chapter 4

optical properties of the ternary chalcopyrite thin films Ag-In-Se and Ag-Ga-Se

Optical absorbance studies of AgInSe₂, AgGaSe₂ and the OVCs AgGa₃Se₅ and AgGa₇Se₁₂ thin films are presented here. The band gap values are elucidated through Tauc plots. The threefold absorption in the fundamental absorption region of the OVC AgGa₇Se₁₂, is analysed to elucidate the three closely spaced band gaps in its valence band due to the lifting of degeneracy of the Γ₁₅ level. Hopfield’s quasi cubic model is employed to extract the crystal-field and spin–orbit splitting parameters and the linear hybridization of orbitals model for evaluating the percentage contribution of Ag d-orbitals and Se p-orbitals to the p–d hybridization of orbitals. Transient photoconductivity analyses have been done to understand the photosensitivity nature of the films.
4.1 Introduction

Investigations on optical behaviour of thin films mainly deal with optical absorption, transmission and reflection properties. The optical absorption spectrum facilitates a simple way to elucidate the optical band gap of the material which may be direct or indirect depending on the electronic transition between the energy levels. Materials in which valence band maximum (VBM) and conduction band minimum (CBM) lies on the same value of k-vector, possess direct band gaps whereas materials in which VBM and CBM do not occur for the same value of k have indirect band gaps, with the electronic transitions assisted by phonons.

The optical band gaps of the ternary AgInSe$_2$ and AgGaSe$_2$ are found to be of direct allowed nature and lies in the visible-near IR range matching the optimum solar spectrum. The fundamental absorption edge may vary from compound to compound based on their electronic band structure. If indium is substituted by gallium in AgInSe$_2$, the band gap changes from 1.25 to 1.75 eV [1-4]. The direct allowed band gap of AgInSe$_2$ and AgGaSe$_2$ within the above mentioned range makes them potential candidates for solar cell applications, though many other factors are to be considered for their efficient use as absorber materials.

The I-III-VI$_2$ compounds are ternary analogues of II-VI binaries with structural similarities and slightly reduced band gap owing to the difference in the uppermost valence band structure between the two. In Ag-based I-III-VI$_2$ compounds the valence band is composed of anion p-orbitals and Ag d-orbitals and under the influence of non-cubic crystalline field and spin-orbit interaction the valence band becomes triply degenerate [5-8]. The threefold absorption in the fundamental absorption region of the optical absorbance spectra is a noteworthy property observed in these ternary chalcopyrites which results in the lifting of the triply degenerate $\Gamma_{15}$ level in its valence band giving three optical band gaps [5-8]. Valence band splitting studies are reported in the case of AgInSe$_2$ and AgGaSe$_2$ compounds by several investigators [9-12]. We have noted the triple degeneracy in the absorption spectra of the OVC AgGa$_7$Se$_{12}$ and evaluated the crystal-field and spin-orbit splitting parameters in order to observe any change in the d-orbital contribution in the OVC due to their specific structure and composition.
In this chapter the valence band splitting studies are elaborated for the OVC 
AgGa\(_7\)Se\(_{12}\) in addition to the band gap estimation of all the other compound thin 
films. A comparative study has been carried out between the valence band splitting 
parameters of OVC AgGa\(_7\)Se\(_{12}\) and that of AgGaSe\(_2\) reported by other investigators. 
The photosensitivity nature of the films is also studied by transient photoconductivity 
measurements.

4.2 Experimental

The absorption spectra of the films are recorded in the wavelength range 300-
2000 nm using a UV-Vis-NIR spectrophotometer of model JASCO V-570 having a 
double beam system with single monochromator, containing deuterium and halogen 
lamps. The film thickness is measured by Fizeau’s interferometric technique and is 
also verified using Stylus profilometer. The thickness of different films used for the 
present study varies from 100 to 170 nm. For the photoresponse measurements an 
FHS quartz halogen lamp is used along with a Keithley 2611A sourcemeter. The 
experimental details of each measurement are explained in chapter 2.

