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KINETICS OF GLASS TRANSITION IN $Te_5(In_xSe_{100-X})_{95}$ GLASSY ALLOYS

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Present paper reports the calorimetric measurements related to the study the effect of increasing indium content on the kinetics of glass transition in the ternary $Te_5(In_xSe_{100}-_x)_{95}$ glassy alloys. DSC scans at different heating rates show the presence of well defined endothermic and exothermic peaks at the glass transition (T_g) and crystallization temperature (T_c). The glass transition temperature is found to increase with heating rate in various alloys. Composition dependence reveals that T_g increases with In% at all heating rates. This behavior seems to be due to formation of three dimensional network bt addition of trivalent In. The activation energy of glass transition has been calculated and is found to vary with indium concentration. The difference in T_c and T_g is obtained from the thermograms for each alloy and the composition dependence of T_c-T_g is analysed.

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Keywords: Glassy alloys, Te-In-Se, Kinetics of glass trasnition

1. Introduction

Chalcogenide glasses are attractive not only due to their electrical and optical properties but also due to their thermal properties. This is largely due to suitability of peculiar properties exhibited by these materials for processing of devices for electrical switching and memories, optical memory applications, x-ray imaging etc. Among these materials selenium in particular exhibits a unique property of reversible transformation [1], which makes these glasses useful as optical memory devices. The effect of alloying Te into a-Se [2,3] is reported to result in dissociation of long polymeric chains and eight member rings of amorphous selenium [4]. This makes Se-Te alloys more important as compared to a- Se due to distinct advantages (greater hardness, better photosensitivity, lesser ageing effects etc.) and hence find applications as recording layer material in optical phase change technique [5]. However, in these alloys limited reversibility [6] and low glass transition and crystallization temperatures are serious problems. These problems can be overcome by addition of third element as a chemical modifier as it is reported to expand the glass forming region and also creates compositional and configurational disorder [7]. The addition of dopant [In] can modify the lattice perfection and optical properties, which play a major role in device preparation. Thus the analysis of the kinetics of glass transition of a-$Te_5(In_xSe_{100-x})_{95}$ alloys is important from basic as well as application point of view.

The experimental details of sample preparation and measurements are described in section 2. Various results of DSC measurements are presented and discussed in section 3. The conclusions drawn from the present work are contained in the last section.

2. Experimental

Various samples of $Te_5(In_xSe_{100-x})_{95}$ glassy system (x = 10, 15, 20 and 25) were prepared in bulk form by melt quenching technique. For each sample, materials of 99.999% purity weighed according to their atomic percentage are sealed in evacuated quartz ampoules (~10^{-5} Torr). The sealed ampoules were then heated to ~1000^o C in an electric furnace at a heating rate of 2-3^{o}C /min. and were frequently rocked for about 10 hours at the highest temperature to make the melt homogenous. The quenching was done in ice-cooled water. X-ray diffraction pattern of the samples confirmed the glassy nature of the material. The samples so obtained were ground to powder form for carrying out DSC measurements. Four heating rates 5, 10, 15 and 20 ^{0} C/ min were selected for DSC measurements. About 10-15 mg. powder was heated at constant heating rate and the changes in heat flow with reference to empty reference pan were measured. The presence of a well-defined

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endothermic peak at the glass transition temperature and an exothermic peak at the crystallization temperature is observed in each DSC scan. The studies were made under almost identical conditions so that the activation energy of glass transition (ΔE_t) could be compared to get an insight into the effect of increasing In concentration.

3. Results and discussion

In a particular glass, the characteristic temperatures such as the glass transition temperature (T_g), crystallization temperature (T_c), melting temerature (T_m) etc. are the factors which determine the stability and resistance to devitrification. In DSC technique the glass transition is exhibited as an endothermic peak or a shift in the base line due to change in specific heat. In case of chalcogenide glasses, an endothermic peak can be observed due to a fast change in enthalpy as the glassy system relaxes quickly due to a decrease in viscosity at the transition temperature. The theory of glass transition and structural relaxation developed by Moynihan and others [8-10] can be used to analyze the kinetics of glass transition from the heating rate dependence of glass transition temperature. The activation energy ΔE_t of molecular motion and rearrangement near glass transition temperature can be calculated using this theory. In chalcogenide glasses, the heating rate dependence of glass transition temperature is interpreted in terms of thermal relaxation phenomenon, where the enthalpy H(T,t) at a particular temperature and time of the glassy system relaxes isothermally towards $H_e(T)$ a new equilibrium value after an isobaric change in temperature. The relaxation equation for such a transition is [8]

$$(\delta H/\delta t)_T = -(H-H_c)/\tau \tag{1}$$

here τ denotes temperature dependent structural relaxation time and is given as:

$$\tau = \tau_o \{\exp(\Delta E_t/RT)\}\{\exp\{-c\,(H - H_c)\}\} \tag{2}$$

where τ_o and c are constants and ΔE_t is the activation energy of relaxation time. The dependence of T_g on heating rate (β) is given as [9,10]

$$d(\ln\beta)/d(1/T_g) = -\Delta E_t/R \tag{3}$$

From equation 3 it is clear that $\ln\beta$ vs. $1/T_g$ plot should be a straight line and the activation energy related to molecular motions and rearrangements around T_g can be obtained from the slope of this plot.

