Chapter-3

STUDY OF STRUCTURAL AND OPTICAL PROPERTIES

3.1 Introduction

In guided wave media and infrared telecommunication systems, chalcogenides are very striking materials due to their wide usage in such fields [1]. Two important properties of these materials used in linear and non-linear optics are large optical non-linearity and high optical transparency. The low vibrational frequencies of chalcogenide bonds is the feature which permits them to transmit into the infrared [2]. When these glasses are exposed to light or any other radiations, they experience a variety of photo-stimulated mechanisms [3-7]. The change in local structure of glassy materials occurs when such glasses are flashed with high-energy particles or light due to which bond cracking and bond rearrangement can happen. These comprise tenuous effects such as shifts in the absorption edge (photo-bleaching and photo-darkening), and more considerable atomic and molecular reconfiguration such as change in photo-induced refractive index and photo-doping effects [8, 9]. A fabrication of large number of optical devices has been possible with the use of these materials due to the changes in optical constants [10, 11] and absorption edge shift [12] which are connected with above mentioned phenomena’s.

The refractive index and optical band gap are the notable factors in semiconducting thin films. The optical nature of material is exploited to deduce its optical constants. The absorbance type calculations can be done ideally with films. Therefore, the optical constants are most
accurately measured. These materials not only are used to record magnitude but also the phase of illumination because of the fact that chalcogenide thin films are known to have the variation in refractive index when exposed to light. The last mentioned is mainly influential in holographic optical information storage and in the construction of distinct integrated optical components and appliances such as selective optical filters, mixers, couplers and modulators [13-16]. The survey of the optical constants of materials is intriguing for several aspects. Firstly, the precise information of optical constants of material over broad limits of wavelength is necessary for the utilization of these materials in optical fibers and reflected coating. Secondly, the atomic and electronic band structure as well as electrical properties of all materials is linked to their optical properties. Therefore, the exact measurement of the electrical as well as optical constants of these materials is significant, not only in order to study the basic mechanisms, but also to employ and evolve their attracting technological operations.

The unusual behavior of electronic interactions existing in layered III—VI semiconductor compounds and also their lurking application in nonlinear optics [17], solar cells [18], memory devices [19] and solid state batteries are the reasons for long and deep study of these compounds. Amidst them, InSe and GaSe, have been investigated interestingly for their intrinsic striking properties as well as for their budding applications in memory devices. The inspection of GaSe draws wide attraction because of its positive properties for nonlinear applications; the first in rank among them is its extreme transparency. The GaSe is a strong candidate for second harmonic generation materials due to their highly anisotropic optical, transport and mechanical
properties and high nonlinear optical coefficients in the infrared range [17].

Chalcogenide glasses based on selenium are very promising materials for various optical and photonic applications in the spectral range 0.4 to 15 pm. These materials are being explored especially for applications as passive devices (lenses, fibers) but these materials are also alluring for construction of active devices such as non-linear components and laser fiber amplifiers. Silver doped chalcogenide glasses have been inspected mostly for their attractive applications such as optical recording media and currently as materials for optical integrated circuits and diffractive optics [20]. Metals as an additive in chalcogenide glasses have attracted widespread [21] attention in optical recording and information storage technologies.

Chalcogenide semiconducting alloys are known to have diverse applications in electrical, thermal as well as in optical media. These glasses have currently induced a ray of light because of distinct applications such as solid state electronics. There exists a unique mechanism of reversible transformation in wide range of amorphous semiconducting glasses for example Selenium. This property allows the use of these glasses in optical memory applications. However, the low sensitivity, short lifetime and thermal stability of pure glassy Selenium are the reason of concern for its practical application. Some additives are added to Se in order to solve these problems. Se-Ga, Se-Sb and Se-In binary alloys are of great importance due to their diverse properties like immense hardness, higher crystallization temperature, higher sensitivity, higher conductivity and lesser ageing effect in comparison to pure Selenium. Indium mono Selenium has an energy band gap of about 1.3 eV which is close to the general optimal value for solar energy
application. Thus, the system, In$_x$Se$_{100-x}$ could have enticing features for solar energy conversion mainly in polycrystalline or amorphous state [22].

### 3.2 Optical Properties of Amorphous Semiconductors

The electronic structure of materials whether it is amorphous or crystalline can be understood with the analysis of their optical properties. So, analysis of optical properties is the most important tool for studying any material. Optical properties of semiconductors generally comprised of their refractive index (n), and absorption coefficient (α) and their dispersion alliances, that is their proportionality on the wavelength (λ) of the electromagnetic radiation or photon energy $h\nu$, and the changes in the dispersion relations with distinct irradiations such as laser, argon plasma, proton, thermal annealing etc. A definite band gap lies between the valence and conduction bands in an intrinsic crystalline semiconductor. In contrast, in an amorphous semiconductor, the allocations of conduction and valence band electronic states do not eliminate suddenly at the band edges. Instead, some of the electronic states, known as tail states, intrude into the vacant gap region [23]. Localized states also exist along with the tail states deep within the gap region [24] in amorphous semiconductors. As an outcome of defects, these localized tail states emerge. As these deep and tail defect states are localized which isolate these localized states from their extended equivalents [25]. Most of the extraordinary properties shown by amorphous semiconductors are due to the existence of these localized tail and deep defect states. When a photon of energy $h\nu$ is irradiated on a thin film, part of its energy is absorbed, part is reflected and rest is transmitted. The optical absorption of thin films alternates with wavelength and thickness. If $h\nu \geq E_g$ (where the band gap energy, $E_g = E_c - E_v$) then an electron can be activated from the top of the
valence band, \( E_v \) to the bottom of the conduction band, \( E_c \), which results in absorption of photon as shown in figure 3.1.

