

PHASE TRANSFORMATION AND CRYSTALLIZATION KINETICS OF $\text{Se}_{90}\text{In}_8\text{Sb}_2$ CHALCOGENIDE GLASS

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The crystallization kinetics of $\text{Se}_{90}\text{In}_8\text{Sb}_2$ chalcogenide glass prepared by melt quenching technique, has been studied by Differential Scanning Calorimetry (DSC) under non-isothermal condition with six different heating rates i.e. 5,10,15,20,25,30 K/min. The DSC traces have been analyzed in terms of activation energy, stability and dimensionality of growth by four different models viz. Kissinger's, Augis-Bennett's, Matusita's and Gao-Wang's equations. The value of the Avrami exponent comes out to be 2.85 ± 0.25 , which shows that crystallization process takes place via two-dimensional growth. Thermal stability has also been determined using various parameters. Besides these, the volume of fractioned crystallized and rate of crystallization as a function of temperature has also been studied. Further, an effort has been made to study the dependence of rate constant on temperature.

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1. Introduction

The last decades have seen a strong interest in the study of glass-crystal transformation. An understanding of kinetics of crystallization in glasses is important for the manufacturing of glass ceramics and in preventing devitrification. Nucleation and crystallization rates are sometimes measured directly in the microscope but this method could not be applied to glasses in which nucleation and crystallization occurred in times below 1 hour [1]. Differential Scanning Calorimetry (DSC) is valuable for the quantitative study of crystallization in different glassy system. This technique is particularly important due to the fact that: (i) it is easy to carry out (ii) it requires little sample (iii) it is quite sensitive and (iv) it is relatively independent of the sample geometry [2]. In calorimetric measurements, two basic methods can be used: isothermal and non-isothermal condition. In the isothermal method, the sample is brought quickly to a temperature above the glass transition temperature (T_g) and the heat evolved during the crystallization process is recorded as a function of time. In non-isothermal method, the sample is heated at a fixed rate and the heat evolved is again recorded as a function of temperature or time.

The selection of Se was made because of its wide commercial applications like switching [3], memory [4] and xerography [5] etc. But in pure state, it has certain disadvantage because of its short lifetime, low sensitivity and low thermal instability. This problem can be overcome by alloying Se with some impurity atoms (Ge, Te, Bi, Sb and In etc.). Selenium also exhibits a unique property of reversible phase transformation. This property makes these systems very useful in optical memory devices [6-8]. The addition of In to Se-Sb system is expected to modify the material properties to make it more suitable for reversible optical recording with an eraser time less than 1 micro second [9]. It has been found that the structure of the glass is considerably modified by the addition of Sb [10].

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2. Experimental details

The bulk material was prepared using well-established melt quenching technique. High purity (99.9999%) Se, Sb and In in appropriate atomic percentage proportions were weighed in a quartz glass ampoule (length 10.5 cm and 8 mm internal diameter). The content of ampoule (5g) were sealed under a vacuum of 10^{-5} Torr and heated in a furnace where the temperature was raised at a rate of 3-4 $^{\circ}\text{C}$ per minute up to 900°C and kept at that temperature for 15 hours. The ampoule was agitated frequently in order to mix the constituents to ensure homogenization of the melt. The molten sample was then quenched in ice-cooled water. The ingot of so produced glassy sample was taken out of ampoule by breaking the ampoule and then grinded gently in mortar and pestle to obtain powder form. The amorphous nature of the alloy was ascertained through X-ray diffraction pattern of the samples using diffractometer with CuK_{α} -radiation source ($\lambda = 1.540 \text{ \AA}$). The XRD pattern of $\text{Se}_{90}\text{In}_8\text{Sb}_2$ glass is shown in Fig 1. The absence of any sharp peak in the XRD pattern confirms the amorphous nature of the sample.