Fig. 1 depicts various thermograms at different heating rates of x = 10 alloy. As seen from the figure, well-defined endothermic and exothermic peaks representing T_g and T_c respectively are present at different heating rates. Similar behavior is observed in other compositions as well. For the sake of comparison Fig. 2 (a) and (b) depict the variation of T_g and T_c in different glasses at a heating rate of 10°C/min.

The glass transition kinetics can be understood in terms of glass transition temperature and activation energy of thermal relaxation and is quite important in glasses. In some of the chalcogenide glassy systems, glass transition temperature T_g is found to vary with the average coordination number. Physical quantities such as, the melting temperature, the magnitude of photo-darkening and width of the band tails in chalcogenide glasses is found to be related with T_g . Therefore, the study of the kinetics of glass transition is one of the most important problems in the area of chalcogenide glasses.

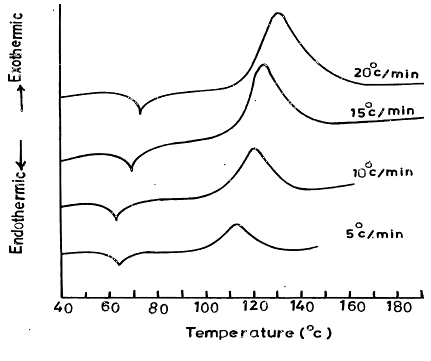

Fig. 1. DSC thermograms for X=10 alloy at different heating rates.

The glass transition temperature (T_g) represents the strength or rigidity of the glassy structure of the alloys. It is well known that T_g of glassy alloys varies with the heating rate [11– 14]. The empirical relation used to analyze the dependence of T_g on heating rate is of the form:

$$T_g = A + B \log\beta \qquad (4)$$

with A and B being the constants. Various results in Table 1 show that this relationship holds good in present set of alloys. Figure 3 depicts the variation of T_g vs. logβ for different glassy alloys. The value of A represents the glass transition temperature for the heating rate of 1K / min. It has been found by various workers that the slope B in the Eqn. (1) is related to the cooling rate of the melt: the lower the cooling rate of melt, the lower the value of B. The physical significance of B seems to be related with the response of the configurational changes within the glass transformation region. The values of B for different glasses have been found to be different, indicating that increasing In content effects structural changes. The values of A and B for different alloys are given in Table 1. The activation energy for glass transition has been calculated using eqn. (3). The plots of lnβ vs. $10^3/T_g$ for all glassy alloys are shown in Fig. 4. The values of ΔE_t for different alloys obtained using equation (3) are also given in Table 1. Various parameters in Table 1 show a marked dependence on In% in present set of glasses as ΔE_t and B show an increase upto x = 20 and A increases monotonically.

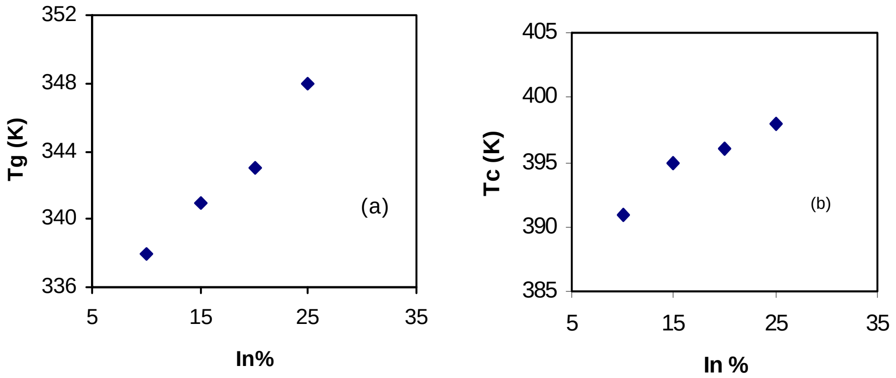

Fig. 2. Variation of T_g and T_c with In % at a heating rate of 10 °C /min.

Table 1: Parameters obtained for different glasses.

