

CRYSTALLIZATION 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. Three different methods have been used for the evaluation of activation energy of crystallization (E_c). The results show that the value of E_c is decreased due to addition of Ag in binary alloy $Se_{70}Te_{30}$. This decrease is explained in terms of mean atomic masses of ternary alloys. The compositional dependence of (E_c) in ternary alloys shows a reversal in the trend at 4 at. % of Ag, which is explained in terms of mechanically stabilized structure at this composition.

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1. Introduction

Recently, great attention has been given to chalcogenide glasses mainly due to their wide range of applications in solid state devices both in scientific and technological fields. Optical data storage based on laser induced amorphous to crystalline (a-c) phase transformation of chalcogenide glasses is an area with on-going research activity [1-10].

Ag - doped chalcogenide glasses have become attractive materials for fundamental research of their structure, properties and preparation [11-15]. They have many current and potential applications in optics and optoelectronics such as photo doping, optical imaging, photo lithography and phase change optical recording [16-26].

The principle of phase change optical recording is straight forward. It is based on the concept that some physical property of microscopic area of recording layer on disc surface is altered. In this technique, spots of a crystalline material are melted momentarily by short laser pulses for recording and the recorded marks are erased through annealing process during which long laser pulses heat the amorphous spots to return in to crystalline phase. The photo structural changes in the optical properties (reflection coefficient, absorption coefficient, transmission coefficient) of chalcogen alloys due to amorphous to crystalline and crystalline to amorphous phase transformations are then used for erasing and recording of bits in the chalcogenide layer.

Chalcogenide glasses containing Ag, generally, exhibit single glass transition and single crystallization temperatures, which is an important condition for rewritable disks. Thin films of chalcogenide glasses containing Ag have found application in erasable PC optical recording [21-26]. Different Ag doped chalcogenide alloys have been developed as recording layer and their good practical performance has been reported [21-26].

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In PC technology, the laser pulse duration used to erase a written spot is usually several hundred nano-seconds. Hence, the a-c phase transformation in PC recording layer material should be very fast so that erasing is possible in such a time scale. For this reason, the study of a-c phase transformation is very important for the development of some new chalcogenide glasses as better PC recording materials.

The crystallization kinetics in chalcogenide glasses can be studied using isothermal and non-isothermal methods. In isothermal method, the sample is brought near to crystallization temperature very quickly and then any physical quantity which changes drastically is measured as a function of time. In non-isothermal method, the sample is heated at a fixed rate and the physical parameter is recorded as a function of temperature. A disadvantage of the isothermal method is the impossibility of reaching a test temperature instantaneously and during the time which system needs to stabilize, no measurements are possible. On the other hand, measurements can be achieved in a relatively rapid and precise manner by non - isothermal technique.

The electrical, optical and structural properties of Ag doped chalcogenide glasses have been studied by various workers [11-20] but there are only a few studies reported on crystallization kinetics in these materials [27-29].

With the above points of view, three different methods of analysis, Kissinger's relation [30], Matusita - Sakka theory [31-32] and Augis - Bennett approximation [33] have been used to study the crystallization kinetics of $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ system ($x = 0, 2, 4, 6$) under non - isothermal condition in the present work.

2. Experimental

Glassy alloys of $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ ($x = 0, 2, 4$ 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 an appropriate temperature (where the temperature was raised at a rate of $3-4$ °C /min.). The ampoules were rocked frequently for 10 hrs 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. 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.

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) were chosen in the present study. Measurements were made under almost identical conditions so that a comparison of activation energy of crystallization E_c could be made in order to understand the effect of increasing the third element (Ag) in given chalcogenide glasses.

3. Results and discussion

Figs. 1-4 show the typical DSC thermograms for $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ alloys ($x = 0, 2, 4, 6$) at a particular heating rate of 20 K / min. Similar thermograms were obtained for other heating rates also (not shown here). It is clear from Figs. 1 - 4 that well defined endothermic and exothermic peaks are observed at glass transition temperature (T_g) and crystallization temperatures (T_c) respectively. The values of peak crystallization temperature (T_c) for all the glassy alloys at different heating rates are given in Table 1.

