CHAPTER FIVE
CHAPTER - FIVE

EFFECT OF THERMAL ANNEALING ON THE OPTICAL PROPERTIES

5.1 Introduction:

In the last few years, particular attention has been devoted to the study of the physical properties of chalcogenide glasses in view of its possible application in photoelectronic devices. Therefore much work has been done on both bulk and thin film samples of glassy chalcogenide regarding electrical and optical properties [108-110]. The common feature of these glasses is the presence of localized states in the mobility gap as a result of the absence of long-range order as well as various inherent defects. The investigation of electron transport in disordered systems has gradually been developed and the investigation of gap states is of particular interest because of their effect on the electrical properties of semiconductors [111,112]. An increase in optical energy gap $E_g$ after annealing at temperature below the glass transition temperature was observed in chalcogenide films [113,114]. The increase in $E_g$ is attributed to the decrease in the density of tail states adjacent to the band edges [115,116]. The value of $E_g$ of as deposited chalcogenide film was found to increase with the film thickness [117, 118]. It has been pointed out, in the Cu Ge-Te system that the bulk glass formation is centered on 20 at % of Ge. Homogeneous glasses could be obtained by progressively replacing Te by Cu up to 10% [119]. Ligero et al. [120] proposed that, the addition of copper to GeTe glasses system increases the
crystallization ability and decreases the forming of Ge-Te glasses system. On the other hand, Barisova [121] suggested as Cu or Ge content increased in Cu-Ge-Te glasses, a progressive replacement of weak van der Waals bonds which strengthening the glass structure. Ramesh et al. [122] studied the crystallization process of \( \text{Cu}_x \text{Ge}_{15} \text{Te}_{85-x} \) glasses. These glasses exhibit a single crystallization stage. Vazquez et al. [123] reported the glass formation and devitrification of alloys in the Cu-Ge-Te system by differential scanning calorimetry. They presented a comparison of various simple quantitative methods to assess the level of stability of the glassy materials in the above mentioned system. All of these methods are based on characteristic temperatures such as the glass transition temperature \( T_g \), the onset temperature of crystallization \( T_{in} \), the temperature corresponding to the maximum crystallization rate, \( T_p \) or melting temperature \( T_m \). Electrical resistivity measurements under pressures at ambient and low temperatures have been carried out on bulk, melt quenched \( \text{Cu}_x \text{Ge}_{15} \text{Te}_{85-x} \) glasses (\( 2 < x < 10 \)) by Ramesh et al. [124]. They found that the resistivities of these samples decrease continuously with pressure. From the above it is clear that very little attention is paid to optical properties of Bi-Se-Zn and Se-In-Pb system. Electrical and optical properties of \( \text{Ge}_x \text{Se}_{1-x} \) thin films have been studied most extensively [125-127]. When tellurium atoms are used instead of selenium, most of the observations are not valid. Thus it appears that Te atoms exhibit typical properties. In this chapter we deal with new results associated with the special features of spectral characteristics of Bi-Se-Zn and Se-In-Pb thin films. The present work is mainly concerned with some experimental observations on
the effect of heat treatment on the optical constants of Bi-Se-Zn and Se-In-Pb thin films.

5.2: Result and Discussion:

5.2.a: Effect of Annealing on Optical parameters in Amorphous Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ Thin Films:

Amorphous Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ (where $x = 0, 0.1, 0.2, 0.5$ and $1.0$) thin films deposited by thermal evaporation were annealed at different temperatures below their crystallization temperatures for two hours. The optical band gap has been studied at different temperature annealed films as a function of photon energy in the wavelength range (400 - 900 nm). It has been found that the optical band gap decreases with increasing annealing temperatures and increases on Zn concentration in the present system. It has been found that refractive index ($n$) and the extinction coefficient ($k$) increases on incorporation of zinc in Bi-Se system.

The absorption coefficient ($\alpha$) has been obtained directly from the absorbance against wavelength curves using the relation,

$$\alpha = \text{OD} / t$$

(5.1)

