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STUDY OF CRYSTALLIZATION KINETICS IN GLASSY $Se_{100-x}Bi_x$ USING ISO-CONVERSIONAL METHODS

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The kinetic of crystallization in $Se_{100-x}Bi_x$ (x = 0.5, 4, 6, 10) has been studied using differential scanning calorimetric (DSC) technique at different heating rates (5, 10, 15,20 K/min). Well defined endothermic and exothermic peaks are obtained at glass transition (T_g) and crystallization temperature (T_c). Five isoconversional methods (Kissinger – Akahira - Sunose (KAS), Flynn-Wall-Ozawa (FWO), Tang, Straink and Friedmann) have been used to determine the activation energy of crystallization (E_c) at different temperatures. The results show that activation energy of crystallization is not constant throughout the crystallization process. It varies with the temperature and hence with the degree of conversion. The activation energy obtained from Friedman method is found to be different as compared with KAS and other methods, is attributed to possible errors involved in the Friedmann method. A discontinuity has also been observed in E_c at 4 at % & 6 at% of Bi, which is explained in terms of a mechanically optimized structure at a particular composition.

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1. Introduction

Chalcogenide glasses have found application in resistance switching [1], which can be used as ON and OFF switch if switching is of threshold type. However, the glasses can be used for memory application if switching is of memory type. Such a memory effect is being used in computer memories. Crystallization studies may be useful in predicting the switching behaviour in these glasses as the type of switching (threshold or memory) depends upon the rate of crystallization.

In addition to the above application, chalcogenide glasses have found application in erasable phase change optical recording also [2-5]. It is difficult to write and erase if the amorphous to crystalline transformation rate is not sufficiently high .For this reason also, the study of crystallization is important for the development of new materials for such applications.

A large majority of a-c phase transformations can be described by a process known as nucleation and growth .Different methods [6-11] have been adopted to study a - c phase transformation. A lot of work has been done on different compositions [12-14].However, different other techniques have also been used to study crystallization in chalcogenide glasses, such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and differential Scanning calorimetry (DSC) [15-17]], the use of isoconversion methods is a trustworthy way of obtaining reliable and consistent kinetic information from both nonisothermal and isothermal DSC data.

The present paper reports the study of the crystallization process in $Se_{100-x}Bi_x$(x = 0.5, 4, 6, & 10) using non – isothermal DSC technique. Activation energy of crystallization has been evaluated by using different isoconversional methods.

2. Experimental details

Glassy alloys of $Se_{100-x}Bi_x$ (x = 0.5, 4, 6 & 10) were prepared by the 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) having a sensitivity of 10^{-4} mg. The materials were then sealed in evacuated (~10^{-5} torr) quartz ampoules (length~5 cm and internal diameter ~ 8 mm). Each ampoule was kept inside the furnace at 1000 ^{0}C (where the temperature was raised at a rate of 3 - 4 ^{0}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 10 hours, the obtained melts were cooled rapidly by removing them from the furnace and dropping them to ice-cooled water rapidly. The ingots of the samples were then taken out by breaking the quartz ampoules.

The glasses thus prepared, were ground to make fine powder for DSC studies. 10 to 20 mg of the powder was heated at a constant heating rate and the changes in the heat flow with respect to an empty reference pan were measured. DSC plus instrument (Rheometric Scientific Company, U.K.) was used at four different heating rates (5, 10, 15 and 20 K/ min).

3. Results

3.1 Heating rate dependence of glass transition and crystallization temperatures

Figs. 1 & 2 show typical DSC thermograms for glassy Se100-xBix (x = 0.5, & 6) at a heating rate of 15 K/min. Similar thermograms were obtained for other heating rates and for other glasses (results not shown here). It is clear from these figures that well defined single endothermic and exothermic peaks are observed at glass transition temperature T_g and crystallization temperature Tc respectively, which indicates that these glasses exist in single phase.The values of crystallization temperature is given in Table 1.