The values of T_c of each alloy are found to be much higher than the room temperature. This is an important advantage of these alloys, which is essential to prevent self transition of recording materials between the two phases: amorphous and crystalline. Hence, one can expect each of these alloys to remain stable in its amorphous and crystalline phases at room temperature. Moreover, each

alloy has been found to stay in single phase during a-c transformation, which is an essential requirement of PC optical recording materials.

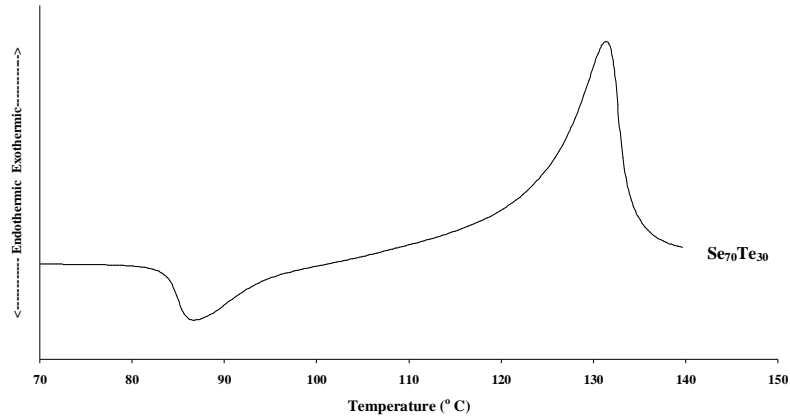


Fig. 1. DSC Thermogram for glassy $\text{Se}_{70}\text{Te}_{30}$ alloy at heating rate of 20 K/min.

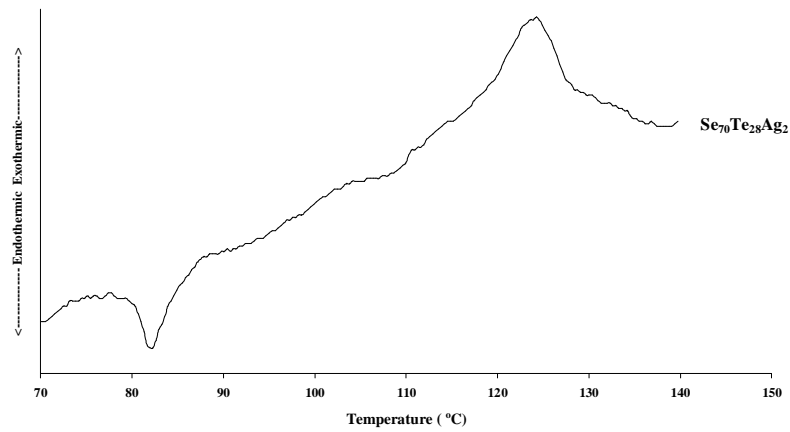


Fig. 2. DSC Thermogram for glassy $\text{Se}_{70}\text{Te}_{28}\text{Ag}_2$ alloy at heating rate of 20 K/min.

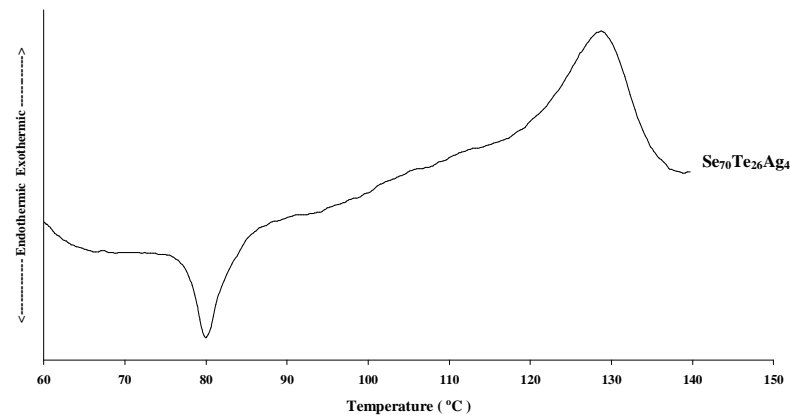


Fig. 3. DSC Thermogram for glassy $\text{Se}_{70}\text{Te}_{26}\text{Ag}_4$ alloy at heating rate of 20 K/min.

