Chapter 5

Optical Properties of $\text{GeS}_x\text{Se}_{1-x}$
($x = 0, 0.25, 0.5, 0.75, 1$) Single Crystals
5.1 INTRODUCTION

Photonic materials are gaining more and more attention of researchers in last few decades. These materials are in various forms e.g. bulk crystalline solids, nano crystals, multilayers, quantum dots etc. are increasingly impacting next generation electronics industry in field like communication, data manipulation and storage, aviation, defence, food processing and packaging, entertainment etc. The optical band gap of a semiconducting material plays a vital role in describing its effectiveness in electronic devices; a detailed study of this parameter is therefore extremely important.

To understand the nature of semiconductors one must consider what happens when similar atoms are brought together to form a solid such as a crystal. As two similar atoms approach each other the wave functions of their electrons begin to overlap. The energy distribution of the states depends strongly on the interatomic distance. It is the extent of the energy gap and the relative availability of electrons that determine whether a solid is a metal, a semiconductor, or an insulator. In a semiconductor the energy gap usually extends over less than about 3 eV and the density of electrons in the upper band is usually less than $10^{20}$ cm$^{-3}$.

Germanium monoselenide and Germanium monosulphide possess interesting optical and photo-absorption properties [1-3]. These semiconducting materials having layered structure. Several studies, mainly on the optical properties have been carried out in the past few years [4-10]. Bassani and Parravicini [11] treated some of the layered material as a two dimensional lattice. Fivaz and Mosser [12-14] discussed anisotropic properties might affect the motion of free carries in layered semiconductors. It was shown that in this structure the free carriers might be localized within individual layers, behaving as if moving a stack of individual layers called as Independent layer approximations.

The optical band gap ‘$E_g$’ of materials is one of the crucial optical parameters for this purpose. It has been found that for maximum solar energy conversion, $E_g$ of any single crystal solar cells should be around 1.4 eV. The semiconducting materials with the band gap value near to this optimum value are therefore considered to be a most suitable for photovoltaic applications. So, the study of optical band gap determination is desirable for all the semiconducting materials.
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The Energy band gap is usually classified in direct allowed and forbidden transition. Direct as well as indirect optical band gap of semiconductor can be determined using the following methods:

1. Optical analysis of absorption Spectra
   (a) Absorption spectra
   (b) Reflectance spectra
   (c) Electroreflectance spectra
   (d) Thermoreflectance spectra
2. Photoelectrochemical Methods
   (a) Quantum yield $\eta$ vs. $h\nu$ plot.
   (b) Action spectrum
   (c) Capacitance measurements
3. Intrinsic conduction measurements at high temperature.
4. Photoemission studies
5. Band structure calculations.

Out of different methods listed above for determining band gap we adopted optical absorption technique. The optical absorption technique is an important technique for finding out the nature of transition of carriers and band gap of a material by investigating measurement of the absorption edge of the material. In this technique, photons of selected wavelength are directed at normal incidence on the sample and their relative transmission is observed. Since the photons with energies greater than the band gap energy are absorbed while photons with energies less than band gap are transmitted. This technique provides an accurate measurement of the energy band gap. The absorption of light from ultraviolet visible region of the spectrum sets valence electrons into oscillation and produces an excitation of the molecule from the ground electronic state to the excited electronic state. On the other hand, the absorption of energy from the far infrared region of the spectrum produces molecular rotation and absorption of near infrared radiation produces the rotation plus atomic vibrations. Thus, the light absorption produces changes in the internal energy of molecules from which much can be learnt about molecular structure and intermolecular forces.
Many investigations have been reported on optically induced transitions on materials including semiconductors [15-23]. Ionic crystals like alkali-halides [15-19] and silica-halides [20-21] absorb strongly in the ultraviolet and reveal interesting features regarding indirect band to band transitions. Spectra of LaMgAl$_{11-x}$O$_{19}$:Ti$_x$ crystals in the range of 606-930 nm showed promising features [24] for tuneable solid state laser systems. The UV-VIS induced absorption bands under the influences of annealing temperature have been used to study radiation hardness of PbWO$_4$ [25-26] and diamond films [27]. The UV-IR measurements made on natural and synthesis diamonds [28, 29] evinced spectrally–broad cathodoluminescence.

The basic theory of the direct and indirect transition has formulated by Moss [30], Pankov [31] and Bardeen et al [32]. The silver halides were also treated in this band model [20-21]. The interaction of the excited electrons with the lattice perturbed by the vibrations or imperfections is in fact responsible for optical absorption in materials and this has been explained quantum mechanically [33]. An electron under impact by incident photons is excited to an intermediate state where it interacts with lattice vibrations or impurities before it reaches a final state and the result is absorption of photon [34]. Dichalcogenides find their important applications in many fields e.g. in the field of Photoelectrochemical solar cell [35].

An important conclusion has been drawn by Lukes and Dub [36] is that the band structure of GeS, GeSe and SnSe are qualitatively similar to each other. It has been observed that GeS is direct gap semiconductor and the absorption near the absorption edge of GeS has been studied by Wiley and his group Wiley et al. [37-39]. However found no evidence of indirect transition whether a three dimensional [40] or a two dimensional [41-42] analysis was used for the absorption spectra. The evidence of indirect transition is GeS and GeSe has been conclusively provided by Elkarashy [43-44] but he also excluded the possibility of direct transition.

However, looking at the importance of optical band gap in GeS$_x$Se$_{1-x}$ (I$_2$) (x=0, 0.25, 0.5, 0.75, 1), the author has carried out a detailed study on the determination of optical band gap in these materials using optical absorption technique. We report here our investigation of optical properties of these crystals by UV-VIS-NIR spectroscopy technique. The results thus obtained have been described and discussed in this chapter.
5.2 UV-VIS-NIR SPECTROPHOTOMETER

Beckman Model DK-A spectrophotometer (UV-VIS-NIR spectrophotometer) (Make: Perkin Elmer, Model: Lambda -19) as shown in Figure 5.1 was used for the analysis of various compounds through the use of radiant energy in the ultraviolet to near infrared regions of the electromagnetic spectrum. Analytical information can be revealed in terms of transmittance, absorbance or reflectance of energy in the wavelength range between 200nm to 3000nm. It utilizes a single beam of energy which is chopped into alternative reference and sample beams to provide a double beam system with the sample compartment. Both sample and reference beam have common detection and amplification components.

