CHAPTER 3

ADSC Studies on Thallium Doped Ge-Se Chalcogenide Glasses

3.1. Introduction

Chalcogenide glassy semiconductors exhibit a number of interesting properties that can be employed in devices. The feasibility of technological applications of chalcogenide glasses has stimulated interest to investigate new compositions. The binary Germanium-Selenide is one of the most studied chalcogenide glassy systems and it has been established that the structure and physical properties in this system are highly composition dependent [1-3]. Unlike most crystalline systems, the structural and physical changes are continuous. Thallium containing Ge-Se chalcogenide glasses have been extensively studied during last few decades. In particular, they have been widely examined for electrical and optical properties by a number of researchers. It is found that the addition of thallium to amorphous chalcogenides is accompanied by a marked change in their structural and physical properties [4-7]. Among thallium doped chalcogenides, bulk Ge-Se-Tl glasses have attracted attention for their potential applications in acousto-optical devices [8, 9].

In the present study, Ge-Se-Tl glasses have been considered for thermal investigations. In particular, the influence of local structure on different thermal properties such as glass transition temperature, crystallization temperature and relaxation enthalpy, etc., of these glasses, has been studied.
3.2. Preparation of Ge-Se-Tl glasses

Vitreous chalcogenides belonging to the Ge$_{10}$Se$_{90-x}$Tl$_x$ system (15 \( \leq x \leq 34 \)) are prepared by melt quenching technique discussed in section 2.2. Appropriate quantities of high purity constituent elements are weighed and transferred in to quartz ampoules, evacuated to \( 10^{-5} \) Torr and sealed. The ampoules are heated in a rotary furnace to a temperature of about \( 980^\circ\)C and maintained at this temperature for 24 hours. The ampoules containing the melt are rotated at 10 rpm to homogenize the melt. The homogenizing temperature is chosen well above the melting points of the constituent elements. After homogenizing, ampoules are subsequently quenched in a mixture of ice water and NaOH to obtain bulk glassy samples. The amorphous nature of the quenched samples is confirmed by X-ray diffraction studies.

3.3. ADSC Studies on Ge-Se-Tl Glasses

ADSC experiments are carried out using a Mettler Toledo 822\textsuperscript{e} DSC instrument with the aid of STAR\textsuperscript{e} software. Temperature calibration is achieved using indium and zinc as standards, and the heat flow calibration is done using indium. A blank run is made prior to the actual measurements, with an empty aluminum pan on the reference side and an empty pan with a lid on the sample side, to calibrate the heat flow signal, to correct the amplitude and to eliminate cell asymmetry. The samples are polished into small pieces nearly of uniform thickness, weighed (~15 mg) and sealed in aluminum pans. An empty aluminum pan is used as a reference. Experiments are undertaken in the temperature range of 30-300°C, at the scanning rate of 3°C/min and a modulation rate of 1/60 Sec. Argon is used as the purge gas at a flow rate of 80 ml/min.

In the ADSC experiments, the inflexion point in the reversible heat flow (RHF) endotherm is taken to be \( T^* \). The enthalpy change \( \Delta H_{\text{NR}} \) (where NR denotes non-reversing) obtained from the non-reversible heat flow (NHF) curve is used as a measure of the relaxation enthalpy of the glass during the glass transition. The first exothermic peak observed in NHF curve is taken to be first crystallization temperature \( T_{\text{cl}} \) and the
corresponding area under this exothermic peak is taken as crystallization enthalpy change $\Delta H_c$.

Figure 3.1. Representative Total Heat Flow curves of Ge$_{10}$Se$_{90-x}$Tl$_x$ samples obtained using ADSC. Compositions with $21 \leq x \leq 29$ show two crystallization reactions, while for $x \leq 19$ and $x \geq 31$, single crystallization reaction is seen.
Figure 3.2. Non-reversible heat flow and reversible heat flow curves of a representative Ge_{10}Se_{67}Tl_{23} sample of the Ge_{10}Se_{90-x}Tl_{x} (15 \leq x \leq 34) series of glasses.

The thermal scans on the samples are repeated at least three times to determine the experimental errors and reproducibility of the measured thermal parameters. The deviation in \( T_g \) and \( T_c \), measured for heating scans are found to be within \( \pm 1^\circ\text{C} \); for \( \Delta H_c \) and \( \Delta H_{NR} \) the deviations are within \( \pm 0.05 \text{ J/g} \).

Figure 3.1 shows the total heat flow curves obtained using ADSC for representative samples of Ge_{10}Se_{90-x}Tl_{x} (15 \leq x \leq 34) series. These results indicate the presence of a single glass transition temperature \( T_g \) and two distinct crystallization temperatures \( T_{c1} \) & \( T_{c2} \) for the composition range \( 21 \leq x \leq 29 \). However, only one crystallization reaction is seen for compositions \( x \leq 19 \) and \( x \geq 31 \). Further, figure 3.2 displays the evaluation of non-reversing and reversing heat flow curves obtained using ADSC, for a representative Ge_{10}Se_{67}Tl_{23} sample.