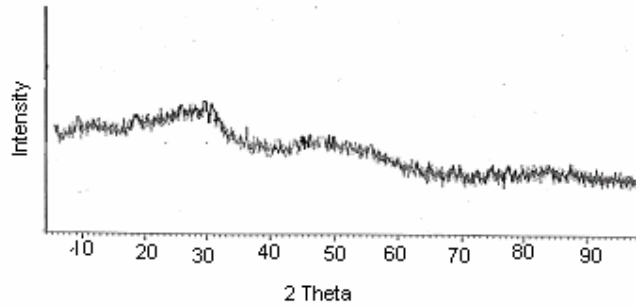


Fig. 1 XRD pattern of $\text{Se}_{90}\text{In}_8\text{Sb}_2$ chalcogenide glass at room temperature.

Differential Scanning Calorimetry (DSC) Rigaku Model 8230 is used to measure the caloric manifestation of the phase transformation and to study the crystallization kinetics under non-isothermal condition. The accuracy of heat flow measurement is $\pm 0.01 \text{ mW}$ and the temperature precision as determined by the microprocessor of the thermal analyzer is $\pm 0.1 \text{ K}$. The DSC runs have been taken at six different heating rates i.e. 5, 10, 15, 20, 25, and 30 K/min on accurately weighed samples taken in aluminum pans. The temperature range covered in DSC was from room temperature to 250°C .

3. Result and discussion

The non-isothermal crystallization data are usually interpreted in terms of Johnson-Mehl-Avrami (JMA) theoretical model [11-13] in which the crystallization fraction χ can be described as a function of time t according to the following equation:

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

where n is the Avrami exponent and K is defined as the effective overall reaction rate, which is usually assumed to have an Arrhenian temperature dependence :

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

where the pre-exponential K_0 is the frequency factor.

Fig.2 shows DSC thermogram at different heating rates for $\text{Se}_{90}\text{In}_8\text{Sb}_2$ glassy alloy under the non-isothermal condition. Two characteristic phenomena (endothermic and exothermic peaks) are evident in the DSC curves in the temperature range of the investigation. From the analysis point of view, the DSC curve is divided into two parts, the first one corresponds to the glass transition region which appears as an endothermic reaction and the other part is related to the crystallization process indicated by exothermic reaction in the DSC curves. The glass transition temperature T_g and the on-set crystallization temperature T_c , have been defined as

temperature corresponding to the intersection of two linear portion adjoining the transition elbow of the DSC trace in the endothermic and exothermic direction, respectively. It is clear from Fig.2 that well-defined endothermic and exothermic peaks are observed at the glass transition temperature.

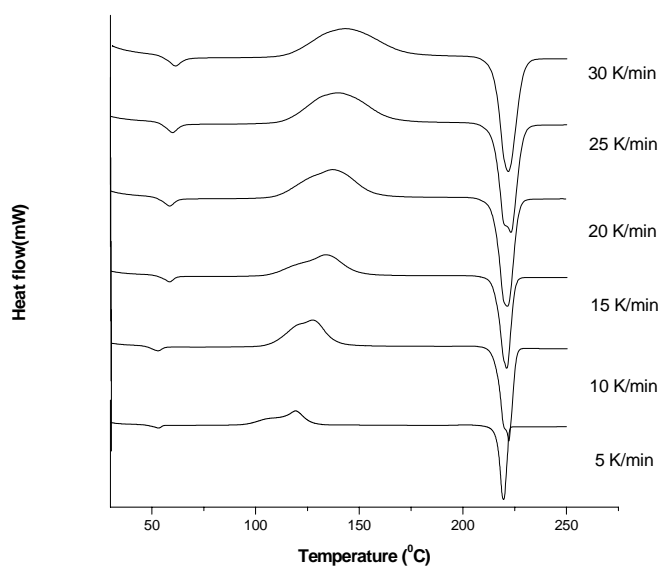


Fig. 2 DSC traces of $Se_{90}In_8Sb_2$ chalcogenide glass at different heating rates

