CHAPTER 3
LINEAR OPTICAL PROPERTIES OF TERNARY Se-Te-Bi AND QUATERNARY Se-Te-Bi-Sn CHALCOGENIDE THIN FILMS
This chapter explains the characterization of linear optical properties of ternary Se$_{85-x}$Te$_{15}$Bi$_x$ and quaternary Se$_{84-x}$Te$_{15}$Bi$_{1.0}$Sn$_x$ chalcogenide thin films. The transmission and reflection spectra of ternary and quaternary chalcogenide thin films have been measured in the spectral range 400-2500 nm by using UV-Vis-NIR spectrophotometer. Swanepoel method has been utilized for the determination of refractive index. The optical band gap has been evaluated through absorption spectra. The behavior of optical band gap with composition is further explained on the basis of different models.

3.1 Introduction

Due to the unique optical properties of chalcogenide glasses viz; transmission in the IR region, high refractive index, low optical losses and low phonon energy make them promising material in optical switching devices, IR optical fibers and anti-reflection coatings [109-111]. Chalcogenide glasses have high refractive index (2-3) and optical band gap lying in sub-band gap region, accordingly they are used as a core material in optical fibers which is further used for transmission, particularly when short length and flexibility is needed [112-114]. Impurity effects in chalcogenide glasses play a vital role in the formation of glassy semiconductors. The influence of impurity atoms in chalcogenide glasses rely on the composition of the glasses, the chemical nature of impurity and the value of impurity concentration. This influence is different for different impurity atoms. Several authors [115-116] have narrated the effect of impurity atoms on the properties of different chalcogenide glasses. Due to their unique phase change properties, chalcogenide glasses are used as a phase change material in phase change optical devices. Phase change recording materials are designed to have at least two structural forms; amorphous and crystalline, which can coexist at room temperature. Difference in optical and electrical properties between amorphous and crystalline phases of the same material are used in phase change applications. In optical storage application small differences (approximately 20 %) in the reflectivity [117] between amorphous and crystalline are used while electronic applications utilize large difference (a factor approximately $10^3$) in electrical conductivity [118]. Most of the device applications utilize these materials in the form of thin films. The optical properties of thin films are responsive to many parameters and one of them is thickness. Also, in amorphous semiconducting thin films, the optical band gap and
refractive index are the essential parameters. These parameters are determined by the optical behavior of the material.

In this chapter for ternary $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ ($x = 0, 1, 2, 3, 4, 5$) chalcogenide thin films, both transmission and reflection spectra have been used for the calculation of optical parameters. In quaternary $\text{Se}_{84-x}\text{Te}_{15}\text{Bi}_{1.0}\text{Sn}_x$ ($x = 0, 2, 4, 6, 8$) chalcogenide thin films transmission spectra has been used for the determination of optical parameters. The linear refractive index and thickness of the film are evaluated using well-known Swanepoel method [119]. Tauc relation [120] has been used for the estimation of optical band gap. Wemple-DiDomenico single oscillator model (WDD) [121] narrates the dispersion behavior of refractive index. Dielectric constant and optical conductivity have also been calculated.

### 3.2 Experimental Details

Bulk samples of ternary $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ and quaternary $\text{Se}_{84-x}\text{Te}_{15}\text{Bi}_{1.0}\text{Sn}_x$ alloys were prepared by melt quenching technique as described in chapter 2. Thin films of the alloys have been deposited using thermal evaporation technique onto the cleaned glass substrate at room temperature and base pressure of $\sim 10^{-4}$ Pa using a molybdenum boat. The thickness of the deposited films is calculated by using digital thickness monitor (DTM-101). XRD technique has been used for the conformation of crystalline or amorphous nature of the thin films. No prominent peak was detected in the spectra which further confirm their amorphous nature. The normal transmission and reflection spectra in the transmission range of 400-2500 nm for $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ ($x = 0, 1, 2, 3, 4, 5$) and $\text{Se}_{84-x}\text{Te}_{15}\text{Bi}_{1.0}\text{Sn}_x$ ($x = 0, 2, 4, 6, 8$) thin films were obtained using a double beam UV-Vis-NIR spectrophotometer (Perkin Elmer Lambda-750). The spectrophotometer was fixed with slit width of 1 nm. All the optical measurements have been done at room temperature.

### 3.3 Methods to determine linear optical properties

When light beams interact with matter it experiences reflection, propagation and transmission. From the total light some of the light is reflected from the front and back surfaces, a part of the light is absorbed and a part is propagated through the matter. The techniques for the determination of optical parameters like refractive index ($n$), extinction
coefficient \((K)\), absorption coefficient \((\alpha)\), thickness of film \((L)\) and optical band gap \((E_g)\) are discussed below:

### 3.3.1 Refractive Index and Extinction Coefficient

In optics, phase of photon is modified by the interaction of photon with matter which leads to change in the direction of propagation of light. The phenomenon is known as refraction of light. The refractive index of material is described as the ratio of velocity of light in vacuum \((c)\) to the velocity of light in medium \((v)\).

\[
n = \frac{c}{v}
\]  

(3.1)

In materials the speed of light decreases as the photons are absorbed and re-emitted by molecules. This decrease is also expressed in Maxwell’s equations [122]. The refractive index is given by

\[
n = \frac{c}{v} = \frac{\sqrt{\mu_r\varepsilon_r}}{\sqrt{\mu_0\varepsilon_0}} = \sqrt{\varepsilon_r\mu_r}
\]

(3.2)

Where \(\mu_r\) and \(\varepsilon_r\) are the relative permeability and relative permittivity respectively.

