Chapter 5

Differential and Alternating Differential Scanning Calorimetry Studies on In-Se-Tl Glasses

Summary

Thermal studies on \( \text{In}_{10}\text{Se}_{90-x}\text{Tl}_x \) \( (7 \leq x \leq 15) \) and \( \text{In}_{15}\text{Se}_{85-x}\text{Tl}_x \) \( (2 \leq x \leq 10) \) bulk glasses are undertaken using Differential Scanning Calorimetry (DSC). On heating, these glasses are found to exhibit a single glass transition \( (T_g) \) and a single crystallization \( (T_c) \). In \( \text{In}_{10}\text{Se}_{90-x}\text{Tl}_x \) glasses, it is found that the glass transition and the crystallization temperatures decrease with the addition of Tl concentration indicating a decrease in the network connectivity. Whereas in the case of \( \text{In}_{15}\text{Se}_{85-x}\text{Tl}_x \) glasses, \( T_g \) and \( T_c \) found to increase with Tl concentration. Alternating Differential Scanning Calorimetry (ADSC) conducted on the both series of glasses, \( T_g \), \( T_c \) and \( \Delta T (= T_c - T_g) \) are obtained from reversing and non-reversing heat flows, respectively. The composition dependence of thermal parameters in \( \text{In}_{10}\text{Se}_{90-x}\text{Tl}_x \) \( (7 \leq x \leq 15) \) and \( \text{In}_{15}\text{Se}_{85-x}\text{Tl}_x \) \( (2 \leq x \leq 10) \) glasses obtained in the DSC and ADSC studies have been understood in the manner in which thallium enters the glassy network and resultant changes in the network connectivity. Further, the effect of Tl incorporation on heat capacities \( \Delta C_{pg} \), \( \Delta C_{pc} \) and \( \Delta C_{pm} \) 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 have been investigated by analyzing the Differential Scanning Calorimetry (DSC) thermogram plots. It is found that the heat capacities of \( \text{In}_{10}\text{Se}_{90-x}\text{Tl}_x \) and \( \text{In}_{15}\text{Se}_{85-x}\text{Tl}_x \) glasses increase initially with the incorporation of thallium \( (upto x \leq 13 \ and \ x \leq 6) \) and reaches the maximum at \( x=13 \) and \( x=6 \), respectively, beyond which it decreases. This behavior seems to follow the change in network connectivity and rigidity and is explained with the help of chemical bond theory of solids.
5.1 Introduction

Chalcogenide glasses are lone pair semiconductors and favor the glass formation. The trend of using amorphous semiconducting chalcogenide materials, rather than properly prepared crystalline semiconductors in electronic devices necessitates further investigation of chalcogenide materials. Glass has a very high viscosity, which gives them the mechanical properties of a solid. Within chalcogen elements, selenium glass is the simplest, stable and two-fold-coordinated polymer. Mainly it consists of chains and rings. When In and/or Tl is added because of their fourfold-bonding property, provide means to cross-link structures with the Se chains and rings [1-5]. The binary In-Se glassy alloys have drawn great attention because of their potential use in solar cells [6,7]. In order to enhance their domain of applications, it is necessary to increase their softening temperature and mechanical strength. The addition of various metals such as Ag, Cu, Sn, Bi, Tl, etc., as a third element which will be acting as a cross-linking agents and increase the dimensionality of the structure and stability of the material [2,8-11]. The thermal analysis of glassy alloys is important from an application point of view. The glass transition temperature, \( T_g \) is one of the most important parameter for the characterization of the glassy state of these materials [12]. The earlier studies on bulk chalcogenide glasses doped with thallium [13,14] have revealed that thallium enters the network with bonding that is more ionic in nature and leads to a reduction in the electrical switching voltage and glass transition temperature. The contributing factors to this reduction are to be increased metallicity and fragmentation of the network. One of the empirical rule in the glass community states that glass-transition temperature increases with the network connectivity and vice-versa [15]. The effect of incorporation of Pb, Te and Bi in In-Se at the expense of In has been studied with the help of DSC technique [16].

Differential Scanning Calorimetry (DSC) studies yield interesting information about the glass forming ability, crystallization tendency, etc., of chalcogenide glasses. In addition, the thermal parameters obtained can throw light on the type of electrical switching exhibited by these materials, the composition dependence of switching voltages, etc., [17-19]. The Alternating Differential Scanning Calorimetry (ADSC), which is equivalent to the Modulated Differential Scanning Calorimetry (MDSC), is one of the most sensitive techniques which provide information on thermal parameters.
in network glasses, thermally induced phase transitions and the effect of network topological effects on thermal properties [20,21]. The ADSC technique offers the possibility of de-convoluting the total heat flow curve into reversing and non-reversing heat flow components. The extraction of the reversing and non-reversing heat flow components of the total heat flow makes possible the separation of overlapping thermal phenomena such as crystallization temperature, non-reversing enthalpy and glass transition. The motivation behind the present study is to systematically investigate and to understand the effect of Tl-doping on thermal parameters and its influence on the composition dependence of switching voltages.

