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THERMAL CHARACTERIZATION OF $Se_{100-x}Sb_x$ GLASSES USING ISOCONVERSIONAL METHOD

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Differential Scanning Calorimetric runs have been taken for $Se_{100-x}Sb_x$ (x = 2, 6, 10) glasses for the thermal study. Well defined endothermic and exothermic peaks are obtained at glass transition (T_g) and crystallization temperature (T_c) .The activation energy of crystallization (E_c) has been calculated by analyzing the data using the isoconversional methods of Kissinger-Akahira-Sunose (KAS) and Friedman for different degree of conversion (α). The results have been compared with the earlier published results, calculated by some non-isothermal methods, i.e., Kissinger's relation, Matusita-Sakka method and the method of Augis and Bennett. The present results show that E_c decreases with increase in α at higher values of α. The results show a decrease in the activation energy for crystallization at higher temperatures. The temperature dependence of E_c is explained in the light of the nucleation theory of Turnbull and Fisher.

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1. Introduction

Chalcogenide glasses have evoked much interest in terms of physics as well as device technology. Device applications like switching, memory and xerography etc. made Se an attractive material. It also exhibits [1] a unique property of reversible transformation. This property makes it very useful in optical memory devices. But in pure state it has disadvantages because of its short lifetime and low sensitivity. To overcome these difficulties certain additives are used. Especially, the use of Se-Te, Se-Ge and Se-In [2, 3] alloys has been of great interest owing to their various properties like greater hardness, higher sensitivity, higher crystallization temperature, higher conductivity and smaller ageing effects as compared to pure amorphous Se [4].

Recently, considerable attention has been focused on glasses of Se-Sb system [5-20] as these materials have found applications for their electrical, optical, dielectric and thermal properties. The effect of Sb alloying on the electrographic properties of a-Se and laser-induced amorphous to crystalline phase transition in glassy Se-Sb alloys is reported by Mikla et. al. [7, 8]. The thermal stability and carrier drift mobilites of a- Se-Sb photoconductors is studied by Tonchev et.al. [9]. Calorimetric studies on Se-Sb thin films have also been reported in literature [18, 19]. The dielectric study on Se-Sb alloys is reported by our group [20].

The activation energy of crystallization E_c plays an important role in determining the utility of chalcogenide glasses as recording material [21]. It has been assumed by many authors that E_c is constant during crystallization process. To test this proposal, E_c was determined from the present measurements using different models. In particular, the isoconversional methods have been used to evaluate the value of E_c at different stages of the transformation. The variation of the activation energy with the degree of crystallization is an important issue in the kinetics of amorphous to crystalline transformation [22]. As pointed out by Vyazovkin [22], this variation of the activation energy with the degree of crystallization, and hence with temperature, can provide useful information about the different mechanisms involved in the transformation process. Different authors have studied crystallization kinetics of various chalcogenide glasses through isoconversional methods [23 – 27].

In the present work, the kinetics of crystallization of amorphous $Se_{100-x}Sb_x$ (x = 2, 6, 10) alloys is studied using the non-isothermal DSC technique at different constant heating rates. The DSC data is analyzed with the help of isoconversional methods to investigate the growth process involved in the transformation. The results have been compared with the E_c calculated by different models based on JMA (Kissinger's etc.). The dependence of the activation energy of crystallization (E_c) on the extent of conversion is discussed.

2. Theoretical basis

The transformation rate equation of a solid-state reaction in isothermal conditions can be generally described by [28-30]:

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

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 an Arrhenian temperature dependence:

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

Where A (s^{-1}) is the pre-exponential (frequency) factor; E (k J mol^{-1}) the activation energy; R is the universal gas constant.

The isothermal transformation rate can be written from Eq. (1) as

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

Under non-isothermal conditions with a constant heating rate of β = dT/dt , Eq.(3) may be rewritten as

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

Since there is a large variety of theoretical models and mathematical treatments to explain the estimation of crystallization kinetics, the two most popular methods have been used in the present work to analyze the crystallization kinetics of the $Se_{100-x}Sb_x$ (x = 2, 6, 10) alloys. An outline of these methods is described as follows:

For various heating rates, β, the Friedman method [36] can be used directly from Eq. (3) at a specific crystallization fraction,α, as

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha i} = Cons\tan t - \frac{E_\alpha}{RT_{\alpha i}} \tag{5}$$

The subscript i denotes different heating rates. The parameter E_α 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 procedure is repeated for many values of α, yielding continuous functions of α for E_α.