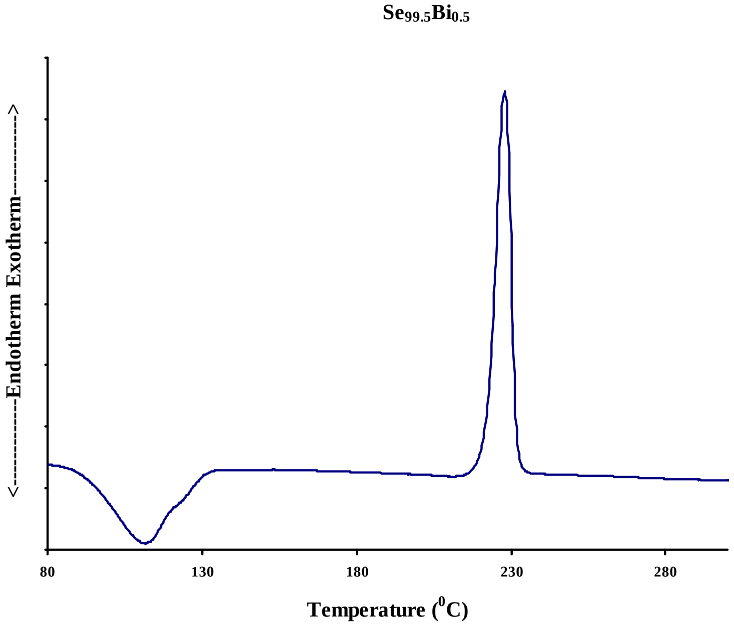

Fig. 1. DSC thermogram for glassy $Se_{94}Bi_{0.5}$alloy for heating rate 15 (K / min).

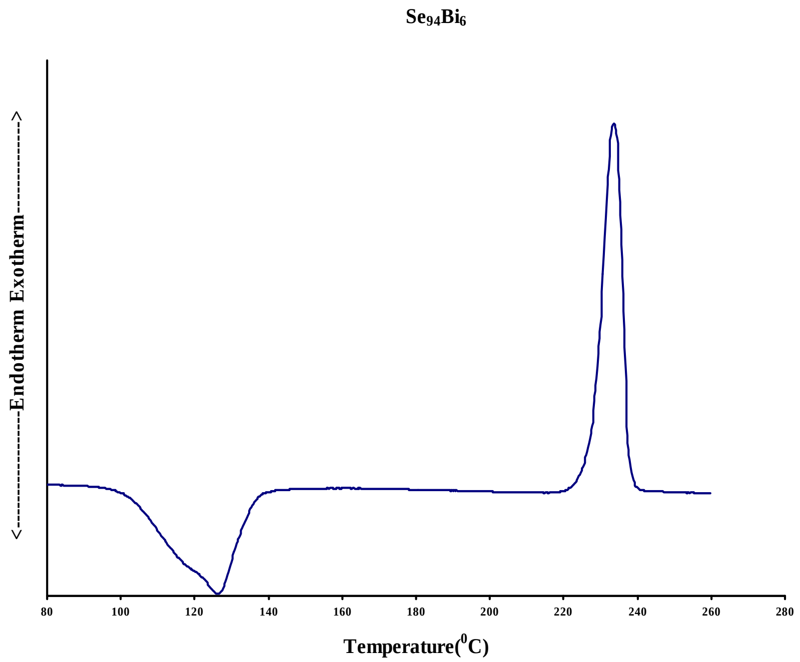

Fig. 2. DSC thermogram for glassy $Se_{94}Bi_6$ alloy for heating rate 15 (K / min).

Table 1. Crystallization temperature T_c at different heating rates in glassy alloy $Se_{100-x}Bi_x$.

	5 (k/min)	**10 (K/min)**	**15 (K/min)**	**20 K/min)**
$Se_{99.5}Bi_{0.5}$	499.3	500.39	501.06	511.20
$Se_{96}Bi_4$	500.12	505.72	508.16	507.13
$Se_{94}Bi_6$	502.64	500.09	506.65	510.13
$Se_{90}Bi_{10}$	498.97	500.39	501.36	504.97

3.2 Activation energy of crystallization

Recent studies in this field have shown that E_c (activation energy of crystallization) is not necessarily constant but show variation in different stages of the transformation [18-21].To see the variation of activation energy with extent of conversion different, isoconversional methods have been used. Fig. 3 shows the variation of α (extent of conversion) with time for $Se_{100-x}Bi_x$(x = 0.5, 4, 6 & 10) as obtained from experimental data.