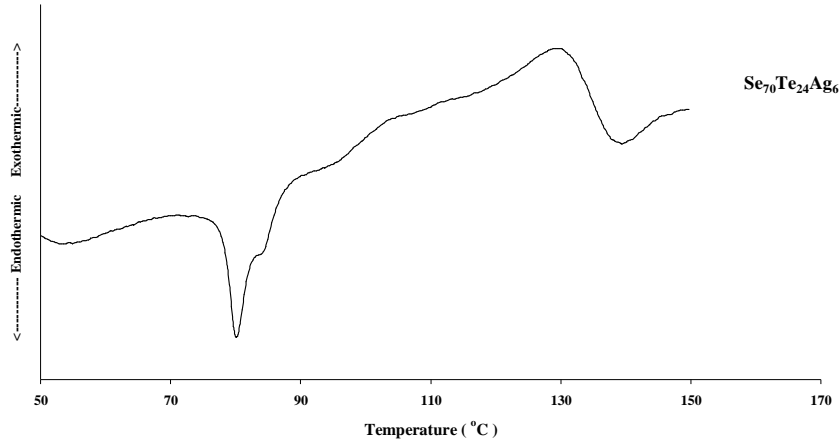


Fig. 4. DSC Thermogram for glassy $\text{Se}_{70}\text{Te}_{24}\text{Ag}_6$ alloy at heating rate of 20 K/min.

Table 1. Values of peak crystallization temperature T_c of glassy $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ ($x = 0, 2, 4, 6$) alloys at different heating rates.

Sample	T_c (K)			
	5 °C/min	10° C/min	15° C/min	20° C/min
$\text{Se}_{70}\text{Te}_{30}$	392.5	400.5	401.6	403.4
$\text{Se}_{70}\text{Te}_{28}\text{Ag}_2$	386.8	-	395.2	396.5
$\text{Se}_{70}\text{Te}_{26}\text{Ag}_4$	388.8	394.0	397.5	401.1
$\text{Se}_{70}\text{Te}_{24}\text{Ag}_6$	389.0	395.6	399.1	401.4

The crystallization kinetics of amorphous alloys has been extensively studied in past using the classical Johnson - Mehl - Avrami (JMA) theoretical model [34 - 36] in which the crystallization fraction (α) can be described as a function of time (t) according to the formula:

$$\alpha(t) = 1 - \exp[-(Kt)^n] \quad (1)$$

where n is the Avrami index and K is the rate constant which is given by:

$$K = K_0 \exp(-E_c / RT) \quad (2)$$

Here E_c is the activation energy of crystallization, R is the universal gas constant and K_0 is also a constant.

According to Kissinger [30], peak temperature of crystallization T_c in terms of the heating rate β , can be expressed as:

$$\ln(\beta / T_c^2) = -E_c / RT_c + \text{constant} \quad (3)$$

This equation is used to calculate the activation energy of crystallization by plotting $\ln \beta / T_c^2$ vs $1 / T_c$ curves. Such plots for glassy $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ ($x = 0, 2, 4, 6$) alloys are shown in Fig. 5.

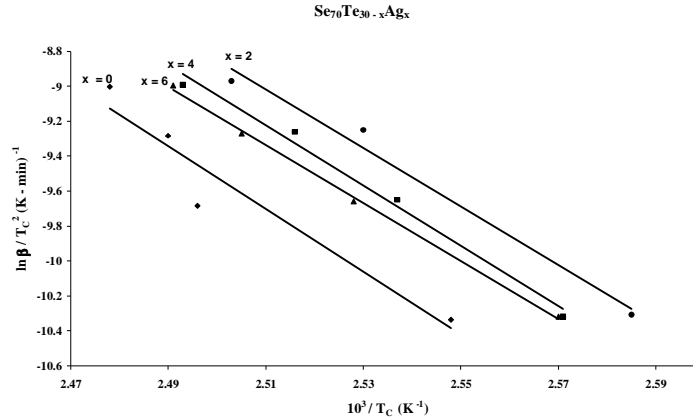


Fig. 5. Plots of $\ln \beta / T_c^2$ vs $10^3 / T_c$ for glassy $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ alloys.

