CHAPTER-4

Thermal conductivity and heat capacity of Bi-Ge-Se and Pb-In-Se glasses exhibiting CTR

4.1 Introduction

Chalcogenide glasses are remarkably resistant to electrical doping by the incorporation of dopant atoms. The Fermi level is considered to be pinned effectively by the presence of charged defect centres [1, 2] and holes are the predominant charge carriers. The discovery that the addition of Bi to Ge-Se glass system changes the conduction type from $p$ to $n$ [3, 4] has therefore attracted a great deal of scientific attention. Later, it has been found that the phenomenon of carrier type reversal (CTR) occurs in some other glass systems also, when doped with Bi or Pb [5-8]. A number of papers have been published on various physical properties of chalcogenide glass systems exhibiting carrier type reversal [9-14].

Several mechanisms have been proposed to account for the doping behaviour of Bi. Most propose that the effect of Bi is to upset the equilibrium between oppositely charged native defect centres ($C^+_i$ and $C^-_i$), being incorporated in a charged state, thereby allowing the Fermi level to become unpinned. Electrical resistivity, thermoelectric power and optical absorption coefficient measurements on $\text{Ge}_{20}\text{Bi}_x\text{Se}_{80-x}$ system of glasses by Tohge et al. [15] shows a gradual decrease in resistivity with increasing Bi content up to 9 at.% and a decrease by about four...
orders of magnitude between $x = 9$ and 10%, but remained almost constant for $x > 10$ at.%. Composition dependence of Seeback coefficient shows a change of sign around 8 at. % of Bi.

In the Pb$_{25-x}$In$_2$Se$_{75}$ system, carrier type reversal occurs at $x = 5$ at. % [7]. Composition dependence of activation energy shows a clear change of slope around the critical composition, while Seebeck coefficient changes its sign from positive to negative. In this case, Pb enters the network in Pb$^{2+}$ ionized state; alter the concentrations of $C_1^+$ and $C_1^-$ centres that result in the unpinning of the Fermi level.

In this chapter we report the results of our work on the composition dependence of thermal parameters viz., thermal diffusivity, thermal effusivity, thermal conductivity and heat capacity of Ge$_{20}$Bi$_x$Se$_{80-x}$ $(2 \leq x \leq 12)$ and Pb$_x$In$_{25-x}$Se$_{75}$ $(2 \leq x \leq 15)$ systems measured using the photopyroelectric (PPE) and photoacoustic (PA) techniques. Thermal parameters show anomalous variations at the critical compositions at which CTR occurs. Experimental details, results obtained and a discussion of the results are given in the following sections.

4.2 Experimental details

Bulk semiconducting glasses with the general formulae Ge$_{20}$Bi$_x$Se$_{80-x}$ $(2 \leq x \leq 12)$ and Pb$_x$In$_{25-x}$Se$_{75}$ $(2 \leq x \leq 15)$ have been prepared by the conventional melt quenching technique described in detail in Chapter 2. Appropriate quantities of high purity constituents are taken in quartz ampoules, which are then evacuated and sealed and kept in a high temperature furnace at a temperature $\approx 1000^\circ$C for nearly 24 hours. Ampoules are then quenched in ice water, at a cooling rate $\sim 200$ Ks$^{-1}$, to obtain the glass samples.
Thermal parameters of the samples are determined using the PPE and PA techniques described already in Chapters 2 and 3. Samples of thickness ~ 0.5mm and area ~ 3x3 mm², prepared by cutting with a slow speed diamond wheel saw and polished by hand lapping are used for the measurements. Optical band gap of PbₓIn₂₋ₓSe₇₅ glasses are determined using a UV-Vis-NIR spectrophotometer following the absorption technique.

4.3 Results and discussion

The optical absorption spectrum of one sample of the Pb-In-Se system under study is shown in Fig. 4.1. Optical band gap is determined graphically from the absorption spectrum. The composition dependence of optical band gap for this glass system is shown in Fig. 4.2. It is seen that the optical band gap decreases with increasing Pb content.

Thermal parameters of the samples are determined using the PPE technique. The thermal thickness of the samples are ensured by plotting the PPE amplitude and phase with modulation frequency. These plots are shown in Figs. 4.3 to 4.6. Thermal diffusivity (\( \alpha \)) of the samples is determined from the PPE signal phase and thermal effusivity (\( e \)) from the PPE signal amplitude.

