

Composition dependence of heat capacity in $\text{Se}_{75}\text{Te}_{15-x}\text{Cd}_{10}\text{In}_x$ ($x=0, 5, 10$ and 15) chalcogenide glasses

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Differential Scanning Calorimetry (DSC) is performed at different heating rates under non-isothermal conditions to study the heat capacities studies of glassy $\text{Se}_{75}\text{Te}_{15-x}\text{Cd}_{10}\text{In}_x$ ($x=0, 5, 10$ and 15) alloys. Heat capacities of $\text{Se}_{75}\text{Te}_{15-x}\text{Cd}_{10}\text{In}_x$ ($x=0, 5, 10$ and 15) chalcogenide glasses at glass transitions (T_g) and crystallisations temperatures (T_c) were mentioned in this work. The evaluated endothermic (ΔC_{pg}) and exothermic (ΔC_{pc}) heat capacities of Se-Te-Cd-In system varies with alloying concentrations and maximum at threshold composition (5 at wt.% of In). This could be explained on the basis of chemical bond theory of the solids.

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1. Introduction

The phase change consequences in chalcogenide glasses (ChGs) are attractive for scientific and technological applications in the area of optoelectronics [1–4]. The structural adjustments that take area in the route of the amorphous-to-crystal transition are an interesting difficulty in modern physics. On this regard, the devitrification manner ought to be slow to obtain excessive-elegance chalcogenide glasses because of their extensive applications within the fabrication of optical fibers, waveguides, and optical elements and lenses. Alternatively, it should be speedy throughout the Erasing method in phase change optical recording in CDs and DVDs [2,3]. Accordingly, the take a look at of crystallization kinetics of newly advanced multi-component chalcogenide glasses has become a primary requirement for their use in the know-how at the back of the device fabrication like phase change optical and electrical memories [4].

Differential scanning calorimetry (DSC) is a notably used technique for the investigation and interpretation of thermal activities in materials. Peaks in DSC lines get up because of thermal relaxation from a nation of higher enthalpy closer to metastable equilibrium states of lower enthalpy. Such procedure of thermal relaxation relies upon on temperature and this event may quite fast near the glass transition temperature. Glass transitions peaks in DSC measurements arises due to abrupt exchange in specific heat and a decrease in viscosity [5]. The crystallisations peak because of the production of excess free-volume.

Glass transition is one of the most captivating problems in physics, however also it remains as one of the toughest ones. Even though this transition has substantial practical and technological importance, nonetheless there may be no consensus about which thermodynamical and structural elements decide the glass transition temperature (T_g) [6]. For chalcogenide glasses, interest has been committed to correlate T_g with other physical and chemical properties, [7] on the

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grounds that such glasses have electric and infrared transmission residences that make them beneficial in technological applications [8]. One of these interesting problems is the change in the properties of the glass because the chemical composition is changed. As an instance, T_g and ΔC_p the jump in the specific heat in the glass transition may be raised or decreased through adding impurities, and the fragility of the glass may be changed from fragile to strong [9]. The specific heat of the material will change quite suddenly as the solid gets converted to liquid. The onset of the alternate in specific heat is frequently used as an indicator of the temperature selection of transition. A literature survey shows that the specific heat provides facts about the solubility and the effect of doping ions on thermal transport properties of glass-forming materials.[10] This parameter has additionally been proven to be valuable for analyzing the structural modifications in the glass transition area of glassy materials.[11-13] but, the reasons for the alteration in the specific heat prior to and subsequent to the glass transition region are diverse in nature. From the above discussion, its miles clear that specific heat measurements provide significant records associated with glass transition phenomenon in glasses.

In our earlier communication, we have reported the glass transition phenomenon in glassy $Se_{75}Te_{15-x}Cd_{10}In_x$ ($x=0, 5, 10$ and 15) alloys [14] and crystallisation kinetics of $Se_{75}Te_{15-x}Cd_{10}In_x$ multi-component chalcogenide glasses [15]. In the present work, we have investigated the effect of In incorporation on the specific heat in ternary Se-Te-Cd system.

