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EFFECT OF INDIUM ADDITIVE ON HEAT CAPACITIES OF Se-Zn-Te MULTICOMPONENT CHALCOGENIDE GLASSES

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In cutting age of science and technology the optoelectronics materials become promising for investigations, due to variable thermophysical properties. Heat capacity of such materials is the essential physical parameter to estimate the energy/data storage capability. Here heat capacities ΔC_{pg}, ΔC_{pc} and ΔC_{pm} of $Se_{93-X}Zn_2Te_5In_X$ (X = 0, 2, 4, 6 and 10) chalcogenide glasses have been described from the analysis of Differential Scanning Calorimetery (DSC) measurements traces. Composition dependence heat capacities of Se-Zn-Te-In systems have been obatined at the glass transitions, onset crystallizations and melting temperatures ($T_{c,}$ $T_{g,}$ T_m). It has obtained that the heat capacities of these materials increases upto threshold composition and afterward decline for higher indium concentration. Up and down behaviours in heat capacities in these materials could be explained with help of chemical bond theory of the solids.

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Keywords: Chalcogenide glasses, DSC, Heat capacity

1. Introduction

Chalcogenide glasses are obtained by mixing the chalcogen elements, viz, S, Se and Te with elements of the periodic table such as Ga, In, Si, Ge, Sn, As, Sb and Bi, Ag, Cd, Zn etc. In these glasses, short-range inter-atomic forces are predominantly covalent: strong in magnitude and highly directional, whereas weak van der Waals' forces contribute significantly to the medium-range order. These materials exhibit unique physical properties that make them good candidates for several potential applications such as infrared transmission and detection, threshold and memory switching [1], optical fibers [2-4] functional elements in integrated-optic circuits [5] non-linear optics [6], holographic & memory storage media [7,8], chemical and bio-sensors [9, 10] and infrared photovoltaics [11] etc. In this respect, the analysis of the compositional dependence of their thermal properties is an important aspect of their study. In order to our systematic study; compositional dependence of glass-forming ability and thermal stability [12], the observation of Meyer Neldel rule and crystallization rate constant stability [13], the optical and FT-IR properties [14], the electrical properties [15] for Se-Zn-Te-In systems.

Differential scanning calorimetry (DSC) is an extensively used technique for the investigation and interpretation of thermal events in materials. Peaks in DSC traces arise due to thermal relaxation from a state of higher enthalpy toward to metastable equilibrium states of lower enthalpy. Such process of thermal relaxation depends on temperature and may quite fast near the glass-transitions temperatures. The glass transitions peaks in DSC measurements arises due to abrupt change in specific heat and decrease in viscosity [16]. While the crystallizations peaks due to the production of excess free-volume and melting peaks owing to quick energy release when alloying element melt. Hence such materials crystallizations temperatures as well as mode of crystallizations widely depend on glass composition [17].

In the present work, we have used DSC to establish the heat capacity jump, ΔC_p at T_g, T_c and T_m [$\Delta C_p = C_{pl} - C_{pg}$, $\Delta C_p = C_{pl} - C_{pc}$, $\Delta C_p = C_{pl} - C_{pm}$ where C_{pl} and C_{pg}, C_{pc} C_{pm} refer to C_p

values of the supercooled liquid and the glass transitions state, crystallizations state, melting state respectively], as a function of composition for $Se_{93-X}Zn_2Te_5In_X$ (X = 0, 2, 4, 6 and 10) glasses.

2. Material preparation and characterizations

Bulk multicomponent glassy materials were prepared by conventional melt-quenched technique. The high purity elements Selenium, Zinc, Tellurium and Indium were used. The desired amounts of elements were weighed by electronic balance and put into clean quartz ampoules (length of ampoules 8 cm and diameter 14 mm). Ampoules were evacuated and sealed under at a vacuum of 10^{-5} Torr to avoid the reaction of glasses with oxygen at high temperature. A bunch of sealed ampoules was heated in electric furnace up to 1173K at a rate of 5-6 K/min and kept at that temperature for 10-11 h. During the melting process ampoules were frequently rocked to ensure the homogeneity of molten materials. After achieved desired melting time, the ampoules with molten materials were frequently quenched into ice cooled water. Ingots of glassy materials were obtained by breaking the ampoules. Obtained materials amorphous nature was confirmed by PHILIPS XRD which shown in Fig.1.