For nonmagnetic substances \(\mu_r = 1\), therefore above equation becomes \(n = \sqrt{\varepsilon_r}\). It relates the optical properties of material with dielectric properties at any particular frequency of interest. The dependence of refractive index on the wavelength of light is called dispersion.

Also, when an electromagnetic wave propagates through a lossy medium, there is loss of energy in the form of generation of phonons (lattice waves), free carrier absorption, scattering etc. Consequently, refractive index becomes a complex function of the frequency of the light wave in such kind of material. From the Maxwell equations, the complex refractive index \((n^*)\), can be resolved into the real and imaginary part as \(n^* = n - iK\) (Figure 3.1), where \(n\) is the refractive index and \(K\) is the extinction coefficient or absorption index. From the application point of view, the knowledge of correct value of wavelength dependent refractive index is very essential. For the determination of optical parameters \(n\) and \(K\), there are different methods but here we are concerned only with those which are appropriate for thin films. An appropriate supporting substrate is utilized for deposition because films are not self-supporting. This results in a system consisting of three dielectrics namely air, film and substrate. The methods for the determination of optical constants of thin films are discussed below:
(i) Reflection and transmission Method

This method utilizes both reflection and transmission spectra taken at normal incidence. The absolute value of $R(\lambda)$ and extinction coefficient ($K$) have been used for the calculation of refractive index $n$ using the following relation [123].

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - K^2}$$  \hspace{1cm} (3.3)

Extinction coefficient ($K$) represents collective effect of absorption coefficient and scattering of incident light. Extinction coefficient ($K$) has been calculated using the relation [124].

$$K = \frac{\alpha \lambda}{4\pi}$$  \hspace{1cm} (3.4)

Where $\alpha$ is the absorption coefficient.

(ii) Transmission Method

J. C. Manificier [125] proposed transmission method for the analysis of linear optical properties of chalcogenide thin films. The model further modified by Swanepoel [119]. Swanepoel used only transmission spectra for the determination of refractive index and absorption coefficient. Swanepoel method has advantage due to its non-destructive nature and yields the dispersion relation over a large range of wavelength without any prior knowledge of film thickness and no parameters have to be introduced.

Suppose a thin film of thickness ($L$) deposited on transparent substrate. The complex refractive index from Maxwell’s Equation can be resolved into the real and imaginary part as $n^* = n - iK$ (Figure 3.1). The thickness of the glass substrate is several orders higher than the thickness of the film. The refractive index ($s$) of glass substrate is $= 1.51$ and absorption coefficient $\alpha_s = 0$. The refractive index of air is taken to be $n_0 \approx 1$. If the thickness of the film is constant, then full transmission spectrum is obtained in the form of interference fringes rather than smooth curve [119]. The optical constants can be evaluated using these interference fringes. The transmission spectrum for thin film is divided into four different regions according to their transmission intensities are shown in Figure 3.2.

The regions are (i) transparent region where $\alpha \approx 0$, transmission is explained on the basis of $n$ and $s$ through multiple reflections (ii) weak absorption region in which transmission starts to reduce (iii) medium absorption region in which $\alpha$ is large and transmission reduces
(iv) transmission reduces extremely in strong absorption region due to effect of $\alpha$.

\[ n^* = n - iK \]

Figure 3.1 System of an absorbing thin film on a thick finite transparent substrate.

In this method, continuous upper and lower envelopes through maximum transmittance ($T_M$) and minimum transmittance ($T_m$) data are generated. Calculation of refractive index using these envelopes is better than using only transmission spectrum because envelopes are gradually varying function with wavelength whereas spectrum is quickly varying with wavelength. Refractive index of the thick substrate is given by

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

Where $T_s$ denotes the transmission of substrate which is given as
Chapter 3

\[ T_s = \frac{2s}{s^2 + 1} \]  \hfill (3.6)

In the transparent region i.e. \( \alpha \approx 0 \), refractive index of the films is determined using minimum transmittance \( (T_m) \) only and is given by

\[ n = [M + (M^2 - s^2)^{1/2}]^{1/2} \]  \hfill (3.7)

Where

\[ M = \frac{2s}{T_m} - \frac{(s^2 + 1)}{2} \]  \hfill (3.8)

In the region of weak and medium absorption where transmission decreases due to the effect of \( \alpha \), refractive index is calculated using both the transmittance maxima \( (T_M) \) and transmittance minima \( (T_m) \). In this case \( M \) in the above equation is given by

Figure 3.2 Different absorption regions in the transmission spectrum.
\[ M = 2s \left( \frac{(T_M - T_m)}{T_M T_m} \right) + (s^2 + 1)/2 \]  

(3.9)

For finding values of refractive index in other parts of the spectrum, values of \( n \) can be tailored in Cauchy’s dispersion formula \([119]\).

\[ n = a + \frac{b}{\lambda^2} \]  

(3.10)

Where \( a \) and \( b \) are used for material dependent constant.

