Effect Of Thallium Additive On Heat Capacities Of In-Se Bulk Chalcogenide Glasses

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ABSTRACT

Chalcogenide glasses are promising materials for optoelectronic device applications. Heat capacity of such materials is the essential physical parameter to estimate the energy/data storage capacity. In the present work, the effect of Tl incorporation on heat capacities \(\Delta C_p\), \(\Delta C_m\) and \(\Delta C_{pm}\) of In\(_{10}\)Se\(_{90-x}\)Tl\(_x\) (7\(\leq\)x\(\leq\)15) and In\(_{15}\)Se\(_{85-x}\)Tl\(_x\) (2\(\leq\)x\(\leq\)10) bulk glasses have been investigated by analyzing the Differential scanning calorimetry (DSC) thermogram plots. Composition dependence of heat capacities of In-Se-Tl glassy systems have been obtained at the peaks of the glass transitions, crystallizations and melting temperatures (\(T_g\), \(T_c\) and \(T_m\)). It is found that the heat capacities of In\(_{10}\)Se\(_{90-x}\)Tl\(_x\) and In\(_{15}\)Se\(_{85-x}\)Tl\(_x\) glasses increases initially with the incorporation of thallium (up to x\(\leq\)13 and x\(\leq\)6) and reaches to 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 may be explained with the help of chemical bond theory of solids.

Further in these glassy materials, at the average coordination \(r=2.46\) (x=13) and \(r=2.42\) (x=6) a sharp slope change is seen in the composition dependence of heat capacity of both the series which is attributed to the rigidity percolation threshold.

1. Introduction

Chalcogenide glasses form an important class of materials having extreme potential applications in science and technology due to their variable electrical, thermal and optical properties [1-3]. The appreciable variation in thermo physical properties of Se with composition helps in designing various passive and active elements for optoelectronic devices. Se rich In-Se-Tl amorphous alloys are used as recording materials in the phase change optical discs [4]. The addition of metallic atoms in selenium based chalcogenide glasses play a dual role as network modifier in Se rich side and network former in Se deficient side, there by influencing the thermo physical properties considerably [5]. In this respect the analysis of the compositional dependence of their thermal properties is an important aspect of their study. The glasses, thus prepared, are crushed to make fine powder for Differential Scanning Calorimetry (DSC) studies. It is an extensively used technique for the investigation and interpretation of thermal events in materials. The main advantages of this technique are: (a) it is easy to carry out, (b) it requires little amount of sample, (c) it is quite sensitive and (d) it is relatively independent of the sample geometry. Peaks in DSC traces arise due to thermal relaxation from a state of higher enthalpy toward to metastable equilibrium states of lower enthalpy. The glass transition peaks in DSC measurements appears due to abrupt change in specific heat and decrease in viscosity [6]. While the crystallization peaks due to the production of excess free-volume and melting peaks owing to quick energy release when composition element melt [7].

In this study DSC endothermic and exothermic phase reversal peaks have been used to establish the heat capacity jump, \(\Delta C_p\) at the glass transition (\(T_g\)), crystallization temperature (\(T_c\)) and melting temperature (\(T_m\)) \(\Delta C_p = C_{p,\text{liquid}} - C_{p,\text{glass}}, \Delta C_p = C_{p,\text{liquid}} - C_{p,\text{crystallization}}, \Delta C_p = C_{p,\text{liquid}} - C_{p,\text{melting}}, \) are due to some “frozen” degrees of freedom lost upon cooling below \(T_g\), which are characteristics of the liquid state [8]; and which are capable of altering the potential energy of the system, as a function of composition for In\(_{10}\)Se\(_{90-x}\)Tl\(_x\) (7\(\leq\)x\(\leq\)15) and In\(_{15}\)Se\(_{85-x}\)Tl\(_x\) (2\(\leq\)x\(\leq\)10) bulk glasses.
2. Experimental details

Bulk In$_{10}$Se$_{90-x}$Tl$_x$ ($7 \leq x \leq 15$) and In$_{15}$Se$_{85-x}$Tl$_x$ ($2 \leq x \leq 10$) glasses have been prepared by vacuum sealed melt quenching method. The amorphous nature of the samples have been checked by X-ray diffraction method. The details of the DSC setup used in the present study and calibration have been presented elsewhere [9].

3. Result and Discussions

A typical DSC thermogram for In$_{15}$Se$_{83}$Tl$_2$ glass at 10 $^\circ$C/ min is shown in figure 1. 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 $\Delta C_p$ can be measured at $T_g$, $T_c$ and $T_m$ by the below expression [10].

$$\Delta C_p = (\Delta H / m)(1/\beta)$$

Where $\Delta H$ is the change of heat flow in the sample of mass m (~5mg) and $\beta$ (10 $^\circ$C/min) is the heating rate.