![Figure 5.1: UV-VIS-NIR Spectrophotometer](image)

Qualitative and quantitative data are obtained with the spectrophotometer by directing radiation into the sample and determining what portion of energy absorbed. Radiation is provided in the wavelength range below 375 nm using hydrogen lamp whereas the tungsten lamp is used in the 320-3500 nm wavelength.

From the source, the radiation enters the optical system. Figure 5.2 shows the path followed by a single ray within the radiation beam. The beam is reflected from the condensing mirror (A) to the slit entrance mirror (B), which directs the beam to the chopper (C).
Figure 5.2: The schematic diagram of UV-VIS spectrometer

The chopped beam passes through the adjustable entrance slit (D) and goes into the monochromator. The beam is reflected from the collimating mirror (E) converted into parallel rays through a reflecting quartz prism (F), which disperses the beam into its spectrum of successive wavelengths. The back surface of prism is aluminized so that the beam is reflected back through the prism and further dispersed as it emerges. Rotation of the prism relative to the collimation mirror changes the angle of incidence and enables the selection of a particular group of wavelengths that comprise a spectral band. This band of rotation is directed back to the collimating mirror, which focuses the entrance slit image on the exit slit (G). Upon passing through the monochromator, the radiation energy is directed by lens (H) into the double beam optical system in the sample compartment. This instrument is a double beam ratio-recording spectrometer, wherein the radiant energies transmitted by the reference and the sample beam (J and M) are compared and the ratio of the sample energy to the references energy is recorded as percentage transmission. The double beam optical system consists of two synchronized semicircular rotating mirrors (I and N) and two stationary mirrors (L and K) in the sample compartment. The rotating mirrors consequently deflect and pass the radiation energy so that it is directed alternatively into sample and reference cells fifteen (or 12.5) times per second. The detector focuses energy transmitted by the sample and reference cells.
Detection of transmitted radiant energy requires two detectors to cover the entire wavelength range of the instrument. One - the lead sulphide cell (P) - responds in the region between 400 - 3500 millimicron. For measurements in the wavelength range extending below 700 nm, a photomultiplier tube (Q) is used. Radiant energy that strikes the detector is converted to a proportional alternating current signal.

5.3 OPTICAL ANALYSIS

The most direct and the simplest method for probing the band structure of semiconductors are to measure the absorption spectrum. The optical absorption is known to arise through the interaction of the excited electrons within the lattice perturbed by vibrations or imperfections. In fact the absorption phenomenon can be considered quantum mechanically [8] as a two-step process in which the electron absorbs a photon and to an intermediate state, where it interacts with the lattice vibrations or impurities and reaches a final state, the net result being the absorption of a photon. Absorption is expressed in terms of coefficient $a(h\nu)$ which is defined as the relative rate of decrease in light intensity $L(h\nu)$ along its propagation path:

$$\alpha = \frac{1}{L(h\nu)} \frac{d[L(h\nu)]}{dx} \quad (5.1)$$

5.3.1 Fundamental absorption

The fundamental absorption refers to band-to-band or to excitons transition, i.e., to the excitation of an electron from the valence band to the conduction band. The fundamental absorption, which manifests itself by a rapid rise in absorption, can be used to determine the energy gap of the semiconductor. However, because the transition are subject to certain selection rules, the estimation of the energy gap from the “absorption edge” is not a straightforward process-even if competing absorption process can be accounted for. Because of the momentum of a photon, $h/\lambda$, ($\lambda$ is the wavelength of light), is very small compared to the crystal momentum $h/a$ (‘a’ is the lattice constant), the photon – absorption process should conserve the momentum of electron. The absorption coefficient $a(h\nu)$ for a given $h\nu$ is proportional to the probability $P_{if}$ for the transition from initial state, $n_i$, and also to the density of available (empty) final state, $n_f$, and this process must be assumed for all possible transition between states separated by an energy difference equal to $h\nu$. 
\[ \alpha(h\nu) = A \sum P_{ij} n_i n_j \quad (5.2) \]

Here, for simplicity we shall assume that all the lower states are filled and that all the upper states are empty, a condition which is true for undoped semiconductor at 0 K.

### 5.3.2 Direct allowed transitions

Let us consider absorption transition between two direct valleys where all the momentum-conserving transition are allowed as shown in Figure 5.3. Every initial state at \( E_i \) is associated with a final state at \( E_f \) such that

\[ E_f = h\nu - |E_i| \quad (5.3) \]

But in parabolic bands,

\[ E_f - E_g = \frac{\hbar^2 k^2}{2m_e} \quad (5.4) \]

and

\[ E_i = \frac{\hbar^2 k^2}{2m_e} \quad (5.5) \]

![Figure 5.3: Allowed transition in bands](image)
Therefore,
\[ h\nu - E_g = \frac{\hbar^2 k^2}{2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) \]  
(5.6)

The density of directly associated states is
\[ N(h\nu)d(h\nu) = \frac{8\pi k^2 dk}{(2\pi)^3} \]  
(5.7)

\[ N(h\nu)d(h\nu) = \frac{(2m_e)^{3/2}}{2\pi^2 \hbar^3} (h\nu - E_g)^{1/2} d(h\nu) \]  
(5.8)

where \( m_r \) is the reduced mass given by \( \frac{1}{m_r} = \frac{1}{m_e} + \frac{1}{m_h} \). Hence the absorption coefficient is [31]:
\[ \alpha(h\nu) = A^*(h\nu - E_g)^{1/2} \]  
(5.9)

where \( A^* \) is given by Bardeen et al. (1956) [32]
\[ A^* \approx \frac{q^2 \left( 2 \frac{m^*_h m^*_e}{m_h + m_e} \right)^{3/2}}{nch^2 m^*_e} \]  
(5.10)

