

## EFFECT OF SOME METALLIC ADDITIVES ON THE KINETICS OF GLASS TRANSITION IN $\text{Se}_{80}\text{Te}_{20}$ GLASSY ALLOY

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Calorimetric measurements have been performed in glassy alloys  $\text{Se}_{80}\text{Te}_{20}$  and  $\text{Se}_{70}\text{Te}_{20}\text{M}_{10}$  ( $\text{M} = \text{Ag}, \text{Cd}, \text{Sb}$ ) to study the effect of these metallic additives on the kinetics of glass transition in glassy  $\text{Se}_{80}\text{Te}_{20}$  alloy. The variation of  $T_g$  with heating rate and composition has been studied. It has been found that increasing sequence of  $T_g$  at all the heating rates in ternary glasses is same as that of the atomic weight of third element. Thus, we can conclude that  $T_g$  in these glasses increases with increase in their mean atomic weights. The activation energy of glass transition process ( $\Delta E_i$ ) has been calculated using the theory of glass transition kinetics and structural relaxation as developed by Moynihan and other workers. It is found that the kinetics of glass transition depends on the addition of third element. The difference ( $T_c - T_g$ ) which is the indicator of glass forming tendency (GFT), has been determined by DSC thermograms for each sample. The activation energy of glass transition process ( $\Delta E_i$ ) is found to be related with ( $T_c - T_g$ ).

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### 1. Introduction

In recent years, optical memory effects in many chalcogenide glasses have been investigated due to their property of reversible transformations between the amorphous and crystalline phases [1 -11]. Since the advent of optical memory effects, amorphous Se (a - Se) has become material of considerable commercial importance in optical memory applications. As the uses of Se have grown, the attempts have been made to improve certain of its properties by alloying with other elements.

The structure of a - Se [12 -15] and the effect of alloying Te into a - Se [16 - 19] have been studied by various workers. Their results have shown that a - Se contains long polymeric chains and eight members rings in various proportions as its structural units, which are dissociated by the addition of Te in a - Se. This makes Se - Te alloys more important due to their attractive advantages (higher photosensitivity, greater hardness and lesser aging effects) as compared to pure a - Se. Due to these advantages, Se - Te alloys can be used as recording layer materials in optical phase change (PC) technique [20, 21]. However, these alloys are found to have some significant problems for this type of application. The two serious problems are the limited reversibility [22] and low glass transition and crystallization temperatures. These problems can be removed by adding a third element as a chemical modifier in Se -Te alloys.

Glassy solid state has a large viscosity, the relaxation kinetics are very slow leaving a few opportunities for local arrangements of bonds and atomic displacements. This type of thermal relaxation depends upon the annealing temperature and may be quite fast near the glass transition temperature.

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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. However, in chalcogenide glasses, such an endothermic peak can also be observed due to a fast change in enthalpy when the glassy system relaxes quickly due to a decrease in viscosity at the transition temperature. DSC technique can, therefore, be quite useful in the study of thermal relaxation in these glasses.

Since  $T_g$  depends upon heating rate  $\beta$  and composition, it is interesting to study such type of dependence in other glassy systems also. The aim of the present work is to report the effect of third element (Ag, Cd, Sb) on the glass transition kinetics in binary alloy  $Se_{80}Te_{20}$  at a particular concentration ( $x = 10$ ).

## 2. Experimental

Glassy alloys of  $Se_{80}Te_{20}$  and  $Se_{70}Te_{20}M_{10}$  ( $M = Ag, Cd, Sb$ ) were prepared by quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of  $10^{-4}$  gm. The materials were then sealed in evacuated ( $\sim 10^{-5}$  Torr) quartz ampoules (length  $\sim 5$ cm and internal diameter  $\sim 8$  mm). Each ampoule was kept inside the furnace at  $1000^\circ C$  (where the temperature was raised at a rate of  $3-4^\circ C / min.$ ). During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly. The ingots of the samples were then taken out by breaking the quartz ampoules.

The samples were kept at room temperature ( $\sim 300$  K) in dark for about one month for the attainment of thermodynamic equilibrium as stressed by Abkowitz [23] in chalcogenide glasses.