4.3 Results and Discussion

4.3.1 Optical absorption and transmission analysis of AgInSe\(_2\) thin films

From the optical absorbance data, the absorption coefficient \(\alpha\) has been 
estimated using the equation (4.1),

\[
T = (1 - R)^2 \exp(-A) = (1 - R)^2 \exp(-\alpha d)
\]

(4.1)

where \(R\) is the reflectance, \(T\) the transmittance, and \(A\) is the absorbance for films with 
thickness \(d\). A graph connecting \((ahv)^{1/\gamma}\) to photon energy \((hv)\) gives the optical band 
gap according to the equation (4.2).

\[
\alpha = A \left( \frac{hv - E_g}{hv} \right)^{\gamma}
\]

(4.2)

where \(\gamma\) is a constant which is equal to 1/2 and 3/2 for allowed and forbidden direct 
transitions respectively and equal to 2 and 3 for allowed and forbidden indirect
transitions in which the phonons are involved, $E_g$ is the optical band gap and $A_c$ is a constant [13].

$$A_c = \left( \frac{q^2 x_m^2 (2m_r)^{1/2}}{\lambda_0^2 c_0 h^3 n} \right)$$

where

$$m_r = \left( \frac{m_h^* m_e^*}{m_h + m_e} \right)$$

where $m_r$ is the reduced mass, $m_h^*$ and $m_e^*$ are the effective masses of the hole and electron respectively, $q$ is the elementary charge, $n$ is the real index of refraction, $\varepsilon_0$ is the vacuum permittivity and $x_{\mu\nu}$ is a matrix element, with units of length and typical value of the same order of magnitude as the lattice constant.

The absorbance spectra and transmission spectra of a typical thin film of AgInSe$_2$ are given in Figure 4.1 (a)-(b). The AgInSe$_2$ films show high transmittance in the infra-red region of the spectrum.

![Figure 4.1 (a)](image)

**Figure 4.1 (a)** The absorbance spectra of a typical thin film of AgInSe$_2$. 
Figure 4.1 (b) The transmittance spectra of a typical thin film of AgInSe$_2$.

The absorption coefficient of the films is of the order of $10^6$/m to $10^7$/m for the wavelength range 2000 to 300 nm. The variation of absorption coefficient with photon energy is given in Figure 4.2.

Figure 4.2 Absorption coefficient Vs photon energy for AgInSe$_2$ thin film.

The $(ahv)^2$ versus $(hv)$ graph (Tauc plot) for a typical film is given in Figure 4.3. The plot indicates direct allowed nature of the band gap and it is elucidated by
extrapolating the straight line portion to \((a\nu)^2 = 0\) axis. The optical band gap value for AgInSe\(_2\) is found to be 1.25\(\pm\)0.03 eV. The obtained band gap value agrees well with the reported values [14, 15].

![Graph](image)

**Figure 4.3** \((a\nu)^2\) Vs \((\nu)\) plot for AgInSe\(_2\) thin film.

### 4.3.2 Optical absorption and transmission analysis of AgGaSe\(_2\) and OVC AgGa\(_3\)Se\(_5\) thin films

The optical absorbance of AgGaSe\(_2\) and OVC AgGa\(_3\)Se\(_5\) are analysed together while that of the OVC AgGa\(_7\)Se\(_{12}\) in the succeeding section 4.3.3 since the important property of valence band splitting is clearly visible in the absorption spectra of that OVC and analysis of which will be useful for the researchers to get information on the properties of OVCs.

The absorbance spectra of AgGaSe\(_2\) and that of its OVC AgGa\(_3\)Se\(_5\) are depicted in Figure 4.4 and the transmittance spectra in Figure 4.5. Both the films have high transmittance in the IR region of wavelengths but less than that for AgInSe\(_2\) films. The darker colour of the Ag-Ga-Se films compared to the AgInSe\(_2\) films is a direct indicative of their higher absorption in the visible range of the spectra.
The absorbance spectra of typical thin films of AgGaSe$_2$ and OVC AgGa$_3$Se$_5$ are shown in Figure 4.4.

The transmittance spectra of typical thin films of AgGaSe$_2$ and OVC AgGa$_3$Se$_5$ are shown in Figure 4.5.