5.2 Experimental

The thermal behavior of 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, prepared by melt-quenching technique have been studied using a Mettler Toledo’s DSC 822e differential scanning calorimetry. The temperature and energy calibration of the DSC system have been carried out using melting temperature and enthalpies of high purity indium and zinc prior to the start of the experiment. In order to study the crystallization kinetics about 10mg of the sample is heated at a constant rate of 10°C/min. Typical error in the measurement of T_g, T_c and T_m is within ±2°C.

ADSC studies have been performed using a Mettler Toledo alternating differential scanning calorimeter (model DSC 822e) with the aid of STAR® software. A blank run for all the samples is made prior to the actual measurements, with an empty aluminum pan on the reference side and an empty pan with a lid at the sample side, in order to calibrate the heat flow signal, to correct the amplitude and to eliminate the cell asymmetry. The samples are polished to small pieces of nearly uniform thickness, weighed (=10mg) and sealed in aluminum pans. The temperature calibration in ADSC studies is achieved using high purity indium as standard. An empty aluminum pan is used as a reference. The ADSC scans have been carried out for all the samples in the temperature range of 30-180°C, at 3°C/min scan rate and a modulation rate of 1°C/min. Flow rate of 75ml/min argon was maintained in order to provide a constant thermal blanket within the DSC cell, thus eliminating thermal gradients and ensuring the validity of the applied calibration standard from sample to sample. Moreover, the
argon purge allows expelling the gases emitted by the reaction, which are highly corrosive to the sensory equipment installed in the DSC furnace.

The inflexion point of the reversible heat flow endotherm is taken as the glass transition temperature ($T_g$) and the heat capacity changes are obtained from the step transition in the reversible heat flow (RHF) and in-phase heat capacity curves. The thermal scans on the samples are repeated at least three times to minimize the effect of experimental errors. The deviations in $T_g$ and $\Delta C_p$ measured for heating scans are found to be within $\pm 1^\circ C$ and $\pm 0.01$ J/g$^\circ C$, respectively.

### 5.3 Results and Discussion

Figure 5.1 shows the DSC thermogram of $\text{In}_{15}\text{Se}_{83}\text{Tl}_2$ glass taken at a heating rate of 10$^\circ C$/min. It is seen from the DSC trace $\text{In}_{15}\text{Se}_{83}\text{Tl}_2$ glass shows a single endothermic glass transition at $T_g$ and single exothermic crystallization peaks at $T_c$. Similar results are obtained for the remaining glassy samples.

![DSC thermogram of In$_{15}$Se$_{83}$Tl$_2$ glass sample at a heating rate of 10°C/min](image)

**Figure 5.1:** DSC thermogram of $\text{In}_{15}\text{Se}_{83}\text{Tl}_2$ glass sample at a heating rate of 10°C/min

Figure 5.2 depicts the evaluation of non-reversing, reversing and total heat flow curves obtained using ADSC, for a representative $\text{In}_{15}\text{Se}_{83}\text{Tl}_2$ glass sample.
5.3.1 Variation of Glass Transition Temperature with Tl Content

The variation of glass transition temperature is obtained from ADSC measurements for In$_{10}$Se$_{90-x}$Tl$_x$ (7 ≤ x ≤ 15) glasses are shown in figure 5.3. The difference in error bar for thermal experiments is due to the little variation in the uniformity of the samples taken for different trials. It is evident from figure 5.3 that the glass transition temperatures decrease with the addition of Tl concentration.

The glass transition temperature of multi-component glasses is known to be dependent on several independent parameters such as band gap, coordination numbers, bond energy, effective molecular weight and the type and fraction of various structural units formed [22-33]. Particularly, in metal chalcogenide glasses, the magnitude of glass transition temperature is essentially determined by the metal chalcogen bonding. It is 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 [34,35].
Figure 5.3: Composition dependence of glass transition temperature ($T_g$) of $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x (7 \leq x \leq 15)$ glasses

Further, Tanaka [36] derived an equation connecting the glass transition temperature with average coordination number $\langle r \rangle$ (equation 5.1) which quantifies the network connectivity:

$$\ln T_g = 1.6\langle r \rangle + 2.3$$ \hspace{1cm} (5.1)

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 [37,38]. Varshneya and co-workers [39] later observed that $T_g$ follows a modified Gibbs-DiMarzio equation in multi-component chalcogenide glasses, to relate $T_g$ and $\langle r \rangle$ (equation 5.2)

$$T_g = \frac{T_o}{1 - \beta(\langle r \rangle - 2)}$$ \hspace{1cm} (5.2)

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 [35].