If \( h\nu \gg E_g \), then the electron is excited to a level higher in the conduction band above \( E_c \). The most of the energy of an electron, \( h\nu - E_c \), in this state is vanished as a result of lattice vibrations (phonons). If \( h\nu < E_g \) then the absorption of photon does not occur. This is correct only if no states exists between the band gap. Here is the comparison between a amorphous and crystalline semiconductor. In amorphous semiconductors due to the presence of localized states within the band gap the photons having energies less than the band gap can create electron hole pairs.

![Diagram](image1.png)

Fig. 3.1 Photon absorption generating electron hole pairs.

![Diagram](image2.png)

Fig. 3.2 Plot of absorption coefficient vs photon energy in a typical crystalline semiconductor to illustrate various absorption processes.
Absorption of photon has to be occurred so that an electron gets stimulated from the valence band to the conduction band. According to Beer Lambert’s law, the spatial decline in intensity of a propagating beam of light, because of progressive conversion of the beam into different forms of energy, can be measured with the help of absorption coefficient ($\alpha$). A typical relationship amongst photon energy absorbed and absorption coefficient in a crystalline semiconductor is shown in figure 3.2.

With the increase in photon energy, the salient attributes in $\alpha$ Vs $hv$ behaviour can be penned down in the following types of absorptions:

a) Reststrahlen or lattice absorption which includes the vibration of the crystal ions resulting in absorption of radiation.
b) Free-carrier absorption in view of the presence of free electrons and holes, an effect that declines with inclination of photon energy.
c) An impurity absorption band because of the various dopants
d) Exciton absorption peaks that are generally experienced at low temperatures and are near to the fundamental absorption edge and
e) Fundamental absorption of photons (band to band absorption), which energize an electron from the valence to the conduction band. Band-to-band absorption has a large absorption coefficient and takes place when the photon energy approaches the bandgap energy $E_g$. There is a good relationship amongst the refractive index and the bandgap of semiconductors in which, wider-bandgap semiconductors have lower refractive indices (i.e. $n$ decreases as $E_g$ increases). The refractive index ($n$) and the extinction coefficient $k$ (or $\alpha$) are linked by the Kramers-Kronig relations [26]. Thus, huge upsurgence in the absorption coefficient for $hv$ near and above the
bandgap energy ($E_g$) also result in rise in the refractive index $n$ Vs $h\nu$ in this region.

3.2.1 Measurement of refractive index ($n$), thickness ($d$) and absorption coefficient ($\alpha$)

The refractive index of the material is one of its most important optical constant which typically resides on the wavelength of the electromagnetic wave by phenomena called dispersion. During the propagation in these materials, an electromagnetic wave can lose its energy due to which the refractive index becomes complex. The real part is generally the refractive index, $n$, and the imaginary part is called the extinction coefficient, $K$. The refractive index of thin films prepared by method discussed in earlier is calculated by Swanepoel’s method [27].

![Fig. 3.3 Thin film deposited on a finite thick transparent substrate.](image)

This method is easiest to apply when thin film does not show much localized absorption band in between interference extremes. This method depends on the upper and lower packets of the optical transmission spectra and is very helpful for determining various optical constants. The transmission spectrum is obtained from VIS/NIR computer-controlled spectrophotometer [SOLAR-TII 2004], in the transmission range 400-
1100 nm. Refractive index of thin film deposited on the transparent substrate is shown in the figure 3.3. The film has thickness $d$ and complex refractive index $n^* = n - ik$, where $n$ is refractive index and $k$ is the extinction coefficient which is related to absorption coefficient ($\alpha$) by following equation

$$\alpha = \frac{4\pi k}{\lambda} \quad (3.1)$$

The transparent substrate on which the film is deposited has thickness much larger than the thickness of the film. The transparent substrate has index of refraction $s$ and absorption coefficient $\alpha_s = 0$. The refractive index of the surrounding air is $n_o = 1$. Multiple reflections at three interfaces are taken into account while calculating transmission. If the thickness $d$ is not uniform, then interference effects are destroyed and the transmission curve will be a smooth curve. However, if the film is of uniform thickness then fringes are obtained in the transmission spectrum as shown in Fig. 3.4. From these fringes optical constants are calculated. There are four regions in the transmission spectrum. In the transparent region, $\alpha = 0$ and the transmission is calculated by $n$ and $s$ through numerous reflections. Although $\alpha$ is less in the weak absorption region it starts to lower the transmission. In the region of medium absorption, $\alpha$ is large and the transmission reduces especially because of $\alpha$. In the region of strong absorption, the transmission weakens intensely almost exclusively due to the impact of $\alpha$. First the solo transmission of the glass substrate in the absence of a film is collected.
The interference-free transmission is given as follows:

\[ T_s = \frac{(1 - R)^2}{1 - R^2} \]  \hspace{1cm} (3.2)

\[ R = [(s - 1)/(s + 1)]^2 \]  \hspace{1cm} (3.3)

\[ T_s = \frac{2s}{s^2 + 1} \]  \hspace{1cm} (3.4)

\[ s = \frac{1}{T_s} + \left( \frac{1}{T_s^2} - 1 \right)^{1/2} \]  \hspace{1cm} (3.5)

The basic equation for interference fringes is given by

\[ 2nd = m\lambda \]  \hspace{1cm} (3.6)

where \( m \) is an integer for maxima and half integer for minima. The transmission \( T \) for the case of Fig 3.4 is a complex function [28, 29] and is given by

\[ T = T(\lambda, s, n, d, \alpha) \]  \hspace{1cm} (3.7)
If s is known, then above equation is written in terms of \( n(\lambda) \) and the absorbance \( x(\lambda) \), where \( x \) is defined in the Eq. (3.15)

\[
T = T(n, x) \tag{3.8}
\]