For an index of refraction \( n=4 \) and assuming the hole and electron effective mass equal to free electron mass, one gets:
\[ \alpha(h\nu) \approx 2 \times 10^4 (h\nu - E_g)^{1/2} \text{cm}^{-1} \]  
(5.11)

### 5.3.3 Direct forbidden transition

In some materials quantum rules forbid direct transition at \( k = 0 \) but allow them at \( k \neq 0 \), with the transition probability increasing with \( k^2 \). In the model Figure 5.3 the transition probability increases proportional to \( (h\nu - E_g) \). Since the density of states linked in transition is proportional to \( (h\nu - E_g)^{1/2} \), the absorption coefficient has the following spectral dependence [31]:
\[ \alpha(h\nu) = A^*(h\nu - E_g)^{3/2} \]  \hspace{1cm} (5.12)

where \( A^* \) given [32]

\[ A^* \approx \frac{4}{3} \frac{q^2 \left( \frac{m^*_e m^*_h}{m_e + m_h} \right)^{5/2}}{n e h \nu} \]  \hspace{1cm} (5.13)

again for \( n=4 \) and \( m^*_e = m^*_h = m \)

\[ \alpha(h\nu) \approx 1.3 \times 10^4 \frac{(h\nu - E_g)^{3/2}}{h\nu} \text{ cm}^{-1} \]  \hspace{1cm} (5.14)

### 5.3.4 Indirect Transition:

When a transition requires a change in both energy and momentum, a double or two-step process is required because the photon cannot provide a change in momentum. Momentum is conserved via a phonon interaction, which is illustrated in Figure 5.4. A quantum of lattice vibration. Although a broad spectrum of phonon is available, only those with the required momentum changes are usable. These are usually the longitudinal and the transverse-acoustic phonon which can participate in the transition process but in different probabilities [45]. Each of this phonon has a characteristic energy \( E_p \). Hence to complete the transition \( E_i \) to \( E_f \) a phonon is either emitted or absorbed. These two processes are given respectively by:

\[
\begin{align*}
  h\nu_e &= E_f - E_i + E_p \\
  h\nu_a &= E_f - E_i - E_p
\end{align*}
\]  \hspace{1cm} (5.15)

In general, however, at high temperature phonons are present and can participate in the absorption process. The optical transition is accordingly said to be non-vertical or indirect. Such indirect transitions are is great importance in semiconductors and provide a means of determining the energy band gap separating the top of the valence band and the bottom of the conduction band when these band extreme occur at different values of the \( k \) vector.
5.4 EXPERIMENTAL TECHNIQUE

The main aim of work presented in this chapter is to make analysis of the absorption spectra obtained from the crystals of GeS$_x$Se$_{1-x}$ (I$_2$) ($x= 0, 0.25, 0.5, 0.75, 1$) and mixture of these compounds. The optical spectra of these crystals were taken with the help of UV-VIS-NIR spectrophotometer in the wavelength range from 200nm – 2000nm at room temperature. For obtaining the absorption spectra spectrophotometer from single crystal specimens, thin flakes of as grown crystals are used. These flakes are pasted on a thick black paper with a cut exposing the crystal flake to the incident light. The reference used is a replica of the black paper, having the cut at exactly the same position as the crystal flake. This arrangement is necessary because the crystal size is smaller than that of the sample compartment. Blank glass slides can also use as replica. For reflectance measurement standard aluminum coated mirror can be used as reference.

For determination of band gap for semiconducting materials, absorption of incident photon by semiconducting material is an important technique. In this technique, photons of selected wavelengths are bombarded on the sample and their relative transmission is observed. Since the photons with energies greater than the band gap are absorbed while photons with energies less than band gap are transmitted, the technique provides an accurate measurement of the energy band gap. The ratio of transmitted to incident radiation intensities is expected to depend on photon wavelength and the thickness of the sample.
When a photon beam of intensity $I_o$ (photon/cm$^2$sec) transmits through a slab of a medium of thickness $x$, the beam of photons attenuates in accordance with the exponential law:

$$I = I_o e^{-\alpha x}$$ \hspace{1cm} (5.16)

where ‘$\alpha$’ is called absorption coefficient and its unit is cm$^{-1}$. This coefficient ‘$\alpha$’ can be obtained simply by measuring $I_o/I$ of the intensities impinging and emerging from the samples respectively.

The relationship that exists for possible transitions across the energy gap of semiconductor, the absorption coefficient ‘$\alpha$’ is proportional as follow [46]:

$$\alpha h\nu = A(h\nu - E_g)'$$ \hspace{1cm} (5.17)

for direct transitions and

$$\alpha h\nu = \sum_j B_j(h\nu - E_g' \pm E_{pj})'$$ \hspace{1cm} (5.18)

for indirect transitions.

Here ‘$\alpha$’ is the absorption coefficient, ‘$h\nu$’ the energy of the incident photon, ‘$E_g$’ the energy for the direct transition ‘$E_g'$’ the energy for indirect transition and ‘$E_{pj}$’ the energies of absorbed or emitted the phonons assisting at indirect transition. $A$ and $B$ are parameters depending in a more complicated way on temperature, photon energy and phonon energies $E_p$.

However, for the analysis of the experimental results obtained at constant temperature, Equations 5.17 and 5.18 are sufficient and they are most often used while interpreting results on absorption spectra obtained from semiconducting materials. The exponent ‘$r$’ in the above equations depends upon whether the transition is symmetry allowed or not and the constants $A$ and $B$ will assume different values for the allowed and forbidden transitions.

For indirect transitions the detailed form of equation 5.18 [47- 49] is given as:
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\[
\alpha_i = \sum_{i=1}^{2} \left\{ \frac{B_{ai}}{E} \left( \frac{1}{e^{\theta_i/i} - 1} \right) (E - E_g + k\theta_i)^\gamma + \frac{B_{ei}}{E} \left( \frac{1}{1 - e^{\theta_i/i}} \right) (E - E_g - k\theta_i)^\gamma \right\} 
\]

(5.19)

Here, \( B_{ai} \) and \( B_{ei} \) are coefficients associated with absorption and emission of \( i^{th} \) phonon. \( E \) the photon energy, \( E_g \) the indirect energy gap and \( \theta_i \) is a phonon equivalent temperature defined by equation:

\[
\theta_i = \frac{E_{pi}}{k}
\]

(5.20)

where \( E_{pi} \) being the \( i^{th} \) phonon energy.

