CRYSTALLIZATION KINETICS IN GLASSY $Se_{100-x} In_x$ SYSTEM USING ISO-CONVERSIONAL METHODS

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Alloys of Se-In glassy system obtained by quenching technique and crystallization kinetics has been studied using differential scanning calorimeter. Activation energy of crystallization is determined using well known Kissinger's relation and Friedman methods. Activation energy is also calculated by the modified Kissinger's relation assuming constant activation energy and it is observed that results are in close agreement at smaller values of extent of crystallization. However, at higher extent of crystallization, the activation energy calculated by isoconversional methods is different and is found to decrease with the increase in extent of crystallization. Effect of In concentration on activation energy is also discussed.

1. Introduction

Chalcogenide glasses are being studied for a long time because of their utility in electronic field [1]. Among these glasses, Se-In glassy alloys have recently gained much importance as these alloys are used in data storage material, charge trapping and transport properties [2]. These materials which have a higher tendency to crystallize, normally show memory switching [3]. Se-In alloys have already been utilized in solar cells [4-5]. They are also found to be more photosensitive and harder than amorphous Se [6]. One of the most interesting problem is the understanding of crystallization kinetics which can be studied in terms of crystallization temperature T_c, and activation energy ΔE_c. The transition from amorphous to crystalline stage is represented by exothermic peaks in DSC scans.

In the present work, we have done non-isothermal measurements using DSC technique to study crystallization kinetics in glassy $Se_{100-x} In_x$ system as the activation energy of crystallization (ΔE_c) plays an important role in determining the utility of these glasses as recording material as reported by Vyazovkin [7].

Dependence of activation energy on the extent of crystallization is analyzed by using Kissinger Akahira Sunose [KAS] method and Friedman method.

KAS method is also used for the study of crystallization Kinetics assuming activation energy constant throughout the crystallization process. Modified form of the KAS method is also applied at different temperatures. It is observed that results are in close agreement with iso-conversional methods at low extent of crystallization.

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2. Theoretical basis of crystallization kinetics

The transformation rate equation of a solid – state reaction in isothermal conditions can be generally described by [8-11]

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

Where k is the reaction rate constant; f (α) the reaction model; α is the conversion fraction that represents the volume of the crystallized fraction. The rate constant, k, usually has Arrhenian temperature dependence:

$$k = A \exp\left(\frac{-\Delta E}{RT}\right) \tag{2}$$

Where A is the pre-exponential factor (frequency factory); ΔE_c (kJ mol^{-1}) the activation energy; R is the universal gas constant.
The isothermal transformation rate can be written from Eq. (1) as

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-\Delta E}{RT}\right) f(\alpha) \tag{3}$$

Under non-isothermal conditions with a constant heating rate of $\beta = \frac{dT}{dt}$, Eq. (3) may be rewritten as

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\left(\frac{1}{\beta}\right) = \frac{A}{\beta}\exp\left(\frac{-\Delta E}{RT}\right) f(\alpha) \tag{4}$$

The Kissinger-Akahira-Sunose method (or generalized Kissinger method as it is called at times) may be obtained through derivation of Eq. (4). Subsequent logarithmic application and rearrangement yield [11-13]

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right) = \text{Constant} - \frac{\Delta E_\alpha}{RT_{\alpha i}} \tag{5}$$

Plots of $\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right)$ vs $1000/T_{\alpha i}$ are plotted and activation energy ΔE_c is calculated from the slopes of these graphs. Plots of $\ln\left(\frac{\beta}{T_c^2}\right)$ versus $1000/T_c$ have also been made and activation energy is calculated from the slopes of these graphs.

For various heating rates β the Friedman method can be used at specific crystallization fraction α as

$$\ln\left(\frac{d\alpha}{dt}\right) = \text{Constant} - \frac{\Delta E_\alpha}{RT_{\alpha i}} \tag{6}$$

The parameter ΔE_c at this specific value of α, is then estimated from a plot of $\ln(d\alpha/dt)_{\alpha i}$ versus $1/T_{\alpha i}$ across different heating rates. The process is repeated for different values of α

3. Material preparation

Glassy alloys of Se_{100-x} In_x were prepared by quenching technique. High purity materials [5 N pure] were weighed according to their atomic percentages and were sealed in quartz ampoules under the vacuum of 10^{-3} Pa. Each ampoule was kept inside the furnace at 1073 K so that all the elements get melted. The temperature was raised at a rate of 3-4 K/ min. 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 ingots of the samples were taken out by breaking the quartz ampoules. The glassy state of alloys was checked by X – ray diffraction technique. For this, X – ray diffraction [XRD] patterns of all the 5 samples were taken at room temperature by using X – ray diffractometer [Philips, PW 1140/09]. The copper target was used as a source of X – rays with I = 1.54 A° [Cu Kal].

