CHAPTER-5

Photoconductivity in chalcogenide glass systems exhibiting CTR

5.1 Introduction

The effect of impurities on the electronic properties of chalcogenide glasses has been a subject of great interest ever since their discovery [1]. In recent years, a great deal of efforts has been expended to understand the role of Bi or Pb in controlling the mechanism of electrical conduction in bulk chalcogenide glasses. It is known that bulk semiconducting glasses behave like intrinsic p-type semiconductors and are insensitive to impurity doping. Fermi level is considered to be pinned due to the equilibrium between positively and negatively charged dangling bonds [2, 3]. However, it is found that when Bi or Pb is added to certain chalcogenide glass systems, a carrier type reversal (CTR) from p to n occurs at certain doping levels [4-9]. Several researchers have reported results on electrical conductivity, activation energy, thermoelectric power, thermal analysis, structure and vibration states of Pb as well as Bi doped glasses across the compositions at which carrier type reversals are reported to occur [10-17].

In this chapter, we report the results of our photoconductivity measurements in Pb$_{20}$Ge$_x$Se$_{80-x}$ (17 ≤ x ≤ 24), Pb$_y$Ge$_{42-y}$Se$_{58}$ (0 ≤ y ≤ 20) and Pb$_x$In$_{25}$Se$_{75}$ (0 ≤ x ≤ 15) systems of glasses, all of them exhibiting CTR at definite compositions. As already stated in Chapter 1, p to n transitions are reported to occur in these systems
at specific compositions. Photoconductivity as well as photodetectivity, which is the ratio of photoconductivity to the corresponding dark conductivity, have been measured as a function of composition, and it is seen that the carrier type reversal gets clearly reflected in these properties. Temperature dependence of these parameters have also been studied and reported. The results are analyzed in terms of the existing photoconductivity models. The experimental methods, results obtained and a discussion of the results are outlined in the following sections.

5.2 Sample preparation and experimental details

Bulk glasses in the required composition range have been prepared by the conventional melt quenching technique. Appropriate quantities of high purity constituent elements are weighed and taken in quartz ampoules, which are then evacuated and sealed. Ampoules are then kept in a high temperature furnace at 1000°C for 24 hours with intermittent rotation of the ampoules for uniform mixing of the constituents. Ampoules are then quenched in ice water at a cooling rate ~ 200 K s⁻¹. The amorphous natures of the samples have been confirmed by XRD technique.

Photoconductivity measurements are carried out as described in Chapter 2. Samples with thickness of the order of 0.5 mm and surface area of the order of 3 x 3 mm² have been used for the present measurements. The sample is sandwiched between two SnO₂ coated conducting, transparent glass plates acting as electrodes. The sample holder is kept in an enclosed chamber, which can be evacuated and heated. The temperature of the sample is measured and controlled within ± 0.1 K using a temperature controller (Lakeshore Cryotronics, Model DRC 82C). A
120mW He-Cd laser ($\lambda = 442$ nm) is used as the source of light to initiate photoconduction. The current is measured using a picoammeter in a two probe setup. Steady state (d. c.) photoconductivity is obtained as the difference between the total conductivity under illumination and the corresponding dark conductivity.

The electrical activation energy of all the samples has been determined by measuring their dark conductivity ($\sigma$) as a function of temperature ($T$) and plotting $\log \sigma$ versus $1/T$.

### 5.3 Results

The composition dependence of photoconductivity and photodetectivity for Pb$_{20}$Ge$_{x}$Se$_{80-x}$ system of glasses are shown in Fig. 5.1. At $x = 21$, which corresponds to the $p \rightarrow n$ transition composition, photoconductivity shows a minimum, while photodetectivity shows a sharp dip. Fig. 5.2 shows the composition dependence of photoconductivity and photodetectivity for the Pb$_{y}$Ge$_{42}$Se$_{58}$ system. In this case, at the critical composition $y = 8$, both photoconductivity and photodetectivity show sharp increases. The composition dependence of photoconductivity and photodetectivity of Pb$_{25}$In$_{25}$Se$_{75}$ system shown in Fig. 5.3, also exhibits a similar behaviour at $x = 5$, which is the critical composition at which CTR occurs.
Fig. 5.1 Composition dependence of photoconductivity and photodetectivity of Pb$_{20}$Ge$_x$Se$_{80-x}$ glasses

Fig. 5.2 Composition dependence of photoconductivity and photodetectivity of Pb$_y$Ge$_{42-y}$Se$_{58}$ glasses
Fig. 5.3 Composition dependence of photoconductivity and photodetectivity of Pb$_x$In$_{25-x}$Se$_{75}$ glasses