73
3.3.1. Glass Transition Temperature and Network Connectivity

![Graph showing composition dependence of glass transition temperature (T_g) of Ge_{10}Se_{90-x}Tlx (15 ≤ x ≤ 34) glasses.]

The dependence of the glass transition temperature $T_g$ on the thallium content, obtained from the reversing component in the ADSC runs is shown in figure 3.3. It is evident from the figure 3.3 that the $T_g$ of Ge_{10}Se_{90-x}Tlx glasses decreases with the thallium concentration, in the composition range 15 ≤ x ≤ 22. Around x = 22, an inflexion is seen in the composition dependence of $T_g$. The decrease in $T_g$ continues in the composition range 23 ≤ x ≤ 29, with a saturation seen around x = 29.

It has been established that the composition dependence of the glass transition temperature of glasses has an intimate relation with the evolution of their network connectivity. It is generally accepted that $T_g$ increases when the connectivity of the network increases. The stochastic agglomeration theory (SAT) provides a quantitative means to predict $T_g$ as a function of glass composition [10, 11]. Further, Tanaka [12] has derived a relation connecting the glass transition temperature and the parameters that quantify the network connectivity, such as the average coordination number 〈r〉, i.e.
\[ \ln T_g = 1.6(r) + 2.3 \quad (3.1) \]

On the basis of thermodynamical consideration, Gibbs and DiMarzio obtained an empirical relationship between the glass transition temperature and the density of cross-linking agents inserted into molecular chains \([13, 14]\). Varshneya and co-workers \([15]\) later observed that \(T_g\) follows a modified Gibbs-DiMarzio equation in multi component chalcogenide glass, expressed as:

\[ T_g = \frac{T_o}{1 - \beta(r - 2)} \quad (3.2) \]

Where \(T_o\) is the glass transition temperature of the initial polymeric chain and \(\beta\) is a system dependent constant, which can be fitted from the experimental data or determined from the nature of the involved atoms \([11]\).

It also been realized recently that the evolution of the glassy network and consequently the glass transition temperature, has a more direct correlation with the average bond energy instead of the mean coordination number. The earlier investigations on several binary and ternary chalcogenide systems, such as Ge-Se, Ge-S, Si-Se, Ge-As-Se, Ge-Sb-Se, Ga-Ge-Se, Ge-Sb-Te, etc., indicate that the glass transition temperature increases with increase in overall mean bond energy \(\langle E \rangle\) \([16]\).

According to covalent bond approach (CBA) proposed by Kerner and Micoulaut \([17-19]\), the mean bond energy of the average cross-linking per atom \(\langle E_c \rangle\) in a \(A_{1-x}B_xC_y\) glassy system at high chalcogen content is given by

\[ \langle E_c \rangle = x r_B E_{A-B} + y r_C E_{A-C} \quad (3.3) \]

Where, \(E_{A-B}\) and \(E_{A-C}\) represent the A-B and A-C bond energies \([20]\). The average bond energy per atom of the remaining matrix \(\langle E_m \rangle\) is defined by:
Chapter 3: ADSC Studies on Thallium Doped Ge-Se Chalcogenide Glasses

\[
\langle E_m \rangle = \frac{2 \left( \frac{\langle r \rangle}{2} - x r_g - y r_c \right) E_{4,4}}{\langle r \rangle} \quad (3.4)
\]

Here \( \langle r \rangle = 2(1 - x - y) + r_g x + r_c y \) \quad (3.5)

The overall mean bond energy of the network \( \langle E \rangle \) is the sum of the above two contributions, i.e.

\[
\langle E \rangle = \langle E_c \rangle + \langle E_m \rangle . \quad (3.6)
\]

Generally, it has been suggested that metal atoms would coordinate tetrahedrally in chalcogenide semiconductors making coordinate bonds with the chalcogen atom [21]. The formation of such tetrahedrally coordinated metal atom in Ge–Se system is reported by Kosek et al [22]. Figure 3.4 shows the composition dependence of mean bond energy \( \langle E \rangle \) of Ge-Se-Tl glasses, obtained using coordination and 4 and 2 for Ge and Se atoms respectively and assuming a coordination of 4 for Tl. It can be seen from figure 3.4 that the calculated mean bond energy \( \langle E \rangle \) for Ge-Se-Tl glasses increases with the addition of thallium atoms. Based on this, one should expect an increase in the glass transition temperature of Ge-Se-Tl glasses, with the addition of thallium. However, it can be seen from figure 3.3 that the \( T_g \) of \( \text{Ge}_{10}\text{Se}_{90-x}\text{Tl}_x \) glasses decreases considerably with the addition of thallium atoms. A similar variation of \( T_g \) with the addition of thallium atoms has been noticed in As-Te-Tl glasses also [23].

