Chapter 4

Thermal Diffusivity and Optical Band Gap Studies on In-Se-Tl Glasses

Summary

Photo-thermal deflection technique and UV visible spectrometer are used to investigate the thermal diffusivity ($\alpha$) and optical band gap ($E_g$) of $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x$ ($7 \leq x \leq 15$) and $\text{In}_{15}\text{Se}_{85-x}\text{Tl}_x$ ($2 \leq x \leq 10$) bulk glasses as a function of composition. It is found that the thermal diffusivity is comparatively high for both the series of glasses, which is consistent with the threshold type of electrical switching behavior exhibited by these samples. The absorption spectra of these materials was obtained at the range of 380-1020nm. The $E_g$ has been estimated from the plot of absorption coefficient as a function of wavelength by using Tauc relation. The composition dependence of thermal diffusivity and optical band gap of $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x$ and $\text{In}_{15}\text{Se}_{85-x}\text{Tl}_x$ glasses exhibits a change in the slope at $\langle r \rangle = 2.46$ ($x=13$) and 2.42($x=6$), respectively, which are attributed to the rigidity percolation threshold in both the systems.
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4.1 Introduction

In most of the chalcogenide glasses, physical properties exhibit extremum or kink or change of slope, etc., at two network topological thresholds known as rigidity percolation threshold and chemical threshold [1,2]. Correlation of the features observed at specific compositions help us in identifying these two thresholds and also to understand the nature of the amorphous state as well as glassy state. In recent years, a great attention was paid to study chalcogenide glasses due to their use in electrical, optical switching and optoelectronic fields [3,4]. It is reported that amorphous Se has special interest, because of its device applications in electronic, electrochemical, solar cells, optical recording, imaging devices, memory and switching devices, etc. [5-9]. The heat dissipation in optoelectronic and microelectronic devices is an important mechanism limiting the device performance and that will provide the knowledge about the thermal degradation of the material at different temperatures [10]. The determination of thermal and optical parameters is an important method for characterization and analysis of chalcogenide glasses for various applications. Photo-thermal deflection technique or the mirage technique, which is non-destructive and non-contact in nature, is one such powerful and highly sensitive technique to measure the thermal diffusivity of solid samples [11-15].

Thermal diffusivity, $\alpha$ is defined as $\alpha = \frac{k}{\rho C}$ where $k$ is the thermal conductivity, $\rho$ is the mass density and $C$ is the specific heat capacity of the material. Physically, the inverse of $\alpha$ is the measure of time required to establish thermal equilibrium in a given material, and it is unique for each material [16]. The phenomenon of electrical switching in glassy chalcogenides has gained a lot of interest in modern times due to various technological applications. Usually, chalcogenide glasses which have high $\alpha$ values exhibit threshold type electrical switching and those with low $\alpha$, show memory behavior [17]. Thus, $\alpha$ measurement is important for characterizing switching glasses and for device modeling & design. Furthermore, the thermal diffusivity is fully dependent upon the effects of compositional and micro-structural variables as well as processing conditions of the glassy material [18]. The present chapter deals with the measurements of thermal diffusivity using photo-thermal deflection technique [19-22] and optical band gap using UV-visible spectrometer on
In$_{10}$Se$_{90-x}$Tlx ($7 \leq x \leq 15$) and In$_{15}$Se$_{85-x}$Tlx ($2 \leq x \leq 10$) glasses [23]. In addition, the thermal diffusivity and the optical band gap variations with composition have been studied systematically and compared with the composition dependence of switching voltages/off-state resistance.

4.2 Experimental

Bulk In$_{10}$Se$_{90-x}$Tlx ($7 \leq x \leq 15$) and In$_{15}$Se$_{85-x}$Tlx ($2 \leq x \leq 10$) glasses are prepared by vacuum sealed conventional melt-quenching technique as described in chapter 2. The amorphous nature of the as-quenched samples has been verified by X-ray diffraction experiments.