The Friedman method is useful because Eq. (5) does not introduce any approximation and the method is not restricted to the constant heating rate mode [37].

The Kissinger - Akahira - Sunose method [38-40] (or the generalized Kissinger method as it is sometimes called) may be obtained through derivation of Eq. (4). Subsequent logarithm application and rearrangement yield:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}{}^2}\right) = Cons\tan t - \frac{E_\alpha}{RT_{\alpha i}} \tag{6}$$

The activation energy of crystallization (E_c) for $Se_{100-x}Sb_x$ (x = 2, 6, 10) glasses has also been obtained from the variation of T_c with the heating rate by following methods:

The first method used is Kissinger's method [41] according to which the peak temperature of crystallization (T_c) is expressed as a function of heating rate by the following equation:

$$\ln (\beta/T_c^2) = \text{constant} – E_c /R\ T_c \tag{7}$$

Plots of $\ln (\beta/T_c^2)$ as a function of $1000/ T_c$ have been made for all the glasses studied and E_c has been derived from the slopes of these plots and the results are given in Table 3.

Another method used is based on the Matusita-Sakka theory [42-43] according to which T_c and the heating rate β are given by:

$$\ln \beta = -E_c / R\ T_c + \text{constant} \tag{8}$$

On plotting $\ln \beta$ versus $10^3/T_c$ curves a straight line is obtained whose slope gives the value of E_c.

The last method used is based on the Augis and Bennett [44] method according to which T_c as a function of β is given by the following equation:

$$\ln (\beta/T_c) \approx (-E_c /RT_c) + \ln K_o. \tag{9}$$

The activation energy of crystallization is evaluated from this equation using the plots of $\ln (\beta / T_c)$ against $10^3/T_c$.

3. Material preparation

Glassy alloys of $Se_{100-x}Sb_x$ (x = 2, 6, 10) 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 five 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 l = 1.54 A ° (Cu Ka1).

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 sample preparation; (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, the wt% loss of a test sample is recorded while the sample is being heated at a uniform rate in an appropriate environment (inert nitrogen gas). The loss in weight over specific temperature ranges provides 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 the 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, UK). The temperature precision of this equipment is 0.1 K with an average standard error of about 1 K in the measured values. Ten to twenty 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. Four heating rates (5, 10, 15 and 20 K /min) were chosen in the present study. Measurements were made under almost identical conditions.

5. Results and discussion

Fig. 1 shows typical DSC thermograms for glassy alloys of $Se_{100-x}Sb_x$ (x = 2, 6, 10) at a heating rate of 15 K/min. Similar thermograms were obtained for other heating rates also (not shown here). It is clear from these figures that well defined and single endothermic and exothermic peaks are observed at the glass-transition temperature (T_g) and the crystallization temperature (T_c) respectively. Crystallization temperatures (T_c) of various glassy alloys of $Se_{100-x}Sb_x$ (x = 2, 6, 10) are given in the table 1 [45]. It is clear from this table that the peak temperature, which is taken as the crystallization temperature, shifts towards higher temperatures as the heating rate is increased from 5 to 20 K/min.