The extent of crystallization (α) at a temperature T is well expressed by the expression:

$$\ln(1 - \alpha)^{-1} = (C / \beta^n) \cdot [(-n E_c) / R T] \quad (4)$$

The above expression is derived by Matusita and Sakka [31-32] from the classical JMA equation. Since the values of α are independent of β at $T = T_c$ [37], so at $T = T_c$, the equation (4) takes the form:

$$\ln \beta = - E_c / R T_c + \text{constant} \quad (5)$$

This equation is used to calculate the activation energy of crystallization by plotting $\ln \beta$ vs. $1 / T_c$ curve. Such plots for glassy $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ ($x = 0, 2, 4, 6$) alloys are shown in Fig. 6.

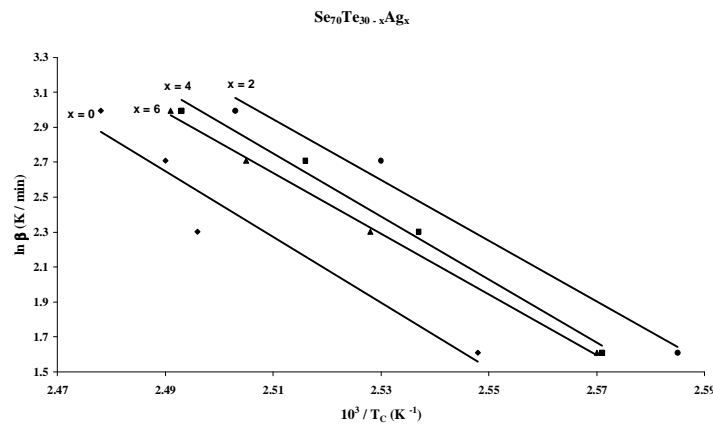


Fig. 6. Plots of $\ln \beta$ vs $10^3 / T_c$ for glassy $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ alloys.

The activation energy of crystallization E_c can also be determined by an approximation method developed by Augis and Bennett [33]. The relation used by them is of the form:

$$\ln(\beta / T_c) = -E_c / RT_c + \ln K_0 \quad (6)$$

The activation energy of crystallization has been evaluated by this equation using the plots of $\ln \beta / T_c$ against $1 / T_c$. Such plots for glassy $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ ($x = 0, 2, 4, 6$) alloys are shown in Fig. 7.

The values of E_c obtained for all the samples using the above three methods are given in Table 2. Comparison of E_c values of different alloys obtained from equations (3), (5) and (6) shows that the values are in good agreement. This means that one can use any of the three equations to calculate activation energy of crystallization.

From Table 2, it is clear that the value of E_c decreases due to addition of Ag in binary alloy $\text{Se}_{70}\text{Te}_{30}$. This decrease in E_c of Ag doped ternary alloys $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ can be explained in terms of atomic weights of Te and Ag. It is well known that the activation energy of crystallization is associated with the nucleation and growth process that dominates the devitrification of most glassy solids [38-41].

Table 2. Values of activation energy of crystallization E_c calculated from different non-isothermal methods.

Non-isothermal method	Activation energy of crystallization, E_c (eV)			
	$\text{Se}_{70}\text{Te}_{30}$	$\text{Se}_{70}\text{Te}_{28}\text{Ag}_2$	$\text{Se}_{70}\text{Te}_{26}\text{Ag}_4$	$\text{Se}_{70}\text{Te}_{24}\text{Ag}_6$
Kissinger's relation	1.549	1.443	1.488	1.432
Matusita & Sakka theory	1.617	1.497	1.557	1.500
Augis and Bennett's approximation	1.584	1.469	1.522	1.465
Average value	1.583	1.469	1.522	1.465

The atomic weight of Ag (107.87 gm / mol) is less than that of Te (127.60 gm / mol). In the present work, Ag is added in binary $\text{Se}_{70}\text{Te}_{30}$ at the cost of Te. Thus, the mean atomic weight of ternary alloys is decreased due to which an increase in the nucleation and growth rate is possible. This is probably the reason why crystallization occurs in present ternary alloys at comparatively lower activation energies.