2. Material preparation and experimental technique

Extremely pure (99.999%) using an electronic balance, the elements Se, Te, Cd, and In were weighed according to their respective atomic weight percent ratios. The substances were expelled into quartz ampoules (length of 8 cm and internal diameter of 12 mm). To prevent any potential of an alloy-oxygen reaction at high temperatures, the ampoules were sealed at a vacuum of 10^{-5} Torr. In the furnace, the ampoules were heated for 12 hours at a rate of 3–4 K/min up to 1098 K. To verify that the samples were homogeneous, they were frequently rocked. To get the alloys in their glassy condition, the molten samples were quickly quenched in ice-cooled water. The X-ray diffraction pattern of the as-prepared samples can be used to confirm the glassy nature of alloys.

Using a DSC equipment, the thermal behaviour of each sample was examined (Model: Shimadzu DSC-60). Standard aluminium pans were used to heat 5 mg of the sample in powder form at four different rates, ranging from 5 to 20 K/min. The heat absorbed or evolved during phase transitions was measured using differential scanning calorimetry (DSC), and the dynamics of crystallisation under non-isothermal circumstances were studied. The thermal analyzer's microprocessor measured the temperature with a precision of 0.1 K and 0.01 mW for the heat flow accuracy.

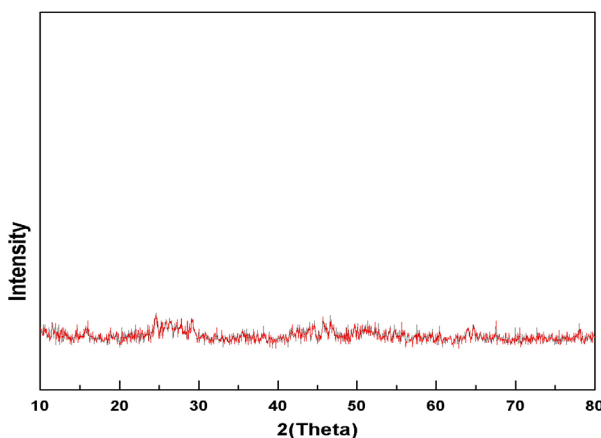


Fig.1. XRD pattern of the $Se_{75}Te_{10}Cd_{10}In_5$ chalcogenide glass.

3. Result and discussion

A typical DSC scan for $\text{Se}_{75}\text{Te}_{10}\text{Cd}_{10}\text{In}_5$ multi-component chalcogenide glasses 15 K/min is given in Figure 2a. The DSC trace surely exhibited the endothermic and exothermic phase reversal peaks at glass transition (T_g) and crystallisation temperature (T_c). The ΔC_p may be evaluated at T_g and T_c by way of the usage of the subsequent relation [16]

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

where ΔH is the exchange of heat go with the flow through a sample of mass m and β is the heating rate. The value of the normalised change of heat flow ($\Delta H/m$) is obtained as outlined in Figures 2b, 2c. The evaluated values ΔH_g , ΔH_c , at glass transition and crystallization regions listed in the Table 1.

Table 1. Obtained values of $-\Delta H_g$ (mW), ΔH_c (mW), C_{pg} , C_{pc} at T_g and T_c for $\text{Se}_{75}\text{Te}_{15-x}\text{Cd}_{10}\text{In}_x$ ($x = 0, 5, 10$ and 15) glassy alloys.

Compositions	ΔH_g (-mW)	ΔH_c (mW)	C_{pg} ($\text{J g}^{-1} \text{K}^{-1}$)	C_{pc} ($\text{J g}^{-1} \text{K}^{-1}$)
In=0	0.37	1.11	0.0049	0.0146
In=5	1.84	2.069	0.024	0.027
In=10	0.67	1.338	0.0089	0.0178
In=15	0.27	1.065	0.0036	0.0142

