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GLASS TRANSITION KINETICS OF SOME Se–Te–Ag CHALCOGENIDE GLASSES

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The present paper reports the Differential Scanning Calorimetric (DSC) study of some Ag doped Se–Te chalcogenide glasses. DSC runs were taken at different heating rates. Well-defined endothermic and exothermic peaks were obtained at glass transition and crystallization temperatures.

The variation of glass transition temperature T_g with Ag concentration has been studied. It has been found that T_g decreases with increase in Ag concentration. The heating rate dependence of T_g is used to evaluate the activation energy of glass transition (ΔE_t). The value of ΔE_t has been found to increase with increase in Ag concentration followed by nearly constant value at higher concentrations of Ag.

Keywords: *chalcogenide glasses, DSC, glass transition kinetics*

Introduction

Chalcogenide glasses exhibit unique IR-transmissions and electrical properties that make them useful for several potential applications. Recently, Ag-doped chalcogenide glasses have become attractive materials for fundamental research regarding their structure, properties and preparation [1–5]. They have many current and potential applications in optics and optoelectronics such as photo doping, optical imaging, photo lithography and phase change (PC) optical recording [6–16].

The optical properties and photostructural changes of Ag-doped chalcogenide glasses have been studied by various workers [6–8]. In our earlier communications [9–10] we have reported photoconductivity and dielectric measurements in Ag-doped Se–Te alloys and found that the ionic character of the glassy samples is important to explain the observed results. Thin films of chalcogenide glasses containing Ag have also been found application in erasable PC optical recording [11–16]. It may be mentioned here that only a few studies have been reported on thermal properties (glass transition and crystallization kinetics) [17–22] in these glasses. We have therefore undertaken the calorimetric studies of Ag-doped glasses in our laboratory.

One of the most important problems in the area of chalcogenide glasses is the understanding of glass transition temperature (T_g). The nature of glass transition is complex and even today remains poorly understood. In some of the chalcogenide glassy systems, glass transition temperature T_g is found to vary with the average coordination number.

The glass transition is exhibited as an endothermic peak or a shift in the base line in Differential Scanning Calorimetry (DSC) due to change in specific heat. The heating rate dependence of T_g is well known, which makes possible the study of glass transition kinetics. The present paper reports the effect of Ag doping in glassy $Se_{70}Te_{30-x}Ag_x$ (x=0, 2, 4 and 6) system on glass transition temperature and activation energy of glass transition.

Experimental

Glassy alloys of $Se_{70}Te_{30-x}Ag_x$ (x=0, 2, 4 and 6) were prepared by quenching technique. High purity materials (5N pure) were weighed according to their atomic percentages and were sealed in quartz ampoules under the vacuum of 10^{-5} Torr. Each ampoule was kept inside the furnace at 1000°C so that all the elements gets melted. The temperature was raised at a rate of 3–4°C min^{-1}. The ampoules were rocked frequently for 10 h at the maximum temperature to make the melt homogeneous. Quenching was done in ice water and the glassy nature of alloys was checked by X-ray diffraction technique. The glasses, thus prepared, were ground to make fine powder for DSC studies.

10 to 20 mg of each sample was heated at a constant heating rate and the changes in heat flow with respect to an empty pan were measured. Four heating rates (5, 10, 15 and 20°C min^{-1}) were chosen in the present study. Measurements were made under almost identical conditions so that a comparison of glass

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transition temperature T_g and activation energy of glass transition ΔE_t could be made in order to understand the effect of increasing the third element (Ag) in the present chalcogenide glassy system.

Results and discussion

Composition dependence of glass transition temperature

Non-isothermal DSC technique has been widely used in literature [23–29] for the study of the glass transition kinetics. This technique is particularly important due to the fact that: (1) it is easy to carry out; (2) it requires little sample preparation; (3) it is quite sensitive and (4) it is relatively independent of the sample geometry. We have therefore used non-isothermal DSC technique for study of glass transition kinetics in the present work.

Figures 1 shows the typical DSC curves for $Se_{70}Te_{30-x}Ag_x$ alloys (x=0, 2, 4, 6) at a particular heating rate of 20 K min^{-1}. Similar curves were obtained for other heating rates also (not shown here). It is clear from Fig. 1 that well defined endothermic and exothermic peaks are observed at glass transition temperature (T_g) and crystallization temperatures (T_c), respectively. We have taken the peak temperature of endothermic peaks as glass transition temperature for each alloy (Fig. 2). The values of glass transition temperature (T_g) for all the glassy alloys at different heating rates are given in Table 1. From this table, it is clear that the glass transition temperature decreases with increase in the concentration of Ag.