4.2.1 Photo-thermal Deflection and Thermal Diffusivity Measurements

Photo-thermal deflection measurements have been undertaken using a custom built setup, in which continuous wave-intensity modulated argon-ion laser (10mW @ 514nm) is used as the pump beam and a He-Ne laser (5mW @ 632nm) as the probe beam. A flat sample piece of $\approx 0.40$mm thickness is kept immersed at the bottom of a quartz cuvette. Carbon tetrachloride (CCl$_4$) is used as the coupling fluid to the sample, which is usually used as a deflection medium in photo-thermal deflection studies. The significant parameters that make CCl$_4$ a potential deflection medium in photo-thermal deflection technique are its low values of thermal conductivity ($k = 0.09$Wm$^{-1}$k$^{-1}$), specific heat capacity ($C_p = 0.85$Jg$^{-1}$k$^{-1}$) and thermal diffusivity ($\alpha = 7.31 \times 10^{-4}$ cm$^2$/sec). The second important parameter which favors the use of CCl$_4$ is that it absorbs mainly below 250nm and has a very high rate of change of refractive index with respect to temperature (($dn/dT = 6.12 \times 10^{-4}$k$^{-1}$), compared to many other liquids [24,25]. The sample is placed horizontally at the bottom of a quartz cuvette. The pump beam is incident normal to the surface of the sample and a mechanical chopper is used to intensity modulate the pump laser beam. The probe laser beam, skimming the surface of the sample is monitored with a position sensitive detector. The entire experimental setup is arranged on a vibration-free table to protect from the ambient vibrations and the probe-beam height above the sample surface is kept as minimum as possible to get non-diffracted (from the sample edge) signal. The details of the PTD setup used in the present study and the calibration methods employed are reported by Pulok et al. [26].
The exposure to an intensity modulated light causes the excitation and the subsequent non-radiative recombination in the sample which are periodic; the periodic non-radiative recombination leads to the generation of a thermal wave in the sample [27], which is propagated to the surrounding liquid medium (CCl₄), setting up a temperature gradient in it. This temperature gradient causes a refractive index variation in the liquid medium above the surface of the sample [28,29]. This refractive index variation causes a deflection in a probe He-Ne laser beam (5mW @ 632nm) skimming the surface of the sample, which is detected by a position-sensitive quadrant detector and a lock-in amplifier. The penetration depth of the thermal waves into the sample is inversely proportional to the chopping frequencies. Hence the measurement of thermal parameter is usually done at lower chopping frequencies because the free carrier contribution starts dominating at higher frequencies [30]. In the present experiment, the amplitude of PDS signal is measured in the frequency range of 0-200Hz.

4.3 Optical Spectroscopy and Optical Band Gap Measurements

UV-visible absorption spectra of Tl-doped In-Se glassy materials are taken using a Perkin-Elmer Spectrometer in the range of 380-1020nm to calculate the band gap of the material. The optical band gap is estimated from absorption coefficient data as a function of wavelength by using Tauc relation [31].

4.4 Results and Discussion

4.4.1 Composition Dependence of Thermal Diffusivity

The variation of the PDS signal amplitude as a function of the chopping frequency of the pump-beam is shown in figure 4.1 for a representative In₁₀Se₈₃Tl₇ glass, which shows that the photo thermal deflection signal amplitude decreases as a function of frequency. The modulation intensity at higher frequencies reduces the time for optical interaction and the carrier generation in the material, which in-turn reduces the phonon contribution and noise contribution from various background sources leading to suppress the signal strength, and consequently accurate measurements are not possible in the high frequency region. Chalcogenide glasses exhibit interesting variations in its thermal diffusivity (α) with composition [32-34]. The metallicity of the
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additive atom is found to be a key factor which determines the composition dependence of $\alpha$

![Figure 4.1: The variation of PDS signal Vs frequency for a representative In$_{15}$Se$_{83}$Tl$_2$ glass](image)