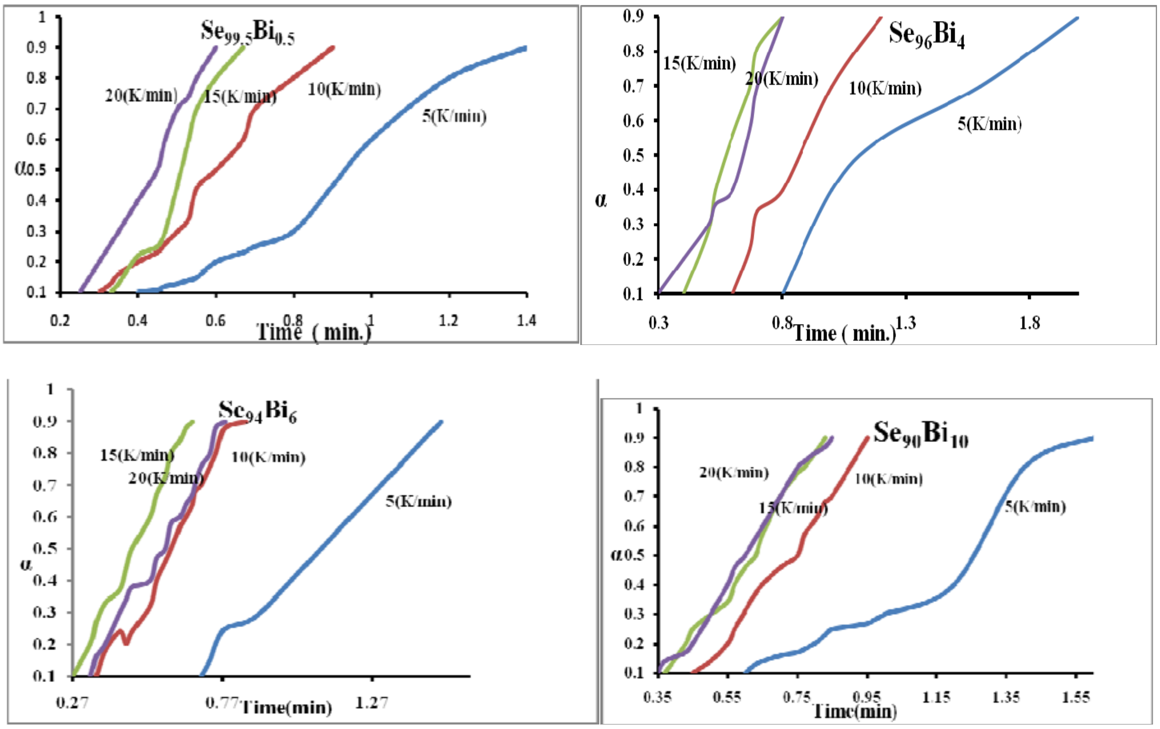

Fig. 3. Variation of α (extent of conversion) with time

For the determination of crystallization activation energy E_c Isoconversional methods can be categorized into one of two main groups. One set of methods relies on approximating the temperature integral.This set of methods includes the Kissinger method [22], Kissinger-Akahira-Sunose (KAS) method [23] and the Flynn-Wall-Ozawa (FWO)method [24]. Another set of methods does not use any mathematical approximation, but instead uses a determination of the reaction rate at an equivalent stage of the reaction at different heating rates such as Friedman-Ozawa method [25]. In an investigation study of the accuracy of known isoconversion methods, Straink [26] reported that the most accurate method are KAS method and the method developed by the author [26,27]. However, the most reliable isoconversion methods as reported by Ozawa [27] are FWO, KAS and the Friedman-Ozawa method.

