowledge of their electronic and optical properties is important. So, these properties have been studied in this work using the pseudopotential method within the DFT framework. The study revealed these materials are semiconductors with good potentials for optoelectronic applications.

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