The absorption coefficient ($\alpha$) variation of the films with photon energy (Figure 4.6) gives $\alpha$ of the order of $10^6$/m to $10^7$/m for the wavelength range 2000 to 300 nm.
Figure 4.6 Absorption coefficient Vs photon energy for typical thin films of AgGaSe₂ and OVC AgGa₃Se₅.

The \((ahv)^2\) versus \(hν\) plots given in Figure 4.7 are used for the estimation of optical band gaps. The optical band gap value for AgGaSe₂ is estimated as \(1.75\pm0.02\) eV which agrees well with the literature values [16-18]. The optical band gap for OVC AgGa₃Se₅ is determined as \(1.84\pm0.02\) eV which is slightly greater than that of the direct allowed band gap obtained for AgGaSe₂ films.

Figure 4.7 \((ahv)^2\) Vs \(hν\) plots for AgGaSe₂ and OVC AgGa₃Se₅ thin films.
By comparing with the enhanced optical band gaps of OVC’s of CuInSe$_2$ and CuGaSe$_2$, the increased band gap for OVC AgGa$_3$Se$_5$ could be explained. In the case of OVC of Cu based I-III-VI$_2$ compounds, p-d interband repulsion plays an important role in widening the band gap compared to that of the stoichiometric compounds [19-21]. According to the molecular orbital theory, the reduction in p-d interband repulsion lowers the valence band maximum (VBM). The OVC structure proposed for AgGa$_3$Se$_5$ indicates the presence of Ag vacancies which reduces the Ag-d and Se-p interband repulsion resulting in the lowering of VBM and hence enhancement of its band gap. The structure of OVC mentioned in chapter 3 explains the introduction of the defect complex (2V$_{Ag}^{-1}$ + Ga$_{Ag}^{+2}$) in the compound where a slight increase in anion displacement has been observed. The slight increase in band gap could be justifiable based on the slightly increased anion displacement in the OVC compounds, in line with that observed for OVC CuIn$_3$Se$_5$ [22].

4.3.3 Optical absorption and transmission analysis of OVC AgGa$_7$Se$_{12}$ thin films and Valence band splitting studies

The absorbance and transmittance spectra of a typical AgGa$_7$Se$_{12}$ thin film are depicted in Figure 4.8 and 4.9.

![Absorbance spectra of AgGa$_7$Se$_{12}$ thin film. Inset: Lower region of the spectra zoomed.](image)
Figure 4.9 The transmittance spectra of AgGa$_7$Se$_{12}$ thin film.

The variation of absorption coefficient with wavelength shown in Figure 4.10, exhibits a threefold structure near the fundamental absorption edge manifesting a threefold absorption. This observation leads to the study of valence band splitting in the compound AgGa$_7$Se$_{12}$. The optical band gaps of these OVC films are found to be direct allowed and could be fitted to equation (4.2).

Figure 4.10 Absorption coefficient Vs photon energy for AgGa$_7$Se$_{12}$ thin film.
Threefold structure is observed in the wavelength range 400 nm to 800 nm of the absorption graph and analysis has been done to estimate the optical band gap energy corresponding to each region. From the absorption graph, using the equation (4.2) the band gap $E_{g1}$ is calculated as $1.612 \pm 0.001$ eV and the corresponding constant $A_1$ as $2.16 \times 10^{13}$ (Figure 4.11).

![Graph showing $(\alpha h\nu)^2$ vs $h\nu$ for AgGa$_7$Se$_{12}$ showing the band gap $E_{g1}$.](image)