4. Experimental

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 amount of sample (3) it is quite sensitive; (4) it is relatively independent of the sample geometry. Before DSC experiment, the thermogravimetric analysis has been made on each glassy sample. Perkin – Elmer TGA7 thermogravimetric instrument is used for this purpose. In thermogravimetric analysis, wt% loss of a test sample is recorded while the sample is being heated at a uniform rate in an appropriate environment [inert N_2 gas]. The loss in weight over specific temperature ranges provide an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability. From TGA scans, it has been found that there is no drastic loss in the weight of the samples over the entire temperature range. The thermal behaviour was investigated using Differential Scanning Calorimeter [Model-DSC plus, Rheometric Scientific Company, U.K.] The temperature precision of this equipment is 0.1 K with an average standard error of about 1 K in the measured values. 10 to 20 milligrams of each sample was heated at a constant heating rate and the changes in heat flow with respect to an empty pan were measured. Five different heating rates [5, 10, 15, 20 and 25 K/min] were chosen in the present study. Measurements were made under almost identical conditions.

5. Results and discussion

The activation energy of crystallization can be calculated by various methods, among which KAS method is an important method [14]. The most widely used model ie. JMA

Non-isothermal Kinetics implies that activation energy ΔE_c should be constant during the transformation process but recent papers in this field show that activation energy of crystallization is not constant throughout the crystallization process and varies at different stage of crystallization [15-18].

DSC scans of the system Se_{100-x} In_x at different heating rates 5, 10, 15, 20 and 25 K/min are taken and crystallization temperature is recorded. It is found that crystallization temperature increases on increasing the heating rate. These results are given in Table 1

Table 1. Heating rate dependence of crystallization temperature

Heating Rates (K/m)	$Se_{95}In_5$	$Se_{90}In_{10}$	$Se_{85}In_{15}$	$Se_{80}In_{20}$	$Se_{70}In_{30}$
5	393	377	387	389	385
10	397	387	395	396	395
15	402	392	403	400	397
20	416	397	408	407	398
25	417	399	409	408	399

It is clear from the Table 1 that all crystallization temperatures are much higher than the room temperature, which prevents the self transition of these glassy alloys which is required for the application as stable glasses

5.1 Evaluation of activation energy (ΔE_c) by modified KAS method & Friedman method

By using Kissinger method graphs are plotted against $\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right)$ vs. $1000/T_{\alpha i}$ at a particular value of α as shown in Figs. 1 & 2 for two samples at α = 0.6. Same process is repeated for different values of α and for all other samples.
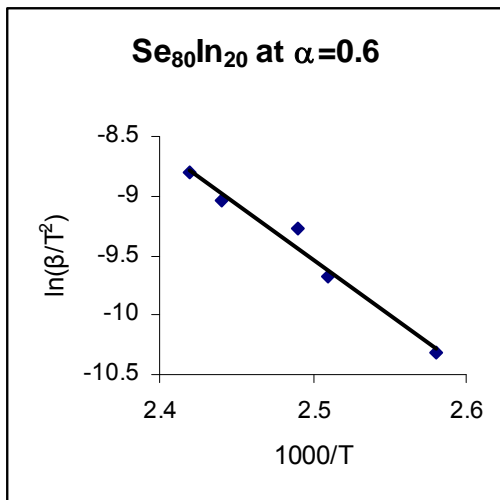
Fig1: $ln(\beta/T^2)$ vs. 1000/T curve for $Se_{80}In_{20}$
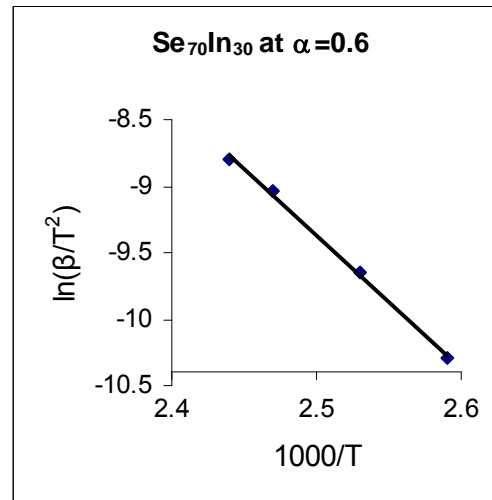
Fig 2: $ln(\beta/T^2)$ vs. 1000/T curve for $Se_{70}In_{30}$