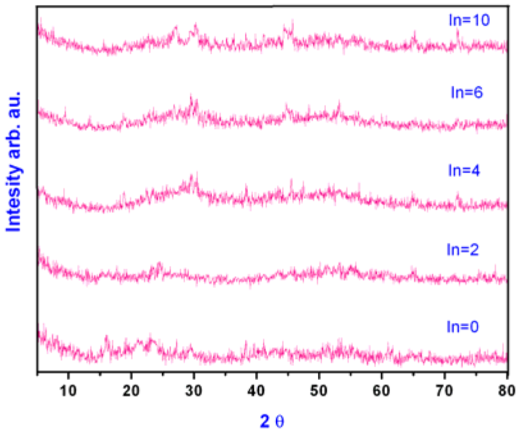

Fig. 1 XRD patterns of $Se_{93-X}Zn_2Te_5In_X$ (X = 0, 2, 4, 6 and 10) chalcogenide glasses

DSC measurements were carried out from SHIMAZADU (Model TA 60, Japan made) with an accuracy of ± 1 K. The instrument was calibrated for each heating rate with materials well-known melting temperatures which supplied with the instrument. The melting enthalpy of indium and lead were used for lower and higher limits. The prepared glassy samples (~ 6-8 mg) were loaded into aluminum pans for each continuous heating rate (β = 5, 10, 15 and 20 K $(\mathrm{min})^{-1}$) and scanned from 308 to 523 K.

3. Results and discussion

A typical DSC scan for $Se_{87}Zn_2Te_5In_6$ glass at 15 K/min is shown in Fig.2. DSC trace 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 evaluated at T_g, T_c and T_m by using the following relation [18]

$$\Delta C_p = \left(\frac{\Delta H}{m}\right)\left(\frac{1}{\beta}\right)$$

where ΔH is the change of heat flow through a sample of mass m and β is the heating rate. The value of the normalized change of heat flow (ΔH/m) is obtained as outlined on Fig.3 (a, b, c).

It is well recognized the heat capacity of such materials widely influence from structural units and/or composition of alloys [19]. The threshold composition material show higher order heat capacity changes at T_g, T_c and T_m critical transitions temperatures. Evaluated heat capacities (C_{pg}, C_{pc} and C_{pm}) values of $Se_{93-X}Zn_2Te_5In_X$ glasses are also consisting with well established view.

Heat capacity at T_g is important to define the rewritable data storage capability of such materials. Present glasses heat capacities variation trend at the glass transitions is shown in Fig.4 and their corresponding values listed in Table.1. Although is also reported that a thermodynamically stable molecular glass has lower value of heat capacity at the glass transition [19] due to rigidity and network complexcity of the material. Here we have obtained the heat capacity in increasing order upto threshold indium composition and beyond this decreased. This kind of heat capacity variation trend probably arises due occurrence of large number unsaturated bonds in complex stoichiometry.

Heat capacity at T_c defines the energy storage capability of the materials for various physical applications. The exothermic heat capacity at T_c arises due to barking of existing covalent bonds in the glassy stoichiometry. Heat capacities variation trend of present glasses is shown in Fig.5. Heat capacity increases with increasing indium atomic percentage upto threshold composition then decrease for higher indium concentration. High value of heat capacity at T_c for threshold indium composition represents high order crystallization rate as compare to other alloys of this series.

Endothermic heat capacities of these materials at T_m reflects the amount of energy liberate when alloying elements completely destroy the solid phase structure. Heat capacity at T_m arises due to braking of all type existing bonds in solid phase cause of thermal agitation. Technologically heat capacity at T_m is less important than heat capacities at T_g and T_c but in order to explore the materials we should aware about this critical transition value. Present glasses heat capacities variation is shown in Fig.6 and their respective values listed in Table.1.Values of endothermic heat capacities at T_m also follow the same variation trend as T_g & T_c and found to be higher at threshold indium composition.