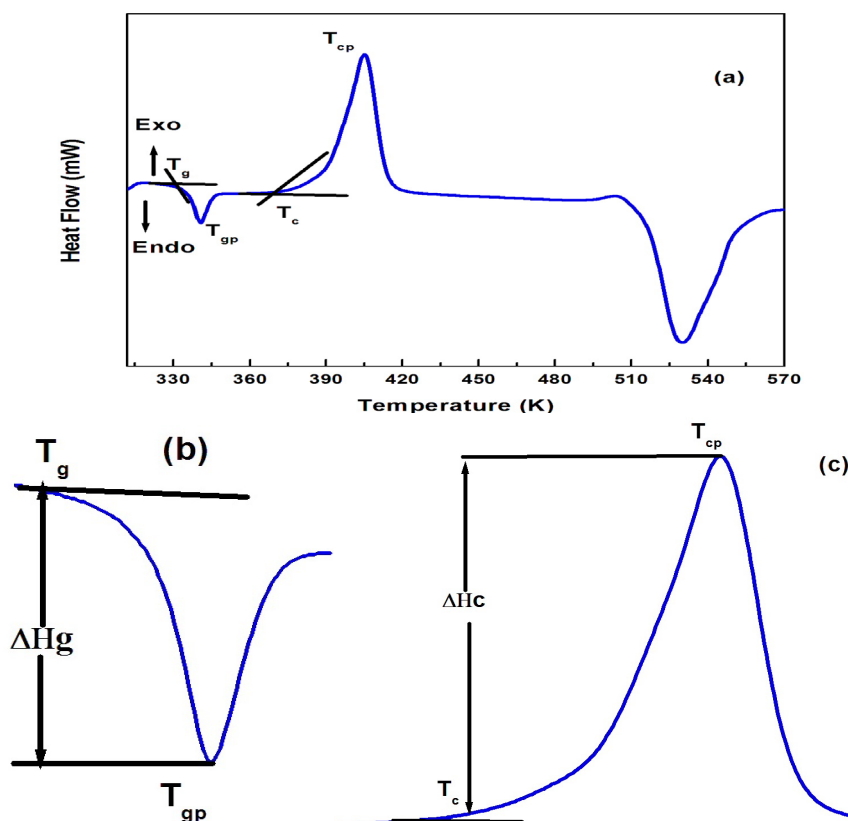


Fig. 2.(a) DSC thermogram of $\text{Se}_{75}\text{Te}_{10}\text{Cd}_{10}\text{In}_5$ chalcogenide glass at 15 K/min heating rate and (b), (c) evaluations of $-\Delta H/m$ and $\Delta H/m$ from the DSC pattern.

Using the values of m and heating rate β the calculated values of ΔC_{gp} and ΔC_{cp} at glass transition temperature and crystallization temperature also listed in Table 1. It is well recognised that the heat capacity of such materials is widely influenced from structural units values and compositions of alloys [17]. At the threshold composition glass normally shows maxima heat capacity at T_g and T_c critical transitions temperatures.

Heat capacity at T_g is useful to classify the rewritable data storage ability of such materials. In the present glassy alloys heat capacity variant shown at the glass transition temperature is shown in Fig. 3 and their corresponding values indexed in table.1. Even as is reported that a thermodynamically stable molecular glassy alloy has lower value of heat capacity at the glass transition [17] because of rigidity and network complexity of the material. In this series we have got acquired the heat capacity in growing order upto threshold indium composition and beyond this reduced. Similar result obtained by A. K. Singh for Se-Zn-Te-In multi-component chalcogenide glasses [18]. A few works on heat capacities has been carried out on ternary chalcogenide glasses having different compositions [19-22]. This kind of heat capacity change trend in all likelihood arises due happening of large number unsaturated bonds in complicated stoichiometry. Heat capacity at T_c defines the energy storage capacity of the materials for various physical applications. The exothermic heat capacity at T_c arises due to breaking of existing covalent bonds in the glassy stoichiometry. The variation of heat capacities at crystallization temperature of Se-Te-Cd-In glassy system shown in Fig 4. Heat capability will increase with growing indium atomic percentage upto 5 at. % of In then decrease for higher indium concentration. High value of heat capability at T_c for this indium composition represents high order crystallization rate as evaluate to other alloys of this glassy system.

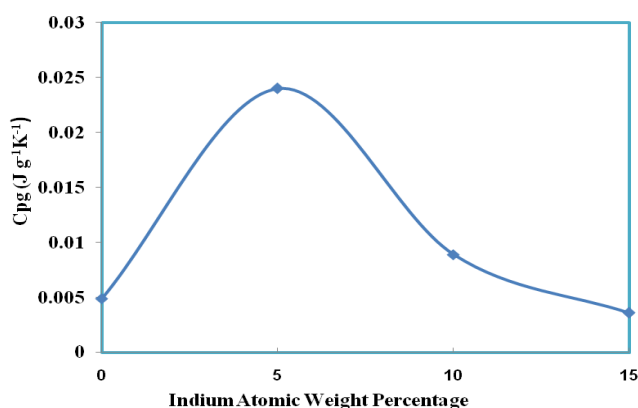


Fig.3. Heat capacities of $Se_{75}Te_{15-x}Cd_{10}In_x$ ($x = 0, 5, 10$ and 15) glassy alloys at T_g .