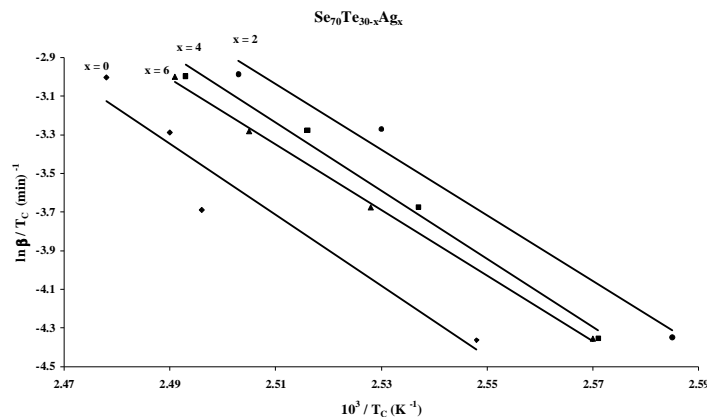


Fig. 7. Plots of $\ln \beta / T_c$ vs $10^3 / T_c$ for glassy $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ alloys.

Further, the compositional dependence of activation energy of crystallization E_c is shown in Fig. 8, which shows a reversal in the trend at 4 at % of Ag. In chalcogenide glasses, a discontinuity in various physical properties has been observed [42-44] at a particular composition when the average co-ordination number $\langle z \rangle$ reaches 2.4. This is explained by Phillips and Thorpe model [45] in terms of a mechanically optimized structure at a critical glass composition.

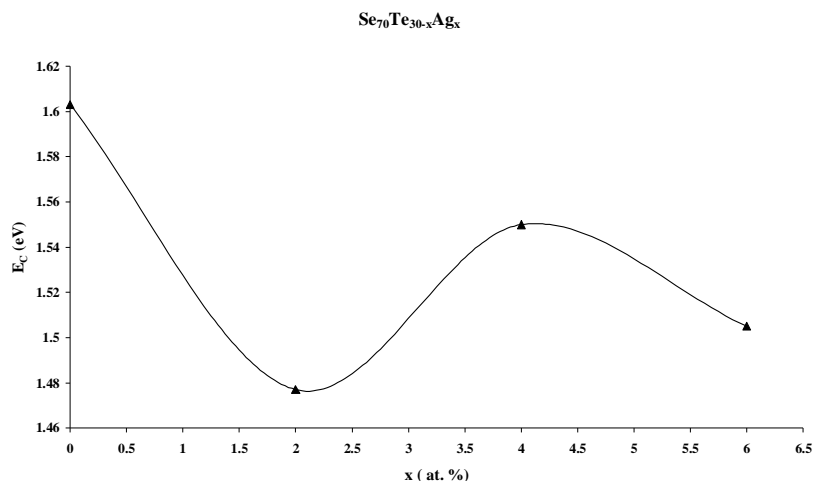


Fig. 8. E_c vs atomic percentage of Ag in glassy $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ alloys.

In the present case, the co-ordination number of Se and Te is 2 and that of Ag is 4. Hence, at the composition $\text{Se}_{70}\text{Te}_{26}\text{Ag}_4$, where a maximum in E_c occurs, $\langle z \rangle$ comes out to be nearly 2.1. However, Phillips and Thorpe model shows a threshold at $\langle z \rangle = 2.4$. The $\langle z \rangle$ value in the present case is slightly less. This may be due to an important limitation of Phillips and Thorpe model. In this model, Phillips considered the interaction between atoms to be purely covalent while arriving at the balance condition. Such an assumption may be valid for glasses showing electronic conduction but is not necessarily valid for system containing Ag. This is due to the fact that Ag doped chalcogenide glasses show ionic conduction [46], which indicates the presence of ionic behaviour of bonds of host materials with Ag. Thus, the ionic character of Ag doped chalcogenide glasses may be responsible for the reversal observed in activation energy of crystallization of ternary alloys at slightly less value of $\langle z \rangle$ in the present work.

4. Conclusions

The study of the crystallization kinetics in glassy $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ ($x = 0, 2, 4, 6$) alloys has been made by three different methods under non - isothermal condition. DSC technique has been used in the present study to calculate the activation energy of crystallization (E_c). It has been found that E_c values are less in ternary $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ ($x = 2, 4, 6$) alloys as compared to binary alloy $\text{Se}_{70}\text{Te}_{30}$. This decrease in ternary alloys is explained in terms of their mean atomic masses.

A reversal in the trend of activation energy of crystallization in ternary alloys has been observed at a particular value of $\langle z \rangle$ which is slightly less than value of $\langle z \rangle = 2.4$ as observed in IV - VI glasses. This may be attributed to ionic behaviour of Ag doped chalcogenide glasses.

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