From the point of technological application, the glass should be thermally stable. This thermal stability of glasses has been ascertained on the basis of calorimetric measurements using the DSC. Usually, unstable glasses show crystallization peak close to the glass transition temperature. Therefore, the temperature difference $T_c - T_g$ is a good indication of thermal stability because the higher the value of this difference, more the delay in nucleation [14]. Two different parameters i.e. Hrubby number [15] and S-parameters [16] are also calculated to determine sample stability. All these parameters show that thermal stability of the sample increases with heating rate. The values of different thermal stability parameters of $Se_{90}In_8Sb_2$ glass are shown in Table 1.

Table 1. Different thermal stability parameters of $Se_{90}In_8Sb_2$ glass at different heating rates:

Heating Rate (K/min)	$T_c - T_g$ (K)	$T_m - T_c$ (K)	Thermal Stability Parameter Hrubby Number $H_R = (T_c - T_g) / (T_m - T_c)$	S- Parameter $S = (T_c - T_g)(T_p - T_c) / T_g$ (K)
5	47.4	125.3	0.378	3.79
10	51.4	120.1	0.428	3.82
15	53.3	115.4	0.462	4.64
20	55.4	112.7	0.492	4.80
25	57.3	111.2	0.515	4.86
30	58.6	108.3	0.541	5.04

Two approaches are used in the analysis of the dependence of T_g on the heating rate (α). The first is the empirical relation that has been suggested by Lasocka [17,18] and has the form

$$T_g = A_g + B_g \ln(\alpha) \quad (3)$$

$$T_c = A_c + B_c \ln(\alpha) \quad (4)$$

where A_g , B_g , A_c and B_c are constants.

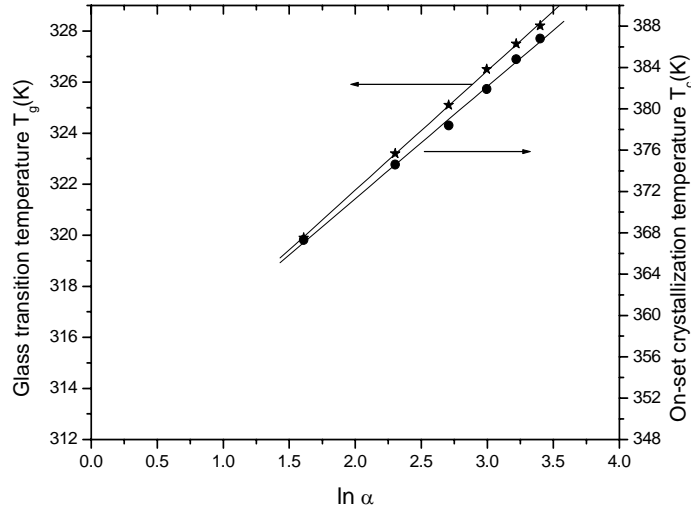


Fig. 3 $\ln(\alpha)$ vs T_g and $\ln(\alpha)$ vs T_c for $Se_{90}In_8Sb_2$ glassy alloy

The plots of $\ln(\alpha)$ vs T_g and $\ln(\alpha)$ vs T_c for $Se_{90}In_8Sb_2$ glassy alloy are shown in Fig.3. The straight line shows the good validity of this relationship for the alloy. The calculated values of A_g , B_g , A_c and B_c are given in Table 2. In Table 2, A_g and A_c depict the glass transition and crystallization temperature at a heating rate of 1 K/min respectively while B_g and B_c are proportional to the time taken by the system to reduce its glass transition and crystallization temperature when its heating rate is lowered from 10 K/min to 1 K/min.

Table 2: calculated values of constants A_g , B_g , A_c and B_c for $Se_{90}In_8Sb_2$ chalcogenide glass.