The mathematical formulae for the transmission \( T \) for a system as shown in figure 3.4 is

\[
T = \frac{Ax}{B - Cx \cos \phi + Dx^2} \tag{3.9}
\]

Where,

\[
A = 16n^2s \tag{3.10}
\]

\[
B = (n + 1)^3(n + s^2) \tag{3.11}
\]

\[
C = 2(n^2 - 1)(n^2 - s^2) \tag{3.12}
\]

\[
D = (n - 1)^3(n - s^2) \tag{3.13}
\]

\[
\phi = \frac{4\pi nd}{\lambda} \tag{3.14}
\]

\[
x = \exp(-\alpha d) \tag{3.15}
\]

The extremes of the interference fringes are as follows:

\[
T_M = \frac{Ax}{B - Cx + Dx^2} \tag{3.16}
\]

\[
T_m = \frac{Ax}{B + Cx + Dx^2} \tag{3.17}
\]

\( T_M \) and \( T_m \) are considered to be continuous functions of \( \lambda \) and thus for \( n(\lambda) \) and \( x(\lambda) \) [30] as shown in figure 3.4.
a. The Transparent region

In the transparent region, $\alpha = 0$ or $x = 1$ in Eqs. (3.16) and (3.17). Substituting Eqs (3.15-3.20) in eq. (3.21) yields

$$T_M = \frac{2s}{s^2 + 1} \quad (3.18)$$

Substituting Eqs (3.15-3.20) in Eq (3.22) for $x = 1$ yields

$$T_m = \frac{4n^2s}{n^4 + n^2(s^2 + 1) + s^2} \quad (3.19)$$

$$n = [M + (M^2 - s^2)\frac{1}{2}]^\frac{1}{2} \quad (3.20)$$

$$M = \frac{2s}{T_m} - \frac{s^2 + 1}{2} \quad (3.21)$$

$T_m$ is thus a function of both $n$ and $s$, and $n$ can be calculated from $T_m$ using Eq (3.25).

b. The region of weak and medium absorption

In this region, $\alpha \neq 0$ and $x < 1$. Subtracting the reciprocal of equation (3.21) from the reciprocal of Eq. (3.22) yields an expression which is independent of $x$

$$\frac{1}{T_m} - \frac{1}{T_M} = \frac{2C}{A} \quad (3.22)$$

Substituting Eq. (3.10-3.15) in Eq. (3.22) and solving for $n$ yields

$$n = [N + (N^2 - s^2)\frac{1}{2}]^\frac{1}{2} \quad (3.23)$$

Where

$$N = 2s \frac{T_M - T_m}{T_mT_M} + \frac{s^2 + 1}{2} \quad (3.24)$$
Eq. (3.23) can be used to calculate \( n(\lambda) \) from \( T_M \) and \( T_m \). It is identical to formulae derived by Manifacier et al. [31] using the theory of infinite substrate. Once \( n(\lambda) \) is known, all the constants in Eqs (3.10-3.15) are known and \( x \) can be calculated in various ways. Eqs. (3.16) and (3.17) are quadratic equations in \( x \) that can be solved for \( x \) and the results are simplified by using Eqs. (3.10-3.16). Solving Eq. (3.16) gives

\[
 x = \frac{E_M - \left[E_M^2 - \left(n^2 - 1\right)^3(n^2 - s^4)\right]^{\frac{1}{2}}}{(n - 1)^3(n - s^2)} \tag{3.25}
\]

Where

\[
 E_M = \frac{8n^2s}{T_M} - (n^2 - 1)(n^2 - s^2) \tag{3.26}
\]

Solving Eq. (3.17) gives

\[
 x = \frac{E_m - \left[E_m^2 - \left(n^2 - 1\right)^3(n^2 - s^4)\right]^{\frac{1}{2}}}{(n - 1)^3(n - s^2)} \tag{3.27}
\]

Where

\[
 E_m = \frac{8n^2s}{T_m} - (n^2 - 1)(n^2 - s^2) \tag{3.28}
\]

Adding the reciprocals of Eqs. (3.17) and (3.18) gives

\[
 \frac{2T_MT_m}{T_M + T_m} = \frac{Ax}{B + Dx^2} \tag{3.29}
\]
Solving for \( x \), above equation gives

\[
x = \frac{F - \left[F^2 - (n^2 - 1)^3(n^2 - s^4)\right]^{1/2}}{(n - 1)^3(n - s^2)}
\]  

(3.30)

where

\[
F = \frac{8n^2s}{T_i}
\]  

(3.31)

and

\[
T_i = \frac{2T_M T_m}{T_M + T_m}
\]  

(3.32)

From Eqs (3.29) and (3.9), it can be seen that \( T_i \) represents a curve passing through the inflection points of the fringes as shown in figure 3.4. The interference-free transmission \( T_\alpha \), can be calculated from the interference fringes by integrating Eq (3.9) between a maximum and an adjacent minimum

\[
T_\alpha = \frac{1}{\pi} \int \frac{A x}{B - Cx \cos \phi + D x^2} \, d\phi
\]  

(3.33)

Assuming a narrow integration region where all parameters are constant, the integral yields

\[
T_\alpha = \frac{A x}{\left[\left(B - Cx + D x^2\right)(B + Cx + Dx^2)\right]^{1/2}}
\]  

(3.34)