Figure (25 - 27) shows the absorption coefficient ($\alpha$) as a function of incident photon energy ($h\nu$) for different films of a- Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ with different annealing temperatures. It has been observed that the value of absorption coefficient ($\alpha$) increases exponentially with the increase in photon energy for different annealed films with the concentration of the zinc. It has also been
Figure 25. Variation of Absorption coefficient ($\alpha$) with photon energy in $\text{a-Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x$ thin films at $60^\circ$C Temperature.
Figure 26. Variation of Absorption coefficient ($\alpha$) with photon energy in $\text{a-Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x$ thin films at 98°C Temperature.
Figure 27. Variation of Absorption coefficient ($\alpha$) with photon energy in a-$\text{Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x$ thin films at 115°C Temperature.
observed that the value of absorption coefficient ($\alpha$) increases with the increase in photon energy for at different temperature of the annealed films. In the absorption process, a photon of known energy excites an electron from a lower to a higher energy state, corresponding to an absorption edge. In chalcogenide glasses, a typical absorption edge can be broadly ascribed to one of the three processes: firstly residual below-gap absorption, secondly Urbach tails and thirdly interband absorption. Chalcogenide glasses have been found to exhibit highly reproducible optical edges, which are relatively insensitive to preparation conditions and only the observable absorption with a gap under equilibrium conditions account for the first process. In the second process the absorption edge depends exponentially on the photon energy according to the Urbach relation. In crystalline materials the fundamental edge is directly related to the conduction and valance band, i.e. direct and indirect band gaps, while in the case of amorphous materials a different type of optical absorption edge is observed. In these materials, $\alpha$ increases exponentially with the photon energy near the energy gap. This optical absorption edge is known as the Urbach edge and is given by equation,

$$\alpha \sim \exp\left(\frac{A(h\nu - h\nu_0)}{kT}\right)$$ ..........................(5.2)

In various absorption processes, the electrons and the holes absorb both a photon and a phonon. The photon supplies the needed energy, while the phonon supplies the required momentum. The variation of $\alpha$ with photon energy can be explained in term of: (i) fundamental absorption (ii) exciton absorption and (iii) valence band acceptor absorption. The measurement of transmission allows
us to determine the absorption coefficient that is the number of absorbed photons per incident photons. The present system obeys the role of indirect transition (n >1) and the relation between the optical gap, optical absorption coefficient $\alpha$ and the energy $h\nu$ of the incident photon is given by equation,

$$(\alpha h\nu)^{1/2} \propto (h\nu - E_g) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5.3)$$

The value of indirect optical band gap ($E_g$) has been calculated from the plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) by taking the intercept on the X-axis.

The variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for different temperature annealed films of $\text{Bi}_{0.5}\text{Se}_{99.5}$, $\text{Bi}_{0.5}\text{Se}_{99.4}\text{Zn}_{0.1}$, $\text{Bi}_{0.5}\text{Se}_{99.3}\text{Zn}_{0.2}$, $\text{Bi}_{0.5}\text{Se}_{99}\text{Zn}_{0.5}$ and $\text{Bi}_{0.5}\text{Se}_{98.5}\text{Zn}_{1.0}$ are shown in figure (28), (29) and (30) respectively. The value of indirect optical band gap ($E_g$) has been calculated by taking the intercept on the X-axis. The calculated values of $E_g$ for all the glassy samples of $\text{Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x$ (at different temperatures annealed films) are given in table - 28 and plotted in figure (31). It is evident from this table and figure that the value of optical band gap decreases with increasing annealing temperature and increases on Zinc concentration. The increase in the optical band gap with increasing zinc concentration may be due to increase in grain size, the reduction in the disorder and decrease in density of defect states, which results in the reduction of tailing of bands. As the temperature increases, the amorphous nature decreases, disorder increases and the regions of strong fluctuations become more and more smaller. Consequently, the localized states reduce in number, the tails reduces and mobility edges $E_c$ and $E_v$ move deeper into the tails. Another phenomenon that is responsible for the reduction in the number of single-electron localized
Figure 28. Variation of $(\alpha hv)^{1/2}$ with photon energy in a- Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 60°C Temperature.
Figure 29. Variation of $(\alpha hv)^{1/2}$ with photon energy in $a\text{-}Bi_{0.5}Se_{99.5-x}Zn_x$ thin films at $98^0C$ Temperature.
Figure 30. Variation of \((\alpha hv)^{1/2}\) with photon energy in a- \(\text{Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x\) thin films at 115°C Temperature.
Figure 31. Variation of the band gap with the different samples of Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ at different annealing temperature
states in chalcogenide glasses is the formation of paired -electron states due to
the polaron effect. The neutral dangling bonds with pairs of electrons (up & down
spins) are formed due to strong attractive interaction between electrons produced
by electron-lattice interaction. These two electron states exist with high density in
the middle of the band gap and pin the Fermi energy [128]

The variations of reflectance (R) for the present system of Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$
(at different annealing temperatures) are shown in figure (32 - 34). These figure
shows that reflectance (R) increases with wavelength.