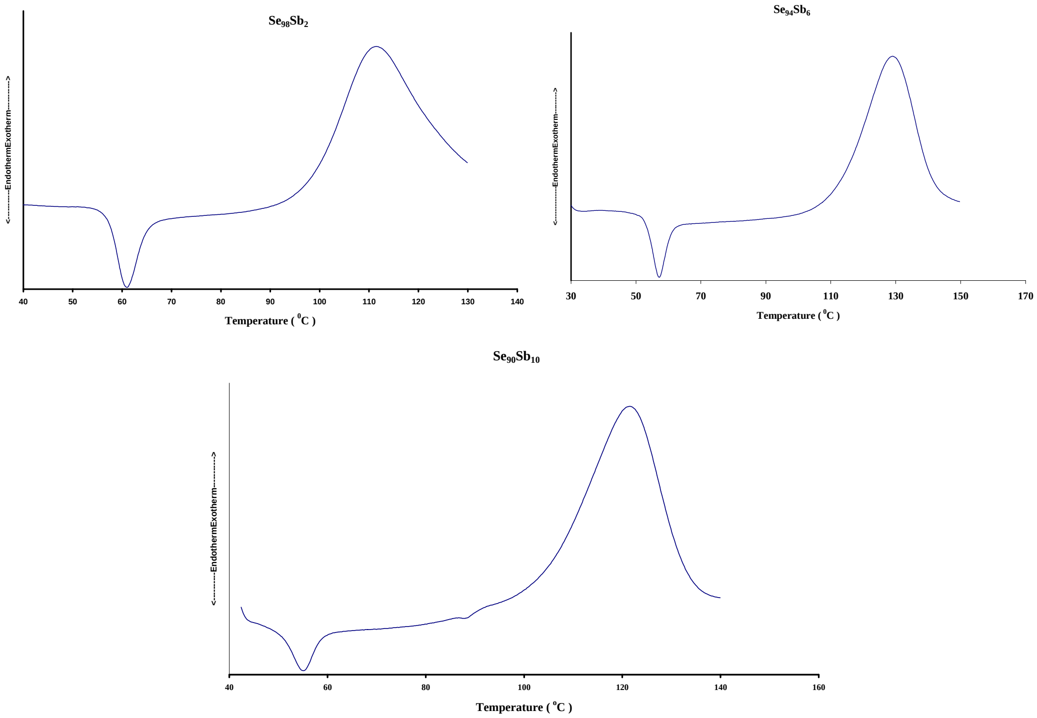


Fig. 1. DSC thermograms for $Se_{100-x}Sb_x$ (x = 2, 6, 10) for 15 (K / min).

Table 1. Crystallization temperatures of $Se_{100-x}Sb_x$ (x = 2, 6, 10) glassy alloys

Heating rate (K / min)	$Se_{98}Sb_2$	$Se_{94}Sb_6$	$Se_{90}Sb_{10}$
5	374	389	381
10	382	398	390
15	385	403	395
20	389	409	400

It is also interesting to note that the crystallization temperatures of all glassy alloys are much higher than room temperature. This is advantageous as a large temperature difference is essential to prevent self transition of recording materials between two phases amorphous and crystalline. Hence, one can expect that each of these alloys may 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 as only one crystallization peak is observed. This is also an essential requirement for PC optical-recording materials.

The most widely used model to obtain activation energy of crystallization is the JMA model for non-isothermal kinetics. This model implies that the Avrami exponent n, and the activation energy E_c, should be constant during the transformation process. By using the slopes of the straight lines obtained in the graphs plotted between ln (β / T_c^2), ln (β), ln (β / T_c) vs 10^3 / T, the activation energy of crystallization can be obtained from Kissinger's method, Matusita-Sakka, and Augis and Bennett theory respectively [45]. Calculated values of the E_c has been given in the Table 2.