Substitution of Eqs (3.17) and (3.18) into (3.39) yields

\[
T_\alpha = \sqrt{T_m T_M}
\]  

(3.35)
$T_\alpha$ is thus just the geometric mean of $T_M$ and $T_m$, and Eq. (3.35) is a very useful relation. Solving Eq. (3.34) for $x$ gives

$$x = \frac{G - [G^2 - (n^2 - 1)^3(n^2 - s^4)]^{\frac{1}{2}}}{(n - 1)^3(n - s^2)}$$  \hspace{1cm} (3.36)

Where

$$G = \frac{128n^4s^2}{T_\alpha^2} - n^2(n^2 - 1)^2(s^2 - 1)^2 + (n^2 - 1)^2(n^2 - s^2)^2$$  \hspace{1cm} (3.37)

Eq. (3.37) is equivalent to a well known equation often used in optical and infrared studies. It can also be used to determine $n$ from $T$, in the transparent region where $x=0$. Putting $x = 1$ in Eq. (3.36) and solving for $n$ gives,

$$n = [H + (H^2 - s^2)^{\frac{1}{2}}]^{\frac{1}{2}}$$  \hspace{1cm} (3.38)

Where

$$H = \frac{4s^2}{(s^2 + 1)T_\alpha^2} - \frac{s^2 + 1}{2}$$  \hspace{1cm} (3.39)

Then, we can use Eq. (3.39) in the linear transmission $T_\alpha$ without interference transmission.

**c. The region of Strong Absorption**

In the region of strong absorption the interference fringes disappear. It is not possible to calculate $n$ and $x$ independently in this region from transmission spectrum alone. Values of $n$ can be estimated by
extrapolating the values calculated in the other parts of the spectrum. The values of $x$ can then be calculated using any of the four formulae presented in the previous section with their appropriate curves. For very large $\alpha$, the four curves $T_M$, $T_a$, $T_i$, $T_m$ converge to a single curve $T_0$ i.e. $T_0 = T_a$. If interference effects are ignored, equation (3.9) can be written for $x \ll 1$ as

$$T_0 = \frac{Ax}{B}$$

(3.40)

or

$$x \cong \frac{(n + 1)^3(n + s^2)}{16n^2s} T_0$$

(3.41)

d. Determination of thickness of thin films
The refractive index of the substrate can be determined by measuring the transmission spectrum of the clean substrate alone and using Eq. (3.5) to calculate the value of $s$. For the calculation of $n$ in the region of weak and medium absorption, the values of $T_M$ and $T_m$ at different $\lambda$ must be obtained. If $n_1$ and $n_2$ are the refractive indices at two adjacent maxima (or minima) at $\lambda_1$ and $\lambda_2$, it follows from Eq. (3.6) that the thickness of thin film ($d$) is given by:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}$$

(3.42)

Owing to the optical absorption, Eqns. (3.6) and (3.42) are not valid at the interference maxima and minima, but are valid at the tangent points. A set of $d$’s is obtained by solving Eq. (3.42) for each pair of consecutive tangent points. The mean ($d$) so calculated is used together with the first
refractive indices, to determine the order numbers from Eq. (3.6): \( m \) being an integer for an upper tangent point and a half integer for a lower tangent point. More accurate values of \( d \)'s are obtained by taking the corresponding integral and half-integral \( m \)'s. Using these \( m \)'s and the mean values of \( d \)'s, a set of \( n \)'s are again calculated. The absorption coefficient can be determined from the Eq. (3.15), where \( x \) is the absorbance given by Eq. (3.25).

### 3.3 Wemple-DiDomenico Dispersion Relation

In a real amorphous material there are disorder potentials due to the "electrostatic" and "elastic" forces. Dow and Redfield [32] have shown that, if we consider only the "electrostatic" part of the disorder potential, the valence and conduction band edges are displaced in parallel. The local gap width does not change and its value coincides with the \( E_{opt} \) obtained by an extrapolation of high frequency interband absorption, which takes place locally. Fig. 3.5 shows an "electrostatic" disorder potential and on the right side the Gaussian variation of the conduction and valence band edges, centered on the most probable values - \( E_{co} \) and \( E_{vo} \). The amorphous semiconductors are transparent for photon energies of subgap (\( hv < E_g \)), but a dispersion of the optical refractive index is observed for energies close to interband transitions. Based on the single-oscillator model, the Wemple-DiDomenico [33, 34] is a semi-empirical dispersion relation for determining the oscillator energy (\( E_0 \)) and the dispersion energy (\( E_d \)) at photon energies below the interband absorption edge in semiconductors. They found that all the data can be described to an excellent approximation by the following relation and is given by:
\[ n^2(\nu) = 1 + \frac{E_d E_0}{E_0^2 - (\nu)^2} \]  (3.43)

Where, \( \nu \) is the frequency, \( h \) is the Planck’s constant, \( E_0 \) the oscillator energy and \( E_d \) the dispersion energy. Thus, \( E_0 \) is the average gap that in our opinion represents \( E_{\text{co}} - E_{\text{vo}} \) as shown in Fig. 3.5. Solomon et al [35] have defined \( E_0 \) like the energy difference between the centre of the valence and conduction band.