The values of refractive index (n) and extinction coefficient (k) have been
calculated by using the theory of reflectivity of light. According to this theory, the
reflectance of light from a thin film can be expressed in term of Fresnel's
coefficient. The reflectivity on an interface can be given by equation,

$$ R = \frac{[\left(n - 1\right)^2 + k^2]}{[\left(n + 1\right)^2 + k^2]} $$

(5.4)

and,

$$ \alpha = \frac{4\pi k}{\lambda} $$

(5.5)

The spectral dependence of refractive index (n) and extinction coefficient
(k) for a- Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films (at different annealed temperature films) is
shown in figure (35 - 40). The value of refractive index (n) decreases, while the
value of extinction coefficient (k) increases with increasing photon energy. The
values of n and k for different concentrations of Zn (at different annealing
temperature films) are shown in table .29 - 31.

The real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the dielectric constant has also
been calculated by using the relation,

$$ \varepsilon'_r = n^2 - k^2 \quad \text{and} \quad \varepsilon''_r = 2nk $$

(5.6)
### Table 28

**Optical band gap in Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ films at different annealing temperatures**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical Band Gap ($E_g$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RT</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.5}$</td>
<td>1.30</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.4}$Zn$_{0.1}$</td>
<td>1.32</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.3}$Zn$_{0.2}$</td>
<td>1.50</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99}$Zn$_{0.5}$</td>
<td>1.60</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{98.5}$Zn$_{1.0}$</td>
<td>1.73</td>
</tr>
</tbody>
</table>

### Table 29

**Optical parameter in Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ films at 700 nm at 60°C**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\alpha$ (cm$^{-1}$) $10^4$</th>
<th>n</th>
<th>$k$  (10$^{-3}$)</th>
<th>R</th>
<th>T</th>
<th>$\varepsilon_\infty$</th>
<th>$\varepsilon'_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.5}$</td>
<td>.4861</td>
<td>1.5845</td>
<td>2.7092</td>
<td>6.35</td>
<td>65.00</td>
<td>2.5107</td>
<td>.0859</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.4}$Zn$_{0.1}$</td>
<td>.7777</td>
<td>3.2013</td>
<td>.43347</td>
<td>43.75</td>
<td>43.54</td>
<td>10.248</td>
<td>.2775</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.3}$Zn$_{0.2}$</td>
<td>.6805</td>
<td>2.3622</td>
<td>.3792</td>
<td>23.96</td>
<td>48.95</td>
<td>5.5800</td>
<td>.1792</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99}$Zn$_{0.5}$</td>
<td>1.0694</td>
<td>3.2013</td>
<td>.5960</td>
<td>43.75</td>
<td>37.50</td>
<td>10.248</td>
<td>.3816</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{98.5}$Zn$_{1.0}$</td>
<td>1.9444</td>
<td>2.6825</td>
<td>1.0836</td>
<td>31.77</td>
<td>22.916</td>
<td>7.1957</td>
<td>.5814</td>
</tr>
</tbody>
</table>
### Table - 30

**Optical parameter in Bi_{0.5}Se_{99.5-x}Zn_x films at 700 nm at 98°C**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\alpha$ (cm$^{-1}$) $10^4$</th>
<th>$n$</th>
<th>$k$ (10$^{-3}$)</th>
<th>$R$ %</th>
<th>$T$ %</th>
<th>$\varepsilon'_r$</th>
<th>$\varepsilon''_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.5}$</td>
<td>1.2566</td>
<td>2.4047</td>
<td>.7003</td>
<td>25.00</td>
<td>36.45</td>
<td>5.7826</td>
<td>.3368</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.4}$Zn$_{0.1}$</td>
<td>2.3180</td>
<td>2.0830</td>
<td>1.2918</td>
<td>17.19</td>
<td>11.66</td>
<td>4.3390</td>
<td>.5382</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.3}$Zn$_{0.2}$</td>
<td>.9236</td>
<td>2.9018</td>
<td>.5147</td>
<td>36.98</td>
<td>28.12</td>
<td>8.4206</td>
<td>.2987</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99}$Zn$_{0.5}$</td>
<td>5.6300</td>
<td>2.3835</td>
<td>3.1377</td>
<td>24.48</td>
<td>7.291</td>
<td>5.6808</td>
<td>1.4957</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{98.5}$Zn$_{1.0}$</td>
<td>1.0208</td>
<td>2.4685</td>
<td>.5689</td>
<td>26.56</td>
<td>16.14</td>
<td>6.0933</td>
<td>.2809</td>
</tr>
</tbody>
</table>