In these cases the density of states is a constant independent of the energy and the expressions showing the dependence of \( \alpha \) in terms of direct and indirect transitions get modified [48] as

\[
\alpha = A (h\nu - E_g)^\gamma
\]

(5.21)

for direct transition and

\[
\alpha_i = \sum_{i=1}^{2} \left\{ \frac{B_{ai}}{E} \left( \frac{1}{e^{\theta_i/i} - 1} \right) (E - E_g + k\theta_i)^\gamma + \frac{B_{ei}}{E} \left( \frac{1}{1 - e^{\theta_i/i}} \right) (E - E_g - k\theta_i)^\gamma \right\}
\]

(5.22)

for indirect transition [ (50)],

5.4.1 Band tailing

While impurity-band formation is an obvious consequence of increased impurity concentration, another important effect occurs is a perturbation of the bands by the formation of tails of states extending the bands into the energy gap. The problem of band tailing has received much theoretical attention [51-55]. An ionized donor exerts an attractive force on the conduction electrons and a repulsive force on the valance holes. Since impurities are distributed randomly in the host crystal, the local interaction will be more or less strong depending on the local crowding of impurities.

Dislocations are also usually present in crystals. They occur at the edge of an extra plane of atoms. The misfit of such an extra plane results in compressional and
dilatational strains, with the consequent onset of both lowering and raising of the potentials in the neighborhood of the dislocation. Hence, one can say that impurities will induce tails in the density states by perturbing the band edge via deformation potential, via coulomb interaction, and by forming a band of impurity states.

**Figure 5.5:** Energy diagram illustrating how absorption probes the conduction band tail of states in a p-type semiconductor. The tail of the valence band has been omitted since, being empty, it does not participate in the absorption process.

The momentum conserving transition between parabolic bands should result in absorption edge which obeys Equation 5.17 ($r = \frac{1}{2}$) i.e. where the absorption constant increases with the square root of the photon energy in excess of the gap energy. For direct transition one expects no absorption below the energy gap and, therefore, a steeply rising absorption edge. But in practice one usually finds an exponentially increasing absorption edge [56-58]. In a number of materials, it is found that $\delta \ln \alpha / \delta (h\nu) = kT$ this is known as Urbach's rule [59].

In the case of degenerate p-type material, the Fermi level is taken to be in the parabolic portion of the valence band, so that the perturbed part of the valence band lies above the Fermi level. Then the density of initial states, $N_i$ is proportional to $(|E_i|)^{1/2}$, where $E_i$ is the energy of the state with respect to what would be the edge of the parabolic valence band as shown in Figure 5.5.
5.5 RESULT AND DISCUSSION

The absorption spectra of GeS$_x$Se$_{1-x}$ (I$_2$) ($x = 0, 0.25, 0.5, 0.75, 1$) single crystal are shown in Figure 5.6 (a) – Figure 5.6 (e). A careful study of these spectra reveals the presence of absorption edge in the spectral range 700nm to 900nm.

In order to analyse the results from these spectra in the vicinity of the absorption edge on the basis of two as well as three – dimensional model, values of absorption coefficients ‘$\alpha$’ were determined at every interval of 1 nm. In absorption curves several peaks observed but the sharp peak is near 700 nm to 800 nm due to absorption in the sample, but respectively weaker peaks may be attribute to excitons formation or interference effects. The interpretation of the experimental results viz. independence of absorption coefficient ‘$\alpha$’ in terms of direct and indirect transitions can be performed with the help of Formulae 5.18 and 5.19 using values of ‘$r$’ given in Table 5.1.

![Graph showing absorption spectra for as grown GeSe (I$_2$) single crystals.](image-url)
Figure 5.6 (b): Absorption spectra for as grown GeS$_{0.25}$Se$_{0.75}$ (I$_2$) single crystals.

Figure 5.6 (c): Absorption spectra for as grown GeS$_{0.5}$Se$_{0.5}$ (I$_2$) single crystals.
Figure 5.6 (d): Absorption spectra for as grown GeS$_{0.75}$Se$_{0.25}$ (I$_2$) single crystals.

Figure 5.6 (e): Absorption spectra for as grown GeS (I$_2$) single crystals.
Table 5.1: Values of exponent ‘r’ for different types of transitions.

<table>
<thead>
<tr>
<th>Type of Transition</th>
<th>Direct 2D</th>
<th>Direct 3D</th>
<th>Indirect 2D</th>
<th>Indirect 3D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allowed (Step Function)</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Forbidden</td>
<td>1</td>
<td>3/2</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Direct optical transition is occurs only when the extremes of the valence and conduction band in K - space for a perfect crystal coincide. But in the case of their non-coincidence, these transitions do not occur, as wave vector of the photon cannot compensate for the change in crystal momentum of the electronic stage. The crystal momentum is however conserved by emission or absorption of phonons during transition due to electron- photon interactions. Both these types of transitions in GeS<sub>x</sub>Se<sub>1-x</sub> (I<sub>2</sub>) (x = 0, 0.25, 0.5, 0.75, 1) single crystals at room temperature are analysed here.

By plotting the graphs of \((\alpha h\nu)^{1/r}\) vs. \(h\nu\) for various values of ‘r’ given in Table 5.1, it is possible to determine which of the following conditions given in this table dominate. Exploration of the plots to zero absorption will give the appropriate value of the energy band gaps of GeS<sub>x</sub>Se<sub>1-x</sub> (I<sub>2</sub>) (x = 0, 0.25, 0.5, 0.75, 1) single crystal.