![Fig. 3.5 Valence and conduction band edges due to the electrostatic part of the disorder potential](image)

The dispersion energy, \( E_d \), gives a measure of the average strength of the interband optical transition.

\[ E_d = \beta N_c Z_a N_e \]  (3.44)

Where, \( N_c \) is the effective coordination number of the cation nearest-neighbor to the anion, \( Z_a \) is the formal chemical valency of the anion, \( N_e \) is the effective number of valence electrons per anion excluding the cores and \( \beta \) is constant that depends on whether the inter-atomic bond is ionic (\( \beta_i \)) or covalent (\( \beta_c \)). Further, empirically,

\[ E_0 = C E_g(D) \]  (3.45)

Where, \( E_g(D) \) is the lowest direct band-gap and \( C \) is a constant. The Wemple-Di Domenico relation has found wide acceptance among experimentalists due to its straightforward simplicity [35, 36]. From
Wemple’s relation (Eq. (3.43)), we determine the oscillator and dispersion energy by using the plot of \( (n^2 - 1)^{-1} \) vs. \( (hv)^2 \), by fitting a linear function, \( E_d \) and \( E_0 \) can be directly determined from the slope, \( (E_d \ E_0)^{-1} \) and the intercept, \( \frac{E_0}{E_d} \), on vertical axis.

3.4 Study of Structural Properties of Pure and Doped InSe Thin Films

3.4.1 Energy Dispersive X-ray Analysis (EDX)

This a technical tool to determine the composition of individual element present in an alloy. The EDX of all samples i.e \((\text{In}_{10}\text{Se}_{90})_{100-x}\text{Sb}_x\) where \( x \) is 0, 2, 5 and 10 was carried out to determine the exact compositions.

![Fig. 3.6 EDX of pure InSe](image)

Table 3.1 Individual wt% of In and Se as determined by EDX of pure InSe

<table>
<thead>
<tr>
<th>Element</th>
<th>At.%</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium</td>
<td>88.43</td>
<td>8.20</td>
</tr>
<tr>
<td>Selenium</td>
<td>11.57</td>
<td>0.98</td>
</tr>
</tbody>
</table>
The above figure 3.6 is EDX spectrum of pure InSe and the table tells the individual stoichiometries of In and Se being 0.98 and 8.02 respectively. This is relative to the composition of our bulk powder i.e \( \text{In}_{10} \text{Se}_{90} \). Therefore, we were able to deposit the films of the same composition as in the bulk parent material.

a. Effect of addition of Pb

As we added the impurity Pb into our sample, and increased the composition, the thin films should also exhibit the presence of a new element in the analysis. This is shown in the EDX of \((\text{In}_{10} \text{Se}_{90})_{98} \text{Sb}_2\), \((\text{In}_{10} \text{Se}_{90})_{95} \text{Sb}_5\) and \((\text{In}_{10} \text{Se}_{90})_{90} \text{Sb}_{10}\) shown below in figures 3.7(a)-(c).
The above table 3.2 summarizes the wt. % of Pb found in thin films of all the samples. Looking at the values, we can conclude that as we increased the doping concentration, the wt. % of Pb element increased.

Table 3.2 The wt. % of Pb increases as we increase the concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt. % of Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{In}<em>{10}\text{Se}</em>{90})_{98}\text{Pb}_2)</td>
<td>1.50</td>
</tr>
<tr>
<td>((\text{In}<em>{10}\text{Se}</em>{90})_{95}\text{Pb}_5)</td>
<td>1.61</td>
</tr>
<tr>
<td>((\text{In}<em>{10}\text{Se}</em>{90})<em>{90}\text{Pb}</em>{10})</td>
<td>2.77</td>
</tr>
</tbody>
</table>

The above table 3.2 summarizes the wt. % of Pb found in thin films of all the samples. Looking at the values, we can conclude that as we increased the doping concentration, the wt. % of Pb element increased.

b. Effect of addition of Sb

The addition of Sb reflects in the EDX spectrum of samples. Figure 3.8 (a)-(c) shows the presence of Sb and the increment in its at. wt. % with increment in the concentration of Sb in the parent material.
XRD is the most powerful and popular tool to gather information about the structure of a material. Based on Bragg’s law of diffraction, x-ray diffractometers are designed to detect the refracted x-rays coming out of a sample. A goniometer is heart of a x-ray machine and it exists in two forms.

Fig. 3.8 EDX of (a) (In$_{10}$Se$_{90}$)$_{98}$Sb$_2$, (b) (In$_{10}$Se$_{90}$)$_{95}$Sb$_5$ and (c) (In$_{10}$Se$_{90}$)$_{90}$Sb$_{10}$ thin films.

### 3.4.2 X-Ray Diffraction (XRD)

XRD is the most powerful and popular tool to gather information about the structure of a material. Based on Bragg’s law of diffraction, x-ray diffractometers are designed to detect the refracted x-rays coming out of a sample. A goniometer is heart of a x-ray machine and it exists in two forms.
modes i.e theta-theta and theta-2theta. Here, we have utilized the theta-2theta geometry to analyze our samples. The incident radiation is CuKα with $\lambda=1.54$ Angstroms. The diffractogram of pure undoped In$_{10}$Se$_{90}$ is shown in figure 3.9.

![Fig. 3.9 XRD of pure In$_{10}$Se$_{90}$](image)

Here it was clearly observed that pure InSe particles were amorphous in nature with characteristic peak observed at $2\theta = 23.2^\circ$ corresponding to (004) crystal plane of pure InSe.

The average crystallite size was calculated as 14.7 nm using Debye-Scherer equation [7]:

$$D = \frac{k\lambda}{\beta \cos \theta}$$  \hspace{1cm} (3.46)

Where, $k$ presents the factor for mean crystallite, $\beta$ (in radians) is the full width at half maxima (FWHM) of crystalline planes. The d-spacing equivalent to maximum crystalline peak was calculated using Bragg’s relation:

$$n\lambda = 2dsin\theta$$  \hspace{1cm} (3.47)
Where, \( n \) is an integer, \( \theta \) is the angle formed between incident and reflected rays and \( \lambda \) is 1.54 Å for Cu target. The d-spacing corresponding to crystalline peak \( 2\theta = 23.2^\circ \) was 3.83 Å.