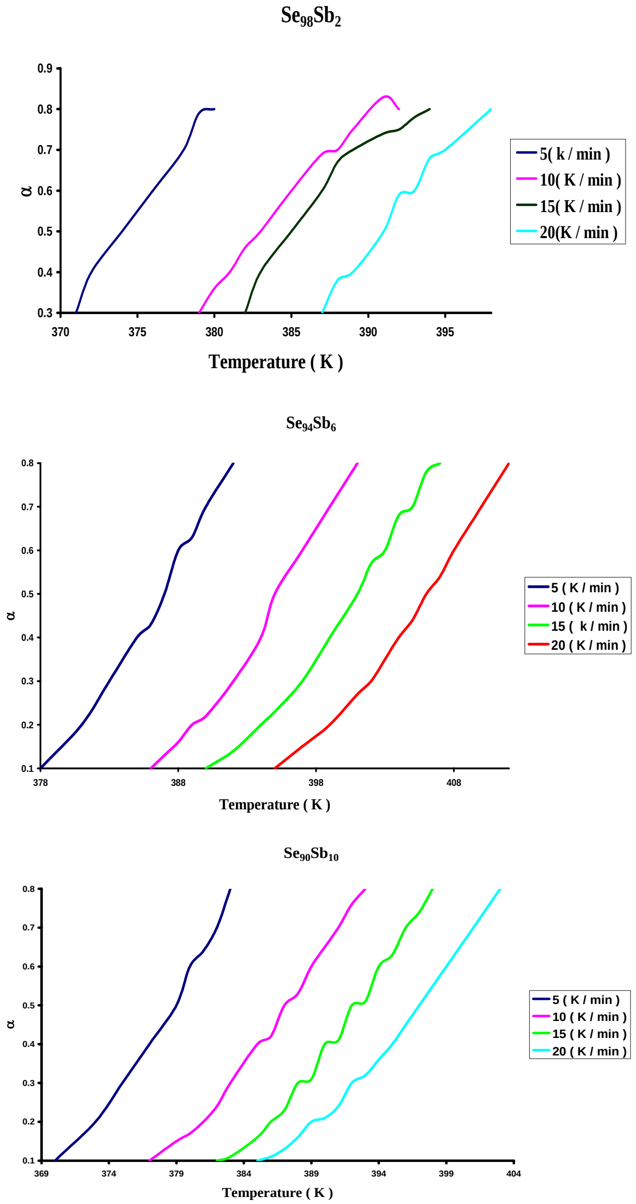
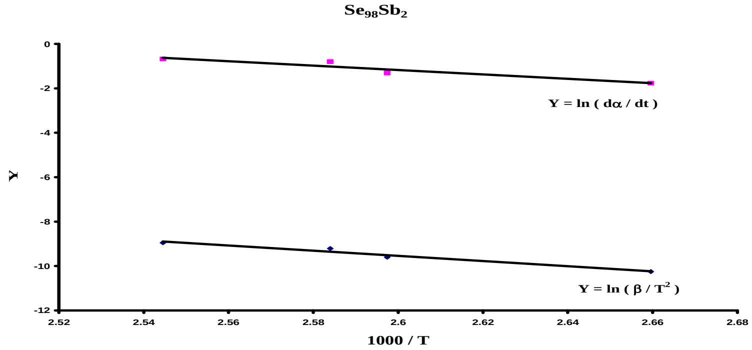
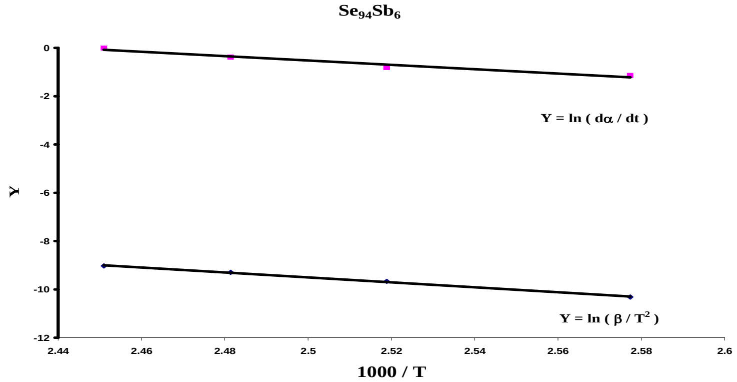


Fig. 2 Crystallization fraction (α) vs. T(k) for $Se_{100-x}Sb_x$ (x = 2, 6, 10).

Table 2. Activation Energy of Crystallization of $Se_{100-x}Sb_x$ (x = 2, 6, 10) glassy alloys

E_c (eV)	$Se_{98}Sb_2$	$Se_{94}Sb_6$	$Se_{90}Sb_{10}$
Kissinger's method	1.10	0.92	0.94
Matusita-Sakka method	1.14	0.98	1.00
Augis and Bennett theory	1.11	0.95	0.97
Average Value	1.12	0.95	o.97





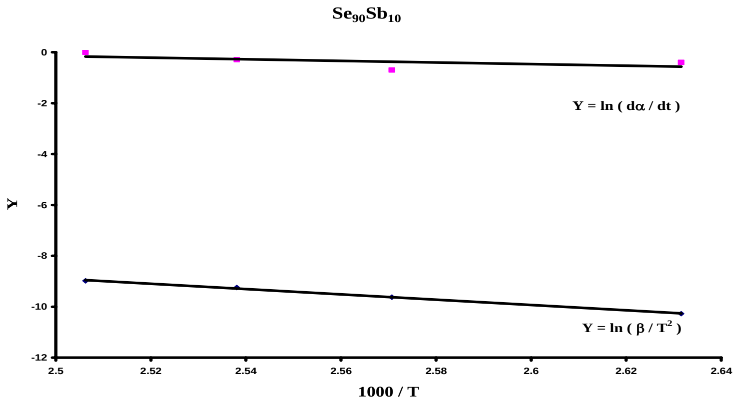
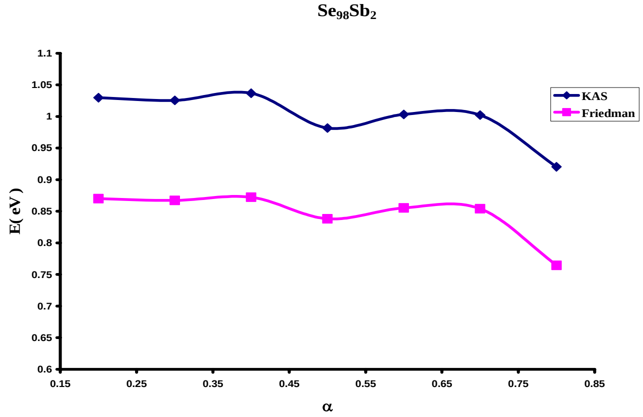