**Figure 4.11** $(\alpha h\nu)^2$ Vs $(h\nu)$ plot for AgGa$_7$Se$_{12}$ showing the band gap $E_{g1}$.

From these values of $E_{g1}$ and $A_1$, the absorption coefficient values $\alpha_{1cal}$ is calculated, but are found to coincide with the experimental $\alpha$ values only for region 1. For higher photon energy values $\alpha_{1cal}$ values are found to be less than the experimental $\alpha$ values which is shown by plot 1 in Figure 4.10. The difference in $\alpha_{1cal}$ values from the experimental values of $\alpha$ indicates an additive absorption towards the higher energies in the films. Thus a second band gap $E_{g2}$ is estimated as $1.847 \pm 0.015$ eV (Figure 4.12) with the constant $A_2$ as $8.32 \times 10^{13}$. 
Using the values of $E_{g2}$ and $A_2$, absorption coefficient ($\alpha_{2\text{cal}}$) values are estimated, but $\alpha_{2\text{cal}}$ values are found to be fitted only to region 2 of the Figure 4.10 as shown by plot 2. Since $\alpha_{2\text{cal}}$ values are found to be less than the experimental $\alpha$ values in the next higher energy range, a third band gap could be predicted. By repeating the analysis as above for the higher energy range, the third band gap $E_{g3}$ is calculated as $2.132\pm0.04$ eV (Figure 4.13) and the corresponding constant $A_3$ as $4.65 \times 10^{14}$. The $\alpha_{3\text{cal}}$ values are found to be in agreement with the experimental values of $\alpha$ as shown by plot 3 in Figure 4.10.
Hence by the careful analysis of the $\alpha$ versus $h\nu$ graph the three optical band gaps are estimated for the OVC AgGa$_7$Se$_{12}$. This reveals lifting of the triple degeneracy of the uppermost valence band which leads towards the valence band splitting studies. The band gaps determined for the OVC AgGa$_7$Se$_{12}$ films are found to fall in the range of the reported values of stoichiometric AgGaSe$_2$ and are given in Table 4.1. The estimated $E_{\text{g1}}$ value is found to be closer to that reported by Bhuiyan and Hasan [23] for a silver deficient Ag-Ga-Se compound having a ratio Ag : Ga : Se = 8.37% : 41.51% : 50.12%.

The optical band gap of I-III-VI$_2$ compounds is usually direct allowed and is less than that of their corresponding binary analogues, because of the difference in the uppermost valence band structure between the two [8, 24-26]. The p-like valence band of AgGaSe$_2$ compound is derived from the triply degenerate $\Gamma_{15}$ level in the zinc blende compounds. The orbital degeneracy in the compound can be completely lifted owing to the combined effects of non-cubic crystalline field and spin-orbit interactions [8]. Under such a condition, the tetrahedral crystal field splits the level $\Gamma_{15}$ such that a singlet $\Gamma_4$ level lies above doubly degenerate level $\Gamma_5$. Due to the additional spin-orbit interaction commonly active in chalcopyrite, the doublet $\Gamma_5$ further splits into $\Gamma_{6v}(B)$ and $\Gamma_{7v}(C)$ while $\Gamma_4$ is converted into $\Gamma_{7v}(A)$ [24-26]. According to the zone-centre valence band structure of AgGaSe$_2$ shown in Figure 4.14, transitions A, B and C correspond to transitions $\Gamma_{7v}(A) \rightarrow \Gamma_{6c}$ (valence band maximum to conduction band minimum), $\Gamma_{6v}(B) \rightarrow \Gamma_{6c}$ (crystal-field split level to conduction band minimum) and $\Gamma_{7v}(C) \rightarrow \Gamma_{6c}$ (spin-orbit split level to conduction band minimum) [24].
The spin-orbit ($\Delta_{SO}$) and crystal-field ($\Delta_{CF}$) splitting parameters are evaluated based on the quasi cubic model put forward by Hopfield [26], applying the three band gaps $E_{g1}$, $E_{g2}$, and $E_{g3}$ in the equation (4.5).

$$E_{1,2} = -\frac{1}{2}[\Delta_{SO} + \Delta_{CF}] \pm \frac{1}{2}\left[(\Delta_{SO} + \Delta_{CF})^2 - \frac{8}{3}\Delta_{SO}\Delta_{CF}\right]^{1/2}$$ \hspace{1cm} (4.5)

