

APPLICATION OF SINGLE SCAN DIFFERENTIAL SCANNING CALORIMETRY TECHNIQUE FOR DETERMINATION OF KINETIC PARAMETERS OF CRYSTALLISATION IN Se-In-Ag

N. YADUVANSHI^{a,*}, D. KUMAR^a, N. RASTOGI^b, A. KUMAR^c

^a*Department of Physics, JSS Academy of Technical Education, Noida 201301, India*

^b*Department of Physics, I.F.T.M University, Moradabad 244102, India*

^c*Department of Physics, Harcourt Butler Technical University, Kanpur, India*

A single scan has been performed in Differential Scanning Calorimetry (DSC) at a heating rate of 15°C/min under non-isothermal conditions to investigate the crystallization kinetics of glassy $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ alloys (where $x=2, 4, 6, 8$). Handerson's theory based on non isothermal method for thermal analysis of single-scan DSC data has been used for this purpose. Activation energy of crystallization and order parameter have been determined and composition dependence of these parameters has been discussed.

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1. Introduction

The intensive development of modern technologies has led to the synthesis of new materials. In recent years there has been a great deal of interest in the study of chalcogenide glasses from the point of view of basic physics [1-3] as well as of device technology [4-6]. They have large applicability in modern technology such as X Ray imaging, switching, photo-voltaic, electro photography, photonics, thermal imaging. Recent studies made on glass transition and crystallization kinetics of amorphous semiconductors provide interesting and important information [7-9]. Crystallization of amorphous semiconductor is due to the simultaneous nucleation and growth of crystallites. Thus, crystal nucleation causes crystallization.

It is well known that Se rich chalcogenide glasses exhibit high resistivity values implying certain limitation in their application. In order to stabilize these glasses, certain additives are added which act as cross linking agents and increase the stability of these selenium based glasses. The properties of the binary glassy chalcogenides on addition of the additives create compositional disorder in the materials which change the optical properties. [10]. Amorphous Selenium based chalcogenides have unique property of reversible transformation, making them useful for optical memory applications. Pure amorphous selenium is unstable because its low glass transition temperature (about 42°C) which is close to room temperature putting it in continuous danger of crystallization. Alloys of Se are very useful for various optical and photonic applications in the spectral range 0.6 μm to 15 μm . These glasses have potential applications in solid state devices. [11-12].

Differential scanning calorimetry (DSC) is commonly used technique for the analysis of kinetics of non isothermal transformation. In the non isothermal measurements, the sample is heated at a fixed rate and heat evolved is recorded as a function of temperature. The DSC [13] is mostly important used for the glass transition and crystallisation kinetics study of glassy materials, since it has high speed and requires a very small amount of glass samples to acquire parameters associated with crystallization and it is more sensitive.

* Corresponding author: nidhiyaduvanshi@jssaten.ac.in

A large majority of Amorphous to crystalline (a-c) phase transformation can be described by a process known as nucleation and growth. Different methods [14–19] have been adopted to study a-c phase transformation which is characterized by an activation energy ΔE_c and an Avrami exponent n according to the Johnson-Mehl-Avrami Kinetic Law. The determination of these parameters can be achieved in a relatively rapid and precise manner by non-isothermal DSC technique, which also allows an immediate observation of the transformation over a wider temperature range. When multiple scan technique is used for the analysis, several DSC curves yields the product $n\Delta E_c$. The actual value of ΔE_c , however, can only be achieved when n and thus the crystallization mechanism is known precisely. Both these values can be determined separately by single scan technique which supplies $\Delta E_c/n$ and ΔE_c independently.

As is widely accepted that the addition of a third element to the binary chalcogenide glasses produces stability in these glasses, the effects of the elements as an additive to binary glasses have been extensively studied[20]. The present paper reports the crystallization in $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ glasses using the DSC technique to understand the mechanism of crystallization in these glasses. The activation energy ΔE_c and Avrami exponent n are calculated using single scan technique. The composition dependence of these parameters has also been discussed.