![DSC thermogram of In$_{15}$Se$_{83}$Tl$_2$ glass at 10 $^\circ$C/ min.](image)

Figure 1. DSC thermogram of In$_{15}$Se$_{83}$Tl$_2$ glass at 10 $^\circ$C/ min.

It has been well established that the heat capacity of such materials are influenced by structural units and as well as composition [11]. The rigidity threshold composition material show 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 rewriteable 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 complexcity 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 due to 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 present glasses heat capacities variation with composition at $T_g$, $T_c$ and $T_m$ is summarized in Table 1.

<table>
<thead>
<tr>
<th>TI</th>
<th>$\Delta H_g$ (mw)</th>
<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>
<th>$C_{pm}$ (Jg$^{-1}$K$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>In$<em>{15}$Se$</em>{85-x}$Tl$_x$ (2≤x≤10)</td>
<td></td>
<td></td>
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<tr>
<td>2</td>
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<td>0.85</td>
<td>5.0</td>
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<td>0.017</td>
<td>0.100</td>
</tr>
<tr>
<td>4</td>
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<td>0.892</td>
<td>6.8</td>
<td>0.0074</td>
<td>0.01784</td>
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</tr>
<tr>
<td>6</td>
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<td>0.946</td>
<td>8.0</td>
<td>0.0079</td>
<td>0.01892</td>
<td>0.160</td>
</tr>
<tr>
<td>8</td>
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<td>0.0720</td>
</tr>
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<td>10</td>
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<td>0.824</td>
<td>3.1</td>
<td>0.0690</td>
<td>0.01648</td>
<td>0.062</td>
</tr>
<tr>
<td>In$<em>{15}$Se$</em>{90-x}$Tl$_x$ (7≤x≤15)</td>
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<tr>
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<td>6.7</td>
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<td>0.134</td>
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</table>

Table 1. Obtained values of $\Delta H_g$, $\Delta H_c$, $\Delta H_m$ and $C_{pg}$, $C_{pc}$, $C_{pm}$.

It is found that the heat capacities at $T_g$, $T_c$ and $T_m$ of In$_{10}$Se$_{90-x}$Tl$_x$ and In$_{15}$Se$_{85-x}$Tl$_x$ glasses increases initially with the incorporation of thallium (upto $x$≤13 and $x$≤6) and reaches to maximum at $x$=13 and $x$=6 respectively beyond which it decreases (Figure 2 a, b, c). This kind of heat capacity variation trend probably arises due to occurrence of large number unsaturated bonds in complex stoichiometry.

![Figure 2(a) Heat capacity of In$_{10}$Se$_{90-x}$Tl$_x$ (7≤x≤15) and In$_{15}$Se$_{85-x}$Tl$_x$ (2≤x≤10) glasses at $T_g$.](image)

Angell [12-15], following Laughlin and Uhlmann [16], classified the super cooled 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 have been extended to glasses and are reflected on the properties such as $\Delta C_p$ and thermal expansion coefficient at $T_g$, $T_c$ and $T_m$ [17].

Figure 2(b) Heat capacity of In$_{10}$Se$_{90-x}$Tl$_x$ ($7 \leq x \leq 15$) and In$_{15}$Se$_{85-x}$Tl$_x$ ($2 \leq x \leq 10$) glasses a $T_c$.

Figure 2(c) Heat capacity of In$_{10}$Se$_{90-x}$Tl$_x$ ($7 \leq x \leq 15$) and In$_{15}$Se$_{85-x}$Tl$_x$ ($2 \leq x \leq 10$) glasses a $T_m$.

Strong glasses have a small $\Delta C_p$ at $T_g$ [18]: 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 transitions 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 [19, 20].
4. Conclusions

The composition dependence of heat capacities of In$_{10}$Se$_{90-x}$Tl$_x$ (7≤x≤15) and In$_{15}$Se$_{85-x}$Tl$_x$ (2≤x≤10) glasses are investigated by using DSC curves. The heat capacities of both the series of glasses lies within the strong glass forming range (Δ$C_p$ should be less than 0.3 J K$^{-1}$ g$^{-1}$ at $T_g$ and $T_c$) at the critical transitions temperatures. The higher values of heat capacities ($C_{pg}$, $C_{pc}$ and $C_{pm}$) at rigidity threshold thallium composition (x=6 and 13) reveals that this concentration alloy is more fragile than other glasses which is useful for various technical applications.

References