Since all the curves indicate some discontinuity straight lines, it is quite possible that they may represent inter-band transitions involving the emission or absorption of phonons. In order to make an accurate determination of the points of discontinuities, we have followed the method earlier successfully used for layer compounds [60- 64].

Figure 5.7(a) - Figure 5.7(e) shows spectral variation of \((\alpha h\nu)^{1/2}\) and \((\alpha h\nu)^{1/3}\) vs. \(h\nu\) respectively.

Accordingly, from the graphical differentiation of the data presented in Figure 5.7 (a) – Figure 5.7 (e) for GeS<sub>x</sub>Se<sub>1-x</sub> (I<sub>2</sub>) (x = 0, 0.25, 0.5, 0.75, 1) single crystal, the dependence of the derivatives \(\delta(\alpha h\nu)^{1/2}/\delta E\) vs. \(h\nu\) has been shown in Figure 5.8 (a) – Figure 5.8 (e). It can be clearly seen from these figure that the derivatives are step function of energy with four steps well defined in the range:
$E_1 < E < E_2,$
$E_2 < E < E_3,$
$E_3 < E < E_4$
$E_4 < E.$

These values of $E_1$, $E_2$, $E_3$ and $E_4$ indicate the points of discontinuities in the plots of $\delta(\alpha h\nu)^{1/2}/\delta E$ vs. $h\nu$.

The indirect energy gaps obtained from these values of $E_1$, $E_2$, $E_3$ and $E_4$ are given by:

$$E'_g = \frac{E_1 + E_4}{2} = \frac{E_2 + E_3}{2}$$

$$E_{\rho 1} = \frac{E_4 - E_1}{2}$$
and
$$E_{\rho 2} = \frac{E_3 - E_2}{2}$$

The values of indirect band gap $E'_g$ phonon energies and some optical parameters thus obtained are presented in Table 5.2.

Figure 5.7 (a): Spectral Variation of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ Vs. Photon Energy of GeSe(I$_2$) single crystal.
Figure 5.7 (b): Spectral Variation of \((\alpha h\nu)^{1/2}\) and \((\alpha h\nu)^{1/3}\) Vs. Photon Energy of \(\text{GeS}_{0.25}\text{Se}_{0.75} (I_2)\) single crystal.

Figure 5.7 (c): Spectral Variation of \((\alpha h\nu)^{1/2}\) and \((\alpha h\nu)^{1/3}\) Vs. Photon Energy of \(\text{GeS}_{0.5}\text{Se}_{0.5} (I_2)\) single crystal.
Figure 5.7 (d): Spectral Variation of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ Vs. Photon Energy of GeS$_{0.75}$Se$_{0.25}$ ($I_2$) single crystal.

Figure 5.7 (e): Spectral Variation of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ Vs. Photon Energy of GeS ($I_2$) single crystal.
Figure 5.8 (a): Spectral variation of $\delta(\alpha h \nu)^{1/2}/\delta E$ vs. photon energy for GeSe (I$_2$) obtained by the graphical differentiation of the data.

Figure 5.8 (b): Spectral variation of $\delta(\alpha h \nu)^{1/2}/\delta E$ vs. photon energy for GeS$_{0.25}$Se$_{0.75}$ (I$_2$) obtained by the graphical differentiation of the data.
**Figure 5.8 (c):** Spectral variation of $\delta(\alpha h\nu)^{1/2}/\delta E$ vs. photon energy for Ge$_{0.5}$Se$_{0.5}$ \((I_2)\) obtained by the graphical differentiation of the data.

**Figure 5.8 (d):** Spectral variation of $\delta(\alpha h\nu)^{1/2}/\delta E$ vs. photon energy for Ge$_{0.75}$Se$_{0.25}$ \((I_2)\) obtained by the graphical differentiation of the data.
Figure 5.8 (e): Spectral variation of \(\delta(\alpha h\nu)^{1/2}/\delta E\) vs. photon energy for GeS (I\(_2\)) obtained by the graphical differentiation of the data.

However, it was found with GeS\(_x\)Se\(_{1-x}\) (I\(_2\)) (\(x = 0, 0.25, 0.5, 0.75, 1\)) single crystals that the best fit is obtained for ‘\(r\)’ = 2, it shows that the compounds are indirect band gap materials where the wave vector difference between electrons in the valence band and the conduction band is supplied by the lattice phonon. It is therefore conjectured that the indirect transition represented by the absorption curves is an indirect allowed type for all the samples while for GeS\(_x\)Se\(_{1-x}\) (I\(_2\)) (\(x = 0.25, 0.5\)) indirect forbidden transition is also occurs. The values of indirect energy band gap \(E_g\) obtained from the intersection of the linear portion of the graphs with energy axis for zero absorption for all the samples are listed in Table 5.3.