This decrease in T_g of Ag doped ternary alloys $Se_{70}Te_{30-x}Ag_x$ can be explained in terms of atomic weights of Te and Ag. The atomic weight of Ag (107.87 g mol^{-1}) is less than that of Te (127.60 g mol^{-1}). In the present work, Ag is added in binary $Se_{70}Te_{30}$ at the cost of Te. Thus, the mean atomic mass of ternary alloys is decreased. This may provide cooperative conditions for thermal relaxation process. This is probably the reason for the decrease in T_g due to addition of Ag.

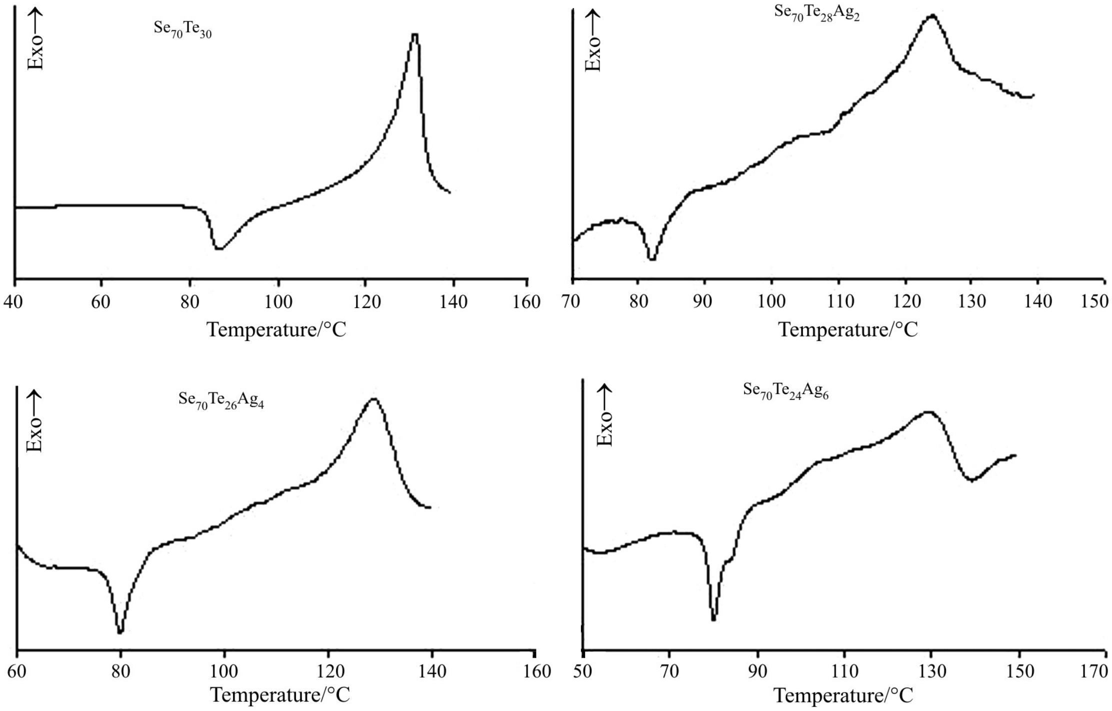

Fig. 1 DSC curve for glassy $Se_{70}Te_{30-x}Ag_x$ alloys at a heating rate of 20 K min^{-1}

Table 1 Values of glass transition temperature T_g of glassy $Se_{70}Te_{30-x}Ag_x$ alloys at different heating rates

Sample	T_g/K			
	5°C min^{-1}	10°C min^{-1}	15°C min^{-1}	20°C min^{-1}
$Se_{70}Te_{30}$	349.9	354.5	357.0	359.5
$Se_{70}Te_{28}Ag_2$	347.8	–	354.3	354.7
$Se_{70}Te_{26}Ag_4$	346.5	350.8	352.4	353.1
$Se_{70}Te_{24}Ag_6$	345.4	348.9	350.9	352.5