Table.1 Obatined values of ΔHg, ΔHc,, ΔHm and Cpg, Cpg, Cpm,at heating rate 15 K/min

Composition	ΔH_g (-mW)	ΔH_c (mW)	ΔH_m (-mW)	C_{pg} (J $g^{-1}K^{-1}$)	C_{pc} (J $g^{-1}K^{-1}$)	C_{pm}(J $g^{-1}K^{-1}$)
In=0	1.27	3.33	20.69	0.0141	0.037	0.2298
In=2	1.49	3.74	23.01	0.0165	0.0415	0.2556
In=4	1.62	4.37	27.86	0.018	0.0485	0.3095
In=6	2.28	6.65	28.87	0.0253	0.0738	0.3207
In=10	1.51	4.18	25.00	0.0167	0.0464	0.2777

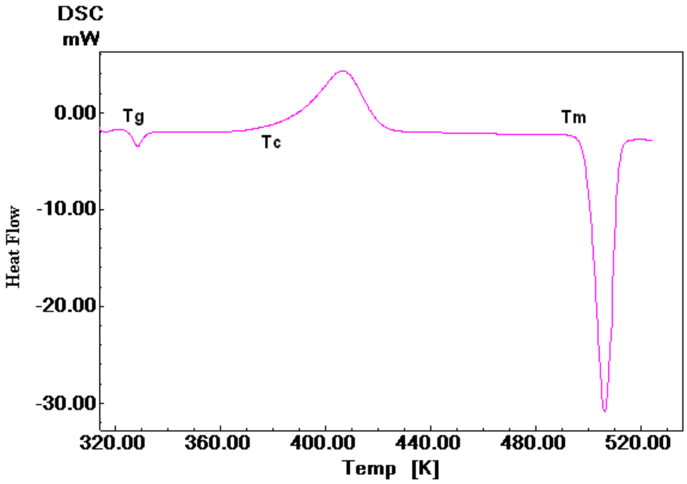

Fig. 2 DSC pattern of $Se_{87}Zn_2Te_5In_6$ chalcogenide glass at 15K/min

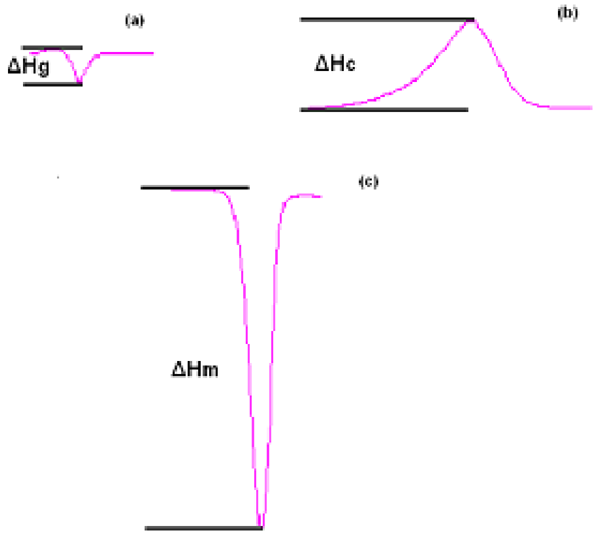

Fig. 3 (a,b,c).Evaluations of enthalpy (ΔH) at T_g,T_c and T_m

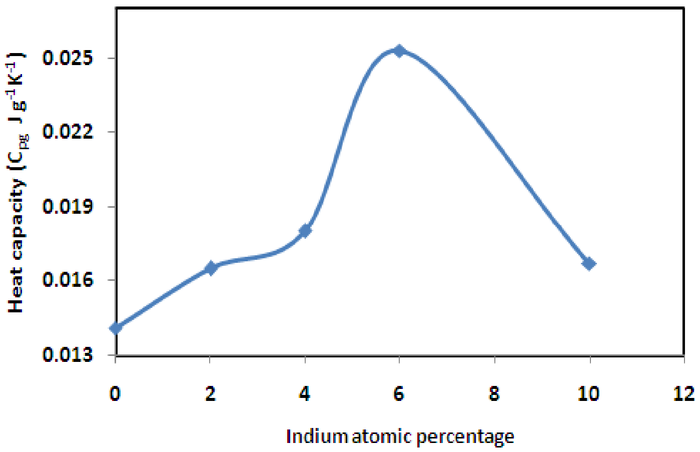

Fig.4 Heat capacities of $Se_{93-X}Zn_2Te_5In_X$ $(0 \leq X \geq 10)$ glasses at T_g