Sample	A_g (K)	B_g (min)	A_c (K)	B_c (min)
$Se_{90}In_8Sb_2$	312.42 ± 0.14	4.67 ± 0.05	349.58 ± 0.73	10.86 ± 0.26

The second approach concern the use of the Kissinger's [19] linear dependence in the form

$$\ln(\alpha/T_g^2) = -E_g/RT_g + \text{constant} \quad (5)$$

Where E_g is the activation energy for the glass transition. Fig.4 shows the plot between $\ln(\alpha/T_g^2)$ and $1000/T$, the slope of which gives the activation energy of the glass transition E_g . The value of E_g deduced using Eq. (5) is $181.33 \pm 2.66 \text{ kJmol}^{-1}$.

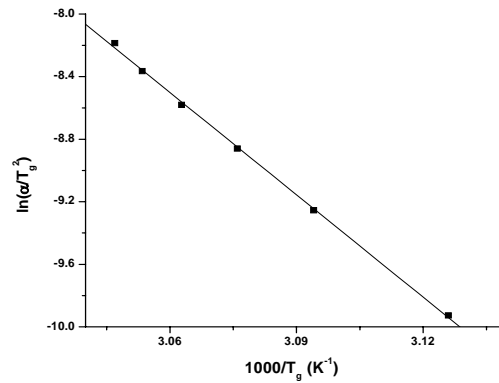


Fig.4 $\ln(\alpha/T_g^2)$ against $10^3/T_g$ for the $Se_{90}In_8Sb_2$ chalcogenide glass

According to Kissinger, the peak crystallization temperature T_p in terms of heating rate (α), can be expressed as

$$\ln(\alpha/T_p^2) = -E_c/RT_p + \text{constant} \quad (6)$$

Eq. (6) is used to calculate the activation energy of crystallization by plotting the curve between $\ln(\alpha/T_p^2)$ vs $10^3/T_p$ as shown in Fig 5.

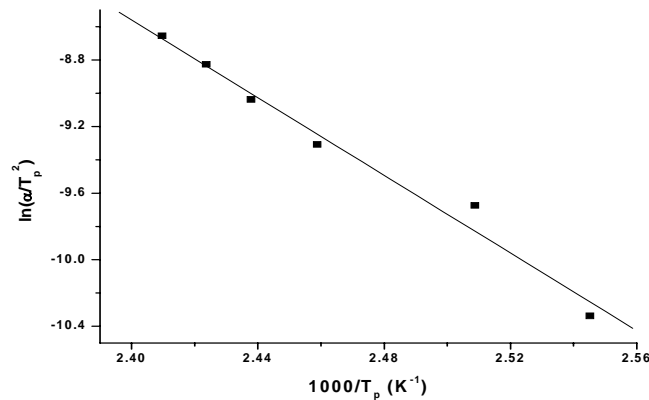


Fig. 5 $\ln(\alpha/T_p^2)$ against $10^3/T_p$ for the $Se_{90}In_8Sb_2$ chalcogenide glass.

The activation energy of crystallization can also be determined by an approximation method developed by Augis and Bennett [20]. The relation used by them is of the form

$$\ln(\alpha/T_c) = -E_c/RT_c + \ln K_0 \quad (7)$$

The activation energy of crystallization can be evaluated by plotting curve between $\ln(\alpha/T_c)$ vs $10^3/T_c$ as shown in Fig 6. This method has an extra advantage that the intercept of the curve gives the value of pre-exponential factor K_0 of Arrhenius equation.