### Table - 31

**Optical parameter in Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ films at 700 nm at 115°C**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\alpha$ (cm$^{-1}$) $10^4$</th>
<th>$n$</th>
<th>$k$ (10$^{-3}$)</th>
<th>$R$ %</th>
<th>$T$ %</th>
<th>$\varepsilon'_r$</th>
<th>$\varepsilon''_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.5}$</td>
<td>.3402</td>
<td>3.1775</td>
<td>.1896</td>
<td>43.23</td>
<td>43.60</td>
<td>10.096</td>
<td>.1205</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.4}$Zn$_{0.1}$</td>
<td>.7291</td>
<td>2.6179</td>
<td>.4063</td>
<td>30.21</td>
<td>11.81</td>
<td>6.8533</td>
<td>.2128</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99.3}$Zn$_{0.2}$</td>
<td>.9236</td>
<td>3.5791</td>
<td>.5147</td>
<td>51.56</td>
<td>36.57</td>
<td>12.810</td>
<td>.3685</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{99}$Zn$_{0.5}$</td>
<td>1.1666</td>
<td>2.5964</td>
<td>.6502</td>
<td>29.69</td>
<td>16.84</td>
<td>6.7415</td>
<td>.3376</td>
</tr>
<tr>
<td>Bi$<em>{0.5}$Se$</em>{98.5}$Zn$_{1.0}$</td>
<td>1.0208</td>
<td>2.5281</td>
<td>.5689</td>
<td>28.02</td>
<td>12.39</td>
<td>6.3911</td>
<td>.2877</td>
</tr>
</tbody>
</table>
Figure 32. Variation of Reflection (R) with wavelength in a- Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 60°C Temperature.
Figure 33. Variation of Reflection (R) with wavelength in a- Bi$_{0.5}$Se$_{99.5-x}$Znx thin films at 98°C Temperature.
Figure 34. Variation of Reflection ($R$) with wavelength in a- $\text{Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x$ thin films at $115^\circ\text{C}$ Temperature.
Figure 35. Variation of Refractive Index (n) with photon energy in a- Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 60°C Temperature.
Figure 36. Variation of Refractive Index (n) with photon energy in a- Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 98$^\circ$C Temperature.
Temperature = 115°C

Figure 37. Variation of Refractive Index (n) with photon energy in a-Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 115°C Temperature.
Figure 38. Variation of Extinction coefficient (k) with photon energy in a-Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 60°C Temperature.
Figure 39. Variation of Extinction coefficient (k) with photon energy in α-
Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 98°C Temperature.
Figure 40. Variation of Extinction coefficient (k) with photon energy in a-Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 115°C Temperature.
The values of real part ($\varepsilon'$) and imaginary part ($\varepsilon''$) of the dielectric constants of as-prepared and annealed films are shown as a function of photon energy in figure (41 - 46).

The variation of the transmittance with the wavelength in different samples of $\text{Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x$ thin films at different annealing temperature is shown in figure (47 - 49). Figure 31 shows the variation of optical band gaps with Zn concentration in $\text{Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x$ at different temperatures annealed films. It is clear from this figure that the optical band gap decreases with increasing annealing temperature and increases with Zinc concentration. The decrease in the optical band gap with increasing annealing temperature may be due to the increase in grain size, the reduction in the disorder and decrease in density of defect states (which results in the reduction of tailing of bands). The increase in the optical band gap with increasing annealing temperature could also be discussed on the basis of density of state model as discussed earlier. Chalcogenide thin films always contain a high concentration of unsaturated bonds or defects. These defects are responsible for the presence of localized states in the amorphous band gap. During thermal annealing at temperature below the crystallization temperature, the unsaturated defects are gradually annealed out producing a large number of saturated bonds. The reduction in the number of unsaturated defects decreases the density of localized states in the band structure consequently increasing the optical band gap. The optical band gap also increases with Zn concentration.
Figure 41. Variation of Real part ($\varepsilon'_r = n^2 - k^2$) of the dielectric constant with photon energy ($hv$) in a- Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 60°C Temperature.
Figure 42. Variation of Real part ($\varepsilon'_r = n^2 - k^2$) of the dielectric constant with photon energy (hv) in a- Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 98°C Temperature.
Figure 43. Variation of Real part ($\varepsilon'_r = n^2 - k^2$) of the dielectric constant with photon energy ($h\nu$) in a- $\text{Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x$ thin films at $115^\circ\text{C}$ Temperature.
Figure 44. Variation of Imaginary part ($\varepsilon'' = 2nk$) of the dielectric constant with photon energy ($h\nu$) in a- $Bi_{0.5}Se_{99.5-x}Zn_x$ thin films at 60°C Temperature.
Figure 45. Variation of Imaginary part ($\varepsilon'' = 2n \kappa$) of the dielectric constant with photon energy ($h\nu$) in a- Bi$_{0.5}$Se$_{99.5}$Zn$_{0.5}$ thin films at 98°C Temperature.
Figure 46. Variation of Imaginary part ($\varepsilon'' = 2nk$) of the dielectric constant with photon energy ($hv$) in a- Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 115°C Temperature.
Figure 47. Variation in Transmission (T) with Wavelength in a- Bi\textsubscript{0.5}Se\textsubscript{99.5-x}Zn\textsubscript{x} thin films at 60° C. Temperature.
Figure 48. Variation in Transmission (T) with Wavelength in a- $\text{Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x$ thin films at $98^\circ\text{C}$ Temperature.
Figure 49. Variation in Transmission (T) with Wavelength in α- Bi$_{0.5}$Se$_{99.5-x}$Zn$_x$ thin films at 115° C Temperature.
The optical absorption measurements on the a- \text{Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x\ films during crystallization indicate that the absorption occurs due to indirect transition. Crystallization of chalcogenide films is accompanied by a change in the optical band gap. The effect of thermal annealing is interpreted on the basis of amorphous-crystalline transformation. The optical band gap decreases on increasing annealing temperature and increases on Zn concentration. This change in the optical band gap may be due to the increase in the grain size and the reduction in the disordered of the system. From the reflectance studies of as-prepared films of \text{Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x, it may be concluded that the refractive index decreases, while the value of the extinction coefficient increases with photon energy. With large absorption coefficients and compositional dependence of reflection, these materials may be suitable for optical disk applications.