Using value of refractive index, absorbance \((\chi)\) is determined by the relation

\[ \chi = \frac{E_M - \left[ E_M^2 - (n^2 - 1)^3 (n^2 - s^4) \right]^{0.5}}{(n-1)^3 (n-s^2)} \]  

(3.11)

Where \( E_M \) is the maximum energy which is given via; the relation and is given by

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

(3.12)

### 3.3.2 Thickness of the film

Swanepoel \([119]\) recommended a formula for the calculation of thickness of film using envelope method. If \( n_1 \) ‘ and \( n_2 \) ‘ are the refractive indices at two consecutive maxima or minima at wavelengths \( \lambda_1 \) and \( \lambda_2 \), respectively then thickness \( L \) is given by

\[ L = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \]  

(3.13)

### 3.3.3 Absorption coefficient and optical band gap

Optical absorption is described in terms of absorption coefficient \((\alpha)\). Low absorption coefficient of a material means that light is imperfectly absorbed and if the material is thin enough it will appear transparent to that wavelength. Interaction of light with film deposited on substrate is shown in Figure 3.1. The nature of the material and wavelength of light that has to be absorbed, determine the value of absorption coefficient of the material. The absorption coefficient is related with the absorbance by the relation:

\[ \alpha = \frac{1}{L} log(1/\chi) \]  

(3.14)

Where \( L \) is the thickness of the film and \( \chi \) is the absorbance.
In semiconductors, the transition between valence band and conduction band starts at the absorption edge which corresponds to the minimum energy difference between the lowest minimum of the conduction band and highest maximum of the valence band. The energy difference between the valence band and conduction band is known as band gap. Therefore band gap is the energy that is mandatory for the movement of the valence electrons into the conduction band. Direct and indirect are the two types of transitions between valence band and conduction band. If the transition from the upper part of the valence band to the lower part of the conduction band take place without the phonon participation and without a change in the crystal momentum then it is called direct transition (Figure 3.3). But if it involves the phonon participation and a change in the crystal momentum, then it is called indirect transition (Figure 3.3) [126].

The separation of energy between bottom of the conduction band and top of the valence band is described using optical absorption edge. This absorption edge can be obtained by plotting graph between $\alpha$ and $hv$. In Figure 3.4, the three parts X, Y, Z of the absorption edge is clearly seen [120].

---

Figure 3.3 Schematic representation of direct and indirect band gap.
(i) **High absorption region**

Region X in Figure 3.4 represents the high absorption region with $\alpha \geq 10^4 \text{cm}^{-1}$. In this region, the optical band gap is evaluated using Tauc relation [120].

$$\alpha h\nu = B(h\nu - E_g)^p$$  \hspace{1cm} (3.15)

Where $E_g$ is the optical band gap and $B$ is the slope of Tauc’s edge called band tailing parameter. $B$ depends on the width of localized states in the energy gap which is of the order of $10^5$ to $10^6 \text{cm}^{-1}\text{eV}^{-1}$.

Absorption in this region is related with the transition from localized valence band states to delocalized conduction band states over mobility edge of conduction band or vice-versa. In the above stated equation, $p = 1/2$ for a direct allowed transition, $p = 3/2$ for a direct forbidden transition, $p = 2$ for an indirect allowed transition and $p = 3$ for an indirect forbidden transition.

(ii) **The exponential region**

In Figure 3.4, region Y represents the intermediate absorption region with absorption coefficients lying between $1 \text{ cm}^{-1} < \alpha < 10^4 \text{cm}^{-1}$. In this region, absorption coefficient with the presence of localized states follows the Urbach exponential relation [127].

$$\alpha = \alpha_0\exp(h\nu/E_e)$$  \hspace{1cm} (3.16)

Where $\alpha_0$ is the constant, $h$ is the plank’s constant, $\nu$ is the frequency of the radiation and $E_e$ is the temperature independent parameter known as Urbach energy. It determines the width of the tail of localized states in gap region and is determined from the slope. The slope drops at high temperature. In this region, absorption is associated through transition among extended states in one band and localized states in the exponential tail of the other band.

(iii) **Weak absorption region**

Part Z of the curve that lies below the exponential region in absorption edge, shows an absorption tail. Many factors viz: preparation technique, purity and nature of the material influence the absorption edge. The study of weak absorption tail in thin films is difficult due to the low absorption level.

3.3.4 **Dielectric constant**

Dielectric is also called an insulator. Dielectric upshots the path of light through the material. The real part of the dielectric constant represents the permittivity and measures
Chapter 3

the polarizability of a material. The imaginary part gives the information about the energy loss in aligning the dipoles. The complex dielectric constant is given as

$$\varepsilon = \varepsilon_r + i\varepsilon_i$$  \hspace{1cm} (3.17)

Here $\varepsilon_r$ is the real part of dielectric constant and $\varepsilon_i$ is the imaginary part of the dielectric constant. The value of $\varepsilon_r$ and $\varepsilon_i$ can be evaluated using the relation [128].

$$\varepsilon_r = n^2 - K^2$$  \hspace{1cm} (3.18)

$$\varepsilon_i = 2nK$$  \hspace{1cm} (3.19)

Figure 3.4 The illustration of absorption edge with its various parts
3.3.5 Optical Conductivity

The optical response of a material is explained in terms of optical conductivity. In Gaussian system of units the dimension of optical conductivity and frequency are same. Using absorption coefficient \( \alpha \) and linear refractive index \( n \), optical conductivity \( \sigma \) is calculated by using the relation [129].

\[
\sigma = \frac{\alpha n c}{4 \pi}
\]  
(3.20)

Here \( c \) is the velocity of light.