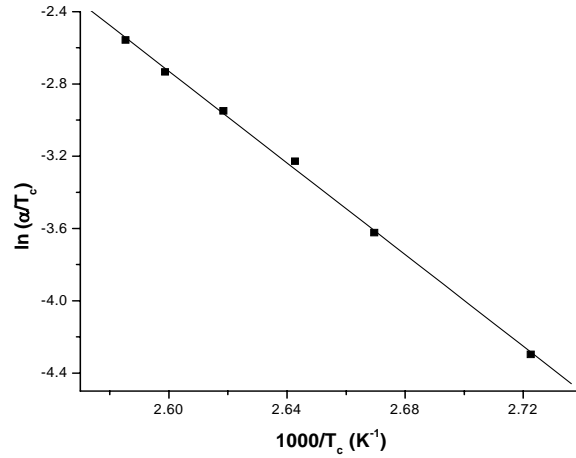


Fig. 6. $\ln(a/T_c)$ against $10^3/T_c$ for the $\text{Se}_{90}\text{In}_8\text{Sb}_2$ chalcogenide glass

Knowing the value of E_c and $\ln K_0$ from Eq.(7), the value of rate constant K has been obtained by Eq.(2). The graph between $\ln K$ and temperature is shown in Fig.7. It is observed that $\ln K$ increases linearly with temperature hence the speed of crystallization increases.

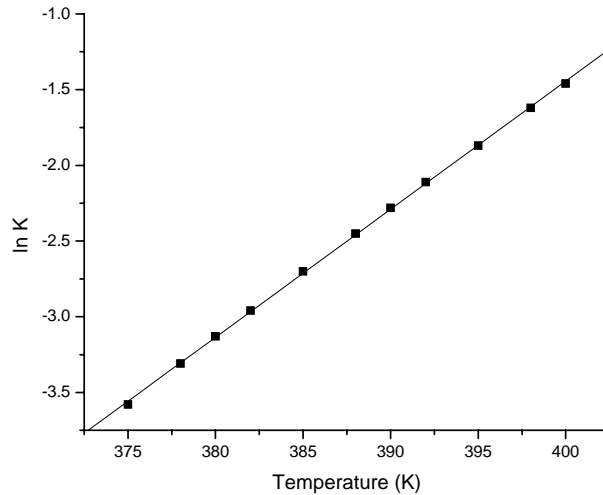


Fig. 7 $\ln K$ against Temperature for the $\text{Se}_{90}\text{In}_8\text{Sb}_2$ chalcogenide glass.

The theoretical basis for interpreting the DSC results is provided by the formal theory of transformation kinetics as developed by Johnson-Mehl and Avrami. In the non-isothermal method, the crystallization fraction (χ) precipitated in the glass heated at constant rate, is related to the activation energy for crystallization (E_c), through the following expression given by Matusita et al. [21]

$$\ln [-\ln(1-\chi)] = -n \ln \alpha - 1.052mE_c/RT + \text{constant} \quad (8)$$

where m and n are integer or half integer numbers that depend on the growth mechanism and the dimensionality of the crystal. The parameter n can be written as $n=b+pm$ where $p=1$ for linear growth and $p=0.5$ for parabolic growth, $m=1,2$ or 3 for one-, two-, or three-dimensional growth, $b=0$, $b<1$ and $b>1$ are chosen for no nucleation, decreasing nucleation and increasing nucleation rate, respectively [22]. The fraction χ

crystallized at any temperature T is given by $\chi = A_T/A$, where A is the total area of the exothermic peak between the on-set temperature T_c (i.e. the temperature from where crystallization starts) and temperature where the peaks end (i.e. crystallization is complete). A_T is the partial area of the exothermic peak between temperature T_c and T .

The plots of $\ln[-\ln(1-\chi)]$ against $\ln(\alpha)$ at three different temperatures are shown in Fig 8. From the slope of this curve, the order of crystallization mechanism or Avrami index (n) can be obtained

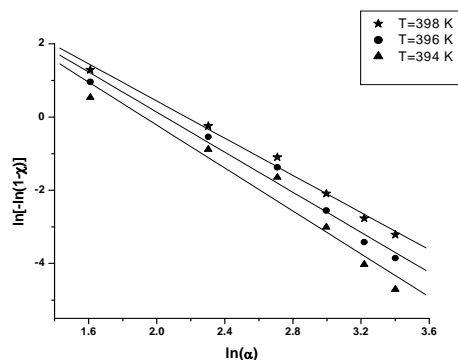


Fig. 8 $\ln[-\ln(1-\chi)]$ against $\ln\alpha$ for the $Se_{90}In_8Sb_2$ chalcogenide glass at different temperature.