2. Experimental

Glass compositions of $\text{Se}_{90}\text{In}_{10-x}\text{Ag}_x$ (where $x= 2, 4, 6, 8$) are prepared by melt quenching technique. The glasses thus prepared were ground to make fine powder for DSC studies. In DSC, the sample is heated at a constant rate and the change in heat flow with respect to an empty reference pan is measured. The thermal behavior is studied using RIGAKU DSV MODEL 823B. In the scan the presence of well defined endothermic peaks at the glass transition temperature and an exothermic peak at the crystallization temperature is observed. The value of T_c and T_g were taken at the temperature corresponding to endothermic and exothermic peak respectively in DSC scan.

3. Theory of measurements

The crystallization mechanism of amorphous materials is controlled by nucleation and growth process which can be characterized by activation energy 'Ec' and the Avrami exponent 'n' which is associated with the nucleation and growth mechanisms. According to John-Mehl-Avrami Law [21–23] the degree of crystallization is given by the following Equations:

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

here α is the extent of crystallization, K is a function of temperature, In general the value of crystallization rate constant K increases exponentially with temperature and hence can be given by

$$K = K_0 \exp\left(\frac{-\Delta E_c}{kT}\right) \quad (2)$$

here E_c is the activation energy of crystallization and k is the Boltzmann's constant.

Crystallisation kinetics of Chalcogenide glassy materials is a thermally activated process. Hendersan [24-29] has suggested single scan technique where non-isothermal DSC curve at a particular heating rate is analyzed. As per this theory the extent of crystallization is related to the activation energy of crystallization by the following equation:

$$\frac{d[\ln\{\ln(1-\alpha)^{-1}\}]}{dT^{-1}} = \frac{-\Delta E_c}{k} \quad (3)$$

It is clear from Eq. (3) $\ln\{\ln(1-\alpha)^{-1}\}$ versus T^{-1} plot should be a straight line and the activation energy ΔE_c involved in the molecular motion and rearrangements around T_c can be calculated from slope of this plot.

$\Delta E_c/n$ can be determined by the same theory proposed by Henderson. According to this theory the natural logarithm of first derivative of crystallization fraction can be expressed as:

$$\ln \frac{d\alpha}{dt} = - \frac{\Delta E_c}{nkT} \quad (4)$$

The derivation of above equation is

$$\frac{d(d\alpha/dt)}{d(T^{-1})} = - \frac{\Delta E_c}{nk} \quad (5)$$

It is clear from Eq. (5) that $\ln \frac{d\alpha}{dt}$ versus T^{-1} should be a straight line and the slope gives $\Delta E_c/n$. The value of 'n' can be calculated if the value of ΔE_c is known from Eq. (3).

4. Results and discussion

From the DSC measurements of $Se_{90}In_{10-x}Ag_x$ [30], at heating rate of $15^\circ C/min$, the value of α is calculated. Here α is the extent of crystallization and is calculated by dividing partial area to the total area of exothermic peak, i.e. $\alpha = A_T / A$. It is found that value of α with increases temperature as shown in Fig. 1.