5.2.b Effect of Annealing on the Optical Band Gap of Amorphous \text{Se}_{75-x}\text{In}_{25}\text{Pb}_x:

The optical band gaps of a-\text{Se}_{75-x}\text{In}_{25}\text{Pb}_x (where \(x = 0, 4, 6\) and 10) have been studied as a function of photon energy in the wave length range (400-900 nm) at different annealing temperature. Thermal annealing for two hour at the temperature below the crystallization temperature induced thin film. It has been found that the value of optical band gap \(E_g\) decreases with increasing the annealing temperature and with Pb concentration. At the higher concentration of Pb \((x=10\%)\), the optical band increases with annealing temperature. At the higher annealing temperature, the optical band increases with Pb concentration. It has
been found that the refractive index (n) and extinction coefficient (k) increases on incorporation of lead in In-Se system.

The absorption coefficient (α) has been obtained directly from the absorbance against wavelength curves using the relation (5.1). The variation of the absorption coefficient (α) as a function of incident photon energy (hv) for different temperature annealed films of Se_{75-x}In_{25}Pb_x with different annealing temperatures of crystallization is shown in figure (50-52). It has been observed that the value of absorption coefficient (α) increases with the increase in photon energy for different temperature annealed films.

The present system also obeys the role of indirect transition (m>1) and the relation between the optical gap, optical absorption coefficient α and the energy hv of the incident photon is given by equation (5.3). The value of indirect optical band gap (E_g) has been calculated from the plot of (αhv)^{1/2} versus photon energy (hv) by taking the intercept on the X-axis. The variation of (αhv)^{1/2} with photon energy (hv) for as-prepared and annealed films of Se_{75}In_{25}, Se_{71}In_{25}Pb_{4}, Se_{69}In_{25}Pb_{6} and Se_{65}In_{25}Pb_{10} are shown in figure (53), (54) and (55) respectively. The value of indirect optical band gap (E_g) has been calculated by taking the intercept on the X-axis. The calculated values of E_g for all the glassy samples of Se_{75-x}In_{25}Pb_x (at different temperatures annealed films) are given in table 34. It is evident from this table that the value of optical band gap (E_g) decreases with increasing the annealing temperature and with Pb concentration. At the higher concentration of Pb (x=10%), the optical band increases with annealing temperature. At the higher annealing temperature, the optical band
Figure 50. Variation of Absorption coefficient (\( \alpha \)) with photon energy in a-Se\(_{75}\)In\(_{25-x}\)Pb\(_x\) thin films at \( T = 60^\circ C \).
Figure 51. Variation of Absorption coefficient ($\alpha$) with photon energy in a-Se$_{75}$In$_{25-x}$Pb$_x$ thin films at $T = 98^\circ$C.
Figure 52. Variation of Absorption coefficient ($\alpha$) with photon energy in a-Se$_{75}$In$_{25-x}$Pbx thin films at $T=115^\circ$C.
Figure 53. Variation of $(\alpha h v)^{1/2}$ with photon energy in a-Se$_{75}$In$_{25-x}$Pb$_x$ thin films at $T = 60^\circ$C.
Figure 54. Variation of $(\alpha h\nu)^{1/2}$ with photon energy in a-Se$_{75}$In$_{25-x}$Pb$_x$ thin films at $T = 98^\circ$ C.
Figure 55. Variation of \((\alpha h\nu)^{1/2}\) with photon energy in a-Se\(_{75}\)In\(_{25-x}\)Pb\(_x\) thin films at \(T = 115^\circ\text{C}\).
increases with Pb concentration. The decrease in optical band gap with increasing annealing temperature may be due to the increase in the grain size, the reduction in the disorderedness of the system. This may also be due to the decrease in the density of defect states, which results in the reduction of tailing of bands. The increase in the optical band gap with increasing lead concentration may be due to increase in grain size, the reduction in the disorder and decrease in density of defect states, which results in the reduction of tailing of bands. As the temperature increases, the amorphous nature decreases, disorder increases and the regions of strong fluctuations become more and more small. Consequently, the localized states reduce in number, the tails reduces and mobility edges Ec and Ev move deeper into the tails. Another phenomenon that is responsible for the reduction in the number of single-electron localized states in chalcogenide glasses is the formation of paired electron states due to the polaron effect. The neutral dangling bonds with pairs of electrons (up & down spins) are formed due to strong attractive interaction between electron electrons produced by electron-lattice interaction. These two electron states exist with high density in the middle of the band gap in the Fermi energy (128).