Generally, when more metallic elements are added, it is found that $\alpha$ value increases, due to the increase in the number of phonon frequency modes. On the other hand, the addition of non-metallic components such as halogens, leads to a decrease in $\alpha$ [17,26]. Figure 4.2(a-e) and 4.3(a-e) shows the plot of the log of the PDS signal amplitude against the square root of the chopping frequencies for all the samples studied for In$_{10}$Se$_{90-x}$Tl$_x$ and In$_{15}$Se$_{85-x}$Tl$_x$ glasses respectively and the curves are found to be almost straight line. The thermal diffusivity ($\alpha$) of In$_{10}$Se$_{90-x}$Tl$_x$ and In$_{15}$Se$_{85-x}$Tl$_x$ glasses are determined from the slope of the straight lines using the relation

$$\alpha = \pi \left( \frac{l}{\text{Slope}} \right)^2 \text{cm}^2/\text{s}.$$  

The thermal diffusivity lie in the range of 0.024-0.086 cm$^2$/s for In$_{10}$Se$_{90-x}$Tl$_x$ and 0.0102-0.0388cm$^2$/s for In$_{15}$Se$_{85-x}$Tl$_x$ glasses, where as that of In$_{10}$Se$_{90}$ and In$_{15}$Se$_{85}$ base glasses are 0.0017 and 0.0014cm$^2$/s [35], respectively.

The higher thermal diffusivity values of the both series of glasses are attributed to the higher metallicity of thallium compared to selenium atoms. In addition to the metallicity factor, network topological effects such as rigidity percolation, chemical
ordering, etc., are found to influence the composition dependence of thermal diffusivity of chalcogenide glasses (figure 4.4).

**Figure 4.2:** A representative plot of the log of PDS signal amplitude against the square root of the chopping frequency for the samples of In$_{10}$Se$_{90-x}$Tlx series
Figure 4.3: A representative plot of the log of PDS signal amplitude against the square root of the chopping frequency for the samples of In$_{15}$Se$_{85-x}$Tl$_x$ series

In many glassy systems, it is observed that $\alpha$ increases with the addition of higher coordinated atoms which increases the network connectivity and structural rigidity [36,37]. A maximum in the $\alpha$ value is observed at the rigidity percolation threshold in
many systems [27,37-41]. The material undergoes a transition from a floppy polymeric glass to a rigid amorphous solid [2,42].

![Graph](image)

**Figure 4.4:** The variations of $\alpha$ and $E_g$ in In$_{10}$Se$_{90-x}$Tl$_x$ glasses ($7 \leq x \leq 15$) with composition/coordination number

Further, the addition of Tl ($x > 13$) favors the formation of Tl-Tl bond which reduces the Se-Se and In-In bond concentrations and results in a slight decrease in $\alpha$ value. That is, the bond length of Se-Se, In-In and Tl-Tl are 232pm, 325pm and 340pm, respectively. The bond length of Se-Se is smaller than Tl-Tl and In-In. The effective molecular weight of glasses decreases as the bond lengths increase and hence the density of localized states decreases [43]. This decrease in the density of localizes states increases the porosity and produces more disordered structure [44], which is responsible for the decrease in the $\alpha$ value.

The average coordination number $<r>$, is an important parameter in determining the composition dependence of various physical properties of chalcogenide glasses. Using the coordination numbers 4, 2 and 4, for In, Se and Tl atoms, respectively [28,29], then the average coordination number $<r>$ of In$_{10}$Se$_{90-x}$Tl$_x$ glasses lies in the range of 2.34-2.5 for the composition studied. According to Phillips’ Constraint Theory [42] and Percolation model [2], the rigidity percolation at which a percolation transition takes place from a polymeric glass to a rigid network or amorphous solid is expected to occur in the In-Se-Tl system at $<r> = 2.40$. It is also suggested that the rigidity
percolation threshold may be shifted towards higher values of $<r>$ in certain glassy systems [45]. The maximum value of $\alpha$ at $x=13$ ($<r>=2.46$) of the In-Se-Tl system is attributed to the mechanical stiffening of rigidity and the corresponding threshold in the internal stress. The number of zero frequency modes would be minimum at $<r>=2.46$ [46]. At this composition, the network offers minimum resistance to the propagating thermal waves and consequently, the thermal diffusivity has a maximum value. Beyond the rigidity threshold, additional vibrational modes characteristic of a rigid elastic network become available and scattering of thermal waves by these modes leads to a reduction in the value of $\alpha$ [38].