3.3.6 Wemple – DiDomenico Model

A model recommended by Wemple and Di-Domineco (WDD), using single-effective-oscillator approach [121] explains the nature of refractive index for various liquids and solids. The dispersion of refractive index of amorphous semiconductors is explained by this model using the relation [130].

\[
\frac{n^2 - 1}{1} = \frac{E_d E_0}{E_0^2 - (h \vartheta)^2}
\]  
(3.21)

Where \( E_o \) is single oscillator energy or average energy gap, \( E_d \) is the dispersion energy and \( h \nu \) is photon energy. Dispersion energy \( (E_d) \) is related with some physical parameters using the simple empirical relation.

\[
E_d = \beta N_c Z_a N_e
\]  
(3.22)

In this relation \( \beta \) is two valued function \( i.e. \) for ionic and covalent materials. Ionic value is taken as 0.26 \( \pm \) 0.03 eV and covalent value is 0.37 \( \pm \) 0.04 eV. \( N_c \) is the coordination number of the cation nearest neighbor to anion and \( N_e \) is effective number of valence electrons per anion. \( Z_a \) is formal chemical valency of anion. The parameter \( E_d \) and \( E_o \), both are independent to each other. The experimental confirmation of equation 3.21 can be done by plotting the graph between \( (n^2-1)^{\dagger} \) and \( (h \nu)^2 \) and obtained straight line gives the value of \( E_d \) and \( E_0 \).

3.4 Result and Discussion

3.4.1 Optical parameters of ternary Se-Te-Bi chalcogenide thin films

3.4.1.1 Refractive index: WDD model

The transmission and reflection spectra of investigated thin films are shown in Figure 3.5 and Figure 3.6 respectively. The fringes in the transparent region are due to interference at different wavelengths in the thin film. The smooth interference fringes in
the transmission and reflection spectra confirm the homogeneity and uniformity of the deposited thin films.

![Figure 3.5 Plot of transmission versus wavelength for ternary Se-Te-Bi thin films.](image)

Figure 3.5 Plot of transmission versus wavelength for ternary Se-Te-Bi thin films.

The optical transmission \( T \) and reflection \( R \) has a strong effect on optical absorption coefficient \( \alpha \) which is evaluated using the relation [131]:

\[
\alpha = \frac{2.303}{L} \log \left( \frac{1 - R}{T} \right)
\]  

(3.23)

Here \( L \approx 500 \) nm is the thickness of the film for all the samples. The obtained values of \( \alpha \) which is of the order of \( 10^4 \) cm\(^{-1} \) are incorporated in Table 3.1. The loss of light due to scattering and absorption per unit distance in the contributing medium is represented by extinction coefficient \( K \). \( K \) has been evaluated using \( \alpha \) via; the equation 3.4. The calculated values of \( K \) are tabulated in Table 3.1 and found to increase with increase of Bi content. The absolute value of reflectance \( R \) and extinction coefficient \( K \) have been used for the evaluation of refractive index of studied thin films using the equation 3.3. The behavior of \( n \) with wavelength \( \lambda \) is shown in Figure 3.7 and it has been observed that with the increase of \( \lambda \), \( n \) is found to decrease which shows the normal dispersion behavior of the system under investigation. Also, it has been observed from the Figure 3.7 that \( n \) increases
Figure 3.6 Plot of reflection versus wavelength for ternary Se-Te-Bi thin films.

Figure 3.7 Plot of refractive index versus wavelength for ternary Se-Te-Bi thin films.
with the increase of Bi content. The high value of \( n \) is advantageous for designing and modeling of interference filters. The increase of refractive index with Bi content may be described on the basis of polarizability. When Bi atom of atomic radius (1.46 Å) enters the host matrix Se-Te, it may replace the Se atom of atomic radius (1.17 Å). Accordingly, larger the atomic radius of the atom, larger will be the polarizability of the system and consequently, larger will be the refractive index [132].

The dispersion of \( n \) has been analyzed using single oscillator Wemple Di-Domenico (WDD) models. The graph between \((n^2-1)^{-1}\) and \((h\nu)^2\) is shown in Figure 3.8. Slope of the graph provides the value for \((E_0E_d)^{-1}\) and intercept on the vertical axis gives the value of \((E_d/E_d)\).

Figure 3.8  Plot of \((n^2-1)^{-1}\) versus \((h\nu)^2\) for ternary Se-Te-Bi thin films.

The static refractive index \((n_0)\) has been obtained by putting \(h\nu=0\) in the equation 3.21. The calculated value of \(E_0\), \(E_d\) and \(n_0\) are tabulated in Table 3.1. It is observed from the Table 3.1 that \(E_d\) and \(n_0\) follows the similar behavior like \(n\) while \(E_0\) is found to decrease with the increase of Bi content.

The real \((\varepsilon_r)\) and imaginary part \((\varepsilon_i)\) of dielectric constant has been determined using
the optical constants $n$ and $K$ using the equations 3.18 and 3.19, respectively. The optical conductivity ($\sigma$) has been determined using the following relation 3.20. The values of $\varepsilon_r$, $\varepsilon_i$ and $\sigma$ are tabulated in Table 3.1. As $\varepsilon_r$, $\varepsilon_i$ and $\sigma$ are directly related to $n$, $K$ and $\alpha$, so follows the similar trend as that of $n$, $K$ and $\alpha$, respectively.

Table 3.1 Values of refractive index ($n$), absorption coefficient ($\alpha$), extinction coefficient ($K$), dispersion energy ($E_d$), oscillator strength ($E_0$), static refractive index ($n_0$), optical band gap ($E_g$), dielectric constant ($\varepsilon_r$), dielectric loss ($\varepsilon_i$) and optical conductivity ($\sigma$) for ternary $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ ($x = 0, 1, 2, 3, 4, 5$) thin films at 1064 nm.