3.2.1 Kissinger and Kissinger-Akahira-Sunose (KAS) method

All of the isoconversion methods require the determination of the temperature$T_{\alpha i}$ at which a fixed fraction α of the total amount is transformed. In the KAS [23] method, the relation between the temperature $T_{\alpha i}$ and the heating rate β is given by

$$\ln (\beta_i/T_{\alpha i}^2) = -E_\alpha / RT_{\alpha i} + \text{constant} \qquad (1)$$

The subscript i denotes different heating rates. For each degree of conversion , α, a corresponding $T_{\alpha i}$ and heating rate are used . Plot of $\ln(\beta_i/T_{\alpha i}^2)$ against $1000/T_{\alpha i}$ enables the calculation of E_α from the linear fits to experimental data Fig. 4. The results have been given in the Tables 2 - 5.

3.2.2 Flynn-Wall-Ozawa (FWO) method

The Flynn-wall-Ozawa (FWO)[48]method has been developed for non-isothermal analysis of crystallization in which final relation is as follows

$$\ln \beta_i = \text{constant} - 1.0518E_\alpha/RT_{\alpha i} \qquad (2)$$

By plotting $\ln \beta$ versus $1/T_\alpha$, for the chosen value of fraction α, the effective activation energy E_α can be determined from Fig. 4. The results are shown in Tables 2 - 5.

3.2.3 Friedman –Ozawa Method

Friedmann-Ozawa method establishes a relation between $\ln(\beta.d\alpha/dT)$ and $1/T_{\alpha i}$ which is as follows

$$\ln(\beta.d\alpha/dT) = \text{Constant} - E_\alpha/RT_{\alpha i} \qquad (3)$$

Plotting of $\ln(\beta.d\alpha/dT)$ against $1/T_{\alpha i}$ enables the calculation of E_α from the linear fits to experimental data of Fig. 4. Results are shown in Tables 2 - 5.

3.3.4 Tang Method

A more precise formula for the temperature integral has been suggested by Tang et al. [28] which is as follows

$$\ln(\beta_i/T_{\alpha i}^{1.894661}) = \text{Constant} - 1.00145033\, E_\alpha/RT_{\alpha i} \qquad (4)$$

The parameter E_α for a particular value of α can be estimated by plotting $\ln(\beta_i/T_{\alpha i}^{1.894661})$ versus $1/T_{\alpha i}$ across different heating rate as shown in Fig. 4. These results are shown in Tables 2 - 5.

3.3.5 Straink Method

According to the method proposed by straink

$$\ln(\beta_i/T_{\alpha i}^{1.92}) = \text{constant} - 1.0008E_\alpha/RT_{\alpha i} \qquad (5)$$

Plot of $\ln(\beta_i/T_{\alpha i}^{1.92})$ against $1/T_{\alpha i}$ enables the calculation of E_α from the linear fits to experimental data of Fig.4. Results are shown in Tables 2 - 5.

Table 2. Activation energy of crystallization(E_c) for $Se_{99.5}Bi_{0.5}$.

Crystallzation Fraction(α)	KAS	Friedmann	FWO	TANG	Straink
0.2	2.15	3.86	2.12	2.14	2.15
0.4	2.01	3.35	1.99	2.01	2.01
0.6	1.89	3.26	1.86	1.87	1.87
0.8	1.81	3.07	1.79	1.81	1.81

Table 3. Activation energy of crystallization(E_c) for $Se_{96}Bi_4$.

Crystallization fraction (α)	KAS	Friedmann	FWO	TANG	Straink
0.2	2.19	4.84	2.17	2.19	2.19
0.4	3.17	6.22	3.09	3.17	3.17
0.6	3.27	6.76	3.19	3.27	3.27
0.8	2.89	5.86	2.83	2.89	2.89

Table 4. Activation energy of crystallization (E_c) for Se $_{94}$Bi$_6$.