Fig. 3 Slopes of Friedman and KAS method for α = 0.6

Recent papers in this field have shown that n and E_c are not necessarily constants, but show variation in different stages of the transformation [46-49].To see the variation of activation energy with extent of conversion, Friedman and KAS isoconversional methods are used. Fig. 2 shows variation of α (extent of conversion) with temperature for $Se_{100-x}Sb_x$ (x = 2, 6, 10) as obtained from experimental data. Using eqs.5 and 6, the plots of ln (dα / dt) vs 10^3 / T and ln (β_i / $T_{\alpha i}^2$) vs 10^3 / T are plotted for various glassy alloys of $Se_{100-x}Sb_x$ (x = 2, 6, 10) for α = 0.6. Such curves are shown in Fig. 3. The slopes of straight lines shown in this figure are used to calculate the activation energy for that particular value of α. This procedure is repeated for other values of α. Fig. 4 shows variation of effective activation energy as a function of the degree of conversion α as observed by two methods (see table 3). Temperature dependence of E_c can be also observed by replacing α by T as shown in Fig.5



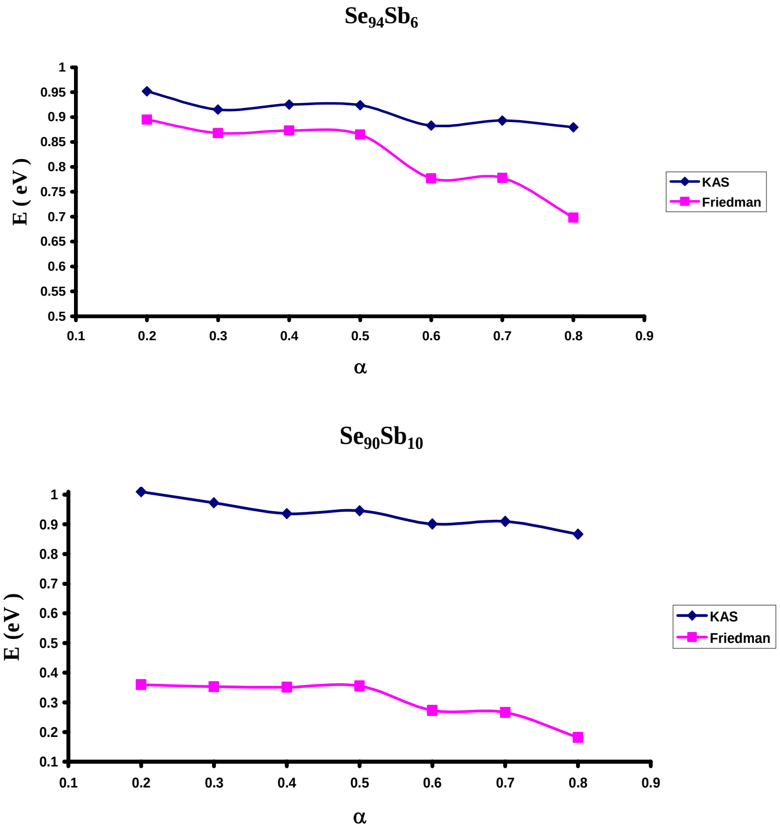


Fig. 4 Activation energy (E) vs. Crystallization fraction (α)

Table 3. Activation energy of crystallization as a function of crystallization fraction

Crystallization Fraction (α)	$Se_{98}Sb_2$		$Se_{94}Sb_6$		$Se_{90}Sb_{10}$	
	KAS	Friedman	KAS	Friedman	KAS	Friedman
0.2	1.03	0.87	0.952	0.90	1.01	0.36
0.3	1.03	0.87	0.92	0.87	0.97	0.35
0.4	1.04	0.87	0.93	0.87	0.94	0.35
0.5	0.98	0.84	0.92	0.87	0.95	0.36
0.6	1.00	0.86	0.88	0.78	0.90	0.27
0.7	1.00	0.85	0.89	0.78	0.91	0.27
0.8	0.92	0.77	0.88	0.70	0.87	0.18

It is clear from table 3 that the activation energy of crystallization is almost same at low values of α. However, at higher values of α, E_c decreases with the increase in α. This trend is evident by Fig. 4. It is also interesting to note that E_c calculated by KAS method, are higher than that obtained by Friedman method. It is possible that this disagreement is due to the fact that the systematic errors, which arise from the numerical differentiation of the experimental data involved in Friedman method can lead to smaller value of E_c. The average value of E_c calculated by the methods shown in table 2 is also closer to the values of E_c calculated by KAS method, which indicates that KAS method may be considered more suitable in the present case.