The optical band gap slight decreases with increasing Pb concentration, and at the higher annealing temperature, the optical band increases with Pb concentration. This may be due to the slight increase in disorderedness of the system (compositional disorder). Since the optical absorption also depends on short-range order in the amorphous states and defects associated with it, the increase in optical band gap may also be explained on the basis of "density of
state model" proposed by Mott and Devis [129]. According to this model, the width of the localized states near the mobility edges depends on the degree of disorder and defects present in the amorphous structure. In particular, it is known that unsaturated bonds together with some saturated bonds are produced as the result of an insufficient number of atoms deposited in the amorphous film [130]. The unsaturated bonds are responsible for the formation of some of the defects in the films, producing localized states in the amorphous solids. The presence of high concentration of localized states in the band structure is responsible for the low values of optical band gap in the case of the amorphous films. These low values may also be due to the shift in Fermi level whose position is determined by the distribution of electrons over the localized states [131].

The variation of reflectance (R) and transmittance (T) for the present system of \(\text{Se}_{75-x}\text{In}_{25}\text{Pb}_x\) is shown in figure (56 - 58) and figure (59 -61). These figures show that both the reflectance (R) and transmittance (T) increase with wavelength.

The values of refractive index (n) and extinction coefficient (k) have been calculated by using the theory of reflectivity of light. According to this theory, the reflectance of light from a thin film can be expressed in term of Fresnel's coefficient. Equation (5.4) and (5.5) can give the reflectivity on an interface. The spectral dependence of refractive index (n) and extinction coefficient (k) for \(\text{a-}\text{Se}_{75-x}\text{In}_{25}\text{Pb}_x\) thin films is shown in figure (62 - 64) and figure (65 - 67). The value of refractive index (n) and extinction coefficient (k) increases with increasing of
Figure 56. Variation of Reflection (R) with wavelength in a-Se$_{75}$In$_{25}$Pb$_x$ thin films at $T = 60^\circ\text{C}$. 

Temperature = 60$^\circ$C
Temperature = 98°C

Figure 57. Variation of Reflection (R) with wavelength in a-Se$_{75}$In$_{25-x}$Pb$_x$ thin films at T = 98°C.
Figure 58. Variation of Reflection (R) with wavelength in a-Se$_{75}$In$_{25-x}$Pb$_x$ thin films at T = 115°C.
Figure 59. Variation in Transmission (T) with Wavelength in a-Se$_{75}$In$_{25-x}$Pb$_x$ thin films at $T = 60^\circ$ C.
Figure 60. Variation in Transmission (T) with Wavelength in a-Se$_{75}$In$_{25}$,Pb$_x$ thin films at $T = 98^\circ$ C.
Figure 61. Variation in Transmission (T) with Wavelength in a-Se₇₅In₂₅₋ₓPbₓ thin films at T = 115°C.
Figure 62. Variation of Refractive Index (n) with photon energy in a-Se_{75}In_{25-x}Pb_x thin films at T = 60°C.
Figure 63. Variation of Refractive Index (n) with photon energy in a-Se$_{75}$In$_{25-x}$Pb$_x$ thin films at T = 98° C.
Figure 64. Variation of Refractive Index (n) with photon energy in a-Se$_{75}$In$_{25}$Pb$_x$ thin films at $T = 115^\circ$C.
Figure 65. Variation of Extinction coefficient (k) with photon energy in a-Se$_{75}$In$_{25-x}$Pbx thin films at $T = 60^\circ$C.
Figure 66. Variation of Extinction coefficient ($k$) with photon energy in $a$-$Se_{75}In_{25-x}Pb_x$ thin films at $T = 98^\circ C$. Temperature = 98°C
Figure 67. Variation of Extinction coefficient (k) with photon energy in a-Se$_{75}$In$_{25-x}$Pb$_x$ thin films at $T = 115^\circ C$. 