The glasses, thus prepared, were ground to make fine powder for DSC studies. 10 to 20 mg of the powder was heated at constant heating rate and the changes in heat flow with respect to an empty reference pan were measured. DSC 2910 Differential Scanning Calorimeter (T. A. instrument, USA) was used at four different heating rates 5, 10, 15 and  $20^\circ C / min.$  Each DSC scan showed a well defined endothermic peak at the glass transition temperature  $T_g$  and an exothermic peak at the crystallization temperature  $T_c$ . Measurements were made under almost identical conditions so that a comparison of activation energy of glass transition ( $E_t$ ) could be made in order to understand the effect of changing the additive element  $M$  (Ag, Cd, Sb) in ternary alloys  $Se_{70}Te_{20}M_{10}$ .

## 3. Theoretical basis

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 [24 - 26] 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 [24]:

$$(\delta H / \delta t)_T = - (H - H_e) / \tau \quad (1)$$

Where  $\tau$  is a temperature dependent structural relaxation time and is given by the following relation:

$$\tau = \tau_0 \exp (- \Delta E_t / RT) \exp [- c (H - H_e)] \quad (2)$$

Where  $\tau_0$  and  $c$  are constants and  $\Delta E_t$  is the activation energy of relaxation time. Using the above equations, it can be shown [25, 26] that;

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

Equation (3) states that  $\ln \beta$  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.

#### 4. Results

Fig. 1 shows a typical DSC thermogram at different heating rates for  $\text{Se}_{70}\text{Te}_{20}\text{Cd}_{10}$  alloys. Similar thermograms were obtained for other glassy alloys. It is clear from Fig. 1 that well defined endothermic and exothermic peaks are observed at  $T_g$  and  $T_c$ . The values of  $T_g$  at different heating rates for various glassy alloys are given in Table 1.

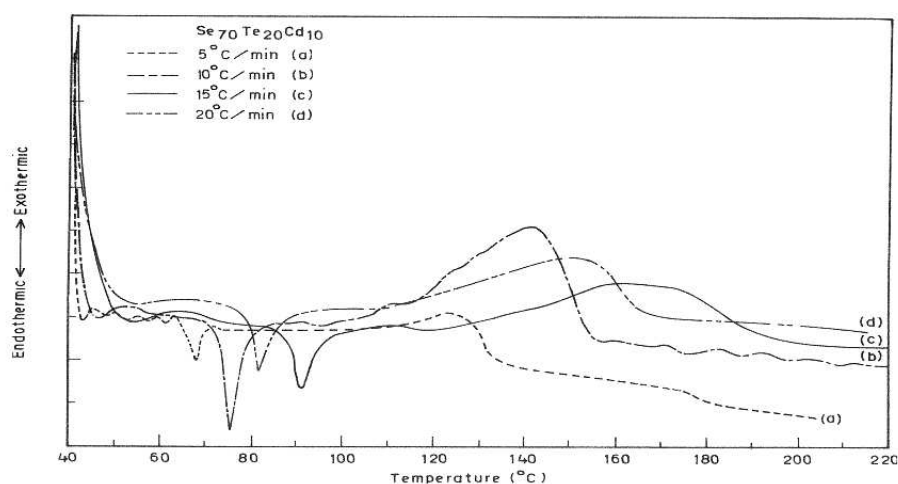


Fig. 1. DSC thermograms of  $\text{Se}_{70}\text{Te}_{20}\text{Cd}_{10}$  alloy at different heating rates.

Table 1. Glass transition temperatures of binary alloy  $\text{Se}_{80}\text{Te}_{20}$  and ternary alloys  $\text{Se}_{70}\text{Te}_{20}\text{M}_{10}$  (M = Ag, Cd, Sb) at different heating rates.

| Sample                                       | $T_g$ ( $^{\circ}\text{C}$ )    | $T_g$ ( $^{\circ}\text{C}$ )     | $T_g$ ( $^{\circ}\text{C}$ )     | $T_g$ ( $^{\circ}\text{C}$ )     |
|----------------------------------------------|---------------------------------|----------------------------------|----------------------------------|----------------------------------|
|                                              | 5 $^{\circ}\text{C}/\text{min}$ | 10 $^{\circ}\text{C}/\text{min}$ | 15 $^{\circ}\text{C}/\text{min}$ | 20 $^{\circ}\text{C}/\text{min}$ |
| $\text{Se}_{80}\text{Te}_{20}$               | 63.80                           | 68.02                            | 69.30                            | 71.12                            |
| $\text{Se}_{70}\text{Te}_{20}\text{Ag}_{10}$ | 60.00                           | 64.50                            | 67.30                            | 67.60                            |
| $\text{Se}_{70}\text{Te}_{20}\text{Cd}_{10}$ | 67.69                           | 72.30                            | 75.88                            | 76.92                            |
| $\text{Se}_{70}\text{Te}_{20}\text{Sb}_{10}$ | 74.63                           | 78.37                            | 80.61                            | 82.04                            |

One of the most important problems in the area of glasses is the understanding of glass transition kinetics which can be studied in terms of glass transition temperature  $T_g$  and activation energy of thermal relaxation ( $\Delta E_t$ ). 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, a study of the kinetics of glass transition is one of the most important problems in the area of chalcogenide glasses.