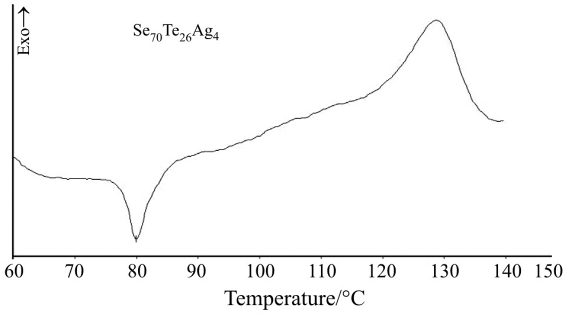

Fig. 2 A typical DSC curve showing peak as glass transition temperature

It was found that lone-pair electron have an important role in chalcogenide glass formation. The chemical environment in the structure has an influence on the role of lone-pair electrons. If there are cations that have high ionicity and strong electrostatic field in the system, unshared electrons may interact with the cations because of electrostatic force and Van der Waals interactions. This action of cation (e.g., Ag^+) constraints the lone-pair electrons of the bridging atoms, and the flexibility of the chemical bond with the lone-pair electrons is decreased. The Ag atom is introduced in chalcogenide system as an Ag^+ ion and its charge is compensated by C_1^- (one-fold coordinated chalcogen). The Ag^+ ion is bonded also by the two, three or four coordinated bonds between free Ag d-orbitals and lone-pair of chalcogens [30]. The expected value of coordination number of Ag in tellurides glasses is 4 [31]. The chalcogenide glass forming ability of Ag atom is very poor, because of high ionicity of Se–Ag and Te–Ag bonds and hence the glass forming ability decreases with the addition of Ag atoms in Se–Te system. This is confirmed from the phase diagram of Se–Te–Ag, which shows that the glass forming region in Se–Te–Ag system is located within narrow boundaries close to 100 at% of Se and comprises concentrations of 38 at% of Te and 17 at% of Ag [32]. This may also explain be the lower values of T_g in the ternary Se–Te–Ag glasses as compared to binary Se–Te glass. Sharma *et al.* [19] also reported the decrease in T_g in $Se_{80-x}Te_{20}Ag_x$ (x=0, 5, 10) with the addition of Ag in glassy $Se_{80}Te_{20}$ alloy.

Evaluation of activation energy of glass transition

The kinetics of glass transition can be studied using the theory of glass transition kinetics and structural relaxation as developed by Moynihan and other workers [33–35] from the heating rate dependence of glass transition temperature. Using such a theory, one can calculate the activation energy of molecular motion and rearrangement near glass transition temperature.

The heating rate dependence of the glass transition temperature in chalcogenide glasses is interpreted in terms of thermal relaxation phenomenon. In this kinetic interpretation, the enthalpy at a particular temperature and time $H(T, t)$ of the glassy system, after an instantaneous isobaric change in temperature, relaxes isothermally towards a new equilibrium value $H_e(T)$. The relaxation equation can be written in the following form [33]:

Table 2 Values of activation energy of glass transition for different chalcogenide glasses

Sample	ΔE_t/kJ mol^{-1}
$Se_{70}Te_{30}$	145.9
$Se_{70}Te_{28}Ag_2$	185.3
$Se_{70}Te_{26}Ag_4$	197.3
$Se_{70}Te_{24}Ag_6$	192.7

$$(\delta H/\delta t)_T = -(H-H_e)/\iota \qquad (1)$$

where ι is a temperature dependent structural relaxation time and is given by the following relation:

$$\iota=\iota_o\exp(-\Delta E_t/RT)\exp[-c(H-H_e)] \qquad (2)$$

where ι_o and c are constants and ΔE_t is the activation energy of relaxation time. Using the above equations, it can be shown [34, 35] that

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

Equation (3) states that ln β *vs.*1/T_g plot should be straight line and the activation energy involved in the molecular motions and rearrangements around T_g can be calculated from the slope of this plot. The plots of ln β *vs.* 1000/T_g is shown in Fig. 3 for glassy $Se_{70}Te_{30-x}Ag_x$ (x=0, 2, 4, 6) alloys. The values of ΔE_t obtained for the different alloys using Eq. (3) are given in Table 2. The plot of ΔE_t *vs.* Ag concentration is shown in Fig. 4. From this plot, it is clear that ΔE_t first increases with Ag concentration and then almost saturates at higher concentration of Ag.

The increase in ΔE_t due to addition of Ag in binary Se–Te system can be explained in terms of average heat of atomization for these alloys. The average heat of atomization, H_S, is based on chemical bonding aspects which is defined for a binary alloy X_aY_b as a direct measure of cohesive energy, i.e., of the average bond strength [36]. H_S can be given as:

$$H_S=[a(H_s)_X+b(H_S)_Y]/(a+b) \qquad (4)$$

For a ternary alloy $X_aY_bZ_c$, it can be expressed as:

$$H_S=[a(H_S)_X+b(H_S)_Y+c(H_S)_Z/(a+b+c)] \qquad (5)$$

where $(H_S)_X$, $(H_S)_Y$, $(H_S)_Z$ are the heat of atomization of atoms X, Y and Z resepectively. The value of H_S for binary alloy $Se_{70}Te_{30}$ and ternary alloys $Se_{70}Te_{30-x}Ag_x$ (x=2, 4, 6) are given in Table 3. From this table, it is clear that the value of H_S is larger for ternary alloys as