Composition (x)	ΔE_t (eV)	B (min)	A °C
10	1.644	12.85	54.01
15	1.552	13.89	55.29
20	1.322	16.01	58.81
25	1.598	12.42	64.32

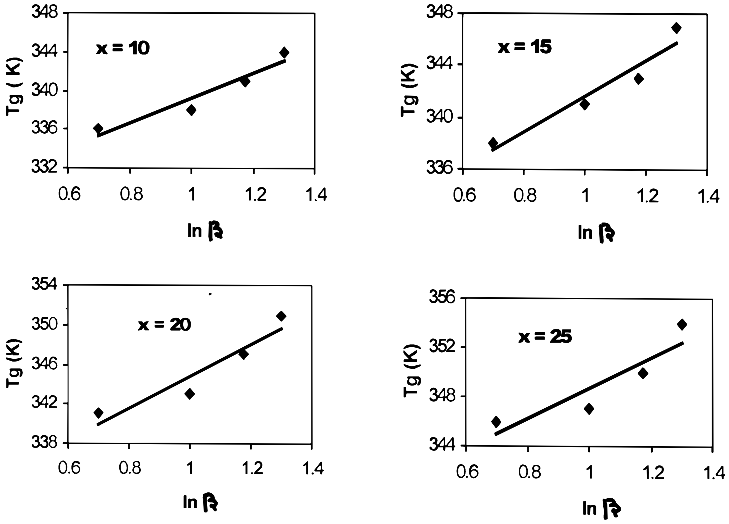

Fig. 3. Variation of glass transition temperature (T_g) with heating rate (lnβ)

In present set of glasses, the activation energy ΔE_t is found to decrease with indium content and shows the minimum value for x =20. Such behavior can be explained in terms of glass forming tendency (GFT) of these glasses. In a glassy alloy, GFT is related to the ease by which melt can be cooled with the avoidance of crystal formation. It has been reported that the difference of T_c and T_g is a strong indication of GFT [15] and higher are the values of (Tc–Tg), the greater is the GFT. For comparison sake, variation of (Tc–Tg) with composition at a heating rate of 10^oC/min is shown in Fig. 5. The values of (Tc–Tg) have been found to be increasing with increasing indium content in present glasses As shown in Figure 5 and Table1, behavior of (Tc–Tg) is just opposite to that of $\Delta E_{t.}$ Hence one can conclude that the activation energy of glass transition process is related to GFT in the present glasses. Higher GFT may require less activation energy for glass transition process as found in the present study.

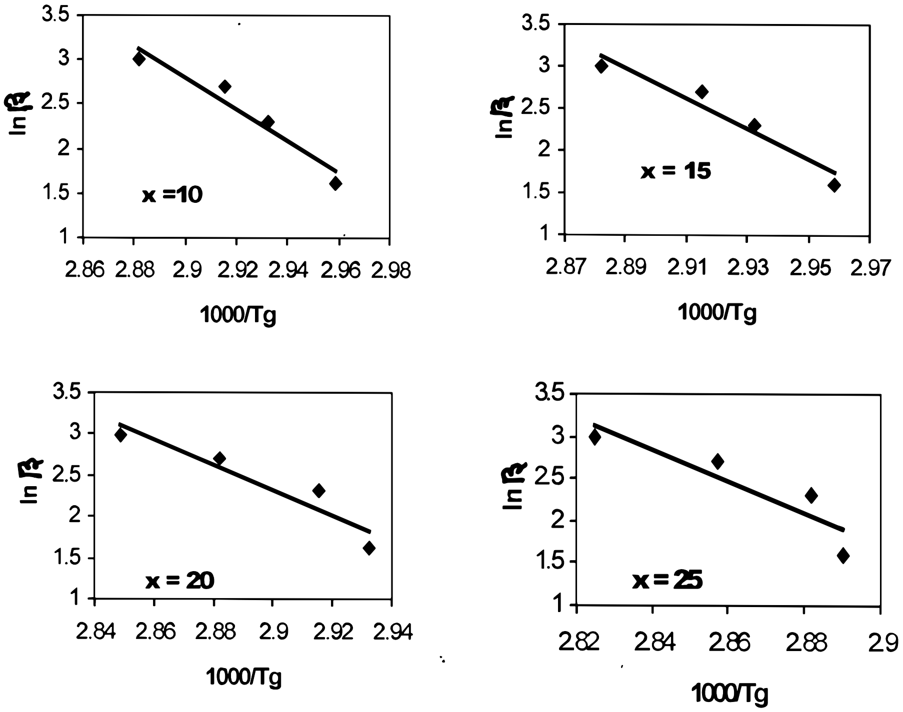

Fig. 4. Variation of $\ln\beta$ *vs.* 10^3 / T_g *in* $Te_5(In_xSe_{100-x})_{95}$ *glassy alloys.*

Se is well known to exist in the form of Se_8 rings and Se-Se chains [4]. Te belongs to same group of the periodic table as Se. Tellurium when mixed into Se probably reduces the rings and goes into Se chains, However, some of the Te atoms may not be incorporated in the chains and exist as ionized impurities forming positively charged localized states since the electron affinity of Te (1.97 eV) is less than that of the Se (2.02 eV). Thus addition of Te in Se system is reported [5] to result in greater hardness, lesser ageing effects etc.