Temperature = 115$^\circ$C
Figure 68. Variation of Real part \( \varepsilon'_r = n^2 - k^2 \) of the dielectric constant with photon energy \( \text{hv} \) in a-Se\(_{75}\)In\(_{25}\)-Pb\(_x\) thin films at T = 60° C.
Figure 69. Variation of Real part ($\varepsilon'_r = n^2 - k^2$) of the dielectric constant with photon energy ($h\nu$) in $a$-Se$_{75}$In$_{25}$Pb$_x$ thin films at $T = 98^\circ C$. 

Temperature = 98°C
Figure 70. Variation of Real part ($\varepsilon'_r = n^2 - k^2$) of the dielectric constant with photon energy (hv) in a-Se$_{75}$In$_{25-x}$Pb$_x$ thin films at $T = 115^\circ$C.
Figure 71. Variation of imaginary part ($\varepsilon'' = 2nk$) of the dielectric constant with photon energy (hv) in a-Se$_{75}$In$_{25}$Pb$_x$ thin films at T = 60°C.
Figure 72. Variation of Imaginary part ($\varepsilon''_r = 2nk$) of the dielectric constant with photon energy (hv) in a-Se$_{75}$In$_{25}$Pb$_x$ thin films at T = 98$^\circ$C.
Figure 73. Variation of Imaginary part ($\varepsilon'' = 2nk$) of the dielectric constant with photon energy ($hv$) in a-Se$_{75}$In$_{25-x}$Pb$_x$ thin films at $T = 115^\circ$C.
Figure 74. Variation of the band gap with the different samples of \( \text{Se}_{75}\text{In}_{25-x}\text{Pb}_x \) at different annealing temperature.
Table - 34
Optical band gap in Se_{75-x}In_{25}Pb_x films at different annealing temperatures

<table>
<thead>
<tr>
<th>Annealing Temperatures</th>
<th>Optical Band Gap (E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Se_{75}In_{25}</td>
</tr>
<tr>
<td>RT</td>
<td>1.50</td>
</tr>
<tr>
<td>60</td>
<td>1.24</td>
</tr>
<tr>
<td>98</td>
<td>1.32</td>
</tr>
<tr>
<td>115</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table - 35
Optical parameter in Se_{75-x}In_{25}Pb_x films at 700 nm 60°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\alpha$ (cm$^{-1}$) $10^4$</th>
<th>n</th>
<th>k (10$^{-3}$)</th>
<th>R %</th>
<th>T %</th>
<th>$\varepsilon'_r$</th>
<th>$\varepsilon''_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se_{75}In_{25}</td>
<td>.5666</td>
<td>1.822</td>
<td>.3203</td>
<td>11.2</td>
<td>22.5</td>
<td>3.3207</td>
<td>.1167</td>
</tr>
<tr>
<td>Se_{71}In_{25}Pb_4</td>
<td>.7000</td>
<td>3.1866</td>
<td>.3957</td>
<td>43.43</td>
<td>45.5</td>
<td>10.155</td>
<td>.2522</td>
</tr>
<tr>
<td>Se_{69}In_{25}Pb_6</td>
<td>1.9666</td>
<td>3.4209</td>
<td>1.1117</td>
<td>48.4</td>
<td>39.8</td>
<td>11.703</td>
<td>.7606</td>
</tr>
<tr>
<td>Se_{65}In_{25}Pb_{10}</td>
<td>1.9000</td>
<td>2.617</td>
<td>1.0740</td>
<td>30.2</td>
<td>31.5</td>
<td>6.8515</td>
<td>.5623</td>
</tr>
</tbody>
</table>
Table – 36
Optical parameter in Se<sub>75-x</sub>ln<sub>25</sub>Pb<sub>x</sub> films at 700 nm 98<sup>0</sup>C