<table>
<thead>
<tr>
<th>X</th>
<th>$n$</th>
<th>$\alpha$ (cm$^{-1}$)</th>
<th>$K$</th>
<th>$E_d$ (eV)</th>
<th>$E_0$ (eV)</th>
<th>$n_0$</th>
<th>$E_g$ (eV)</th>
<th>$\varepsilon_r$</th>
<th>$\varepsilon_i$</th>
<th>$\sigma \times 10^{13}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.86</td>
<td>14473.1</td>
<td>0.0103</td>
<td>15.18</td>
<td>2.65</td>
<td>2.59</td>
<td>1.47</td>
<td>9.61</td>
<td>0.076</td>
<td>1.14</td>
</tr>
<tr>
<td>1</td>
<td>2.91</td>
<td>19684.9</td>
<td>0.0347</td>
<td>15.77</td>
<td>2.54</td>
<td>2.68</td>
<td>1.38</td>
<td>10.11</td>
<td>0.271</td>
<td>4.26</td>
</tr>
<tr>
<td>2</td>
<td>2.99</td>
<td>25418.2</td>
<td>0.0448</td>
<td>15.92</td>
<td>2.47</td>
<td>2.72</td>
<td>1.33</td>
<td>10.84</td>
<td>0.373</td>
<td>5.89</td>
</tr>
<tr>
<td>3</td>
<td>3.04</td>
<td>28024.1</td>
<td>0.045</td>
<td>16.05</td>
<td>2.43</td>
<td>2.75</td>
<td>1.31</td>
<td>11.43</td>
<td>0.382</td>
<td>5.92</td>
</tr>
<tr>
<td>4</td>
<td>3.24</td>
<td>35320.7</td>
<td>0.054</td>
<td>16.18</td>
<td>2.41</td>
<td>2.78</td>
<td>1.28</td>
<td>12.31</td>
<td>0.502</td>
<td>8.90</td>
</tr>
<tr>
<td>5</td>
<td>3.64</td>
<td>41053.8</td>
<td>0.0633</td>
<td>16.71</td>
<td>2.40</td>
<td>2.82</td>
<td>1.25</td>
<td>16.18</td>
<td>0.510</td>
<td>1.25</td>
</tr>
</tbody>
</table>

3.4.1.2 Optical band gap ($E_g$)

In the high absorption region ($\alpha \geq 10^4$ cm$^{-1}$), the optical band gap of amorphous semiconductors has been determined using “non-direct transition model” recommended by Tauc [120] (equation 3.15). Figure 3.9 shows the variation of $(\alpha h\nu)^{1/2}$ as a function of $h\nu$. The extrapolation of best fit line between $(\alpha h\nu)^{1/2}$ and $h\nu$ to intercept the $h\nu$ axis determines the value of $E_g$. The nonlinear nature of the graph indicates that the transition in the forbidden gap is of indirect type. From the graph it is clear that $E_g$ decreases from 1.47 eV to 1.25 eV with the increase of Bi content (Table 3.1). The drop in the $E_g$ with the incorporation of Bi content may be ascribed on the basis of electronegativity.

The valence band in chalcogenide glasses are formed by lone pair electrons, proposed by Kashner et al. [14]. The energy of the lone pair electrons is closer to the electropositive atoms as compared to electronegative atoms. Since the electronegativity of Bi (2.0) is less
than Se (2.4) and Te (2.1), therefore the incorporation of electropositive Bi atoms for Se may increase the energy of some lone pair states and hence expand the valence band inside the forbidden band gap. This indicates the tailing of valence & conduction band and consequently decreases the optical band gap. The decrease in optical band gap with the substitution of Bi may also be described on the basis of valence alteration pairs (D⁺, D⁻). The localized states in the gap are formed due to these strained and dangling bonds, which is further responsible for the drop of optical band gap of the thin films under study.

3.4.2 Optical properties of quaternary Se-Te-Bi-chalcogenide thin films

3.4.2.1 Refractive index: WDD model

The transmission spectra of quaternary Se₈₄ₓTe₁₅Bi₁₀.ₓSnₓ thin films are shown in Figure 3.10. Interference fringes, with alternate maxima and minima are observed at different wavelengths. A blue shift is observed at the short-wave cut-off boundary, while the concentration of Sn is increased in the host Se-Te-Bi ternary glass. This may be due to the weaker metallic character of bonds between the constituents.

The optical parameters like refractive index (n), thickness of the film (L) and extinction coefficient (K) are calculated using well known Swanepoel method [119]. In this method

Figure 3.9 Plot of \((ahv)^{1/2}\) versus \(hv\) (eV) for ternary Se-Te-Bi thin films.
Figure 3.10 Plot of optical transmission versus wavelength (nm) for quaternary Se-Te-Bi-Sn thin films.

The upper and lower envelopes are generated to the ellipsometric curves through the tangents of maximum and minimum of fringes.

Figure 3.11 depicts the behavior of $n$ as a function of wavelength ($\lambda$). It is observed that $n$ decreases with increase in $\lambda$, while in the transparent region it is found to be static. Also it is clearly seen that on Sn addition refractive index decreases first and with the further addition of Sn, $n$ increases. The decrease in the refractive index with Sn addition at 2 atomic percent of Sn may be due to change in the film density [133] and deviation from stoichiometry [134]. The calculated values of $n$ at 1064 nm are presented in Table 3.2.