The absorption data has been analysed from the absorption curve on the basis of 2D Model for various values of ‘\(r\)’ is given in Table 5.3 using Equation 5.18.
Table 5.2: Calculated optical parameters for GeS<sub>x</sub>Se<sub>1-x</sub> (I<sub>2</sub>) (x = 0, 0.25, 0.5, 0.75, 1) single crystals in 3D model.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>GeSe (I&lt;sub&gt;2&lt;/sub&gt;)</th>
<th>GeS&lt;sub&gt;0.25&lt;/sub&gt;Se&lt;sub&gt;0.75&lt;/sub&gt;(I&lt;sub&gt;2&lt;/sub&gt;)</th>
<th>GeS&lt;sub&gt;0.5&lt;/sub&gt;Se&lt;sub&gt;0.5&lt;/sub&gt;(I&lt;sub&gt;2&lt;/sub&gt;)</th>
<th>GeS&lt;sub&gt;0.75&lt;/sub&gt;Se&lt;sub&gt;0.25&lt;/sub&gt;(I&lt;sub&gt;2&lt;/sub&gt;)</th>
<th>GeS (I&lt;sub&gt;2&lt;/sub&gt;)</th>
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<tr>
<td>E&lt;sub&gt;1&lt;/sub&gt; (eV)</td>
<td>1.0983</td>
<td>1.2109</td>
<td>1.3418</td>
<td>1.40891</td>
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<td>1.2169</td>
<td>1.3477</td>
<td>1.416952</td>
<td>1.5896</td>
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<td>E&lt;sub&gt;3&lt;/sub&gt; (eV)</td>
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<td>1.2229</td>
<td>1.3535</td>
<td>1.423457</td>
<td>1.6208</td>
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<td>E&lt;sub&gt;4&lt;/sub&gt; (eV)</td>
<td>1.1490</td>
<td>1.2301</td>
<td>1.3595</td>
<td>1.43166</td>
<td>1.6585</td>
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<tr>
<td>E&lt;sub&gt;p1&lt;/sub&gt; (eV)</td>
<td>0.0253</td>
<td>0.0096</td>
<td>0.0088</td>
<td>0.011</td>
<td>0.058</td>
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<tr>
<td>E&lt;sub&gt;p2&lt;/sub&gt; (eV)</td>
<td>0.0757</td>
<td>0.00299</td>
<td>0.00293</td>
<td>0.0032</td>
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<td>294.09</td>
<td>111.320</td>
<td>102.24</td>
<td>131.8873</td>
<td>767.17</td>
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<td>87.79</td>
<td>34.7515</td>
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<td>37.6798</td>
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<tr>
<td>E&lt;sub&gt;g&lt;/sub&gt; (eV) Direct</td>
<td>1.46</td>
<td>1.45</td>
<td>1.48</td>
<td>1.53</td>
<td>1.68</td>
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<td>E&lt;sub&gt;g'&lt;/sub&gt; (C) (eV)</td>
<td>1.12</td>
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<td>1.34</td>
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<td>1.60</td>
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<td>E&lt;sub&gt;g'&lt;/sub&gt; (E) (eV)</td>
<td>1.12</td>
<td>1.02</td>
<td>1.34</td>
<td>1.42</td>
<td>1.60</td>
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<td>B&lt;sub&gt;α1&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;eV&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>4410.54</td>
<td>30423.1669</td>
<td>3529.94</td>
<td>-10958.03</td>
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<td>-22679.2729</td>
<td>3474.61</td>
<td>7283.3479</td>
<td>4017.71</td>
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<tr>
<td>B&lt;sub&gt;ε1&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;eV&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>124.81</td>
<td>27347.2407</td>
<td>924.4665</td>
<td>-9400.875</td>
<td>5960.08</td>
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<td>B&lt;sub&gt;ε2&lt;/sub&gt; (cm&lt;sup&gt;-1&lt;/sup&gt;eV&lt;sup&gt;2&lt;/sup&gt;)</td>
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<td>-24980.8948</td>
<td>1389.17800</td>
<td>8365.3689</td>
<td>3478.10</td>
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Figure 5.9 (a) to Figure 5.9 (e) shows the spectral variation of (α) and (α)1/2 vs. hν respectively. The according to the Two Dimension Model, the Indirect transition can be confirmed to be the Allowed type. The values of the indirect band gaps in 2D model obtained from the extrapolation of the linear portion of the curves show as inset in Figure 5.9 (a, b, c, d, e) are presented in Table 5.3.

Since for GeSe (I<sub>2</sub>) single crystal the curves indicate some discontinuity straight lines, it is quite possible that it may represent inter-band transitions involving the emission or absorption of phonons.

To make an accurate determination of the points of discontinuities, we have followed the method earlier successfully used for layer compounds [60-64] which is shown in Figure 5.10 (a) - Figure 5.10 (e). The values of indirect band gap E<sub>g'</sub>,
phonon energies and some optical parameters in two dimensional model thus obtained for GeS\textsubscript{x}Se\textsubscript{1-x} (I\textsubscript{2}) single crystals are presented in Table 5.4.

For the determination of the three dimensional direct band gap \(E_g\) the spectral variation of \((ahv)^2\) and \((ahv)^{2/3}\) vs. \(hv\) as shown in Figure 5.11 (a) - Figure 5.11(e) has been analyzed. The best fit of all the experimental points was observed in the case of \((ahv)^2\) vs. \(hv\). The values of \(E_g\) obtained from the intersection of the straight line portion of the curve on the \(hv\) axis for zero absorption are shown in Table 5.3.

The values of direct and indirect band gaps obtained from the mentioned curves match with the reported value [65, 66]. The spectral variation of \((\alpha)^2\) vs. \(hv\) has been shown in Figure 5.12 (a) – Figure 5.12(e) and the curves are analysed.

The energy band gap \(E_g\) obtained from the extrapolation of the straight line portion of the curve on energy axis for zero absorption is determined. The value of direct band gap for the entire sample GeS\textsubscript{x}Se\textsubscript{1-x} (I\textsubscript{2}) \((x = 0, 0.25, 0.5, 0.75, 1)\) represented in Table 5.3 which clearly confirms that the transition is direct allowed. From the Table 5.3 it is observed that the two dimensional (2D) model nearly gives the optical direct energy band gap for GeS\textsubscript{x}Se\textsubscript{1-x} (I\textsubscript{2}) \((x = 0, 0.25, 0.5, 0.75, 1)\) crystals as those obtained from three dimensional (3D) model. So finally we can conclude direct and indirect symmetry allowed transition gives a good account of the optical absorption edge in our as grown GeS\textsubscript{x}Se\textsubscript{1-x} (I\textsubscript{2}) \((x = 0, 0.25, 0.5, 0.75, 1)\) single crystals which match with others single crystals in both 2D and 3D models.

**Table 5.3:** Values of Indirect and Direct band gaps using 3D and 2D Model of GeS\textsubscript{x}Se\textsubscript{1-x} (I\textsubscript{2}) \((x = 0, 0.25, 0.5, 0.75, 1)\) single crystals.