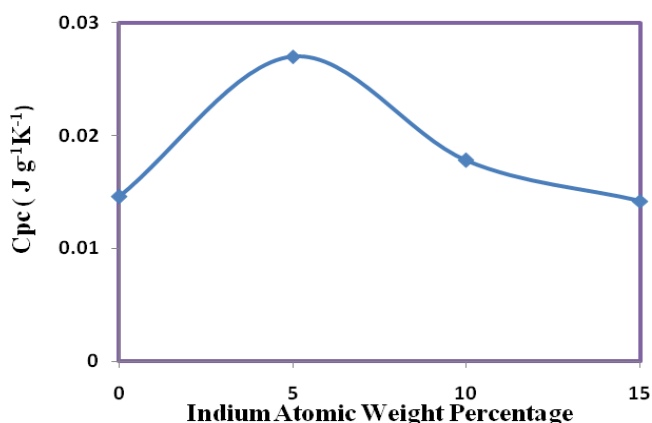


Fig.4. Heat capacities of $Se_{75}Te_{15-x}Cd_{10}In_x$ ($x = 0, 5, 10$ and 15) glassy alloys at T_c .

Based totally on full size investigations, Angell [23] categorized the glass-forming liquids in keeping with the temperature dependence of their viscosity. Liquids showing an Arrhenius temperature dependence of the viscosity are defined as strong glass forming liquids. The liquids which show off non-Arrhenius dependence (the ones defined by a Vogel-Tammann-Fulcher equation) are recognized as fragile glass forming liquids. Ionic glass former has poor directionality in bonding in fragile-forming liquids. Currently, the strength-fragility concept of glass-forming liquids has been extended to the glassy state [24]. The values of ΔC_p at T_g , and T_c also can be connected to strength-fragility idea of the materials. As outlined by means of Angell [23], glasses displaying a high ΔC_p value ($\Delta C_p \geq 0.3 \text{ J K}^{-1} \text{ g}^{-1}$) at T_g and T_c are far from their thermodynamic equilibrium. Such glass-forming structures established as thermodynamically fragile [25, 26].

The high value of ΔC_{pg} and ΔC_{pc} for fragile glasses is due to the extra translational or rotational modes made available with the aid of the breakage of bonds formation of the glass network is because of addition of impurity. The values of ΔC_{pg} and ΔC_{pc} in this series is maximum for $\text{Se}_{75}\text{Te}_{10}\text{Cd}_{10}\text{In}_5$ glassy alloy. Further increase the Indium concentration the values of ΔC_{pg} and ΔC_{pc} are decreases. An abrupt outcome of the critical values of ΔC_{pg} and ΔC_{pc} at T_g and T_c for fragile glasses is because of systems breaks down unexpectedly with increasing temperature near and above said critical transitions temperatures and consequently a large number of configurations are made to available for the threshold composition glass. On contradictory low values of ΔC_{pg} , ΔC_{pc} at important transitions temperatures for rigid glass indicates that their structures resist the configurational modifications near and above critical transitions temperatures is because of the ones having less degree of freedom in density of state. For that reason in heat capacities at critical transitions temperatures are carried out on both sides of the structural threshold.

4. Conclusions

Calorimetric measurements have been performed in glassy $\text{Se}_{75}\text{Te}_{15-x}\text{Cd}_{10}\text{In}_x$ ($x=0, 5, 10$ and 15) alloys to study the effect of In additive on the heat capacity in the ternary Se-Te-Cd system. The results of this investigation demonstrated that the structurally threshold alloy composition exhibited maxima for both the endothermic (ΔC_{pg}) and exothermic (ΔC_{pc}) heat capacities. Higher value of heat capacity of $\text{Se}_{75}\text{Te}_{10}\text{Cd}_{10}\text{In}_5$ composition glass is explained on the basis of bond theory of the solids.

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