It is also 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 systems such as Ge-Se, Ge-S, Si-Se, etc., and ternary systems Ge-As-Se, Ge-Sb-Se, Ge-Ge-Se, Ge-Sb-Te, etc., indicate that the glass transition temperature increases with increase in overall mean bond energy $\langle E \rangle$ [40].

According to covalent bond approach (CBA) proposed by Kerner and Micoulaut [41-43], the mean bond energy of average cross-linking/atom $\langle E_c \rangle$ in a $A_{1-x-y}B_xC_y$ glassy system at high chalcogen content is given by

$$\langle E_c \rangle = x_{B}E_{A-B} + y_{C}E_{A-C}$$

(5.3)

Where $E_{A-B}$ and $E_{A-C}$ represent the A-B and A-C bond energies [44]. The average bond energy/atom of the remaining matrix $\langle E_{rm} \rangle$ is defined by

$$\langle E_{rm} \rangle = \frac{2\left(\frac{\langle r \rangle}{2} - x_{B} - y_{C}\right)E_{A-A}}{\langle r \rangle}$$

(5.4)

Here $\langle r \rangle = 2(x - y) + r_{B}x + r_{C}y$ (5.5)

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

$$\langle E \rangle = \langle E_c \rangle + \langle E_{rm} \rangle$$

(5.6)

Generally, it is assumed that the metal atoms would coordinate tetrahedrally in chalcogenide semiconductors making coordinate bonds with the chalcogen atom [45]. Kosek et al. [46] reported the formation of such tetrahedrally-coordinated metal atoms in Se-rich chalcogenide glassy system. Figure 5.4 shows the composition dependence of mean bond energy $\langle E \rangle$ of In$_{10}$Se$_{90-x}$Tl$_{x}$ glasses obtained using coordination 4, 2 and 4 for In, Se and Tl atoms, respectively. It is seen from figure 5.4 that the calculated mean bond energy $\langle E \rangle$ of In-Se-Tl glasses increases with the addition of thallium atoms. Based on this, one should expect an increase in the glass transition temperature of In-Se-Tl glasses, with the mean bond energy or the addition of thallium concentration. However, it can be seen from figure 5.3, that the $T_g$ of In$_{10}$Se$_{90-x}$Tl$_{x}$ glasses decrease with the addition of thallium atoms. A similar variation of $T_g$ with the addition of thallium atoms is noticed in Ge-Se-Tl [47] and As-Te-Tl glasses also [48]. The Se or
Te rich glassy system is completely cross-linked three-dimensional structural units [1,49].

![Figure 5.4: Composition dependence of mean bond energy $\langle E \rangle$ of $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x$ ($7 \leq x \leq 15$) glasses](image)

![Figure 5.5: Composition dependence of glass transition temperature ($T_g$) of $\text{In}_{15}\text{Se}_{85-x}\text{Tl}_x$ ($2 \leq x \leq 10$) glasses](image)
When Tl concentration increases in In\textsubscript{10}Se\textsubscript{90-x}Tl\textsubscript{x} (7 \leq x \leq 15) glassy system, more and more Se-Se bonds are broken and probability of ionic Se-Tl bond formation increases. Therefore, in the In\textsubscript{10}Se\textsubscript{90-x}Tl\textsubscript{x} network, connectivity is achieved by the weaker bond formation. The progressive addition of Tl results in the formation of weaker Se-Tl bonds at the expense of stronger In-Se and Se-Se bonds. Hence, there is a net decrease in the network connectivity and rigidity of In\textsubscript{10}Se\textsubscript{90-x}Tl\textsubscript{x} glasses with the addition of Tl atoms, leading to a decrease in $T_g$ as shown in figure 5.3.

![Figure 5.6: Composition dependence of mean bond energy $\langle E \rangle$ of In\textsubscript{15}Se\textsubscript{85-x}Tl\textsubscript{x} (2 \leq x \leq 10) glasses](image)

It is well established that the $T_g$ in network glasses is taken as a global measure of the connectivity [50]. The composition dependence of $T_g$ in the In\textsubscript{15}Se\textsubscript{85-x}Tl\textsubscript{x} (2 \leq x \leq 10) system, as depicted in figure 5.5 shows a linear increase with Tl addition. This indicates a progressive increase in network connectivity with the addition of Tl. It is also seen in figure 5.6 that the mean bond energy $\langle E \rangle$ increases with Tl content.