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  $\beta$  [27 – 31]. The empirical relation used to analyze the dependence of  $T_g$  on  $\beta$  is of the form:

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

Where A and B are constants. The results shown in Table 2 indicate the validity of this relationship for binary alloy  $\text{Se}_{80}\text{Te}_{20}$  and ternary alloys  $\text{Se}_{70}\text{Te}_{20}\text{M}_{10}$  (M = Ag, Cd, Sb). The plots of  $T_g$  vs  $\log \beta$  for glassy alloys are shown in Fig. 2. The value of A indicates 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 with in the glass transformations region. The values of B for binary and ternary alloys have been found to be different, indicating that binary  $\text{Se}_{80}\text{Te}_{20}$  undergoes structural changes after doping of different metallic additives (Ag, Cd, Sb). The values of A and B for different alloys are given in Table 2.

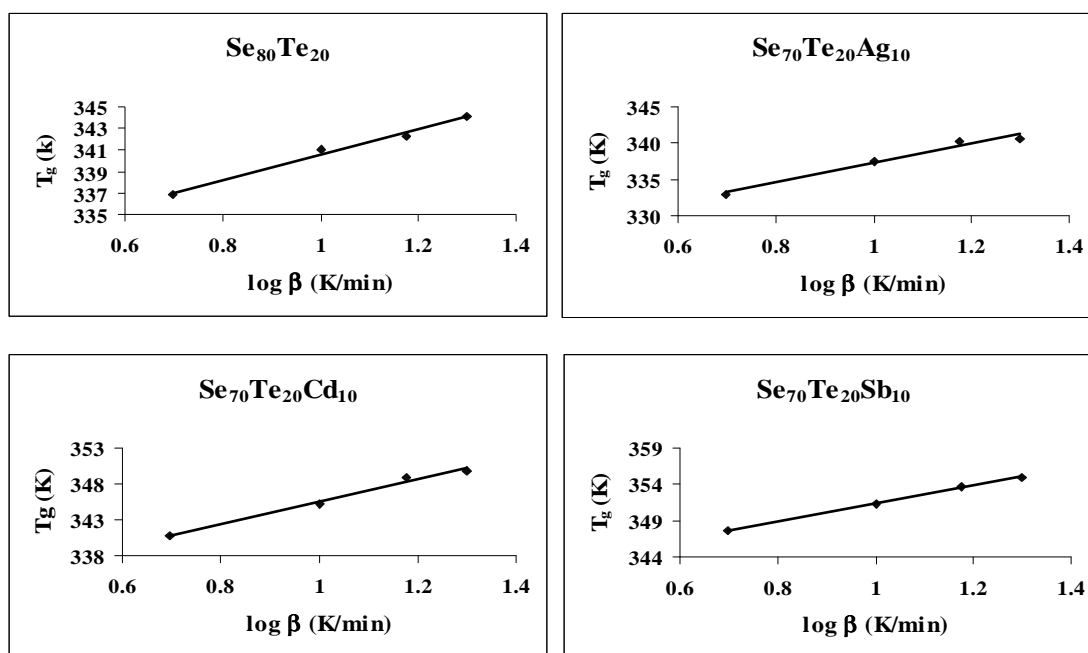


Fig. 2. Plot of  $T_g$  vs  $\log \beta$  for various glassy alloys.