The accuracy of $n$ determination of investigated films is $\pm 1\%$ over the whole transmission range. The value of $n$ is found to lie in the range of 2-3, which is quite advantageous for strong optical field confinement, leading to compact circuit design. According to Lorentz-Lorenz relationship [132] effective increase in $n$ may be attributed to the increased
polarizability of the system with the incorporation of highly polarized Sn, having larger atomic radius (1.41 Å) compared to Se (1.17 Å).

Figure 3.11 Plot of refractive index \((n)\) versus \(\lambda\) (nm) for quaternary Se-Te-Bi-Sn thin films.

Moreover according to Fajan’s rule [8] polarizing power of the cation increases with its decreasing size, number of filled orbital’s and with the increase in its positive charge. Polarizability of a cation must be higher in the columbic field of anion while the polarizability of anion should be lower in the field of a cation. The effective increase in \(n\) may also be attributed to the increase in the density of glassy system from 5.13 to 5.52 due the addition of denser Sn at the expense of Se. The observed values of \(n\) can be analyzed to obtain the high frequency lattice dielectric constant \(\varepsilon_L\). The method describes the contribution of free charge carrier and lattice vibrational modes of dispersion. In this method \(n, \varepsilon_L\) and \(\lambda^2\) are related to each other by the relation [135],

\[
n^2 = \varepsilon_L - B\lambda^2
\]  

(3.24)
Where \( B = \frac{e^2 N}{4\pi^2 c^2 \epsilon_0 m^*} \), \( N \) is the charge carrier concentration and \( m^* \) is the effective mass. The values of \( \epsilon_0 \) and \( N/m^* \) are deduced from the plots of \( n^2 \) versus \( \lambda^2 \) (Figure 3.12) and these values are reported in Table 3.2.

The spectral dependence of \( n \) in the visible to near infrared region is analyzed using WDD model based upon single oscillator approach [121] given by (equation 3.21).

![Figure 3.12 Plot of \( n^2 \) versus \( \lambda^2 \) for quaternary Se-Te-Bi-Sn thin films.](image)

The values of WDD parameters are evaluated from the linear fit of \((n^2-1)^{-1}\) against \((hv)^2\) (Figure 3.13) using intercept \( E_d/E_d \) and slope \((E_0/E_d)^{-1}\) respectively. The value of static refractive index \( n_0 \) is determined by substituting \( hv=0 \) in equation (3.21). The values of \( E_d, E_0 \) and \( n_0 \) are tabulated in Table 3.2. It is observed that \( E_d \) and \( n_0 \) follow the similar trend as that of \( n \), however \( E_0 \) is found to increase monotonically with increase in Sn concentration. Moreover \( E_0 \) is found to be in good approximation with Tauc gap [136] \((E_0=2E_g)\). The rise in \( E_d \) with increasing Sn content reveals that Sn is more coordinated in the matrix and confirms the average increase of cation coordination number with increasing Sn content.
### 3.4.2.2 Absorption coefficient and Optical band gap

The optical absorption spectra of Se-Te-Bi thin films with various content of Sn

![Graphs showing absorption coefficient](image)

Figure 3.13 Plot of \((n^2 - 1)^{-1}\) versus \((h\nu)^2\) for quaternary Se-Te-Bi-Sn thin films.

Impurity are shown in Figure 3.14. It is essential to study the optical absorption spectra of chalcogenide glasses since it gives the information about certain optical properties like the band structure and band gap of semiconducting materials. Optical absorption spectra in the lower wavelength region provides the knowledge of electronic states in the material while in the higher wavelength region of the spectrum corresponds to atomic vibrations. The absorption coefficient \(\alpha\) is measured in the high and intermediate absorption regions and not in the weak absorption region. Absorption coefficient \(\alpha\) of the studied thin film is determined by the relation \([140]\) \(\exp(-\alpha L) = T\), where \(L\) is the thickness of the film and \(T\) is transmittance. In photonic materials the extinction coefficient also known as absorption index represents the collective effect of absorption coefficient and scattering of light.

Average extinction coefficient of studied materials is obtained by using the equation 3.4. The calculated values of \(K\) for the films under investigation at 1064 nm wavelength are
Chapter 3

The behavior of $K$ as a function of wavelength is shown in Figure 3.15. Optical band gap ($E_g$) of amorphous semiconductor is described as the minimum energy required for optical excitations. For the investigated thin films of quaternary chalcogenides $E_g$ is determined in the strong absorption region ($\alpha \geq 10^4 \text{cm}^{-1}$).

Table 3.2 Values of refractive index ($n$), extinction coefficient ($K$), dispersion energy ($E_d$), static refractive index ($n_0$), oscillator strength ($E_0$), Urbach energy ($E_e$), lattice dielectric constant ($\epsilon_L$) and $\frac{N}{m^*}$ ratio for Se$_{84-x}$Te$_{15}$Bi$_{1.0}$Sn$_x$ ($x = 0, 2, 4, 6, 8$) thin films.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$n$</th>
<th>$K \times 10^4$</th>
<th>$E_d$ (eV)</th>
<th>$n_0$</th>
<th>$E_0$ (eV)</th>
<th>$E_e$ (eV)</th>
<th>$\epsilon_L$</th>
<th>$\frac{N}{m^*} \times 10^4$ ($m^3 \text{Kg}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.67</td>
<td>5.14</td>
<td>8.51</td>
<td>2.27</td>
<td>2.06</td>
<td>0.26</td>
<td>7.13</td>
<td>3.97</td>
</tr>
<tr>
<td>2</td>
<td>2.18</td>
<td>4.28</td>
<td>7.39</td>
<td>1.94</td>
<td>2.67</td>
<td>0.247</td>
<td>4.78</td>
<td>1.48</td>
</tr>
<tr>
<td>4</td>
<td>2.30</td>
<td>3.71</td>
<td>9.52</td>
<td>2.12</td>
<td>2.71</td>
<td>0.282</td>
<td>5.34</td>
<td>1.63</td>
</tr>
<tr>
<td>6</td>
<td>2.69</td>
<td>2.56</td>
<td>13.83</td>
<td>2.26</td>
<td>3.35</td>
<td>0.286</td>
<td>7.14</td>
<td>4.44</td>
</tr>
<tr>
<td>8</td>
<td>2.99</td>
<td>1.99</td>
<td>16.72</td>
<td>2.35</td>
<td>3.70</td>
<td>0.295</td>
<td>8.86</td>
<td>7.69</td>
</tr>
</tbody>
</table>