By using Friedman method graphs are plotted for ln(dα/dT) vs. $1000/T_{\alpha i}$ at a particular value of α as shown in Figs. 3 & 4 for two samples at α = 0.6. Same process is repeated for different values of α and for all other samples.
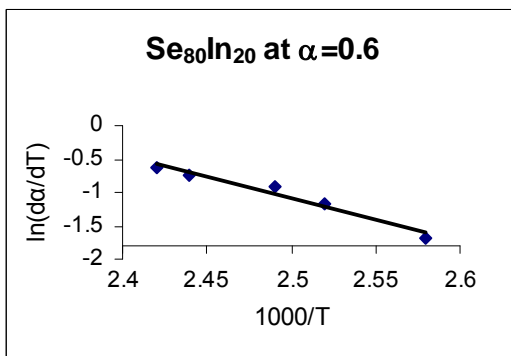

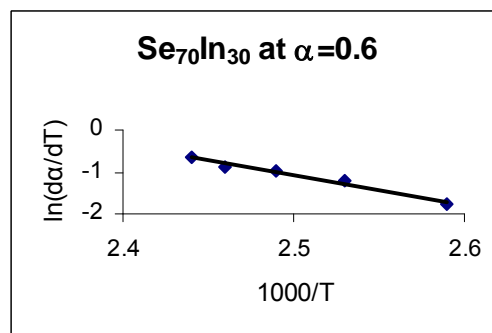Fig 3: $ln(d\alpha/dT)$ vs. $1000/T_{\alpha i}$ curve by Friedman

Fig 4: $ln(d\alpha/dT)$ vs. $1000/T_{\alpha i}$ curve by Friedman

From the slopes of these plots, activation energy is calculated at a given value of α. Activation energy for different values of α by both the methods are given in Table 2

Table 2. Activation Energy ΔE_c (in eV) at different extent of crystallization by KAS & Friedman methods.

α	$Se_{95}In_5$		$Se_{85}In_{15}$		$Se_{80}In_{20}$		$Se_{70}In_{30}$	
	KAS	Fd.	KAS	Fd.	KAS	Fd.	KAS	Fd.
0.3	0.46	0.73	0.85	1.11	0.92	0.83	0.95	0.71
0.4	0.50	0.63	0.75	0.84	0.9	0.82	0.95	0.70
0.5	0.49	0.59	0.79	0.63.	0.83	0.66	0.86	0.71
0.6	0.45	0.54	0.70	0.55	0.81	0.56	0.86	0.61
0.7	0.43	0.49	0.63	0.44	0.74	0.51	0.77	0.50
0.8	0.39	0.50	0.64	0.42	0.70	0.82	0.68	0.44

It is observed that for all samples used here, activation energy ΔE_c decreases on increase of percentage of crystallization as shown in Figs 5 & 6 for $Se_{80}In_{20}$ and $Se_{70}In_{30}$ respectively. Similar results are found in other samples also. It is clear from the Table 2 that activation energy is not same for the samples by both methods but variation trend is same by both methods i.e. it decreases on increasing the extent of crystallization.
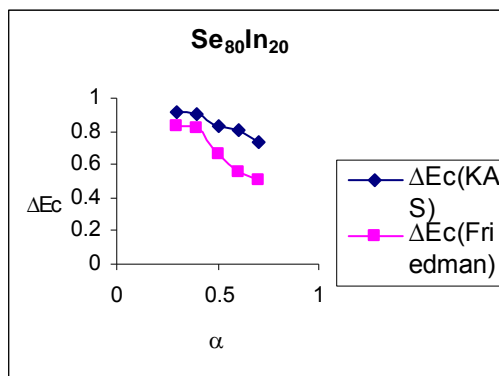

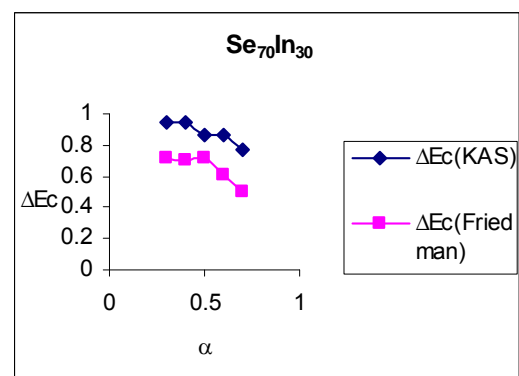Fig 6. α dependence of ΔE_c in $Se_{80}In_{20}$ Fig 6. α dependence of ΔE_c in $Se_{70}In_{30}$

It is also noted that activation energy calculated by both methods changes on In incorporation in pure Se. It increases at 10 at% of In incorporation and decreases at 15 at% of In incorporation then again it shows a rise and increases gradually up to 30 at% of In . These results are shown in Figs 5 & 6 at α=0.4 & α=0.6 respectively. Similar results were obtained at other values of α.