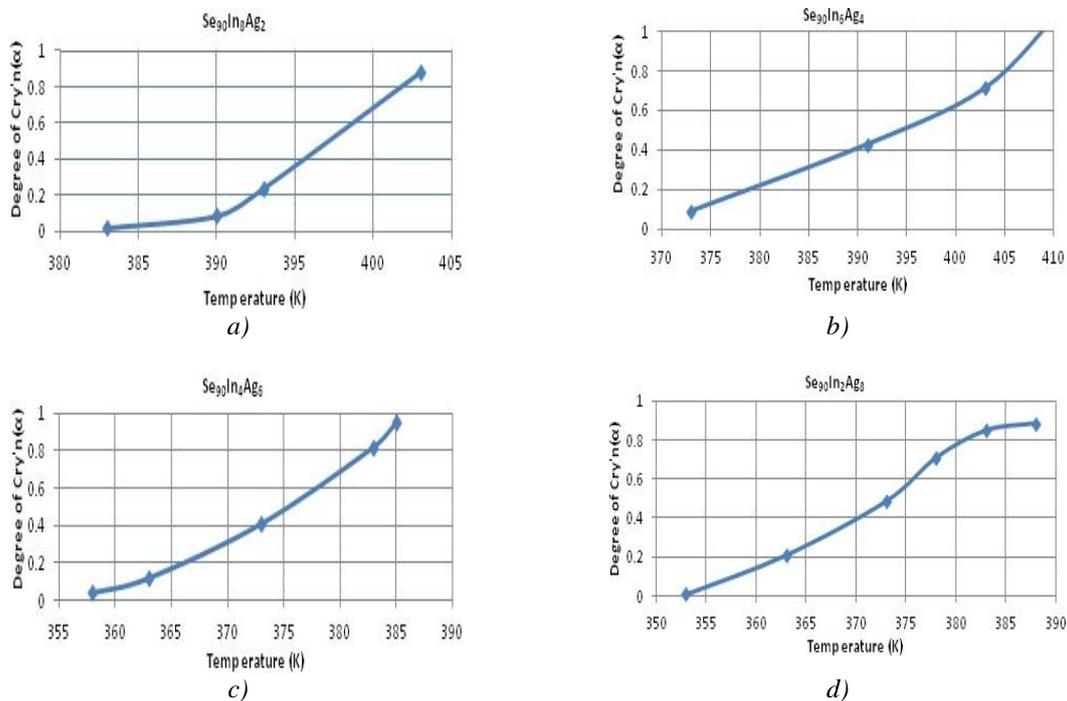


Fig. 1. Degree of crystallization (α) versus temperature for $Se_{90}In_{10-x}Ag_x$ glassy alloys: (a) Variation of Degree of crystallization (α) versus temperature (T) for $Se_{90}In_8Ag_2$; (b) Variation of Degree of crystallization (α) versus temperature (T) for $Se_{90}In_6Ag_4$; (c) Variation of Degree of crystallization (α) versus temperature (T) for $Se_{90}In_4Ag_6$; (d) Variation of Degree of crystallization (α) versus temperature (T) for $Se_{90}In_2Ag_8$.

Fig. 2 shows plots between $\ln(\ln 1/(1-\alpha))$ versus $1/T$ which is a straight line for all the glassy alloys used, showing the validity of Eq 3. From the slopes of these graphs the values of ΔE_c is calculated for each glassy alloy. Table 1 shows these calculated values for all the glass alloys.