The variations of thermal diffusivity ($\alpha$) and optical band gap in In$_{15}$Se$_{85-x}$Tlx $(2 \leq x \leq 10)$ glasses with composition/average coordination number are shown in figure 4.5. It is found that with the addition of thallium to the base In$_{15}$Se$_{85}$ glass, thallium enters the network with two types of valencies, as a trivalent Tl$^{3+}$ species which is covalent in nature and a monovalent Tl$^{1+}$ which is more ionic [47].

![Figure 4.5: The composition dependence of $\alpha$ and $E_g$ of In$_{15}$Se$_{85-x}$Tlx glasses](image)

In the present study, it is found that the additional thallium enters as the ionic Tl$^{1+}$ and contributes to the fragmentation effect of the network. The progressive fragmentation of the network causes more resistance to the propagation of the thermal waves in the sample leading to the decrease in thermal diffusivity.
4.4.2 Optical Band Gap

The optical band gap has a prime effect on the electrical properties of semiconducting materials [48,49]. It is observed that the composition has a significant influence on the band gap of glassy chalcogenide semiconductors [50-52]. The absorption spectrum shows that (figure 4.6) In-Se-Tl ternary glasses can absorb considerable amount of visible light making them potentially usable for photochemical reactions.

![Absorbance spectra of In_{10}Se_{90-x}Tl_x and In_{15}Se_{85-x}Tl_x glasses](image)

Figure 4.6: Absorption spectra of In_{10}Se_{90-x}Tl_x and In_{15}Se_{85-x}Tl_x glasses

Based on the chemically-ordered network model, the Se rich In_{10}Se_{90-x}Tl_x (7≤x≤15) glassy system is described as a completely cross-linked three-dimensional structural units consisting of In-Se, Se-Se and Se-Tl bonds. The bond energies of various possible bonds involved in the formation of this network system namely, In-Se, Se-Se, In-In, Se-Tl and Tl-Tl are 247, 205.8, 100, 158 and 64.5kJ/mol, respectively. When Tl concentration increases, more and more Se-Se bonds are broken and the probability of ionic Se-Tl bond formation increases. As the In-Se heteropolar bonds and the Se-Se homopolar bonds have comparatively more bond energy compared to Se-Tl bonds. This attribute to the reduction of the energy of the conduction band edge resulting in a decrease in E_g (figure 4.4). The plot of (αhυ)^2 versus hυ for the In_{15}Se_{85-x}Tl_x and In_{10}Se_{90-x}Tl_x glassy samples is as shown in figure 4.7(a-j).

Extrapolation of linear region of the plot to (αhυ)^2 = 0 gives corresponding direct energy band gap. It is evident from the graph that the direct band gap increases with the increase in Tl concentration upto x ≤ 6, beyond which it decreases.
In the present study, the increase in band gap (figure 4.5) it may be explained on the basis of the decrease in the lattice parameters for the thallium content upto 6% which is due to smaller size of Tl$^{3+}$ (ionic radii $\approx 0.095$ nm) as compared to Se$^{2+}$ (ionic radii $\approx 0.198$ nm) but as the doping of Tl is made 8 or 10%, the band gap decreases as the lattice parameter increases. The increases in the band gap can also be studied on the basis of Moss-Burstein effect [53]. When the Fermi level shifts close to the conduction band due to increase in carrier concentration, the lower energy transitions are blocked and the value of the band gap increases for doping upto 6%. Further, the decrease in band gap when Tl concentration level increases to above 6% may be due to the formation of a new orbital Tl mixed and to the transitions between partially forbidden valance band and conduction band.