Figure 3.14 Plot of $\alpha$ versus $(hv)$ for quaternary Se-Te-Bi-Sn thin films.
using Tauc Power Law (equation 3.15). Optical band gap has been determined by plotting \((ah\nu)^{1/2}\) versus \(h\nu\) (Figure 3.16) assuming that the transition is of indirect type as is the case of chalcogenide glasses. Obtained values of \(E_g\) with an accuracy of \(\pm 0.03\) eV for different compositions are in Table 3.3.

Figure 3.15 Plot of extinction coefficient \((K)\) versus \(\lambda\) (nm) for quaternary Se-Te-Bi-Sn thin films.

In the low absorption region \((\alpha \leq 10^4 \text{ cm}^{-1})\) the absorption coefficient \(\alpha\) shows an exponential dependence on \(h\nu\) and obeys the Urbach relation (equation 3.16). Calculated values of \(E_e\) are listed in Table 3.2. It can be observed from the Table 3.2 that optical band gap increases from 1.27 eV to 1.64 eV, when Sn content is increased from 0 to 8 atomic %.

This increase in \(E_g\) is attributed to increase in the cohesive energy \((CE)\) of the composite chalcogenide material. Cohesive energy defined as stabilization energy of an infinitely large cluster of the material per atom is a measure of average bond energy of the system and is determined by using the formula [137].

\[
CE = \sum C_iD_i/100
\]  
(3.25)

Bond energies of the heteropolar bonds are calculated by the approach suggested by Pauling [138].
\[ D(A - B) = [D(A - A) \times D(B - B)]^{0.5} + 30(\chi_A - \chi_B)^2 \] (3.26)

Where \( \chi_A \) and \( \chi_B \) are the electronegativities of the atoms A and B and D (A-A) and D(B-B) are the bond energies of A-A and B-B bonds, respectively. Considering the bond energies of homopolar bonds as 44 Kcal/mol, 33 Kcal/mol, 25 Kcal/mol and 34.76 Kcal/mol for Se-Se, Te-Te, Bi-Bi and Sn-Sn homopolar bonds respectively, the calculated values of bond energy for heteropolar bonds is found to be 44.18 Kcal/mol, 41.6 Kcal/mol and 49.55 Kcal/mol for Se-Te, Se-Bi and Se-Sn bond, respectively.

Figure 3.16 Plot of \((\alpha h \nu)^{0.5}\) versus \(h \nu\) for quaternary Se-Te-Bi-Sn thin films.

Applying the chemical bond approach [139] to the present system, since the bonds are formed in the sequence of decreasing bond energy and heteropolar bonds are preferred over homopolar bonds, the bond formation probability in absence of Sn is highest for Se-Te bond. However when Sn is added to the network the formation of Sn-Se bond is preferred over Se-Te bond. Since the bond energy of Se-Sn bond is higher compared to Se-Te bond, the average bond energy and hence the CE of the system as a whole increases. Since \( E_g \) is a direct consequence of CE, it is also found to follow the similar trend. The distribution of bonds and CE of the quaternary chalcogenide glassy system are listed in
Table 3.3. In chalcogenide glasses containing high concentration of chalcogen the valence band is constituted by lone pair electrons and antibonding band forms the conduction band. In any composition number of different bonds determines the number of states in the conduction band whereas lone pair electrons of chalcogenide determine the number of states in the valence band. The number of lone pair electrons are calculated by using the relation \[ LPE = V - \langle r \rangle \], where \( LPE \) is the number of lone pair electrons, \( V \) is the number of valence electrons and \( \langle r \rangle \) is the coordination number of the system. The number of lone pair electrons formed in the system is listed in Table 3.3. It is clear from Table 3.3 that \( LPE \) decreases with the increasing Sn content indicating the lowering of number of states in the valence band. Therefore the increase in \( E_g \) with Sn content is attributed to the narrowing of valence band caused by decrease in lone pair electrons.

Table 3.3 Values of lone pair electron (\( LPE \)), distribution of chemical bonds, band gap \( E_g \), and cohesive Energy (\( CE \)), dielectric constant \( \varepsilon_r \), dielectric loss \( \varepsilon_i \) and optical conductivity \( \sigma \) for quaternary Se\(_{84-x}\)Te\(_{15}\)Bi\(_{1.0}\)Sn\(_{x}\) (\( x = 0, 2, 4, 6, 8 \)) thin films.