It is clear from the Fig.8 that n is temperature independent and hence the average value can be calculated. Thus average value of n obtained from these results is 2.85 ± 0.25 . From the value of n , the crystallization mechanism is concluded to be two-dimensional growth.

The activation energy of crystallization (E_c) can be obtained from Matusita's equation by plotting $\ln[-\ln(1-\chi)]$ against $1000/T$ as shown in Fig 9. The slope of this gives activation energy of crystallization. The curve is a straight line for most of the temperature range but shows break in linearity at higher temperatures, which is attributed to the saturation of nucleation sites in the final stages of crystallization or due to restriction of the crystal growth by the small size of the particles [23].

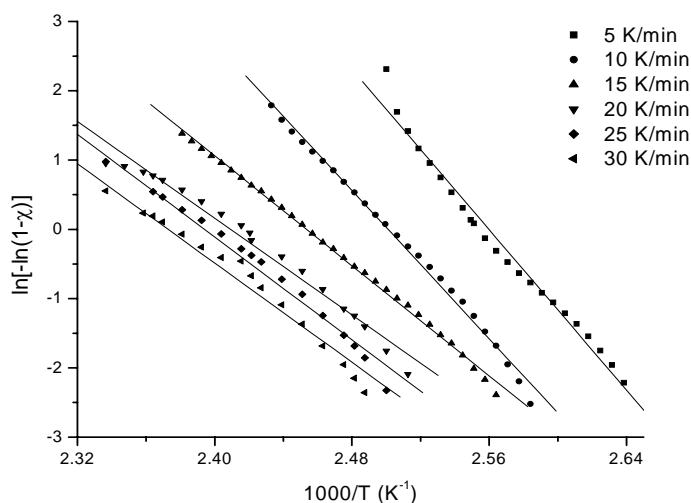


Fig. 9 $\ln[-\ln(1-\chi)]$ against $10^3/T$ for the $Se_{90}In_8Sb_2$ chalcogenide glass at different heating rates

The area under the crystallization peak is directly proportional to the total amount of alloy crystallized. The ratio between the ordinates and the total area of the peak gives the corresponding crystallization rates, which make it possible to plot the curves between volume crystallization fraction and temperature. Fig.10 shows the plot of volume crystallization fraction (χ) as a function of temperature. Differentiating these curves we can obtain the relationship between crystallization rate $d\chi/dt$ and the temperature. Fig.11 shows the plot of

crystallization rate ($d\chi/dt$) as a function of temperature. From Fig.10 and Fig.11, one can infer that the saturation of crystallization shifts towards the higher temperature as the heating rate increases as reported earlier [1,4].

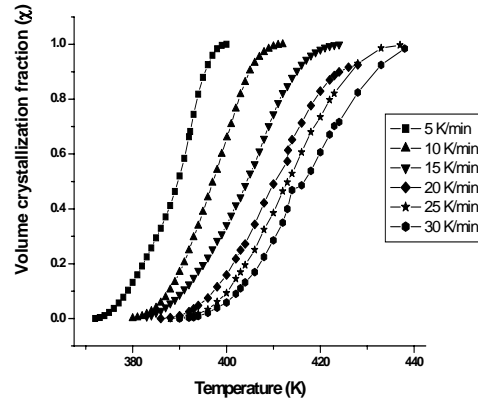


Fig. 10 Volume crystallization fraction (χ) vs temperature at different heating rates

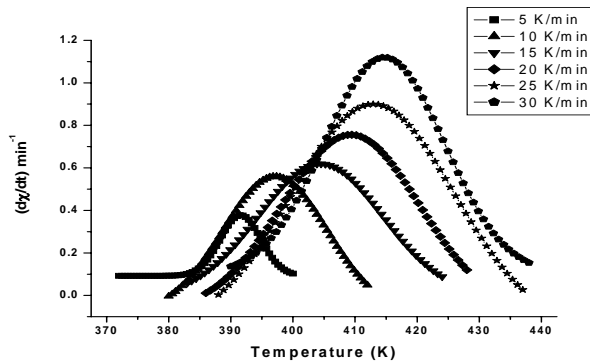


Fig. 11 Rate of crystallization ($d\chi/dt$) vs temperature at different heating rates.