Temperature dependence of photoconductivity and photodetectivity has also been carried out on selected compositions on either side of the critical composition for all the three glass systems. The results are shown in Figs. 5.4, 5.5 and 5.6. It may be noted that for all the compositions in the three series, photoconductivity increases with temperature, while photodetectivity decreases with temperatures. Figs. 5.7, 5.8 and 5.9 show the composition dependence of activation energy for electrical conduction for the three systems. Uncertainties in the measured values are less than 2%. Anomalous variations occur at the transition compositions for all the three glass systems.
Fig. 5.4a Temperature dependence of photoconductivity of Pb$_{20}$Ge$_x$Se$_{80-x}$ glasses

Fig. 5.4b Temperature dependence of photodetectivity of Pb$_{20}$Ge$_x$Se$_{80-x}$ glasses
Fig. 5.5a Temperature dependence of photoconductivity of Pb$_2$Ge$_{42-y}$Se$_{58}$ glasses.

Fig. 5.5b Temperature dependence of photodetectivity of Pb$_2$Ge$_{42-y}$Se$_{58}$ glasses.
Fig. 5.6a Temperature dependence of photoconductivity of Pb$_{x}$In$_{25-x}$Se$_{75}$ glasses

Fig. 5.6b Temperature dependence of photodetectivity of Pb$_{x}$In$_{25-x}$Se$_{75}$ glasses
Fig. 5.7 Composition dependence of activation energy of \( \text{Pb}_{20}\text{Ge}_{x}\text{Se}_{80-x} \) glasses

Fig. 5.8 Composition dependence of activation energy of \( \text{Pb}\text{yGe}_{12-y}\text{Se}_{58} \) glasses
5.4 Discussion of Results

The results show that the \( p \rightarrow n \) transitions exhibited by the Pb-Ge-Se and Pb-In-Se systems are clearly reflected in photoconductivity measurements. For \( \text{Pb}_2 \text{Ge}_x \text{Se}_{80-x} \) system, photoconductivity decreases up to the transition composition and then increases, exhibiting a threshold minimum, while photodetectivity shows a sharp dip. For \( \text{Pb}_2 \text{Ge}_{12} \text{Se}_{58} \) and \( \text{Pb}_2 \text{In}_{25} \text{Se}_{75} \) systems, both photoconductivity and photodetectivity show sharp increases at the critical composition.

Presence of charged defect pairs of the type \( C_i^+ \) and \( C_i^- \) are characteristic of chalcogenide glasses [18]. Their formation can be represented by a reaction of the form,

\[
2C_i^0 \rightarrow C_i^- + C_i^+
\]  

(5.1)
where $C$ represents a chalcogen. The superscript is the formal charge on the chalcogen and the subscript denotes the number of covalent bonds by which the chalcogen atom is connected to other atoms. Charge transport in chalcogenide glasses occurs through the participation of charged defects. The motion of $C_i^-$ centres in chalcogenide glasses is more facile than that of $C_i^+$ centres so that chalcogenide glasses are generally $p$-type conductors.

When Pb is introduced into the Ge-Se network, $C_i^-$ centres are created and their concentration is equal to that of Pb itself. Vaidhyanathan et al. [16] have calculated the values for the ratios of different types of defects in Pb$_x$Ge$_{42-y}$Se$_{58}$ glasses. It is seen that as the Pb atom concentration increases from 5 to 20, the value of $[C_i^-]/[C_2^0]$ increases by a factor of 10, while the value of $[C_i^+]/[C_2^0]$ decreases by a factor of 10. This means that the ratio, $[C_i^-]/[C_i^+]$ vary by nearly two orders of magnitude. For low values of $y$, $C_i^+$ centres are major charge carriers and the glasses are $p$-type. As $y$ increases, $C_i^-$ centres become the dominant charge carriers and the system switches to an $n$-type semiconductor. At the same time, the activation energy decreases with $y$, which means that the concentration of $C_i^+$ increases with $y$, and so the transition is gradual in this case. For Pb$_{20}$Ge$_x$Se$_{80-x}$ system, activation energy increases with increasing $x$. Therefore, the concentration of $C_i^+$ decreases and $C_i^-$ increases, so that $p \rightarrow n$ transition in this system is rather sharp.