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \alpha \left( \text{cm}^{-1} \right) \times 10^4 )</th>
<th>( n )</th>
<th>( k \left( 10^{-3} \right) )</th>
<th>( R % )</th>
<th>( T % )</th>
<th>( \varepsilon'_r )</th>
<th>( \varepsilon''_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se&lt;sub&gt;75&lt;/sub&gt;ln&lt;sub&gt;25&lt;/sub&gt;</td>
<td>.3402</td>
<td>2.0698</td>
<td>.1896</td>
<td>16.87</td>
<td>60.41</td>
<td>4.2843</td>
<td>.0785</td>
</tr>
<tr>
<td>Se&lt;sub&gt;71&lt;/sub&gt;ln&lt;sub&gt;25&lt;/sub&gt;Pb&lt;sub&gt;4&lt;/sub&gt;</td>
<td>.7291</td>
<td>6.8715</td>
<td>.4063</td>
<td>86.25</td>
<td>42.70</td>
<td>47.21</td>
<td>.5585</td>
</tr>
<tr>
<td>Se&lt;sub&gt;69&lt;/sub&gt;ln&lt;sub&gt;25&lt;/sub&gt;Pb&lt;sub&gt;6&lt;/sub&gt;</td>
<td>.9236</td>
<td>3.2128</td>
<td>.5147</td>
<td>44.00</td>
<td>60.41</td>
<td>10.322</td>
<td>.3308</td>
</tr>
<tr>
<td>Se&lt;sub&gt;65&lt;/sub&gt;ln&lt;sub&gt;25&lt;/sub&gt;Pb&lt;sub&gt;10&lt;/sub&gt;</td>
<td>1.1666</td>
<td>1.9360</td>
<td>.6502</td>
<td>13.75</td>
<td>50.00</td>
<td>3.7482</td>
<td>.2518</td>
</tr>
</tbody>
</table>

Table – 37
Optical parameter in Se<sub>75-x</sub>ln<sub>25</sub>Pb<sub>x</sub> films at 700 nm 115<sup>0</sup>C

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \alpha \left( \text{cm}^{-1} \right) \times 10^4 )</th>
<th>( n )</th>
<th>( k \left( 10^{-3} \right) )</th>
<th>( R % )</th>
<th>( T % )</th>
<th>( \varepsilon'_r )</th>
<th>( \varepsilon''_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se&lt;sub&gt;75&lt;/sub&gt;ln&lt;sub&gt;25&lt;/sub&gt;</td>
<td>.3743</td>
<td>4.1401</td>
<td>.20861</td>
<td>61.45</td>
<td>42.70</td>
<td>17.140</td>
<td>.1727</td>
</tr>
<tr>
<td>Se&lt;sub&gt;71&lt;/sub&gt;ln&lt;sub&gt;25&lt;/sub&gt;Pb&lt;sub&gt;4&lt;/sub&gt;</td>
<td>.8020</td>
<td>3.1069</td>
<td>.4470</td>
<td>41.66</td>
<td>68.75</td>
<td>9.6532</td>
<td>.2778</td>
</tr>
<tr>
<td>Se&lt;sub&gt;69&lt;/sub&gt;ln&lt;sub&gt;25&lt;/sub&gt;Pb&lt;sub&gt;6&lt;/sub&gt;</td>
<td>1.0159</td>
<td>4.9159</td>
<td>.5662</td>
<td>71.87</td>
<td>37.91</td>
<td>24.166</td>
<td>.5567</td>
</tr>
<tr>
<td>Se&lt;sub&gt;65&lt;/sub&gt;ln&lt;sub&gt;25&lt;/sub&gt;Pb&lt;sub&gt;10&lt;/sub&gt;</td>
<td>1.1666</td>
<td>2.5323</td>
<td>.65021</td>
<td>28.12</td>
<td>26.04</td>
<td>6.4127</td>
<td>.3293</td>
</tr>
</tbody>
</table>
the photon energy. The values of n and k for different concentration of lead are shown in tables 35 – 37.

The real \( (\varepsilon'') \) and imaginary \( (\varepsilon'''') \) parts of the dielectric constant has also been calculated by using the relation (5.6). The values of real part \( (\varepsilon') \) and imaginary part \( (\varepsilon'') \) of the dielectric constants of different films are shown in table 35 - 37. The variation of real part \( (\varepsilon') \) and imaginary part \( (\varepsilon'') \) of the dielectric constants of different films with photon energy \( h\nu \) in \( \text{Se}_{75-x}\text{In}_{25}\text{Pb}_x \) seriessaamles at different annealing temperatures is shown in figure (68 –73). It is evident from this table that both increases on incorporating lead in the present system.

Figure 74 shows the variation of optical band gap with Pb concentration in \( \text{Se}_{75-x}\text{In}_{25}\text{Pb}_x \). It is clear from this figure that the optical band gap decreases with increasing annealing temperature up to \( x<6 \), and the optical band gap increases with increasing annealing temperature for \( x>6 \).

From the above results and discussion, it may be concluded that the optical band gap decreases with increasing annealing temperature up to \( x<6 \), and the optical band gap increases with increasing annealing temperature for \( x>6 \). This may be due to the increase in the grain size, the reduction in the disorderedness of the system. This may also be due to the decrease in the density of defect states, which results in the reduction of tailing of bands. The refractive index \( (n) \) and extinction coefficient \( (k) \) increases on incorporation of lead in In-Se system with photon energy for as-prepared films.