**Effect of dopant on structural properties of pure InSe**

**a. Effect of addition of Pb**

The introduction of foreign element into parent material leads to some or the other change in its structure or properties. In the present work, we have used lead and antimony as dopants. Considering Pb first, the introduction of 2% lead into \( \text{In}_{10}\text{Se}_{90} \) makes it \( \text{In}_{10}\text{Se}_{90.98}\text{Pb}_{2} \). From the XRD of this composition (figure 3.9(a)), we can see that the characteristic peak of InSe at \( 23.2^\circ \) is present. No new phase is visible with this much concentration which might be due to very low amount of dopant added. When we increased the concentration of Pb to 5%, enhancement in crystallinity of the sample was observed. The XRD of \( \text{In}_{10}\text{Se}_{90.95}\text{Pb}_{5} \) is shown in figure 3.9(b). Apart from the characteristic (004) phase, some new phase is coming into picture but the intensity is very low.

![XRD of (a) \( \text{In}_{10}\text{Se}_{90.98}\text{Pb}_{2} \) and (b) \( \text{In}_{10}\text{Se}_{90.95}\text{Pb}_{5} \)](image)

Fig. 3.9 XRD of (a) \( \text{In}_{10}\text{Se}_{90.98}\text{Pb}_{2} \) and (b) \( \text{In}_{10}\text{Se}_{90.95}\text{Pb}_{5} \)
n increasing the concentration to 10% Pb, three more peaks at $2\theta = 25.4^\circ$, $29.1^\circ$ and $42.1^\circ$ corresponding to (220), (311) and (440) crystal planes come into picture (see figure 3.10).

![Fig. 3.10 XRD of (In$_{10}$Se$_{90}$)$_{95}$Pb$_5$](image)

Therefore, the pattern (shown in figure 3.11) vividly proved that with the addition of Pb in InSe system, the amorphous nature of the sample was converted into nano crystalline and the degree of crystallinity was further enhanced with increase in wt% of Pb.

![Fig. 3.11 The enhancement in crystallinity with increment in percentage concentration of Pb](image)
b. Effect of addition of Sb

The introduction of antimony lead to the following compositions: (In$_{10}$Se$_{90}$)$_{98}$Sb$_2$, (In$_{10}$Se$_{90}$)$_{95}$Sb$_5$ and (In$_{10}$Se$_{90}$)$_{90}$Sb$_{10}$ The diffractogram of (In$_{10}$Se$_{90}$)$_{98}$Sb$_2$ is shown in figure 3.12. Just like the previous result, the characteristic peak at 23.3° is visible in the XRD pattern and no new phase has been introduced.

![Fig. 3.12 XRD of (In$_{10}$Se$_{90}$)$_{98}$Sb$_2$](image)

![Fig. 3.13 XRD of (a) (In$_{10}$Se$_{90}$)$_{95}$Sb$_5$ and (b) (In$_{10}$Se$_{90}$)$_{90}$Sb$_{10}$](image)
On increasing the concentration to 5% Sb and 10% Sb, no new phase is introduced into the sample. There is an enhancement in the intensity of existing phase as the characteristic peak at 23.2° is intensified with increment in dopant concentration as seen in figure 3.13.

3.4.3 FESEM (Field Effect Scanning Electron Microscopy)

![Fig. 3.14 Top view of As-dep undoped In<sub>10</sub>Se<sub>90</sub> thin films](image)

This is a new and powerful technique to get complete insight of the structural transformations in a material. We characterized all the seven samples to investigate the effect of dopants and their increasing concentrations on the parent material. The Field Effect Scanning Electron Microscopic (FE-SEM) micrographs of pure InSe are shown in figure 3.14. Perfectly defined grain boundaries of spherical shaped nanoparticles are seen in the images.
As we introduced Pb into the sample, some nanoparticles lose their perfect shape and face distortion. This is shown in (figure 3.15) the FESEM images of (In$_{10}$Se$_{90}$)$_{98}$Pb$_2$. Further, the addition of higher atomic wt. % of Pb in the sample lead to even more distortion and agglomeration of nanoparticles.

Fig. 3.15 Top view of (In$_{10}$Se$_{90}$)$_{98}$Pb$_2$ thin films

Fig. 3.16 Top view of (In$_{10}$Se$_{90}$)$_{95}$Pb$_5$ thin films
The FESEM micrographs of \((\text{In}_{10}\text{Se}_{90})_{95}\text{Pb}_5\) and \((\text{In}_{10}\text{Se}_{90})_{90}\text{Pb}_{10}\) are shown in figures 3.16 and 3.17 respectively. Maximum agglomeration is observed at the highest wt. % i.e \((\text{In}_{10}\text{Se}_{90})_{90}\text{Pb}_{10}\).

Fig. 3.17 Top view of \((\text{In}_{10}\text{Se}_{90})_{90}\text{Pb}_{10}\) thin films

Similar trend is observed with Sb as the dopant. As seen in figure 3.18 (a) to (c), the nanoparticles tend to agglomerate with the rise in dopant concentration. By virtue of this, undefined grain boundaries and shapeless crystallites come into picture.

Fig. 3.18 Top view of (a) \((\text{In}_{10}\text{Se}_{90})_{98}\text{Sb}_2\), (b) \((\text{In}_{10}\text{Se}_{90})_{95}\text{Sb}_5\) and (c) \((\text{In}_{10}\text{Se}_{90})_{90}\text{Sb}_{10}\) thin films
3.4.4 TGA and DSC

Thermo-gravometric Analysis (TGA) and Differential Scanning Calorimetry) are techniques for thermal analysis of the material. It basically tells us the temperature up to which a material retains its structure before its losing weight.