Table 2. Values of  $\Delta E_t$  using Eqn. (3) and values of the slope B and intercept A using Eqn. (4) for different alloys.

| Sample                                       | $E_t$ (eV) | B (min)  | A ( $^{\circ}\text{C}$ ) |
|----------------------------------------------|------------|----------|--------------------------|
|                                              | Eqn. (3)   | Eqn. (4) | Eqn. (4)                 |
| $\text{Se}_{80}\text{Te}_{20}$               | 1.867      | 11.83    | 55.7                     |
| $\text{Se}_{70}\text{Te}_{20}\text{Ag}_{10}$ | 1.626      | 13.28    | 60.00                    |
| $\text{Se}_{70}\text{Te}_{20}\text{Cd}_{10}$ | 1.466      | 15.87    | 56.60                    |
| $\text{Se}_{70}\text{Te}_{20}\text{Sb}_{10}$ | 1.972      | 12.35    | 66.00                    |

The activation energy for glass transition has been calculated using eqn. (3). The plots of  $\ln \beta$  vs.  $10^3 / T_g$  for all glassy alloys are shown in Fig. 3. The value of  $\Delta E_t$  for the different alloys were obtained from equation (3) are given in Table 2.

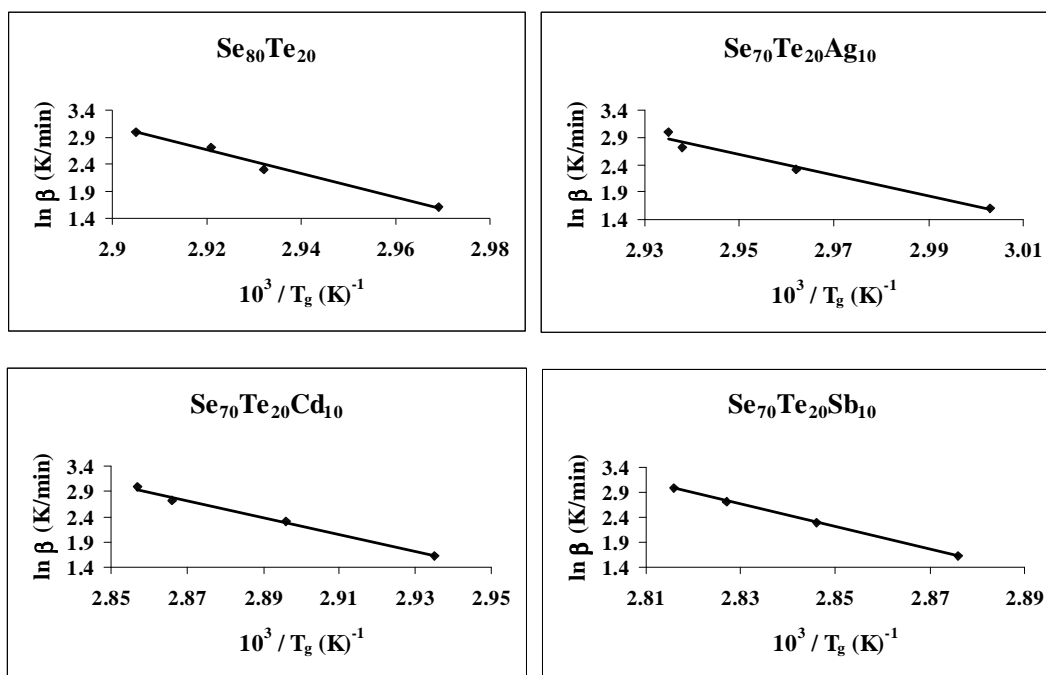


Fig. 3. Plot of  $\ln \beta$  vs  $10^3 / T_g$  for various glassy alloys.

## 5. Discussions

The structure of chalcogenide glasses represents the short range order. 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 the ternary alloys  $\text{Se}_{70}\text{Te}_{20}\text{M}_{10}$  ( $M = \text{Ag}, \text{Cd}, \text{Sb}$ ) has been found to be increasing in the order  $(T_g)_{\text{Ag}} < (T_g)_{\text{Cd}} < (T_g)_{\text{Sb}}$  for all the four heating rates. The  $T_g$  of a multicomponent glass is known to be depend on several independent parameters such as the band gap, coordination number, mean atomic volume and mean molecular weight [32 – 42].

The increasing sequence of  $T_g$  in ternary alloys may, therefore, be associated with the increase in the mean atomic weights of ternary glasses in the same sequence due to addition of third element (Ag, Cd, Sb) in Se – Te system [see Table 3].