Crystallization fraction (α)	KAS	Friedmann	FWO	TANG	Straink
0.2	2.55	4.15	2.51	2.55	2.55
0.4	2.13	3.20	2.11	2.13	2.13
0.6	1.97	2.50	1.95	1.97	1.97
0.8	1.83	2.40	1.82	1.83	1.83

Table 5. Activation energy of crystallization(E_c) for Se $_{90}$Bi$_{10}$.

Crystallization fraction (α)	KAS	Friedmann	FWO	TANG	Straink
0.2	4.54	5.62	4.39	4.53	4.54
0.4	4.08	5.10	3.96	4.08	4.08
0.6	3.79	4.46	3.63	3.79	3.79
0.8	3.25	3.46	3.17	3.25	3.25

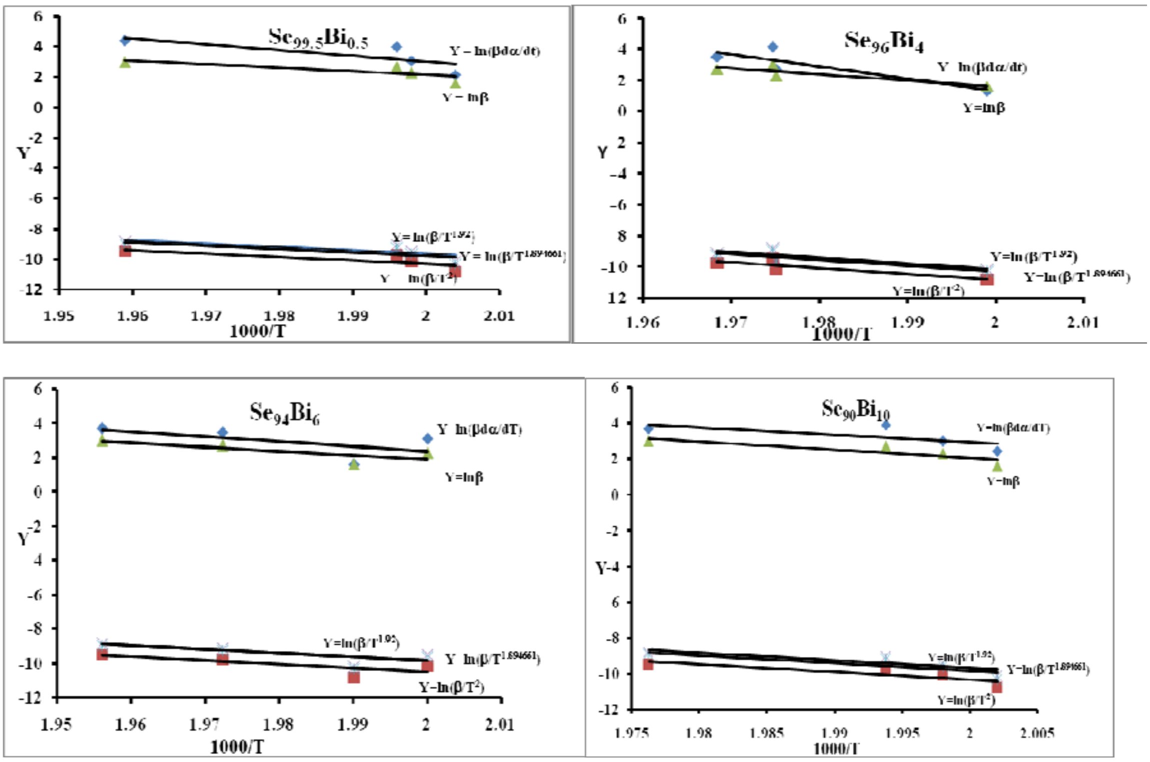

Fig. 4. Slopes of KAS, Friedmann, FWO, Tang & straink method for α = 0.6

It is clear from the above tables that E_c (activation energy of crystallization) is not constant but varies with extent of conversion. It can be seen from the tables 2 - 5 that E_c (activation energy of crystallization) is almost same at low value of α but at higher values of α, E_c decreases. This can also be seen in Fig. 5 which plots the variation of E_c with α. It is also worth to note that there is good agreement among all the four methods (Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa(FWO), Tang, Straink) except Friedman method .This disagreement may be due to the systematic error, which arise from the numerical differentiation of the experimental data involved in Friedman method.