![Graph showing TGA and DSC analysis](image)

Fig. 3.19 DSC and TGA of As-dep undoped In$_{10}$Se$_{90}$

From the figure, it is clear that the temperature upto which the sample remains stable is around 170°C which is also confirmed by the inset of the crystallisation peak in the DSC curve.

a. Effect of addition of Pb to the thermal stability of In$_{10}$Se$_{90}$

The addition of Pb significantly increases the thermal stability of InSe. As shown in figure 3.20, the temperature at which the material loses its weight increases from 170°C to 450°C in (In$_{10}$Se$_{90}$)$_{98}$Pb$_2$. 
Increasing the dopant concentration to 5 at. wt. % Pb, (figure 3.21) the thermal stability remains the same as the temperature at which the sample...
loses its maximum mass is same (450°C). Even at the maximum Pb concentration of 10 at. wt. % the degradation temperature remains the same (figure 3.22).

![DSC and TGA of (In$_{10}$Se$_{90}$)$_{90}$Pb$_{10}$](image)

Fig. 3.22 DSC and TGA of (In$_{10}$Se$_{90}$)$_{90}$Pb$_{10}$

This suggests that introduction of Pb as dopant, greatly enhances the thermal stability of our parent material but the its concentration has no effect afterwards.

**b. Effect of addition of Sb on thermal stability of InSe**

![DSC and TGA of (In$_{10}$Se$_{90}$)$_{98}$Sb$_{2}$](image)

Fig. 3.23 DSC and TGA of (In$_{10}$Se$_{90}$)$_{98}$Sb$_{2}$
The DSC and TGA curves of samples with Sb as impurity show different results. The graphs are shown in figures 3.23, 3.24 and 3.25. The degradation temperature for all doped samples has significantly increased from $170^\circ\text{C}$ to $400^\circ\text{C}$ but remains constant thereafter. The crystallization peaks also represent the same temperature for crystallization.

Fig. 3.24 DSC and TGA of $(\text{In}_{10}\text{Se}_{90})_{95}\text{Sb}_5$

Fig. 3.25 DSC and TGA of $(\text{In}_{10}\text{Se}_{90})_{90}\text{Sb}_{10}$
3.5 Optical Properties

Optical properties of materials like absorption coefficient, refractive index, extinction coefficient etc can be determined with UV-Vis-NIR spectroscopy. It contains three modes, i.e. Reflectance, Transmittance and Absorbance.

Absorbance gives us the amount of incident electromagnetic radiation absorbed by the sample, Transmittance gives us amount of radiation it transmits after absorbing and reflectance gives the amount of radiation reflected by the sample. Total incident radiation is always the sum of all these three i.e. \( I = T + A + R \). Therefore, if we know any two of the three, third one can be easily calculated as the incident radiation is always known.

The absorbance spectroscopy gives the absorbance spectrum which is the graph plotted between absorbance values and the incident wavelength. Our range of experiment is 200nm to 100 nm. From this data, we can calculate the absorption coefficient (\( \alpha \)):

\[
\alpha = \frac{(2.303 \times A)}{d}
\]  \hspace{1cm} (3.48)

Where,

A: Absorbance values at particular wavelength (\( \lambda \)) of incident radiation.

d: thickness of the film

The band gap of a material can be determined using the absorption peak corresponding to transformation from valence band to conduction band. The relationship between absorption coefficient (\( \alpha \)) and incident energy (\( hv \)) from the power law given by Tauc can be written as:
\[ \alpha = \frac{A(h\nu - E_g)^n}{h\nu} \]  

(3.49)

Where, A is constant and E \(_g\) is the optical band gap. The n may have values 1/2, 2, 3/2 and 3, depending on the type of transition and it corresponds to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively [9].

The absorption coefficient was further used to plot the Tauc plot [e.g fig 3.27] which gives us the value of energy bandgap (E\(_g\)) as follows:

\[ a h\nu = C (h\nu - E_g) \]  

(3.50)

This is the popular Tauc relation, a graph plotted between \((a h\nu)^n\) vs. \(h\nu\) gives us the tauc plot having a linear portion in the graph, which is extrapolated to meet the abscissa at the value of \(E_g\). Here, n is the factor which tells us about the kind of transition taking place in our material. It is 2 for an indirect transition and \(1/2\) for a direct transition. The absorbance and transmittance spectrum of pure In\(_{10}\)Se\(_{90}\) is given in figure 3.26.

Fig. 3.26 Absorbance and Transmittance Spectrum of pure undoped InSe thin films
The tauc plot drawn from the above data, looks like figure 3.27.

![Tauc plot](image)

**Fig. 3.27** Tauc plot of pure InSe thin film gives $E_g$ as 1.72 eV

**a. Effect of addition of Pb on $E_g$ of pure InSe thin films**

Dopants lead to change in optical bandgap of a material depending upon its atomic mass, atomic weight and electronegativity. Here Pb is added in increasing concentration from 2% to 10% to see how much it affects the optical properties of our parent material.

![Absorbance spectrum](image)

**Fig. 3.28** Variation in Absorbance spectrum with concentration of Pb as dopant
Firstly, with the addition of 2 at wt.% Pb, 5 at wt.% Pb and 10 at wt.% Pb leads to the absorption and transmission spectrum as shown in figure 3.28 and 3.29 respectively.