Addition of indium in Se system, Se-In bonds form, carrier concentration increases, hence energy band gap of the system decreases. Further addition of indium in Se system, In-In bond formation takes place. Volume of this system decreases, molecular density increases, thus decreasing carrier density of this system, hence increasing energy band gap. Such type of behavior of energy gap with increasing indium content in Se-In glasses may be explained by considering the structural changes due to increasing indium concentration. Different bonds expected to occur in Se-In system are Se-Se, In-In and Se-In with bond energies 79.5, 24.0 and 54.0 K cal/mol respectively [16]. The Se-Se, In-In are homopolar and Se-In are heteropolar. The average energy of homopolar bonds is almost equal to the energy of heteropolar bonds. As strong Se-In bonds are energetically favored compared to In-In bonds [17], it is predicted that the system exhibits a tendency for chemical ordering, which tends to form microscopic molecular species. Addition of indium in Se system introduces In-In and In-Se bonds in Se_8 rings. It may be noted that the bond length of In-In is larger than Se-Se bond, which may increase the volume of the system, hence effective molecular weight decreases.

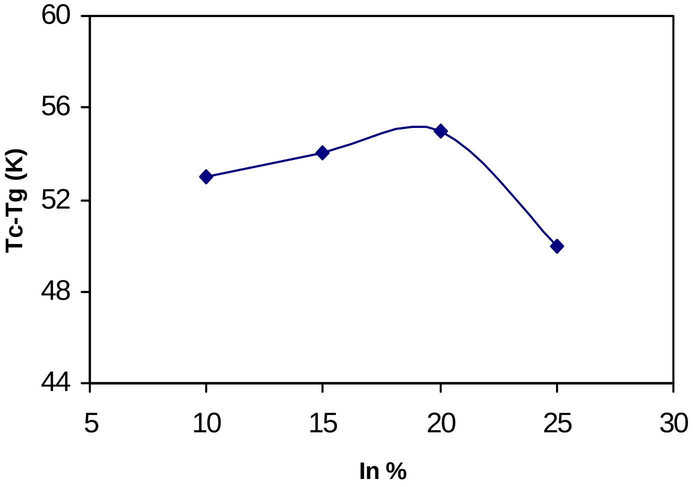

Fig. 5. Variation of T_c-T_g with indium content in ternary $Te_5(In_xSe_{100-x})_{95}$ glasses

Chalcogenide glasses are characterized by short-range order and due to lack of translational symmetry, the properties of chalcogenide glasses strongly depend upon the character and concentration of chemical bonds, which holds the atoms together in the glassy network. The glass transition temperature T_g in present set of alloys has been found to be increasing with indium content. In multi-component glasses, T_g is known to depend on several independent parameters such as the band gap, coordination number, mean atomic volume and mean molecular weight [18-28]. The atomic weight of Indium is greater than Selenium. The increasing sequence of T_g in present alloys with increasing In content may, therefore, be associated with the increase in the mean atomic weights of present set of glasses.

Moreover, the effect of indium content at the expense of Se concentration may also be due to the decreasing number of Se_8 ring structure. As In belongs to the 3rd group of the periodic table, it will cross-link the Se-Se chains and thus giving more rigidity to the structure and increases the glass transition temperature. Further, the electron affinity of Te<Se, formation of In-Se bonds is more likely as compared to In-Te bonds and thus results in decreasing ring concentration with increasing In content.

4. Conclusions

DSC measurements have been made in ternary $Te_5(In_xSe_{100-x})_{95}$ glassy alloys. The effect of increasing indium concentration on the glass transition kinetics has been studied. It is observed that the glass transition temperature (T_g) in present set of ternary glasses increases with increase in In%. Such behavior may be attributed to an increase in their mean atomic weight. The activation energy of glass transition process (ΔE_t) decreases with increasing indium content and shows a minimum for x = 20. Tc–Tg increases in reverse sequence and shows the maximum value at x = 20. In present set of glasses it can be concluded that the activation energy of glass transition process is related to GFT in the present glasses and the chalcogenide glasses having higher activation energy for glass transition process shows less GFT.

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