<table>
<thead>
<tr>
<th>X</th>
<th>LPE</th>
<th>Distribution of chemical bonds</th>
<th>( E_g ) (eV)</th>
<th>( CE ) (Kcal/mol)</th>
<th>( \varepsilon_r )</th>
<th>( \varepsilon_i )</th>
<th>( \sigma \times 10^{13} ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.98</td>
<td>0.81 0.177 0.018 - -</td>
<td>1.27</td>
<td>43.34</td>
<td>5.8</td>
<td>0.0026</td>
<td>2.6</td>
</tr>
<tr>
<td>2</td>
<td>3.9</td>
<td>0.75 0.183 0.018 0.0488 -</td>
<td>1.36</td>
<td>43.57</td>
<td>4.2</td>
<td>0.0017</td>
<td>1.9</td>
</tr>
<tr>
<td>4</td>
<td>3.82</td>
<td>0.69 0.188 0.019 0.1 -</td>
<td>1.47</td>
<td>43.82</td>
<td>4.8</td>
<td>0.0015</td>
<td>1.2</td>
</tr>
<tr>
<td>6</td>
<td>3.74</td>
<td>0.63 0.192 0.019 0.1539 0.0006</td>
<td>1.54</td>
<td>44.09</td>
<td>5.5</td>
<td>0.0011</td>
<td>1.20</td>
</tr>
<tr>
<td>8</td>
<td>3.66</td>
<td>0.57 0.197 0.019 0.2105 0.002</td>
<td>1.64</td>
<td>44.36</td>
<td>6.1</td>
<td>0.0008</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Moreover it is noticed from the observed values of Urbach energy \( E_u \), that band width of localized states decreases as the concentration of Sn content is increased, which probably may be attributed to the decrease in the degree of disorder and hence leads to broadening of forbidden energy gap.
Chapter 3

The real \((\varepsilon_r)\) and imaginary \((\varepsilon_i)\) parts of dielectric constant of \(\alpha\)-Se\(_{84-x}\)Te\(_{15}\)Bi\(_{1.0}\)Sn\(_x\) thin films are evaluated using refractive index and extinction coefficient. The values of \(\varepsilon_r\) and \(\varepsilon_i\) are calculated using equation 3.18 and equation 3.19, respectively and are incorporated in Table 3.3. It has been observed that trend of \(\varepsilon_r\) with Sn concentration is same as that of refractive index i.e increases while the values of \(\varepsilon_i\) decreases with Sn content. Using the values of absorption coefficient \((\alpha)\) and refractive index \((n)\), the optical conductivity \((\sigma)\) has been evaluated using the relation [129] (equation 3.20). The behavior of optical conductivity \((\sigma)\) with photon energy is shown in Figure 3.17.

Values of \(\sigma\) are tabulated in Table 3.3. The behavior of optical conductivity is same as that of absorption coefficient i.e it increases with photon energy for all the composition while optical conductivity decreases when Sn is added with the base composition Se-Te-Bi thin films.

![Figure 3.17 Plot of \(\sigma\) versus \(h\nu\) for quaternary Se-Te-Bi-Sn thin films.](image)

3.5 Conclusion

The optical parameters of ternary Se\(_{85-x}\)Te\(_{15}\)Bi\(_x\) have been determined in the spectral range 400-1500 nm by using transmission and reflection spectra. The refractive index is found to increase with the addition of Bi content. The increase in refractive index is related
with the increased polarizability of larger atomic radii of Bi atoms (1.46 Å) as compared to smaller atomic radii of Se atoms (1.17 Å). The dispersion parameters $E_d$, $E_0$, and $n_0$ are discussed in terms of WDD model. The result indicates that $E_d$ & $n_0$ increases, while $E_0$ decreases with the increase of Bi content. The optical band gap has been determined in high absorption region using Tauc relation and found to decreases from 1.47 eV to 1.25 eV with the increase of Bi content. The dielectric constant and optical conductivity have been determined for the studied thin film and found to follow the same behavior like refractive index.

The vacuum evaporated quaternary $\text{Se}_{84-x}\text{Te}_{15}\text{Bi}_{1.0}\text{Sn}_x$ thin films utilized transmission spectra in the spectral range of 400-2500 nm for the calculation of various optical parameters. Addition of Sn content in the base composition shows that there is a blue shift in the transmission spectra. Envelope method recommended by Swanepoel has been used for the estimation of refractive index and thickness of the film. It is found from the results that on Sn addition refractive index decreases first and with the further addition of Sn, $n$ increases. The decrease in refractive index on 2 atomic percent of Sn may be due to change in the film density and deviation from stoichiometry. The increase in refractive index is associated with the increased polarizability of larger atomic radii (1.41 Å) Sn atoms as compared to smaller atomic radii (1.17 Å) Se atoms. Increase in refractive index may also be explained on the basis of increase of density of the system on addition denser Sn atoms. High frequency dielectric constant ($\varepsilon_L$) also is analyzed using refractive index values. Dispersion energy ($E_d$), oscillator energy ($E_0$) and static refractive index ($n_0$) are all calculated using WDD model. It is found that $E_d$ and $n_0$ follows the same behavior as that of $n$, however $E_0$ is found to increase monotonically with increase in Sn concentration. It is found that values of absorption coefficient and extinction coefficient decreases on addition of Sn concentration. In high absorption region, the optical band gap has been calculated by Tauc extrapolation method and found that the value of band gap increases from 1.27 eV to 1.64 eV with the addition of Sn content. The observed behavior of $E_g$ is explained on the basis of CE, Lone pair electrons and Urbach energy $E_e$ of the chalcogenide glass system. The optical conductivity is found to be increased with photon energy for all the compositions, however optical conductivity decreases when Sn added to the base composition of Se-Te-Bi chalcogenide thin films.