<table>
<thead>
<tr>
<th>Types of Transition</th>
<th>GeSe(I\textsubscript{2})</th>
<th>GeSe\textsubscript{0.25}Se\textsubscript{0.75}(I\textsubscript{2})</th>
<th>GeSe\textsubscript{0.5}Se\textsubscript{0.5}(I\textsubscript{2})</th>
<th>GeSe\textsubscript{0.75}Se\textsubscript{0.25}(I\textsubscript{2})</th>
<th>GeS(I\textsubscript{2})</th>
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<td>3D Model (Indirect Transition)</td>
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<td></td>
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<tr>
<td>Allowed</td>
<td>0.78</td>
<td>1.24</td>
<td>1.34</td>
<td>1.42</td>
<td>1.54</td>
</tr>
<tr>
<td>Forbidden</td>
<td>0.34</td>
<td>1.28</td>
<td>1.30</td>
<td>1.41</td>
<td>1.06</td>
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<tr>
<td>3D Model (Direct Transition)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1.45</td>
<td>1.48</td>
<td>1.53</td>
<td>1.61</td>
</tr>
<tr>
<td>Forbidden</td>
<td>1.01</td>
<td>1.43</td>
<td>1.34</td>
<td>1.43</td>
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</table>
### Chapter 5: Optical Properties

#### Types of Transition

<table>
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<tr>
<th></th>
<th>GeSe(I₂)</th>
<th>GeS₀.₂₅Se₀.₇₅(I₂)</th>
<th>GeS₀.₅Se₀.₅(I₂)</th>
<th>GeS₀.₇₅Se₀.₂₅(I₂)</th>
<th>GeS(I₂)</th>
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<td><strong>2D Model (Indirect Transition)</strong></td>
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<td>1.60</td>
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<td></td>
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</tr>
<tr>
<td>Allowed</td>
<td>----</td>
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</tr>
<tr>
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<td>1.4</td>
<td>1.45</td>
<td>1.56</td>
<td>1.52</td>
<td>1.59</td>
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**Figure 5.9 (a):** Spectral variation of $(\alpha)$ and $(\alpha)^{1/2}$ vs. Photon energy of GeSe(I₂) single crystal.
Figure 5.9 (b): Spectral variation of $(\alpha)$ and $(\alpha)^{1/2}$ vs. Photon energy of Ge$_{0.25}$Se$_{0.75}$ (I$_2$) single crystal.

Figure 5.9 (c): Spectral variation of $(\alpha)$ and $(\alpha)^{1/2}$ vs. Photon energy of Ge$_{0.5}$Se$_{0.5}$ (I$_2$) single crystal.
Figure 5.9(d): Spectral variation of ($\alpha$) and ($\alpha$)$^{1/2}$ vs. Photon energy of GeS$_{0.75}$Se$_{0.25}$ (I$_2$) single crystal.

Figure 5.9 (e): Spectral variation of ($\alpha$) and ($\alpha$)$^{1/2}$ vs. Photon energy of GeS (I$_2$) single crystal.
Figure 5.10 (a): Spectral Variation of $\frac{\delta\alpha}{\delta E}$ vs. Photon energy by graphical data presentation for GeSe ($I_2$) single crystal.

Figure 5.10 (b): Spectral Variation of $\frac{\delta\alpha}{\delta E}$ vs. Photon energy by graphical data presentation for Ge$S_{0.25}$Se$0.75$ ($I_2$) single crystal.
**Figure 5.10 (c):** Spectral Variation of $\delta\alpha/\delta E$ vs. Photon energy by graphical data presentation for GeS$_{0.5}$Se$_{0.5}$ (I$_2$) single crystal.

**Figure 5.10 (d):** Spectral Variation of $\delta\alpha/\delta E$ vs. Photon energy by graphical data presentation for GeS$_{0.75}$Se$_{0.25}$ (I$_2$) single crystal.
Figure 5.10 (e): Spectral Variation of $\delta \alpha / \delta E$ vs. Photon energy by graphical data presentation for GeS (I$_2$) single crystal.

Figure 5.11 (a): Spectral Variation $(\alpha h \nu)^{2/3}$ and $(\alpha h \nu)^2$ vs. Photon energy for GeSe (I$_2$) single crystal.
Figure 5.11 (b): Spectral Variation $(\alpha h\nu)^{2/3}$ and $(\alpha h\nu)^2$ vs. Photon energy for GeS$_{0.25}$Se$_{0.75}$ (I$_2$) single crystal.

Figure 5.11 (c): Spectral Variation $(\alpha h\nu)^{2/3}$ and $(\alpha h\nu)^2$ vs. Photon energy for GeS$_{0.5}$Se$_{0.5}$ (I$_2$) single crystal.
Figure 5.11 (d): Spectral Variation \((\alpha h \nu)^{2/3}\) and \((\alpha h \nu)^2\) vs. Photon energy for GeS\(_{0.75}\)Se\(_{0.25}\) (I\(_2\)) single crystal.

Figure 5.11 (e): Spectral Variation \((\alpha h \nu)^{2/3}\) and \((\alpha h \nu)^2\) vs. Photon energy for GeS (I\(_2\)) single crystal.
Figure 5.12 (a): Spectral variation of $(\alpha)^2$ vs. Photon energy for GeSe (I$_2$) single crystal.

Figure 5.12 (b): Spectral variation of $(\alpha)^2$ vs. Photon energy for GeS$_{0.25}$Se$_{0.75}$ (I$_2$) single crystal.

Figure 5.12 (c): Spectral variation of $(\alpha)^2$ vs. Photon energy for GeS$_{0.5}$Se$_{0.5}$ (I$_2$) single crystal.
Figure 5.12 (d): Spectral variation of $(\alpha)^2$ vs. Photon energy for Ge$_{0.75}$Se$_{0.25}$ (I$_2$) single crystal.

Figure 5.12 (e): Spectral variation of $(\alpha)^2$ vs. Photon energy for GeS (I$_2$) single crystal.