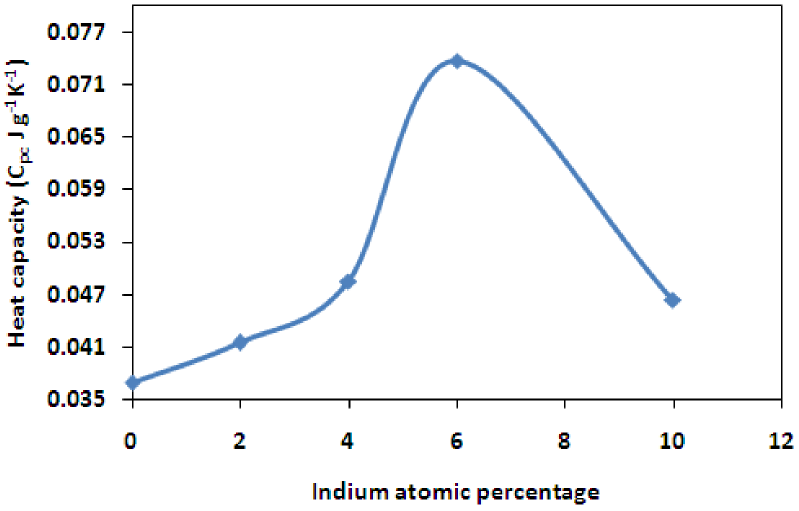

Fig. 5 Heat capacities of $Se_{93-X}Zn_2Te_5In_X$ $(0 \leq X \geq 10)$ glasses at T_c

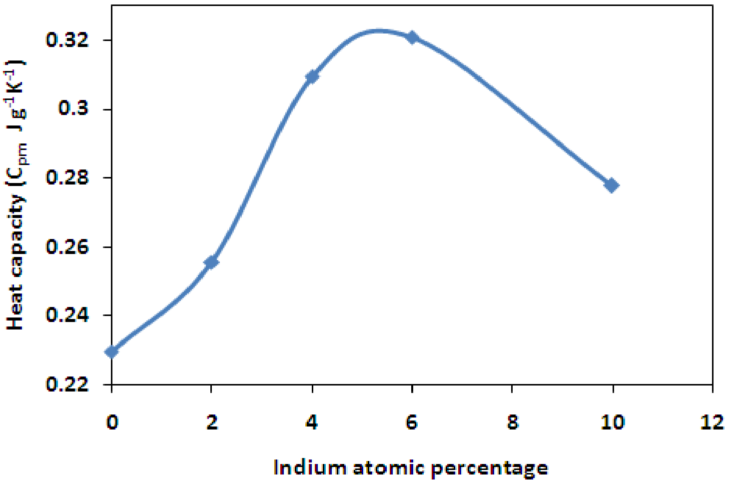

Fig.6 Heat capacities of $Se_{93-X}Zn_2Te_5In_X$ *(0 ≤ X ≥ 10) glasses at* T_m

Based on extensive investigations, Angell [20] classified the glass-forming liquids according to the temperature dependence of their viscosity. Liquids exhibiting an Arrhenius temperature dependence of the viscosity are defined as strong glass forming liquids. The liquids which exhibit non-Arrhenius dependence (those described by a Vogel-Tammann-Fulcher equation) are identified fragile glass forming liquids. 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. Recently, the strength-fragility concept of glass-forming liquids has been extended to the glassy state [21]. The values of ΔCp at T_g, T_c and T_m can also be connected to strength-fragility concept of the materials. As outlined by Angell [20], glasses exhibiting a high ΔCp value (ΔCp ≥ 0.3 J K-1 g-1) at T_g and T_c are far from their thermodynamic equilibrium. Such glass-forming systems demonstrated as thermodynamically fragile [22, 23].

The high value of ΔCp 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 values of ΔCp at T_g, T_c and T_m for fragile glasses is that their structures breaks 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 responsible for the equilibrium liquid transforms to non-equilibrium glass. On the contrary, the low ΔCp at critical transitions temperatures for rigid glasses (Those having less degree of freedom in density of state) indicates that their structures resist the changes and undergo fewer configurational changes near and above critical transitions temperatures. As consequence fewer values of heat capacities at critical transitions temperatures are achieved both side the chemical threshold composition.

4. Conclusions

In summary, one has discussed the heat capacities of $Se_{93-X}Zn_2Te_5In_X$ (X = 0, 2, 4, 6 and 10) chalcogenide glasses and found it lies within the strong glass forming range (ΔCp 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 threshold indium composition reveal this concentration alloy is more fragile than other glasses of the series. Thus on basis of obatined results it can be concluded that threshold composition alloy is most fragile glass which useful for technical uses.

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