where $\Delta_{SO}$ is the splitting of valence band due to spin-orbit interaction and $\Delta_{CF}$ is the splitting due to tetragonal crystal-field interaction in the valence band of the compound. The $\Delta_{SO}$ and $\Delta_{CF}$ values are tabulated in Table 4.1 along with the reported values for stoichiometric AgGaSe$_2$ compounds by other investigators. The crystal-field splitting $\Delta_{CF}$ is found to be negative but slightly greater than most of the reported values for stoichiometric AgGaSe$_2$, and the slight difference could be correlated with the structural parameters of this compound as follows.
Table 4.1 The band gap values $E_{g1}$, $E_{g2}$ and $E_{g3}$ and spin-orbit and crystal-field splitting parameters (in eV).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{g1}$</th>
<th>$E_{g2}$</th>
<th>$E_{g3}$</th>
<th>$\Delta_{SO}$</th>
<th>$\Delta_{CF}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgGa$<em>7$Se$</em>{12}$</td>
<td>1.612</td>
<td>1.847</td>
<td>2.132</td>
<td>0.343</td>
<td>-0.293</td>
<td>Present study</td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>1.82</td>
<td>2.02</td>
<td>2.28</td>
<td>0.31</td>
<td>-0.25</td>
<td>[8]</td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>1.76</td>
<td>1.96</td>
<td>2.22</td>
<td>0.311</td>
<td>-0.251</td>
<td>[24]</td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>1.76</td>
<td>1.95</td>
<td>02.25</td>
<td>0.35</td>
<td>-0.24</td>
<td>[9]</td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>1.77</td>
<td>2</td>
<td>2.25</td>
<td>0.30</td>
<td>-0.28</td>
<td>[11]</td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>1.58</td>
<td>2.03</td>
<td>2.36</td>
<td>0.42</td>
<td>-0.54</td>
<td></td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>1.62-1.74</td>
<td>2.07-2.19</td>
<td>-</td>
<td>0.329-0.527</td>
<td>0</td>
<td>[23]</td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>1.75</td>
<td>1.95</td>
<td>2.20</td>
<td>0.30</td>
<td>-0.25</td>
<td>[25]</td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>1.67-1.75</td>
<td>2.05-2.08</td>
<td>-</td>
<td>0.33-0.40</td>
<td>0</td>
<td>[10]</td>
</tr>
</tbody>
</table>

It has been suggested that $\Delta_{CF}$ value depends on the factors: (1) existence of two different cations, $A\neq B$, (2) tetragonal deformation $\eta \neq 1$ and (3) anion displacement $u \neq \frac{1}{4}$ [5, 6]. Jaffe and Zunger [5] reported that for ABC$_2$ chalcopyrite materials with tetragonal compression ($\eta < 1$), $\Delta_{CF}$ value is greatly decided by the second factor mentioned above. Therefore the slight increase in $\Delta_{CF}$ values (deviation from $\eta = 1$, the ideal value) obtained for AgGa$_7$Se$_{12}$ could be attributed to the slightly enhanced compression, as it is detailed in the structural analysis given in chapter 3, due to the obviously different composition of this OVC when compared to that of stoichiometric AgGaSe$_2$ compounds.

The $\Delta_{SO}$ value in the ternaries of chalcopyrite are usually less than that for its binary analogues due to the hybridization of group I-d levels with the p-like valence bands of group VI; the spin–orbit parameter for d-bands being opposite in sign to that of p-bands. It has been reported that while there is a strong evidence for a large admixture of Cu d-bands in Cu-based chalcopyrite such d-mixing is significantly reduced in Ag-based compounds, which probably might be the reason for the
reduced effect of hybridization exhibited by the Ag-based compounds [8, 27]. The experimental $\Delta_{SO}$ value for the OVC AgGa$_7$Se$_{12}$ is found to be in the range of the reported values on stoichiometric AgGaSe$_2$ as depicted in Table 4.1.

The spin-orbit splitting is related to p- and d-orbital contribution through the following equation (4.6) based on the linear hybridization of orbitals model (LHO),

$$\Delta_{SO} = \beta \Delta p + (1 - \beta) \Delta d$$  \hspace{1cm} (4.6)

where $\beta$ and $(1-\beta)$ are the fractional admixtures of p and d levels in the uppermost valence band [22, 28]. The percentage of p-orbital contribution and d-orbital contribution to the hybridization are evaluated by taking the quasi cubic value of $\Delta p = 0.42$ eV and $\Delta d = -0.28$ eV [8] and are determined to be 89% and 11% respectively. Tell et al. [8] reported a d-orbital contribution of 16% and about 13% by Bhuyian et al. [10] in AgGaSe$_2$, compared to that the d-orbital contribution is found to be slightly lesser in this OVC. This decrement in the percentage contribution of d-orbitals in the OVC AgGa$_7$Se$_{12}$ films compared to the reported values for stoichiometric AgGaSe$_2$ compounds could be attributed to the reduced atomic percentage of Ag in the composition of the former.