![Graph showing absorption and transmission spectrum](image)

**Fig. 3.29** Variation in Transmittance spectrum with concentration of Pb as dopant

Now, to calculate the value of $E_g$ of samples with different doping concentrations, we need to draw the tauc plot. Starting with $(\text{In}_{10}\text{Se}_{90})_{98}\text{Pb}_2$, the plot is shown in figure 3.30.

![Graph of Tauc plot](image)

**Fig. 3.30** Tauc plot of $(\text{In}_{10}\text{Se}_{90})_{98}\text{Pb}_2$ gives the value of $E_g$ as 1.69 eV
As we can see in the figure 3.30, the value of optical bandgap has decreased from 1.72eV to 1.69 eV with the introduction of 2 at wt. % of Pb into the parent material. When we increased the doping concentration to 5 at wt. % of Pb, $E_g$ reduces by the same difference again (see figure 3.31). This suggests that increment in amount of Pb impurity is leading to decrement in $E_g$ of the material.

![Tauc plot](image)

Fig. 3.31 Tauc plot of $(\text{In}_{10}\text{Se}_{90})_{95}\text{Pb}_5$ gives the value of $E_g$ as 1.67 eV

The maximum fall in $E_g$ was observed with the highest doping concentration i.e. 10 at. Wt. % of Pb. This is shown in figure 3.32.

From the plots the value of band gap value $E_g$ for pure and different weighted doped samples were calculated and summarized in Table 3.3. The modifications in band gap with different atomic wt% of Pb in InSe glasses were graphically shown in figure 3.33.
Table 3.3 Variation in band-gap with doping concentration

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample</th>
<th>Band gap (E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Pure InSe</td>
<td>1.72</td>
</tr>
<tr>
<td>2.</td>
<td>(InSe)Pb_2</td>
<td>1.69</td>
</tr>
<tr>
<td>3.</td>
<td>(InSe)Pb_5</td>
<td>1.67</td>
</tr>
<tr>
<td>4.</td>
<td>(InSe)Pb_{10}</td>
<td>1.55</td>
</tr>
</tbody>
</table>

The changes in band gap (E_g) with different weighted Pb concentrations are displayed in Fig. 3.33. This variation could be made clear by describing the composition dependent bond energy variation of amorphous film.
Pauling suggested [37] that when two atoms A and B with different electronegativity values $\chi_A$ and $\chi_B$ combine to form a heteronuclear compound then, the mono covalent bond energy of homonuclear $D(A-A)$ and $D(B-B)$ could be used to estimate the bond energy of heteronuclear bond $D(A-B)$ using the relation:

$$D (A - B) = [D (A - A)X D (B - B)]^{1/2} + 30 (\chi_A - \chi_B)^2 \quad (3.51)$$

The single bond energy values of In-In are 84.5kJ mol$^{-1}$, Se-Se is 206.1kJ mol$^{-1}$ and Pb-Pb is 85.7 kJ mol$^{-1}$ [38]. Also Allred-Rockow electronegativity values were made use of, for estimating In-Se and Pb-Se single bond energy values which were found to be 257.5 kJ mol$^{-1}$ and 231.2 kJ mol$^{-1}$ respectively. With the addition of Pb in InSe chalcogenide glasses, In-Se bonds were thoroughly replaced by Pb-Se bonds. Since the bond energy of Pb-Se bond is comparatively lower than In-Se bond, the increased concentration of Pb in InSe glasses form 2 at wt% to 10 at wt% would results in more decrease in bond energy of solid. As optical band gap is directly and strongly influenced by bond energy, therefore this
decrease in average bond energy would in turn decreases the band gap of the material. Hence a decreasing trend in optical band gap was observed with increasing Pb at wt% whose variation is graphically depicted in figure 3.33.

b. Effect of Sb on optical properties of Undoped InSe thin films

Just like Pb, Sb also introduced changes in the absorbance and transmittance spectrum of undoped parent material. This variation is shown in figure 3.34.

![Graph showing absorbance and transmittance spectra with varying concentrations of Sb](image)

Fig. 3.34 (a) Variation in Absorbance spectrum with concentration of Sb

![Graph showing transmittance spectra with varying concentrations of Sb](image)

Fig. 3.34(b) Variation in Transmittance spectrum with concentration of Sb as dopant
The tauc plots of various concentrations of Sb are shown in figure 3.35.

![Tauc plots](image)

Fig. 3.35 Tauc plots for (In\textsubscript{10}Se\textsubscript{90})\textsubscript{100-x}Sb\textsubscript{x} where x is 2, 5 and 10

Here, we can see that the energy bandgap shows no particular trend. It decreases from 1.69 eV to 1.36 eV with 2 at. wt. % Sb. As we increase the doping concentration the bandgap increases from 1.36 eV to 1.61 and then again decreases to 1.43 eV with 10 at. wt. % Sb. This is summarized in table 3.4.
Table 3.4. Variation in bandgap with doping concentration of Sb

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample</th>
<th>Band gap (E&lt;sub&gt;g&lt;/sub&gt;) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Pure InSe</td>
<td>1.72</td>
</tr>
<tr>
<td>2.</td>
<td>(InSe)Sb&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.36</td>
</tr>
<tr>
<td>3.</td>
<td>(InSe)Sb&lt;sub&gt;5&lt;/sub&gt;</td>
<td>1.61</td>
</tr>
<tr>
<td>4.</td>
<td>(InSe)Sb&lt;sub&gt;10&lt;/sub&gt;</td>
<td>1.43</td>
</tr>
</tbody>
</table>

References:


[35] Nicolae Tomozeiu, University of Bucharest, Faculty of Physics, IEEE (1997).