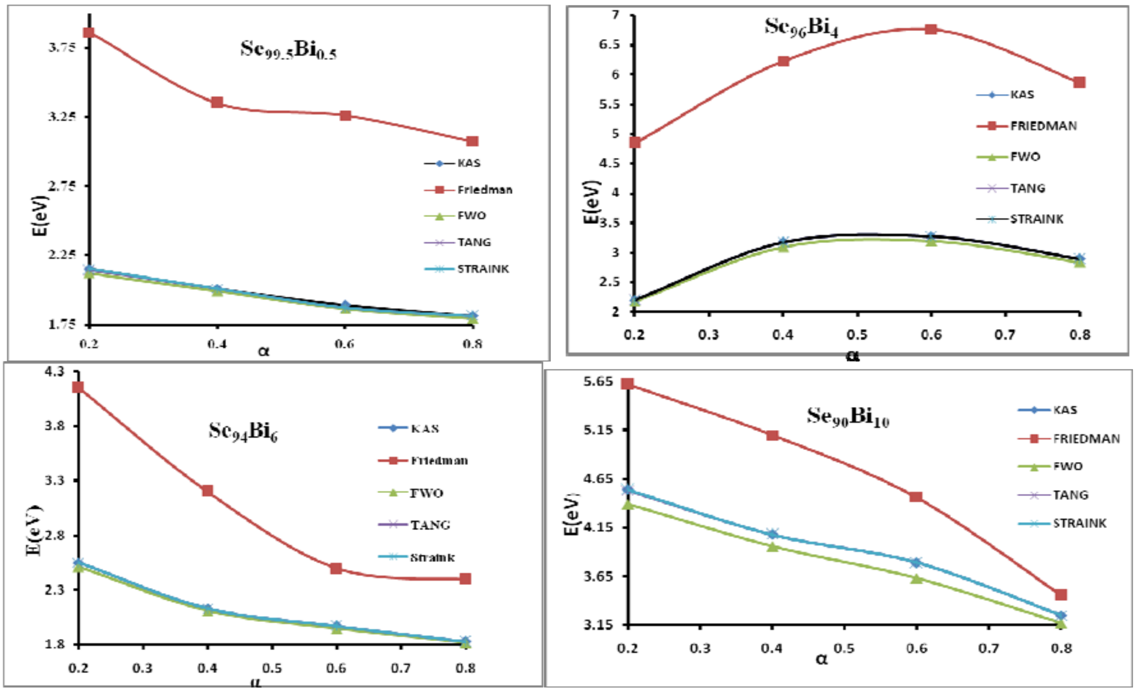

Fig.5 Activation energy E_c vs. crystallization fraction (α).