The deformation potential, $b$ in the OVC AgGa$_7$Se$_{12}$ is calculated using the equation (4.7) and is determined to be -1.01 eV.

$$\Delta_{CF} = \frac{3}{2} \frac{b}{a} \left( 2 - \frac{c}{a} \right)$$  \hspace{1cm} (4.7)

where $a$ and $c$ are the lattice parameters.

Here the negative sign indicates the compressive distortion in this compound and is usually observed in the case of AgGaSe$_2$ chalcopyrite also [27]. Hence it is inferred that the optical analysis of this OVC AgGa$_7$Se$_{12}$ are in concordance with the structural and compositional findings explained in chapter 3. This work on the valence band splitting studies of the OVC is published in the reference [29].
4.3.4 Transient Photoconductivity Analysis

Photoconductivity analysis is a promising tool for the investigation of electron-hole dynamics and transport properties of a compound useful for device applications. In the present work, photoresponse measurements have been done for a comparative study on the sensitivity nature and recombination process in the different Ag-based ternary thin films. The transient photoconductivity curve for the AgGaSe$_2$ thin film is given in Figure 4.15.

\[ I = I_0 \left( e^{-t/\tau_d} \right) \]

where $\tau_d$ is the decay time and $I_0$ is the maximum photocurrent [30].

The decay of photocurrent after the illumination is cut off shows an exponential behaviour with the decay time $\tau_d \sim 236$ seconds, indicating a very slow decay of
photocurrent which could be due to the presence of a number of trap levels in the compound film.

The OVC AgGa$_3$Se$_5$ and AgGa$_7$Se$_{12}$ also show similar photoresponse behaviour (Figure 4.16 and 4.17) with an exponential decay of the photocurrent, as that of the parent compound AgGaSe$_2$ with decay time of about 221 seconds and 247 seconds respectively.

**Figure 4.16** Photoconductivity Vs time graph for AgGa$_3$Se$_5$ thin film with exponential fit for the decay curve.

**Figure 4.17** Photoconductivity Vs time graph for AgGa$_7$Se$_{12}$ thin film with exponential fit for the decay curve.

The presence of a number of defect levels is revealed through the larger decay times in the OVC films also. The positive photoresponse of all the Ag-Ga-Se thin films
irrespective of the composition variation is revealed through the photoconductivity analysis.

In AgInSe$_2$ thin films the photo response is rapid, but not stable compared to that for AgGaSe$_2$ films. Here the carrier formation is fast on illumination, but it seems from the decay current data that the carriers disappear even in light, suggesting presence of defects levels that combine with the carriers as soon as they are formed. The native defects present in the sample could lead to high trap density giving an unstable photoresponse.

4.4 Conclusion

Evaluation of optical band gaps for the thin films has been done, which gives a direct optical band gap $\sim 1.25$ eV for AgInSe$_2$ and $\sim 1.75$ eV for AgGaSe$_2$. Slightly increased band gap $\sim 1.84$ eV for the OVC AgGa$_3$Se$_5$, is accounted by the reduced p-d inter band repulsion in the OVC films. The threefold optical absorbance of the OVC AgGa$_7$Se$_{12}$ thin films indicates the crystal-field and spin-orbit interactions in the ternary chalcopyrite films leading to the valence band splitting studies. The crystal-field and spin-orbit splitting parameters are elucidated as $\Delta_{CF} = -0.293$ eV and $\Delta_{SO} = 0.343$ eV respectively. The p-orbital contribution and d-orbital contribution to the p–d hybridization of Se p-orbitals and Ag d-orbitals are estimated as 89% and 11% respectively. The reduced d-orbital contribution is correlated with the reduced percentage of Ag in the OVC film. A positive photoresponse is exhibited by all the films revealing the photosensitive nature of the films.
References