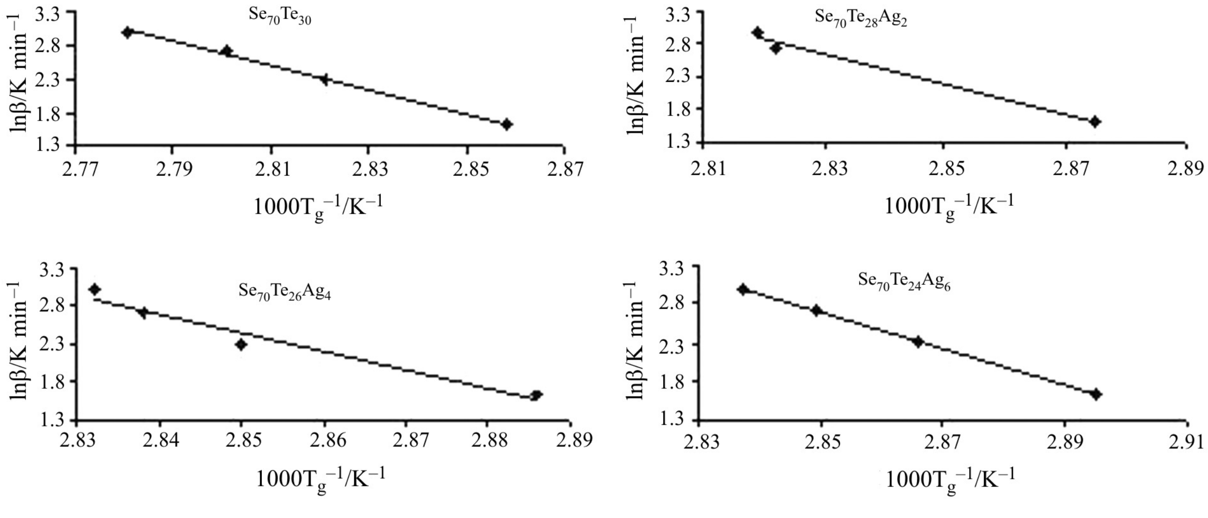

Fig. 3 Plots of ln β *vs.* $10^3/T_g$ for glassy $Se_{70}Te_{30-x}Ag_x$ alloys

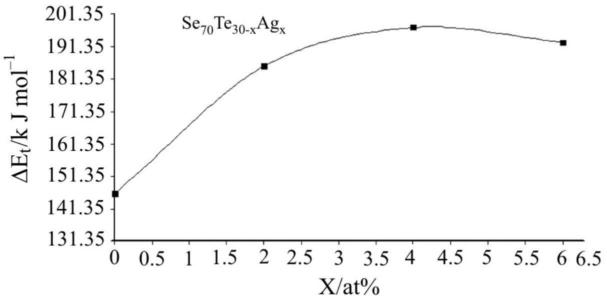

Fig. 4 Plot of ΔE_t *vs.* Ag concentration

Table 3 The average bond strength of ternary $Se_{70}Te_{30-x}Ag_x$ (x=0, 2, 4, 6) alloys

Sample	H_s/kJ mole atoms^{-1}
$Se_{70}Te_{30}$	218.0
$Se_{70}Te_{28}Ag_2$	219.7
$Se_{70}Te_{26}Ag_4$	221.5
$Se_{70}Te_{24}Ag_6$	223.2

compared to that of binary alloy. This explains the higher values of ΔE_t for ternary alloys as compared to that of binary $Se_{70}Te_{30}$ alloy.

Conclusions

The study of the glass transition kinetics in glassy $Se_{70}Te_{30-x}Ag_x$ (x=0, 2, 4, 6) alloys has been made using DSC technique. The glass transition temperature decreases with increase in the concentration of Ag. This decrease in T_g of ternary alloys is explained in terms of reduced mean atomic masses of these alloys and the poor chalcogenide glass forming ability of Ag atom, because of high ionicity of Se–Ag and Te–Ag bonds.

The activation energy of glass transition (ΔE_t) has been evaluated using the relation suggested by Moynihan. The value of ΔE_t has been found to increase with increase in Ag concentration and it becomes nearly constant at higher concentrations of Ag. The higher value of ΔE_t for ternary alloys as compared to that of binary $Se_{70}Te_{30}$ alloy is explained in terms of average heat of atomization for these alloys.

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