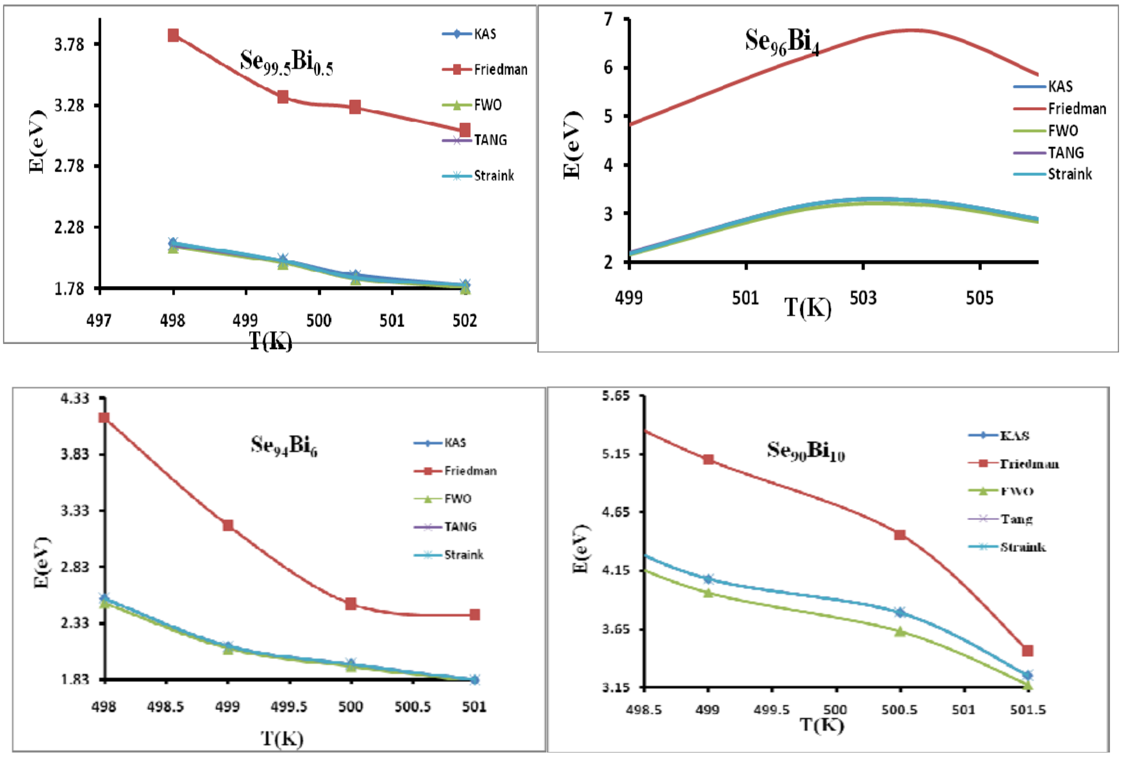

Fig. 6. Activation energy E_c vs. T(K).