### 5.3.2 Composition Dependence of the Crystallization Temperature $T_c$

The plot of In\textsubscript{10}Se\textsubscript{90-x}Tl\textsubscript{x} (7 \leq x \leq 15) crystallization temperatures ($T_c$) obtained from the non-reversing component of ADSC measurements with composition is shown
in figure 5.7. From the figure 5.7, it is clear that the crystallization temperature decrease with the addition of Tl atom into the network. A similar decrease in T_c has been reported to occur in many other Se based ternary glassy systems such as Ge-Se-Tl, Ge-Se-Ag and Ge-Se-Te[51-53].

**Figure 5.7:** Composition dependence of crystallization temperatures of In_{10}Se_{90-x}Tl_x 
(7 \leq x \leq 15) glasses

Figures 5.8 shows the variation of (T_c - T_g), which reflects the thermal stability of glasses with composition. It is found that (T_c - T_g) of In_{10}Se_{90-x}Tl_x (7 \leq x \leq 15) glasses decreases with increase in Tl concentration, indicating that the In_{10}Se_{90} glass become more easily devitrifiable with the addition of Tl. The decrease in thermal stability also contributes for the observed decrease in the switching voltages of In_{10}Se_{90-x}Tl_x (7 \leq x \leq 15) glasses with Tl content.

The plot of In_{15}Se_{85-x}Tl_x (2 \leq x \leq 10) crystallization temperatures (T_c) obtained from the non-reversing component of ADSC measurements with composition is shown in figure 5.9. It is seen from the figure 5.9 that the crystallization temperature increases with the addition of Tl atom into the network.
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Figure 5.8: Composition dependence of \((T_c - T_g)°C\) on In\(_{10}\)Se\(_{90-x}\)Tl\(_x\) \((7 \leq x \leq 15)\) glasses.

Figure 5.9: Composition dependence of crystallization temperatures of In\(_{15}\)Se\(_{85-x}\)Tl\(_x\) \((2 \leq x \leq 10)\) glasses.

Figures 5.10 show the variation of the difference between the glass transition and crystallization temperature of In\(_{15}\)Se\(_{85-x}\)Tl\(_x\) glasses with composition. It is interesting to note that \((T_c - T_g)\) of In\(_{15}\)Se\(_{85-x}\)Tl\(_x\) \((2 \leq x \leq 10)\) glasses, which is representative of the
glass forming ability of the system [54-56] goes through a local maximum at \( x = 8 \) \(<r>= 2.46\). This confirms the glassy system varies from floppy mode to rigid mode.

![Graph](image)

**Figure 5.10:** Composition dependence of \((T_g - T_c)\)°C in \( \text{In}_{15}\text{Se}_{85-x}\text{Tl}_x \) \( (2 \leq x \leq 10) \) glasses

### 5.3.3 Measurement of Heat Capacity \( \Delta C_p \) at \( T_g \), \( T_c \) and \( T_m \)

A typical DSC thermogram for \( \text{In}_{15}\text{Se}_{83}\text{Tl}_2 \) glass at 10°C/min is shown in figure 5.11. DSC curve clearly exhibit endothermic and exothermic phase reversal peaks at the glass transition \( (T_g) \), crystallization temperature \( (T_c) \) and melting temperature \( (T_m) \). The \( \Delta C_p \) is measured at \( T_g \), \( T_c \) and \( T_m \) by using the equation 5.7 [57].

\[
\Delta C_p = (\Delta H/ m)(1/\beta)
\]

(5.7)

Where \( \Delta H \) is the change of heat flow in the sample of mass \( m \) \((\approx 5 \text{ mg})\) and \( \beta \) \( (10^\circ\text{C/min}) \) is the heating rate. It is well established that the heat capacity of such materials are influenced by structural units as well as composition [58]. The rigidity threshold composition material shows higher order heat capacity changes at \( T_g \), \( T_c \) and \( T_m \), critical transition temperatures, which are consistent with well-established view.
The significance of the heat capacity at $T_g$ is that, it helps to understand the rewritable data storage capability of these materials. It is also mentioned that a thermodynamically stable molecular glass has lower value of heat capacity at the glass transition due to rigidity and network complexity of the material. Similarly the heat capacity at $T_c$ gives the information about the energy storage capability of the materials for various technical applications. Further, $\Delta C_p$ at $T_m$ reflects the amount of energy liberated when glassy elements completely destroy the solid phase structure. Further, $C_p$ at $T_m$ reflects the amount of energy liberated by breaking all types of existing bonds in glassy alloys due to thermal agitation. Though $C_{pm}$ is technologically least important compared to $C_{pg}$ and $C_{pc}$, it is important to know about it to explore the materials at this critical transition value. The heat capacities of various glasses studied in both the series of $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x$ and $\text{In}_{15}\text{Se}_{85-x}\text{Tl}_x$ glasses at $T_g$, $T_c$ and $T_m$ are summarized in Table 5.1.