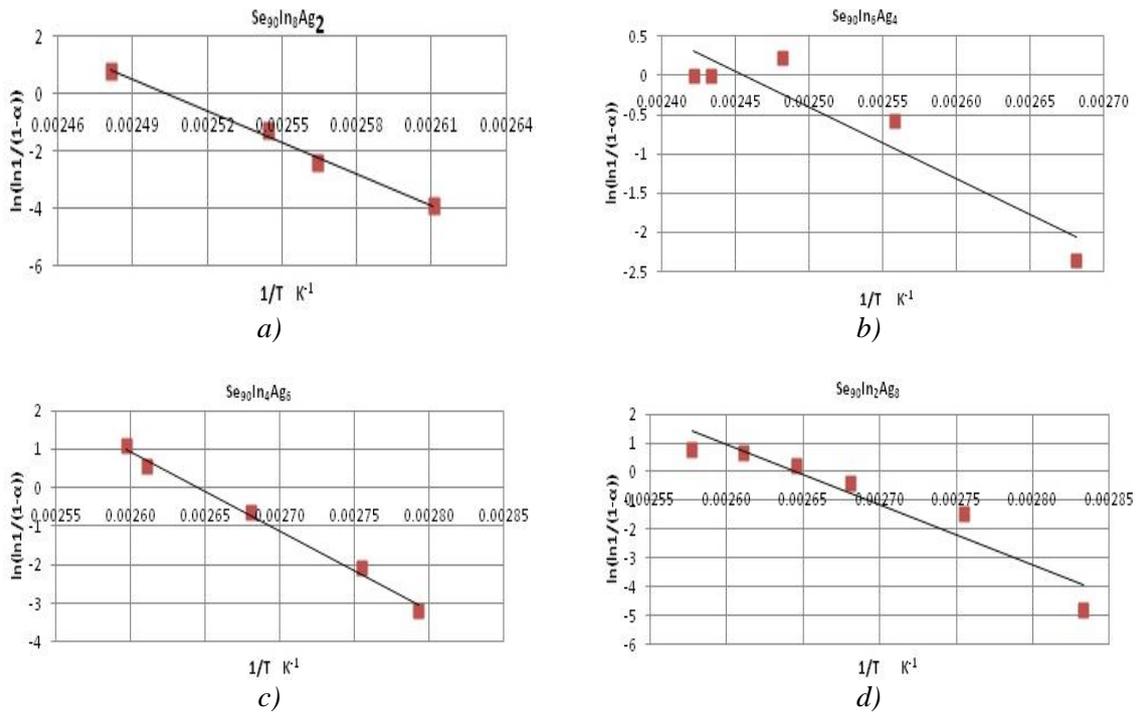


Fig. 2. $\ln(\ln 1/(1-\alpha))$ versus $1/T$ curves for $Se_{90}In_{10-x}Ag_x$ glassy alloys: (a) Variation of $\ln(\ln 1/(1-\alpha))$ versus $1/T$ for $Se_{90}In_8Ag_2$; (b) Variation of $\ln(\ln 1/(1-\alpha))$ versus $1/T$ for $Se_{90}In_6Ag_4$; (c) Variation of $\ln(\ln 1/(1-\alpha))$ versus $1/T$ for $Se_{90}In_4Ag_6$; (d). Variation of $\ln(\ln 1/(1-\alpha))$ versus $1/T$ for $Se_{90}In_2Ag_8$.

Table 1. Crystallization parameters E_c and n in a $Se_{90}In_{10-x}Ag_x$ alloy.

S. No.	Sample	E_c (KJ/mole)	n
1.	$Se_{90}In_8Ag_2$	302	0.2
2.	$Se_{90}In_6Ag_4$	76.4	0.7
3.	$Se_{90}In_4Ag_6$	171.2	0.88
4.	$Se_{90}In_2Ag_8$	174.3	0.92

It is clear from this table those ΔE_c first decreases with Ag concentration and then increases again at higher concentration showing a minima at 4 atomic percent of Ag.

From the α versus T curves as shown in Fig. 1, da/dT is calculated at various temperatures for each glassy alloy and da/dt is calculated by multiplying da/dT to the heating rate (β).

Fig. 3 shows plots of da/dt as function of $1/T$ for all glassy alloys studied here. It is clear from these figures that such plots are straight lines, showing the validity of eq 5. Values of $\Delta E_c/n$ are calculated from the slopes of these curves for all glassy alloys used. Using the value of ΔE_c calculated above (as shown in Table 1), and order parameter (n) is calculated for each glassy alloy and values are given in table 1. It is clear from the table that the value of n are less than 1 for all the glasses studied, indicating one dimensional crystal growth in these alloys.