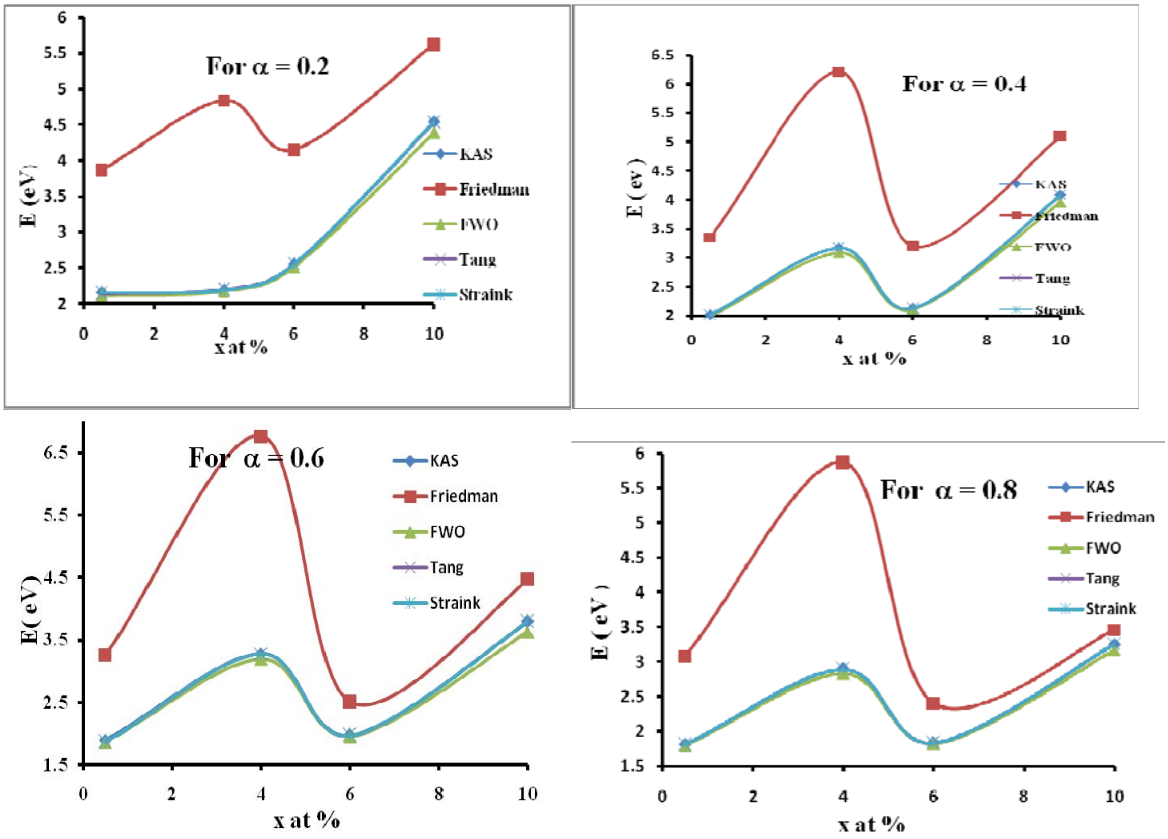

Fig.7. Variation of activation energy E_c with concentration of Bi.

Fig.6 shows the variation of E_c (activation energy of crystallization) with temperature. The values of E_c decreases with the increase in temperature, which simply indicates that the crystallization rate increases with increasing temperature. This behaviour demonstrates that the rate constant of crystallization is, in fact, is determined by the rates of two processes, nucleation and diffusion. Because these two mechanisms are likely to have different activation energies, the effective activation energy of the transformation will vary with temperature [29].This interpretation is based on the nucleation theory proposed by Fisher and Turnbull [30].

Fig.7 shows the variation of activation energy E_c with concentration of Bi. It has been found that E_c first increases with concentration, becomes maximum at 4 at % of Bi. This type of discontinuity has been found at almost all fraction of crystallization (α□= 0.2, 0.4, 0.6, 0.8).

4. Discussion

In chalcogenide glasses a discontinuity in various physical properties has been observed [31-38] at a particular composition when the average co-odination numbe <r> reaches 2.4. This is explained by Phillips and Thorpe [39] in terms of a mechanically optimised structure at a critical glass composition.

In the present case the co-ordination number of Se is 2 and that of Bi is 3. Hence, for a composition where the maximum in E_c is occurring, <r> comes out to be 2.04 following the model of Phillips and Thorpe [39]. IV-VI glasses, however, show a threshold at <r> = 2.4 as pointed out by Phillips [40-42].

It may be mentioned here that Phillips considered the interaction between atoms to be purely covalent while arriving at the balance condition .Such an assumption may be valid for Ge-Se glasses but not for systems containing heavier elements such as Bi.The presence of heavier element may lead to partial covalent bonding .This can affect the balance condition .There are several other shortcomings in the simple theory, such as the assumption of the 8-N rule. It has been reported [43] that the co-ordination number of elements changes with composition and that the simple assumption of the co-ordination number of the elements on the basis of the 8-N rule in the balance condition is not strictly valid for such cases.

However, it should be noted that the the above explanation for this anomaly are highly qualitative and it is difficult to get any quantitative information from such explanations. Future experiments on the local structure of these glasses could reveal the exact origin and nature of the anomaly.

5. Conclusions

Crystallization kinetics of glassy alloys of $Se_{100-x}Bi_x$ (x = 0.5, 4, 6 & 10) has been studied with the help of DSC technique using non-isothermal process at four heating rates (5, 10, 15 & 20 k / min). Activation energy of crystallization (E_c) has been evaluated by five iso-conversional methods (Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO), Tang, Straink and Friedmann). A good agreement has been obtained among four methods except Friedmann method.

Activation energies of crystallization (E_c) have been found temperature dependent at higher extent of conversion. It decreases as temperature increases. The temperature dependence of activation energy of crystallization is explained in the light of the nucleation theory of Turnbull and Fisher. Present work shows that the transformation from amorphous to crystalline phase in $Se_{100-x}Bi_x$ (x = 0.5, 4, 6 & 10) is a complex process involving different mechanisms of nucleation and growth, particularly at higher values of the extent of crystallization.

A discontinuity has been found in E_c at 4at % of Bi, which is explained in terms of a mechanically optimized structure at a particular average co-ordination number.

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