It is found that the heat capacities at $T_g$, $T_c$ and $T_m$ of $\text{In}_{15}\text{Se}_{85-x}\text{Tl}_x$ and $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x$ glasses increases initially with the incorporation of thallium (upto $x \leq 6$ and $x \leq 13$) and reaches to a maximum at $x = 6$ and $x = 13$, respectively, beyond which it decreases (figures 5.12 to 5.14). This kind of heat capacity variation trend probably
arises due to the occurrence of large number of unsaturated bonds in complex stoichiometry.

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<th>$\Delta H_c$ (mw)</th>
<th>$\Delta H_m$ (mw)</th>
<th>$C_{pg}$ (Jg$^{-1}$K$^{-1}$)</th>
<th>$C_{pc}$ (Jg$^{-1}$K$^{-1}$)</th>
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Table 5.1: Obtained values of $\Delta H_g$, $\Delta H_c$, $\Delta H_m$ and $C_{pg}$, $C_{pc}$, $C_{pm}$.

Figure 5.12: Heat capacity of $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x$ (7 ≤ x ≤ 15) and $\text{In}_{15}\text{Se}_{85-x}\text{Tl}_x$ (2 ≤ x ≤ 10) glasses at $T_g$. 

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Angell [59-62], following Laughlin and Uhlmann [63], classified the supercooled liquids as strong and fragile depending on whether their temperature dependence of viscosity is Arrhenius or non-Arrhenius, respectively. Departure from Arrhenius behavior marks the instability of the liquid against variation of temperature. It is well known that oxide glass formers such as GeO$_2$ and SiO$_2$ with well-formed tetrahedral network structures and directional bonds belong to the category of strong-forming liquids. On the other hand, ionic glass formers with poor directionality in
bonding are fragile forming liquids. These ideas are extended to glasses and are reflected on the properties such as $\Delta C_p$ and thermal expansion coefficient at $T_g$, $T_c$ and $T_m$ \[64\].

Strong glasses have a small $\Delta C_p$ at $T_g$ \[65\]. This means that the structure of the liquid, when cooled is not affected much, implying smaller number of accessible configurations; and the structure of the glass thus formed closely resembles to that of the liquid. On the contrary, the high value of $\Delta C_p$ ($\Delta C_p \geq 0.3$ J K$^{-1}$ g$^{-1}$) for fragile glasses is due to the addition of translational or rotational modes (due to addition of impurity) made available by the breakage of bonds forming the glass network. An immediate consequence of the high value of $\Delta C_p$ at $T_g$, $T_c$ and $T_m$ for fragile glasses is that their structures break down rapidly with increasing temperature near and above said critical transition temperatures and thus, a large number of configurations are made available for the threshold composition glass. Thus, the structural rearrangements are responsible for the equilibrium liquids transformation to non-equilibrium glass \[66,67\].

5.4 Conclusion

The thermal behavior of melt-quenched In$_{10}$Se$_{90-x}$Tlx ($7 \leq x \leq 15$) and In$_{15}$Se$_{85-x}$Tlx ($2 \leq x \leq 10$) glasses is investigated using DSC and ADSC techniques. Both the series of glasses are found to exhibit one endothermic glass transition reaction and one exothermic crystallization reaction upon heating. Further, the glass transition temperature and crystallization temperature of In$_{10}$Se$_{90-x}$Tlx ($7 \leq x \leq 15$) glasses are found to show a decrease with increase in Tl content suggesting a decrease in the network connectivity. The composition dependence of $T_g$ in the In$_{15}$Se$_{85-x}$Tlx ($2 \leq x \leq 10$) system found to exhibit linear increase with Tl addition. This indicates a progressive increase in network connectivity with the addition of Tl. It is found that the mean bond energy $\langle E \rangle$ also increases with Tl content. Further, it is found that the heat capacities of In$_{15}$Se$_{85-x}$Tlx and In$_{10}$Se$_{90-x}$Tlx glasses increase initially with the incorporation of thallium (upto $x \leq 6$ and $x \leq 13$) and reaches to a maximum at $x=6$ and $x=13$, respectively, beyond which it decreases. This behavior seems to follow the change in network connectivity and rigidity.
References


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