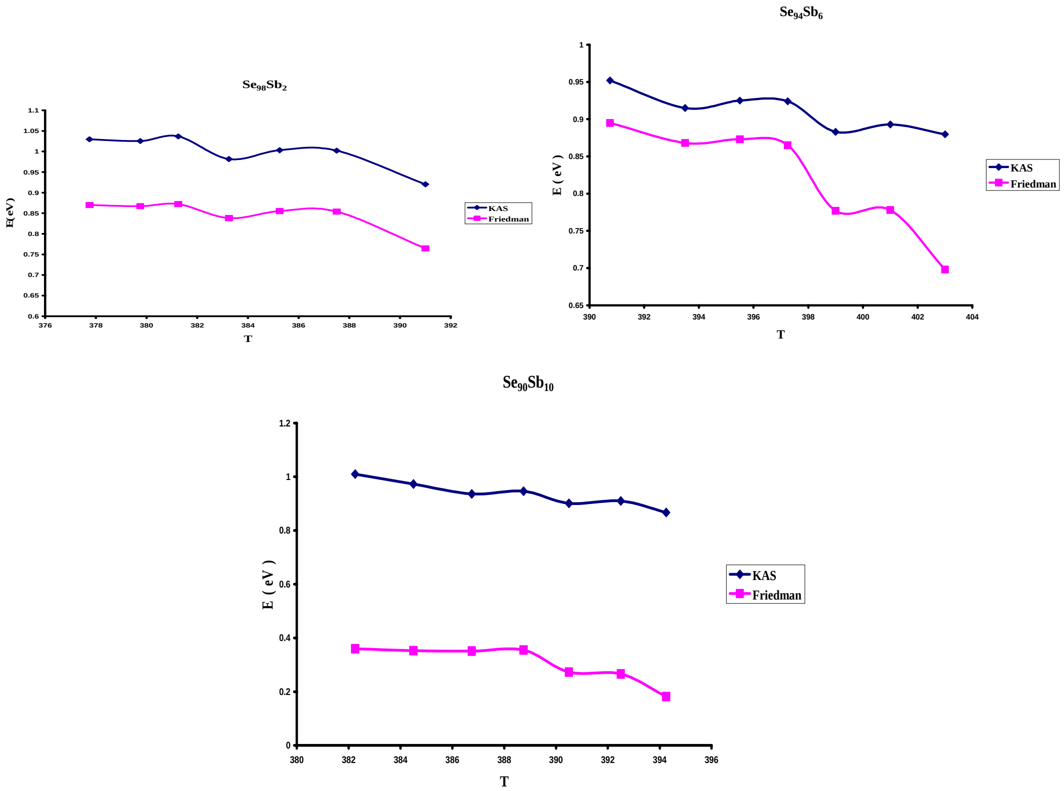


Fig. 5 Activation energy (E) vs. Temperature T(K)

The values of E_c decreases with temperature also for both the methods used (see Fig. 5), which simply indicates that the crystallization rate increases with increasing temperature. This behaviour demonstrates that the rate constant of crystallization is, in fact, determined by the rates of two processes, nucleation and diffusion. Because these two mechanism are likely to have different activation energies, the effective activation energy of the transformation will vary with temperature [50].This interpretation is based on the nucleation theory proposed by Fisher and Turnbull [51].

6. Conclusions

The crystallization kinetics in glassy $Se_{100-x}Sb_x$ (x = 2, 6, 10) alloys has been studied under non-isothermal conditions. The DSC technique has been used to determine the activation energy of crystallization (E_c). By applying two isoconversional methods, the activation energies of crystallization of $Se_{100-x}Sb_x$ have been determined found that they are strongly temperature-dependent at the high extent of crystallization only. The results show a decrease in the activation energy for crystallization with increasing temperature at higher extent of crystallization. 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 $Se_{100-x}Sb_x$ (x = 2, 6, 10) is a complex process involving different mechanisms of nucleation and growth particularly at higher values of the extent of crystallization.

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