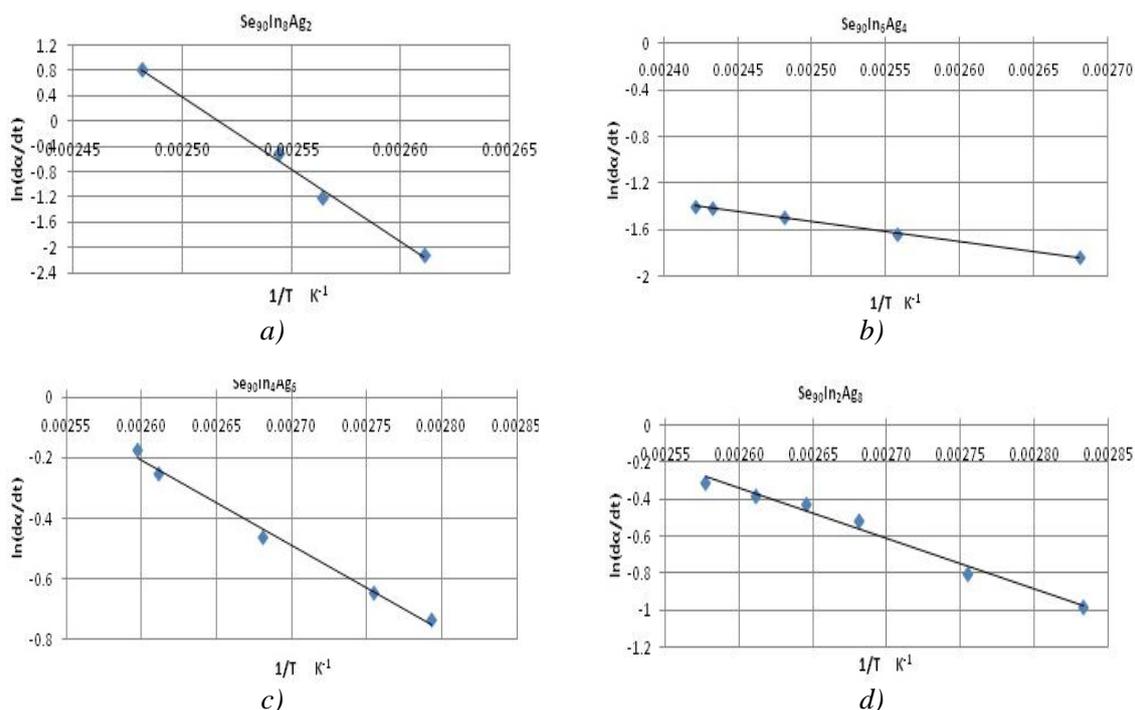


Fig. 3. $\ln(da/dt)$ versus $1/T$ for $Se_{90}In_{10-x}Ag_x$ glassy alloy: (a) Variation of $\ln(da/dt)$ versus $1/T$ for $Se_{90}In_8Ag_2$; (b) Variation of $\ln(da/dt)$ versus $1/T$ for $Se_{90}In_6Ag_4$; (c) Variation of $\ln(da/dt)$ versus $1/T$ for $Se_{90}In_4Ag_6$; (d) Variation of $\ln(da/dt)$ versus $1/T$ for $Se_{90}In_2Ag_8$.

The thermal stability [31] and glass forming tendency (GFT) is an important feature of chalcogenide alloys which is useful as recording materials due to the fact that phase change optical recording and erasing techniques are based on the laser induced thermal amorphization and crystallisation of chalcogenide glasses. This develops interest [32-35] in the study of thermal stability and GFT. Recently some work has been done in this area [36-37]. T_g determines the strength and rigidity of the glass structure in chalcogenides. The difference between T_c and T_g provides complete information about thermal stability as well as GFT. Higher is value of $(T_c - T_g)$, greater is the GFT, because it delays the nucleation process [37]. Using the peaks of endothermic and exothermic peaks of T_g and T_c [30], the values of $(T_c - T_g)$, are calculated from DSC Scans and given in Table 2 below.

Table 2. Thermal stability in glassy $Se_{90}In_{10-x}Ag_x$ alloy.

Heating rate 15°C/min		
S.No.	Glassy Alloy	$T_c - T_g$
1.	$Se_{90}In_8Ag_2$	88.7
2.	$Se_{90}In_6Ag_4$	81.3
3.	$Se_{90}In_4Ag_6$	51.1
4.	$Se_{90}In_2Ag_8$	65.2

Graph is plotted for thermal stability ($T_c - T_g$) versus Ag concentration. It is observed that, $T_c - T_g$ decreases with Ag concentration, which indicates thermal stability is lower at higher concentration of Ag. Compositional dependence of thermal stability shows a discontinuity at an Ag concentration of 6%, which is explained in terms of mechanically optimised structure at a particular average coordination number.

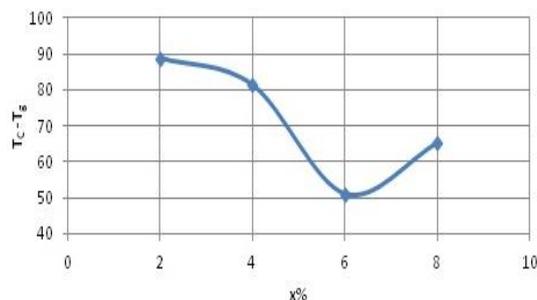


Fig. 4. Variation of $T_c - T_g$ with Ag concentration in $Se_{90}In_{10-x}Ag_x$ alloys.

5. Conclusion

Calorimetric studies have been made in glassy $Se_{90}In_{10-x}Ag_x$ alloys. Single scan technique has been used to calculate the Activation energy of crystallization ΔE_c , order parameter (n) and thermal stability ($T_c - T_g$). The results shows that ΔE_c is highly composition dependent while n is found to be less than 1 for all glassy alloys studied, indicating no change in crystallization mechanism. Thermal stability is also reported at various concentration of Ag. It decreases with higher concentration of Ag showing a minima at 6 atomic percent.

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