

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 ΔC_{pg} , ΔC_{pc} and ΔC_{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 $\langle r \rangle = 2.46$ ($x=13$) and $\langle r \rangle = 2.42$ ($x=6$) 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 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, ΔC_p at the glass transition (T_g), crystallization temperature (T_c) and melting temperature (T_m) [$\Delta C_p = C_{p,liquid} - C_{p,glass}$, $\Delta C_p = C_{p,liquid} - C_{p,crystallization}$, $\Delta C_p = C_{p,liquid} - C_{p,melting}$, 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 $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x$ ($7 \leq x \leq 15$) and $\text{In}_{15}\text{Se}_{85-x}\text{Tl}_x$ ($2 \leq x \leq 10$) glasses 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 $\text{In}_{15}\text{Se}_{83}\text{Tl}_2$ glass at $10^\circ\text{C}/\text{min}$ 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 ΔC_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 ΔH is the change of heat flow in the sample of mass m ($\sim 5\text{mg}$) and β ($10^\circ\text{C}/\text{min}$) is the heating rate.

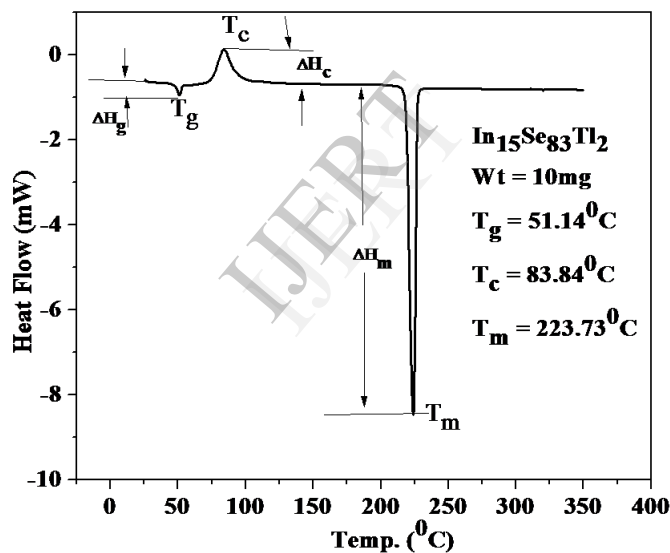


Figure 1. DSC thermogram of $\text{In}_{15}\text{Se}_{83}\text{Tl}_2$ glass at $10^\circ\text{C}/\text{min}$.

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 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 ΔC_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.

Tl	ΔH_g (-mw)	ΔH_c (mw)	ΔH_m (-mw)	C_{pg} ($Jg^{-1}K^{-1}$)	C_{pc} ($Jg^{-1}K^{-1}$)	C_{pm} ($Jg^{-1}K^{-1}$)
$In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$)						
2	0.35	0.85	5.0	0.007	0.017	0.100
4	0.37	0.892	6.8	0.0074	0.01784	0.136
6	0.395	0.946	8.0	0.0079	0.01892	0.160
8	0.354	0.885	3.6	0.00708	0.0177	0.0720
10	0.354	0.824	3.1	0.0690	0.01648	0.062
$In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$)						
7	0.035	0.8	4.6	0.0007	0.0160	0.092
9	0.05	1.0	6.5	0.0010	0.020	0.130
11	0.078	1.0	7.8	0.00156	0.022	0.156
13	0.100	1.3	8.2	0.002	0.026	0.164
15	0.076	1.0	6.7	0.0152	0.020	0.134

Table 1. Obtained values of ΔH_g , ΔH_c , ΔH_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 $x \leq 13$ and $x \leq 6$) 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.