Vaidhyanathan et al. have proposed a band structure model to account for the transition exhibited by the Pb-Ge-Se system [16]. The proposed band energy diagram is shown in Fig. 5.10. Here it is assumed that Ge is always tetrahedrally coordinated and Pb is octahedrally coordinated. In this structure, the top of the lone
pair band is constituted of $C_1^-$ states. Electron transport between $C_1^-$ states takes place through an empty sp$^3$d$^2$ state. When the Pb concentration is increased, sp$^3$d$^2$ band as well as the $C_1^-$ states increases rapidly, and hence the electronic contribution to conductivity also increases. Thus, the $p\rightarrow n$ transition in Pb$_y$Ge$_{42-y}$Se$_{58}$ system occurs due to the spreading of the sp$^3$d$^2$ band, which causes a decrease in the sp$^3$d$^2$ lone pair band gap. In Pb$_{20}$Ge$_x$Se$_{80-x}$ system, for small values of $x$, sp$^3$d$^2$ band is well above the lone pair band. As the value of $x$ increases, the lone pair band spreads upwards in energy because of the perturbation of lone pair levels caused by the presence of larger number of tetrahedrally bonded centres. As a result, the sp$^3$d$^2$ band and the lone pair band become closer, and the electronic contribution to the conductivity increases. Thus the CTR in Pb$_{20}$Ge$_x$Se$_{80-x}$ system occurs due to the upward movement of the lone pair levels, closing in the sp$^3$d$^2$ lone pair band gap.

For Pb$_y$Ge$_{12-y}$Se$_{58}$ system, the composition dependence of photoconductivity shows that photoconductivity increases with $y$, with a sharp increase at $y \approx 8$. For this series activation energy decreases with $y$, with a clear slope change at the critical composition. Also, in this case, a spreading of the sp$^3$d$^2$ band occurs resulting in CTR. For the Pb$_{20}$Ge$_x$Se$_{80-x}$ system, photoconductivity shows a minimum at $x = 21$. For this series, activation energy shows a maximum at that composition and CTR occurs due to an upward shift of the lone pair levels.

In the case of Pb$_x$In$_{25-x}$Se$_{75}$ system, it is seen that both photoconductivity and photodetectivity show sharp increases at $x = 5$, the critical composition. In this case also, it is assumed that Pb atoms are present in the Pb$^{2+}$ ionized state. The formation of negatively charged Se centres, which occurs as a result of the addition of Pb,
disturbs the equilibrium between Se$_{1}^{-}$ and Se$_{3}^{+}$ centres. Since Pb is more electropositive than selenium or indium, the lone pair electrons adjacent to Pb atoms will have higher energies than those remote from Pb atoms, causing a broadening and tailing of the lone pair valence band.

Photoconductivity, which is the excess conductivity due to incident radiation, can be expressed as [19].

$$
\Delta \sigma = e(\Delta n \mu_n + \Delta p \mu_p)
$$

(5.2)

where $\Delta n$ and $\Delta p$ are the changes in the electron and hole densities due to irradiation and $\mu_n$ and $\mu_p$ are their respective mobilities in the medium. The photoconducting behaviour of these samples is close to that of a Type II photoconductor as per the ABFH model [20]. According to this model, the photoconductivity behaviour of
Chalcogenide glasses have been classified into Type I and Type II. For Type I photoconductors, photoconductivity has a maximum at a specific temperature $T_m$. For $T < T_m$, photoconductivity magnitude is generally larger than the dark conductivity, while for $T > T_m$, it is smaller than dark conductivity. For Type II photoconductors, the photoconductivity maximum is absent. Photoconductivity increases monotonically with increasing temperature and in general, photoconductivity is much smaller than dark conductivity. On the basis of the energy level diagram suggested by the ABFH model, transitions from localized to localized states are dominant in a Type II photoconductor, over the whole measurable range. The temperature dependence of photoconductivity of Pb-Ge-Se and Pb-In-Se systems show that photoconductivity increases monotonically with temperature in the temperature range in which measurements are carried out. Moreover, the magnitude of photoconductivity is less than that of dark conductivity. This means that the photoconductivity behaviour of these samples is close to that of a Type II photoconductor.

5.5 Conclusions

Photoconductivity measurements in Pb$_{20}$Ge$_{75}$Se$_{80-x}$, Pb$_3$Ge$_{42}$Se$_{58}$ and Pb$_3$In$_{25-x}$Se$_{75}$ systems of glasses have been carried out. All the three systems exhibit $p \rightarrow n$ transition, and these transitions are clearly reflected in the present measurements. Temperature dependence of photoconductivity and photodetectivity has been reported and the results are analyzed in terms of the existing models. The results show that all the samples under study show photoconductivity properties close to Type II photoconductors as per the ABFH model.
References