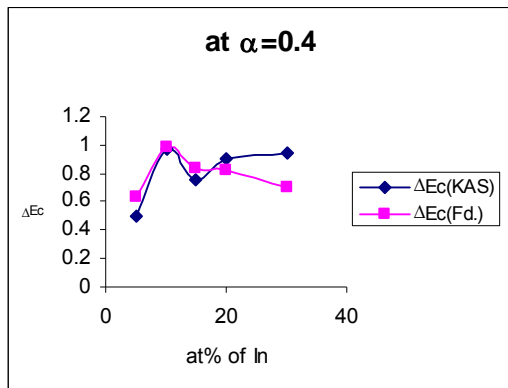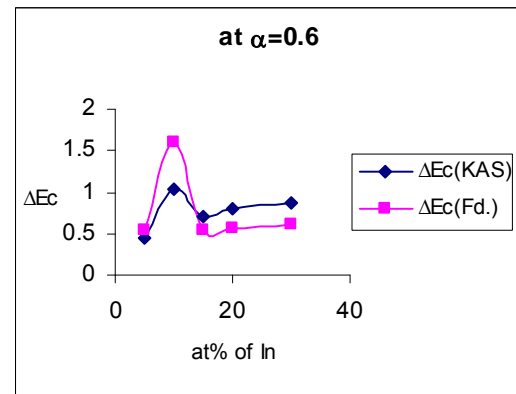Fig 7. Concentration dependence of ΔE_c at
$\alpha=0.4$

Fig 8. Concentration dependence of ΔE_c at
$\alpha=0.6$

5.2 Evaluation of activation energy ΔE_c by KAS method at crystallization temperature T_c

In this method it is assumed that ΔEc is constant through out the process of crystallization. In this case plots of $\ln\left(\dfrac{\beta}{T_c{}^2}\right)$ versus $1000/T_c$ are straight lines and activation energy is calculated from the slopes of these graphs & then energy variation is observed.

The concentration dependence of ΔE_c is shown in Fig 7.It is intresting to note that the results are of similar nature as obtained by modified KAS method.
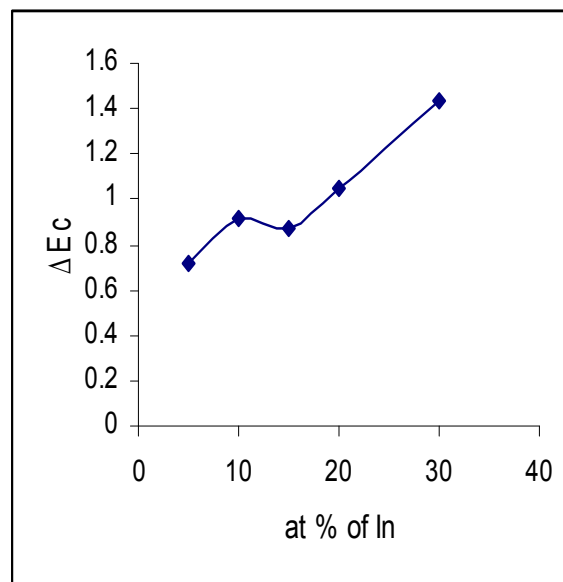

Fig 9. Concentration dependence of ΔE_c by KAS methods

6. Conclusions

Glassy alloys of $Se_{100-x}\,In_x$ are prepared by quenching technique . Crystallization kinetics of these glasses are studied using non isothermal method by Differential Scanning Calorimetery.

In the present work it is shown that activation energy of crystallization is not constant throughout but varies with percentage of crystallinity. It decreases as percent of crystallinity

increases .It is also observed that activation energy changes according to percentage of In incorporation. Activation energy increases at 10 atomic % of In incorporation at a particular α but decreases at 15 at% of In incorporation thereafter it again increases. Similar composition dependence is also observed by using constant ΔE_c in KAS method.

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