Composition dependences of \( \alpha \) and \( e \) for the two sets of glasses are shown in Figs. 4.7 and 4.8. Using the PA technique \( \alpha \) has been independently determined and these are shown in Figs. 4.9 and 4.10, which agrees well with the values obtained by PPE technique.
Fig. 4.1 Optical absorption spectrum of Pb$_2$In$_{23}$Se$_{75}$ glass

Fig. 4.2 Composition dependence of optical band gap ($E_g$) of Pb$_2$In$_{25}$, $x$Se$_{75}$ glasses. Uncertainties in the values are less than 2%
Fig. 4.3 Frequency dependence of PPE amplitude of Ge_{20}Bi_{x}Se_{80-x} glasses

Fig. 4.4 Frequency dependence of PPE phase of Ge_{20}Bi_{x}Se_{80-x} glasses
Fig. 4.5 Frequency dependence of PPE amplitude of Pb$_{1-x}$In$_x$Se$_{75}$ glasses

Fig. 4.6 Frequency dependence of PPE phase of Pb$_{1-x}$In$_x$Se$_{75}$ glasses
Fig. 4.7 Composition dependence of thermal diffusivity and thermal effusivity of Ge$_{20}$Bi$_x$Se$_{80-x}$ glasses employing PPE technique

Fig. 4.8 Composition dependence of thermal diffusivity and thermal effusivity of Pb$_x$In$_{25-x}$Se$_{75}$ glasses employing PPE technique
Fig. 4.9 Composition dependence of thermal diffusivity of Ge_{20}Bi_{x}Se_{80-x} glasses employing PA phase lag technique.

Fig. 4.10 Composition dependence of thermal diffusivity of Pb_{x}In_{25-x}Se_{75} glasses employing PA phase lag technique.
Sample mass densities have been determined using Archemedis principle, with liquid paraffin used as the densiometric fluid. Figs. 4.11 and 4.12 show the composition dependence of densities of Ge$_{20}$Bi$_x$Se$_{80-x}$ and Pb$_x$In$_{25-x}$Se$_{75}$ systems of glasses respectively. It is seen that density increases with Bi content for the first set and increases with Pb content for the second set.

Thermal conductivity and heat capacity of the samples have been determined using the relations \( K = e(\alpha)^{1/2} \) and \( c_p = e/\rho(\alpha)^{1/2} \). Figs. 4.13 and 4.14 show the composition dependence of \( K \) and \( c_p \) for Ge-Bi-Se and Pb-In-Se systems of glasses respectively. It can be seen that anomalous variations occur at the compositions corresponding to CTR in the composition dependence of thermal parameters.

From Fig. 4.7 it is seen that \( \alpha \) increases gradually with Bi content up to 7 at.% of Bi, beyond which it decreases, which agrees with an earlier report [16]. Thermal effusivity also shows a maximum at 7 at. % of Bi which corresponds to the \( p \rightarrow n \) transition composition. However, density increases monotonically with Bi content, as can be seen from Fig. 4.11. Thermal conductivity shows a maximum at \( x = 7 \), beyond which there is a sharp decrease. Heat capacity shows a sharp decrease around the critical composition (Fig. 4.13).

Various structural models have been put forward to account for CTR observed in Ge-Bi-Se glasses. These could be viewed as two groups, normally the electronic [17] and the structural inhomogeneity [18] groups. The electronic model considers the existence of Bi in various defect configurations, which perturbs the concentration of VAPs and results in the unpinning of the Fermi level. On the other hand, the structural inhomogeneity model assumes these glasses as phase separated into \( n \)-type tetradymite Bi$_2$Se$_3$ clusters with diameter less than 40Å [10] in the rest of
Fig. 4.11 Composition dependence of density of Ge$_{20}$Bi$_x$Se$_{80-x}$ glasses

Fig. 4.12 Composition dependence of density of Pb$_x$In$_{25-x}$Se$_{75}$ glasses
Fig. 4.13 Composition dependence of thermal conductivity and heat capacity of Ge$_{20}$Bi$_x$Se$_{80-x}$ glasses employing PPE technique

Fig. 4.14 Composition dependence of thermal conductivity and heat capacity of Pb$_x$In$_{25-x}$Se$_{75}$ glasses employing PPE technique
the matrix at the microscopic level. Therefore at the conductivity percolation [18], or mechanical threshold [10], these glasses show a conductivity change. Measurements on the double stage crystallization in these glasses support the phase separations at the microscopic level [19].

According to the constraints theory by Phillips and Thorpe [10, 20], for the IV$_x$-V$_{100-x}$ binary glasses, mechanical threshold occurs around $x_c = 20$ at. %. However, for Ge$_x$Se$_{100-x}$ glasses, mechanical threshold occurs at a slightly higher value of $x$ ($x = 23$ at. %) [21]. This is attributed to the fact that not all the bond bending constraints are effective in hindering intercluster motion. Ge$_{20}$Bi$_x$Se$_{80-x}$ glasses can be represented as Bi$_{2x}$Se$_{3x}$ + Ge$_{20}$Se$_{80-5y}$. At lower Bi percentage, the localized unconstructed Se$^-$ defects are present at the Bi$_2$Se$_3$ tetramite surfaces. Theses clusters are uniformly dispersed in the rest of GeSe$_2$ and Se flexible chains, which make the material $p$-type. As the value of $x$ increases, the mechanical stiffness of the combined medium increases. At $x = 6$ at. %. Bi$_6$Ge$_{20}$Se$_{74} = Bi_6Se_9 + Ge_{20}Se_{65}$ and Ge$_{20}$Se$_{65} = Ge_ySe_{100-y}$ with $y = 24$, which agrees with the elastic stiffness threshold composition $y_c = 23$ of the glasses found in other experiments [21]. For $x \geq 6$ at. % the mechanical misfit between these clusters is high, which leads to the plastic deformation of tetradyrmite clusters and as a result, the Se$^-$ density increases. The high density of these Se$^-$ defects evolves in a percolative manner at mechanical threshold and produces the $n$-type conduction in these glasses.