Using absorption spectra, transmission (T) and reflection (R) coefficients have been computed by equations 5.25 and 5.26 [67- 68].

\[
A = - \log T \tag{5.25}
\]

\[
R = 1 - (T + A) \tag{5.26}
\]

where symbols have their usual meanings. The relation between T and R in graphical form is shown in Figure 5.13 (a) – Figure 5.13(e)

Figure 5.13 (a) – Figure 5.13 (e) and Figure 5.6(a) – Figure 5.6 (e) it implies that reflectance and absorbance posses the same trend but the value of reflectance is low so the surface of the grown crystal is less shiny.
Furthermore, the reflectivity, the optical constant (k) and the refractive index (n) of crystals at certain constant wavelength are related through the following equation.

\[ K = \frac{a_\lambda}{4\pi} \]  
(5.24)

\[ R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \]  
(5.25)

Using these relation values of k and n have been calculated at different input wavelengths. The change in the optical parameters is presented graphically in Figure 5.14 (a), (b), (c), (d) and (e).

In GeS_xSe_1-x (I_2) (0, 0.25, 0.5, 0.75, 1) single crystal the transmittance and the reflectance shows almost the same trend. There is a large change in them in the wavelength range 750 nm to 900 nm.

**Figure 5.13 (a):** The variation of reflectance (R) and transmittance (T) of GeSe (I_2) single crystal with wavelength.
Figure 5.13 (b): The variation of reflectance (R) and transmittance (T) of Ge$_{0.25}$Se$_{0.75}$ (I$_2$) single crystal with wavelength.

Figure 5.13 (c): The variation of reflectance (R) and transmittance (T) of Ge$_{0.5}$Se$_{0.5}$ (I$_2$) single crystal with wavelength.
Figure 5.13 (d): The variation of reflectance (R) and transmittance (T) of GeS$_{0.75}$Se$_{0.25}$ (I$_2$) single crystal with wavelength.

Figure 5.13 (e): The variation of reflectance (R) and transmittance (T) of GeS (I$_2$) single crystal with wavelength.
Figure 5.14 (a): Spectral variation of the extinction co-efficient (k) and refractive index (n) with wavelength for GeSe (I$_2$) single crystal.

Figure 5.14 (b): Spectral variation of the extinction co-efficient (k) and refractive index (n) with wavelength for GeS$_{0.25}$Se$_{0.75}$ (I$_2$) single crystal.
Figure 5.14 (c): Spectral variation of the extinction coefficient (k) and refractive index (n) with wavelength for GeS$_{0.5}$Se$_{0.5}$ (I$_2$) single crystal.

Figure 5.14 (d): Spectral variation of the extinction coefficient (k) and refractive index (n) with wavelength for GeS$_{0.75}$Se$_{0.25}$ (I$_2$) single crystal.
Figure 5.14 (e): Spectral variation of the extinction co-efficient (k) and refractive index (n) with wavelength for GeS (I_2) single crystal.

The general trend of variation in n and k is fairly the same for GeS_xSe_{1-x} (I_2) (0.25, 0.5, 0.75) materials. The values of k and n increase gradually up to 854 nm for GeS_{0.25}Se_{0.75} (I_2), 783 nm for GeS_{0.5}Se_{0.5}(I_2), 796 nm for GeS_{0.75}Se_{0.25}(I_2) and then decreased sharply up to 799 nm for GeS_{0.25}Se_{0.75}(I_2), 732 nm for GeS_{0.5}Se_{0.5}(I_2) 756 nm for GeS_{0.75}Se_{0.25}(I_2) single crystals. While In GeSe (I_2) it remains constant up to 980 nm and then sharply decreases up to 1020 nm and again becomes constant up to 1400 nm and in GeS (I_2) however the values of k and n increases sharply at 1000 nm and then it becomes constant.

Figure 5.13(b) - Figure 5.13(d) shows that at both its extreme ends GeS_xSe_{1-x} (I_2) (0.25, 0.5, 0.75) shows the steep depressions at the same position, the reflectance, R, of the same crystal exhibits two shallow depressions. This behavior indicates the existence of two strong absorptions bands in both IR and UV ends of spectrum. This conclusion will be confirmed below more qualitatively as shown in Figure 5.13(b) - Figure 5.13(d). Crystal shows abrupt depression in the both the near IR and the UV sides of the spectrum. At the same region of the spectrum, R, of the same crystal steadily increases while it exhibits a few narrow ripples indicating the existence of a
couple of sharp absorption bands overlapping broad conduction band characteristics for semiconducting material [69].

5.6 CONCLUSION

In the present work author has found that from an accurate analysis of the absorption spectra for GeS\textsubscript{x}Se\textsubscript{1-x} (I\textsubscript{2}) (x= 0, 0.25, 0.5, 0.75, 1) single crystal it is possible to find both direct as well as indirect transitions simultaneously in the same spectra thus supporting the views expressed by Willet et. al. [38, 39].

From the study of two dimensional and three dimensional model it has been found that in GeS (I\textsubscript{2}) and GeSe (I\textsubscript{2}) indirect transitions are of allowed type while in rest of the samples both the allowed and forbidden transitions take place. And indirect symmetry allowed transition gives a good account of the optical absorption edge in our as grown GeS\textsubscript{x}Se\textsubscript{1-x} (I\textsubscript{2}) (x= 0, 0.25, 0.5, 0.75, 1) single crystals. So both two dimensional and three dimensional models can be used satisfactorily to describe the indirect transitions in GeS\textsubscript{x}Se\textsubscript{1-x} (I\textsubscript{2}) (x= 0, 0.25, 0.5, 0.75, 1).

A careful study of the results on energy band gaps presented in Table 5.2 and Table 5.4 reveals that the value of both direct as well as indirect band gap increases as the content of sulphur increases. This is due to the imperfection caused by the off–stoichiometry in these samples.

On the basis of two and three dimensional models suggest us to conclude that it is perhaps not appropriate to classify GeS\textsubscript{x}Se\textsubscript{1-x} (I\textsubscript{2}) (x= 0, 0.25, 0.5, 0.75, 1) as a truly layered like compounds but it should be considered as an intermediate case between two dimensional and three dimensional system or more appropriately pseudo-two dimensional system.

The low value of Phonon energy in Table 5.2 favourable match with values of Phonon energies in far infra red spectrum of grown crystals.

Several optical parameters such as transmittance, reflectance, refractive index, extinction coefficient could be determined from the measured values of absorbance of all the materials under investigation.
REFERENCES