Table 3. Atomic weights of additives.

| Name of Additive Elements | Atomic weight<br>(gm – mol <sup>-1</sup> ) |
|---------------------------|--------------------------------------------|
| Silver (Ag)               | 107.86                                     |
| Cadmium (Cd)              | 112.41                                     |
| Antimony (Sb)             | 121.75                                     |

The activation energy  $\Delta E_t$  in the ternary alloys is found to be increasing in the order  $(\Delta E_t)_{Cd} < (\Delta E_t)_{Ag} < (\Delta E_t)_{Sb}$ . This sequence can be explained in terms of glass forming tendency (GFT) of these glasses. GFT of a glassy alloy is related to the ease by which melt can be cooled with the avoidance of crystal formation. It has been found that the difference of  $T_c$  and  $T_g$  is a strong indication of GFT [43]. The higher the values of  $(T_c - T_g)$ , the greater is the GFT. The values of  $T_c$  and  $(T_c - T_g)$  at all heating rates are given in Table 4.

Table 4. Values of  $T_c$  and  $(T_c - T_g)$  for ternary alloys at different heating rates.

| $\beta$<br>(°C/min) | $Se_{70}Te_{20}Ag_{10}$ |             | $Se_{70}Te_{20}Cd_{10}$ |             | $Se_{70}Te_{20}Sb_{10}$ |             |
|---------------------|-------------------------|-------------|-------------------------|-------------|-------------------------|-------------|
|                     | $T_c$                   | $T_c - T_g$ | $T_c$                   | $T_c - T_g$ | $T_c$                   | $T_c - T_g$ |
| 5                   | 103.30                  | 43.30       | 125.60                  | 57.91       | 87.62                   | 12.99       |
| 10                  | 109.70                  | 45.20       | 130.00                  | 57.70       | 92.00                   | 13.63       |
| 15                  | 115.30                  | 48.00       | 136.47                  | 60.59       | 95.00                   | 14.39       |
| 20                  | 118.40                  | 50.80       | 139.23                  | 62.31       | 100.00                  | 17.96       |

The values of  $(T_c - T_g)$  have been found to be increasing in the order  $Sb < Ag < Cd$  in ternary alloys  $Se_{70}Te_{20}M_{10}$ . This sequence of  $(T_c - T_g)$  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. This is confirmed from the plots of  $\Delta E_t$  vs.  $(T_c - T_g)$  at all the four heating rates [see Fig. 4].

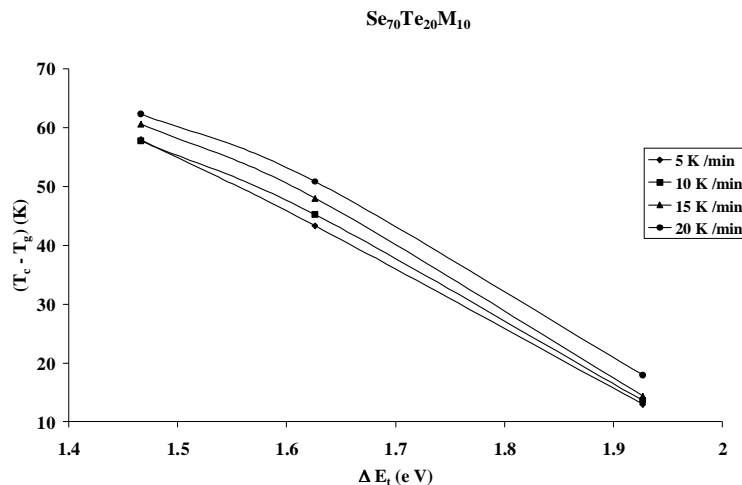


Fig. 4. Plot of  $E_t$  vs  $(T_c - T_g)$  of ternary alloys  $Se_{70}Te_{20}M_{10}$  ( $M = Ag, Cd, Sb$ ) at different heating rates.

## 6. Conclusions

The calorimetric measurements have been performed in binary  $Se_{80}Te_{20}$  and ternary  $Se_{70}Te_{20}M_{10}$  ( $M = Ag, Cd, Sb$ ) alloys using DSC technique. The effect of addition of some metallic

additives (Ag, Cd, Sb), at a particular concentration (10 %), on the glass transition kinetics in glassy Se<sub>80</sub>Te<sub>20</sub> binary alloy has been studied by non-isothermal DSC technique.

It has been found that increasing sequence of T<sub>g</sub> in ternary glasses is same as that of the atomic weight of third element. Thus, we can conclude that T<sub>g</sub> in these glasses increases with increase in their mean atomic weights. The activation energy of glass transition process ( $\Delta E_t$ ) is found to be related with (T<sub>c</sub>-T<sub>g</sub>) in reverse sequence. Hence one can conclude 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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