According to the charged dangling bond model, when bismuth is added to the Ge-Se network, the equilibrium between positively and negatively charged dangling bonds which pin the Fermi level near the middle of the gap gets affected
[3]. As a result, the Fermi level gets unpinned and moves towards the conduction band.

Elliot and Steel [22] have suggested that the $p\rightarrow n$ transition in these glasses is accompanied by a significant change in the local structural order surrounding the Bi impurity atoms. At low Bi concentrations, Bi-Se bond remains covalent in character and at higher Bi concentrations it becomes partially ionic with slight increase in bond lengths. According to them, the process of dissolution of Bi impurity in the Se rich regions at lower concentrations produce Se$^-$ centres making the Bi impurities positively charged. Further addition of Bi in larger concentrations do not produce appreciable additional defects as it enters in a modified network. Consequently, the absorption edges are not appreciably affected. According to Bhatia et al. [23], at lower Bi concentrations there is little change in activation energy $E_{av}$, where as at higher concentrations, a considerable decrease in $E_{av}$ is observed, which can be explained on the basis of the shift of the Fermi level towards the conduction band.

The dependence of thermal diffusivity and thermal conductivity on Bi concentration show maxima at the critical compositions that lies close to the mechanical threshold predicted by the constraints model. The increase in $\alpha$ and $K$ may be attributed to the mechanical stiffening of Ge-Se network with Bi$_2$Se$_3$ clusters dispersed in it. The elastic misfit between the Bi$_2$Se$_3$ cluster and GeSe$_2$ network is relieved by distortions of the Se atom chains for $x < 7$. When $x \geq 7$, the grown up Bi$_2$Se$_3$ clusters find themselves embedded in a matrix of increased mechanical rigidity. Heat capacity shows a sharp decrease around the transition composition, which is in agreement with an earlier report [19].
For Pb$_2$In$_{25-x}$Se$_{75}$ system, carrier type reversal occurs around $x = 5$ at. % \cite{7}. From Fig. 4.2, it can be seen that the optical band gap decreases with increasing Pb content. Thermal diffusivity ($\alpha$) shows a minimum and thermal effusivity ($\epsilon$) a maximum at $x = 5$. Thermal conductivity ($K$) and heat capacity increase up to the critical composition corresponding to CTR and thereafter decrease.

According to Mehra \textit{et al.} \cite{7}, the Fermi level is pinned and placed towards the valence band at an energy of 0.73 eV for In$_{25}$Se$_{75}$. However, when Pb enters the network, the band picture changes drastically. It is assumed that Pb enters the network in Pb$^{2+}$ ionized state as in other Pb containing chalcogenide glasses. Consequently Se$^{\cdot}$ centres are formed, and the equilibrium between Se$^{\cdot}$ and Se$_3^{\cdot}$ centres gets disturbed. As a result, the Fermi level gets unpinned and moves towards the conduction band resulting in $n$-type conductivity.

Since Pb is more electro positive than Se or In, the lone-pair electrons adjacent to Pb atoms will have higher energies than those remote from Pb atoms. This results in a broadening and tailing of the valence band. This leads to the observed decrease in $E_g$ with increasing Pb concentration.

The thermal parameters viz., $\alpha$, $\epsilon$, $K$ and $c_p$ of Pb$_2$In$_{25-x}$Se$_{75}$ glasses show anomalous variations at $x = 5$. While $\alpha$ shows a minimum, $\epsilon$ shows a maximum. $K$ and $c_p$ decrease beyond $x = 5$. As already stated in Chapter 3, thermal conductivity in these glasses is dominated by the transport of heat by the vibration modes of the network. As the electron concentration is increased during $p\rightarrow n$ transition, the phonon mean free path gets reduced. This results in the decrease in thermal conductivity beyond the critical composition.
4.4 Conclusions

Thermal parameters of Ge-Bi-Se and Pb-In-Se systems of glasses exhibiting carrier type reversal are studied as functions of compositions. It is found that the carrier type reversal gets reflected in the thermal parameters measured using the PPE technique. A decrease is observed in thermal conductivity beyond the $p$-$n$ transition composition. This is explained on the basis of enhancement in carrier concentration in the samples.
References

1. R. A. Street and N. F. Mott, Phys. Rev. Lett. 35 (1975) 1293