The earlier investigation on Ge-Se-Tl glasses, reveal that Tl does not form bonds with Ge, and the units that may constitute the local structure are [24, 25]:

\[
\text{Se}^-\text{Tl}^+ \\
-\text{Se} - \text{Ge} - \text{Se} - \\
\text{Se}^-\text{Tl}^+
\]

or \( \text{Tl}^+\text{Se}^-\text{GeSe}_{2/3}\text{Se}^-\text{Tl}^+ \)

76
Chapter 3: ADSC Studies on Thallium Doped Ge-Se Chalcogenide Glasses

3.3.2. Crystallization Behavior of Ge-Se-Tl Glasses

The variation of the first crystallization temperature \( T_{cl} \) with the thallium concentration obtained from the non-reversing component in the ADSC runs is shown in figure 3.5. A similar multistage crystallization has been reported to occur in many other Ge-Se based glassy systems such as Ge-Se-Ag [26], Ge-Se-Te [27], etc. It is seen from the figure that the composition dependence of \( T_{cl} \) of Ge\(_{10}\)Se\(_{90-x}\)Tl\(_x\) glasses is very similar to that of \( T_g \) for lower thallium content; \( T_{cl} \) of Ge\(_{10}\)Se\(_{90-x}\)Tl\(_x\) glasses decreases with the
thallium concentration, in the composition range $15 \leq x \leq 22$. Around $x = 22$, an inflexion is seen in the composition dependence of $T_{c1}$. A marginal decrease is seen in $T_{c1}$ in the range $23 \leq x \leq 29$. Above $x = 29$, $T_{c1}$ is found to increase with $x$.

![Figure 3.5](image)  

**Figure 3.5.** Compositional variation of first crystallization temperature ($T_{c1}$) of $Ge_{10}Se_{90-x}Tlx$ ($15 \leq x \leq 34$) glasses.

It is generally known that in non-isothermal study, the stability of the glasses is usually investigated in terms of two independent factors i.e., ($T_{c1} - T_g$) and $\Delta H_c$. In the present study, experimental evaluation of the enthalpy released, $\Delta H_c$ during crystallization has been determined by measuring the area under the crystallization peak, obtained from the non-reversing component in the ADSC runs.

Figure 3.6 shows the compositional dependence of $T_{c1} - T_g$ and crystallization enthalpy change $\Delta H_c$ obtained from the ADSC runs at a heating rate of $3^\circ C/min$. It is evident from figure 3.6, that $T_{c1} - T_g$ exhibits an initial increase in the composition range $15 \leq x \leq 19$. Above $x = 19$, a decrease is seen in $T_{c1} - T_g$, which leads results in a broad trough in the composition range $21 \leq x \leq 25$. A sharp increase is seen in $T_{c1} - T_g$ above $x = 25$. On the other hand, $\Delta H_c$ exhibits an initial decrease in the composition range $15 \leq
$x \leq 19$. A sharp increase is seen in $\Delta H_c$ above $x = 20$, which leads to a local maximum around $x = 22$. A continuous decrease is seen in $\Delta H_c$ in the composition range $22 \leq x \leq 33$.

![Figure 3.6](image)

**Figure 3.6.** Composition dependence of $(T_{cl} - T_g)$ and crystallization enthalpy ($\Delta H_c$) of $Ge_{10}Se_{90-x}Tl_x$ ($15 \leq x \leq 34$) glasses.

Since the release of energy $\Delta H_c$ is associated with the meta-stability of the glasses, large values of $\Delta H_c$ are normally associated with the least stable glasses, corresponding to a lower $(T_{cl} - T_g)$ values [24, 28]. The present results indicate that when compared to other compositions, the $Ge_{10}Se_{90-x}Tl_x$ glasses in the composition range ($29 \leq x \leq 34$) have higher $T_{cl} - T_g$ values & also lower $\Delta H_c$ values and hence are likely to be more thermally stable against crystallization [29].