Similar results were also observed in other Se-based binary and ternary glassy samples such as Se$_{1-x}$Te$_x$, Se$_{96-x}$Te$_x$Ag$_x$ and Se$_{80}$Te$_{20-x}$Pb$_x$ with composition [54-56]. So
it can be said that optical band gap values are consistent with the data found from literature.

\[
\alpha_h \nu = \frac{\hbar \nu}{E_g}\left(\frac{\hbar \nu}{m}\right)^{1/2}
\]

\[
E_g = 1.25 \text{ eV}
\]

\[
E_g = 1.51 \text{ eV}
\]

\[
E_g = 1.42 \text{ eV}
\]

\[
E_g = 1.37 \text{ eV}
\]

\[
E_g = 1.39 \text{ eV}
\]

**Figure 4.7:** A representative plot of \((\alpha_h \nu)^2\) vs. photon energy \((\hbar \nu)\): (e)\(\text{In}_{15}\text{Se}_{75}\text{Tl}_{10}\) (f) \(\text{In}_{10}\text{Se}_{83}\text{Tl}_{7}\) (g) \(\text{In}_{10}\text{Se}_{81}\text{Tl}_{9}\) (h) \(\text{In}_{10}\text{Se}_{79}\text{Tl}_{11}\) (i) \(\text{In}_{10}\text{Se}_{77}\text{Tl}_{13}\) and (j) \(\text{In}_{10}\text{Se}_{75}\text{Tl}_{15}\) samples

The chalcogenide glassy materials are intrinsic-like and the conductivity activation energy is half the optical band gap [43]; therefore an increase in optical band gap indicates an increase in conductivity activation energy and consequently, the
resistivity of the glassy material. It is known that the switching voltages of glassy chalcogenides are directly related to the resistivity of the sample. Thus, the composition dependence of optical band gap and the variation of switching voltages with Tl concentration of amorphous In$_{15}$Se$_{85-x}$Tl$_x$ bulk samples are consistent.

4.5 Conclusion

The thermal diffusivity ($\alpha$) of bulk In-Se-Tl glasses is measured using photothermal deflection technique. The $\alpha$ value of In$_{10}$Se$_{90-x}$Tl$_x$ and In$_{15}$Se$_{85-x}$Tl$_x$ glasses lie in the range of 0.024-0.086cm$^2$/s and 0.0102-0.0388cm$^2$/s, respectively, depending on the thallium content. Whereas that of In$_{10}$Se$_{90}$ and In$_{15}$Se$_{85}$ base glasses are 0.0017 and 0.0014cm$^2$/s, respectively. It is found that the thermal diffusivity is comparatively high for both the series of glasses, which is consistent with the threshold type of electrical switching exhibited by these samples. The absorption spectra of these materials are obtained in the range of 380-1020nm. The $E_g$ is estimated from the plot of absorption coefficient as a function of wavelength by using Tauc relation. The $\alpha$ of these glasses increases and $E_g$ decreases with Tl upto $x$=13, beyond which trend reverses. Further, a maximum in $\alpha$ and minimum in $E_g$ are observed at the average coordination $<r>$ = 2.46 ($x$=13). Further, a minimum is observed in the composition dependence of $\alpha$ and a maximum in $E_g$ at the average coordination $<r>$ = 2.42 ($x$=6) is attributed to the rigidity percolation threshold. Correlation of the variation in OFF-state resistance with that of $\alpha$ is in agreement with the variation in threshold switching voltages observed earlier in both the series. These observations are consistent with the concepts of rigidity percolation in covalent networks.
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References