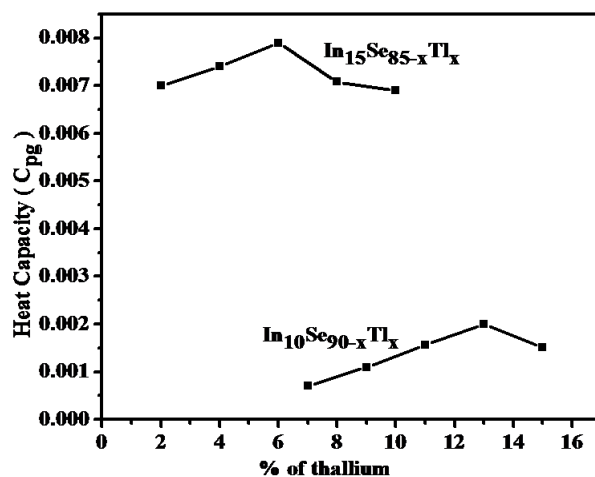


Figure 2(a) Heat capacity of $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) and $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses at T_g .

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 ΔC_p and thermal expansion coefficient at T_g , T_c and T_m [17].

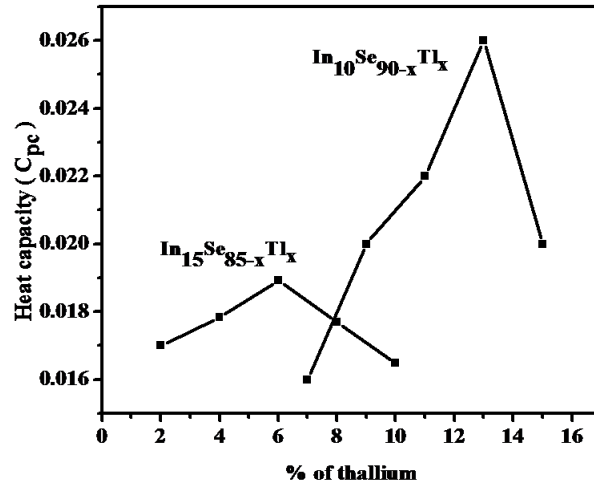


Figure 2(b) Heat capacity of $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x$ ($7 \leq x \leq 15$) and $\text{In}_{15}\text{Se}_{85-x}\text{Tl}_x$ ($2 \leq x \leq 10$) glasses at T_c .

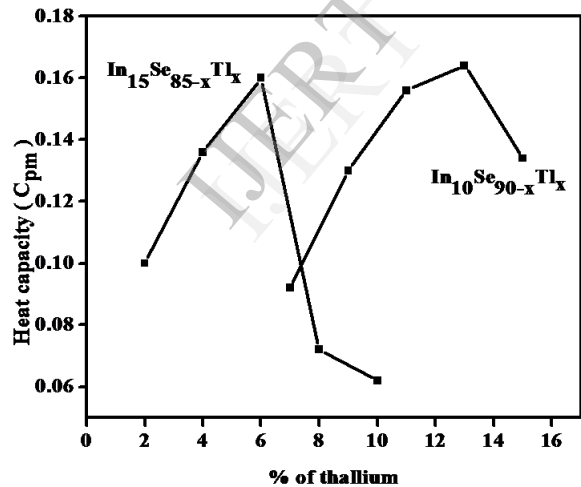


Figure 2(c) Heat capacity of $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x$ ($7 \leq x \leq 15$) and $\text{In}_{15}\text{Se}_{85-x}\text{Tl}_x$ ($2 \leq x \leq 10$) glasses at T_m .

Strong glasses have a small ΔC_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 ΔC_p ($\Delta C_p \geq 0.3 \text{ J K}^{-1} \text{ g}^{-1}$) 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 ΔC_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 $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x$ ($7 \leq x \leq 15$) and $\text{In}_{15}\text{Se}_{85-x}\text{Tl}_x$ ($2 \leq x \leq 10$) glasses are investigated by using DSC curves. The heat capacities of both the series of glasses lies within the strong glass forming range (ΔC_p should be less than $0.3 \text{ J K}^{-1} \text{ g}^{-1}$ 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.

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