### 3.3.3. Composition Dependence of Relaxation Enthalpy

Figure 3.7 shows the variation of the change in the enthalpy at the glass transition with Tl content, obtained from the non-reversing heat flow ($\Delta H_{NR}$) for Ge-Se-Tl glasses. It is known that $\Delta H_{NR}$ is connected with kinetic processes and the enthalpic changes
accompanying structural reorganization of the glass network as it softens near $T_g$. The $\frac{dH_{NR}}{dT}$ term shows a peak precursor to the glass transition and the integrated area-under-the-peak $\Delta H_{NR}$ in relaxed bulk glasses gives the relaxation enthalpy. Besides, the non-reversing endotherm $\Delta H_{NR}$ is a signature of ergodicity-breaking events when structural changes of a glass forming liquid cease near $T_g$. Recent studies have revealed that $\Delta H_{NR}$ nearly vanishes across the compositional window, and the glass transitions become thermally reversing in character. The glass compositions in this thermally reversing window are said to be non-ageing and stress free [30-32]. The minimum observed in $\Delta H_{NR}$ of Ge$_{10}$Se$_{90-x}$Tl$_x$ glasses around $x = 22$, indicates the possibility of a self-organized glassy network in the Ge$_{10}$Se$_{90-x}$Tl$_x$ glasses in the composition range $19 \leq x \leq 24$. The anomalies in the thermal parameters observed, such as the inflexion in the composition dependence of $T_g$ & $T_c$, the trough in $T_c - T_g$ and the maximum in $\Delta H_c$ are associated with the thermally reversing window in Ge$_{10}$Se$_{90-x}$Tl$_x$ glasses around the composition $x = 22$.

![Figure 3.7](image-url)  

**Figure 3.7.** Compositional variation of relaxation enthalpy ($\Delta H_{NR}$) obtained from the non-reversing heat flow of Ge$_{10}$Se$_{90-x}$Tl$_x$ ($15 \leq x \leq 34$) glasses.
3.4. XRD Studies

Powder X-ray diffraction studies (using the Cu K\textsubscript{a} line with $\lambda = 1.5405$ Å) of bulk glasses are taken after annealing well above their crystallization temperatures for 2hrs to find out the products of the crystallization reactions. Figure 3.8 shows the XRD pattern of a representative Ge\textsubscript{10}Se\textsubscript{59}Tl\textsubscript{31} sample annealed well above its first crystallization temperature, $T_{c1}$ for 2hours, which indicates the existence of tetragonal-Tl\textsubscript{2}Se\textsubscript{2} and GeSe\textsubscript{4}Tl\textsubscript{2} phases in the annealed sample.

![XRD Pattern](image)

**Figure 3.8.** The X-ray diffraction pattern of a representative Ge\textsubscript{10}Se\textsubscript{59}Tl\textsubscript{31} sample annealed well above $T_{c1}$ for 2hours.

3.5. Micro-Structural Studies

The micro structural observations have also been performed using Scanning Electron Microscopy (SEM). Figure 3.9 shows the SEM microphotograph of a representative Ge\textsubscript{10}Se\textsubscript{68}Tl\textsubscript{22} glassy sample, indicating the presence of phase separation (also revealed by the presence of two crystallization temperatures). The growth of
crystallites is clearly seen in figure 3.10, which is a micrograph of the Ge_{10}Se_{68}Tl_{22} sample annealed at $T_{c2}$ for 2 hours.

**Figure 3.9.** SEM micrograph of a representative Ge_{10}Se_{68}Tl_{22} sample showing phase separation.

**Figure 3.10.** SEM micrograph of a representative Ge_{10}Se_{68}Tl_{22} sample annealed for 2 hours.

### 3.6. Summary

The thermal behavior of melt quenched Ge_{10}Se_{90-x}Tl_x (15 ≤ x ≤ 34) glasses has been investigated using ADSC. Glasses in the present series have been found to exhibit single glass transition temperature. On the other hand, these glasses are found to exhibit two distinct crystallization reactions at temperatures $T_{c1}$ & $T_{c2}$ in the composition range 21 ≤ x ≤ 29 but single crystallization temperature for compositions x ≤ 19 and x ≥ 31. The glass transition temperature, $T_g$, which is a measure of global connectivity decreases substantially with the addition of Tl content suggesting a decrease in the network connectivity.

Further, the composition dependence of $T_g$ & $T_{c1}$ of Ge_{10}Se_{90-x}Tl_x (15 ≤ x ≤ 34) glasses are found to exhibit an inflexion around the composition x = 22. Also, a trough is
seen in the variation with composition of thermal stability \((T_{cl} - T_g)\) and a maximum is noticed in the crystallization enthalpy \((\Delta H_c)\) around this composition. In addition, the relaxation enthalpy has been found to exhibit a minimum in the composition range \(19 \leq x \leq 24\), which indicates the presence of a self-organized network in the Ge-Se-Tl glassy system. The anomalies in the composition dependence of \(T_g\), \(T_{cl}\), \(T_{cl} - T_g\) and \(\Delta H_c\) are associated with the thermally reversing window in Ge\(_{10}\)Se\(_{90-x}\)Tl\(_x\) glasses occurring around the composition \(x = 22\).
Chapter 3: ADSC Studies on Thallium Doped Ge-Se Chalcogenide Glasses

References