Further, Gao and Wang [24] have proposed a slightly different method to analyze DSC thermograms in terms of the activation energy (E_c), the dimensionality (m), the rate constant (K_p), the frequency factor (K_0) during the crystallization process. The theory is based on the same fundamental assumption imposed on the JMA transformation equation. It assumes that the nucleation is randomly distributed, and that the growth rate of the new phase depends on the temperature but not on time. The theory provides the relationship between the maximum crystallization rate and the peak crystallization temperature

$$\ln (d\chi/dt)_p = -E_c/RT_p + \text{constant} \quad (11)$$

where $(d\chi/dt)_p$ is the peak crystallization rate which is proportional to the peak height. A plot between $\ln(d\chi/dt)_p$ and $1000/T_p$, as shown in Fig 12, gives the value of activation energy of crystallization E_c .

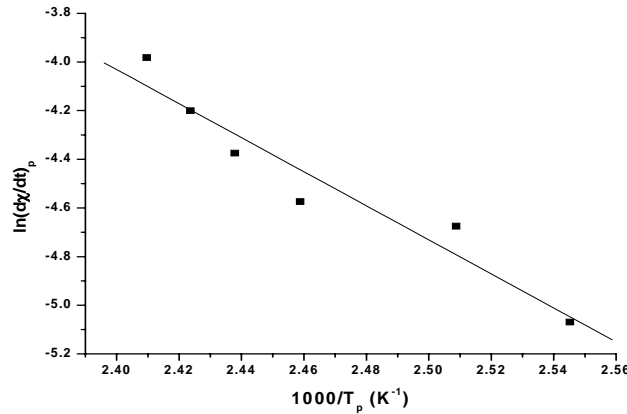


Fig. 12 $\ln(dx/dt)_p$ against $10^3/T_p$ for the $Se_{90}In_8Sb_2$ chalcogenide glass

Using $\ln(dx/dt)_p$, activation energy and other experimental data, the value of K_p and the Avrami exponent (n) are then determined from the following relations:

$$K = K_0 \exp(-E_c/RT), \quad (12)$$

$$K_p = \alpha E_c / RT_p^2, \quad (13)$$

$$(dx/dt)_p = (0.37)nK_p, \quad (14)$$

where the pre-exponential factor (K_0) known as the frequency factor, gives the number of attempts per second made by the nuclei to overcome the energy barrier, reflecting the information about the number of nucleation sites. The different parameters obtained from Gao-Wang's equation are given in Table 3.

Table 3: The parameters of crystallization of $Se_{90}In_8Sb_2$ glass.

Heating Rate (K/min)	$(dx/dt)_p$ (s ⁻¹)	K_p (s ⁻¹)	Avrami index (n)
5	0.0063	0.0038	4.48
10	0.0093	0.0073	3.44
15	0.0103	0.0106	2.63
20	0.0126	0.0139	2.45
25	0.0150	0.0171	2.37
30	0.0187	0.0203	2.49

From the above, we know that the activation energies of an amorphous alloy calculated by means of the different theoretical models differ substantially from each other. This difference in the activation energy as calculated with the different models, even for the same sample, may be attributed to the different approximations used in the models. The Kissinger equation was basically developed for studying the variation of the peak crystallization temperature with heating rate. According to Kissinger's method, the transformation under non-isothermal condition is represented by a first-order reaction, and this is also the case with the Ozawa model. Moreover, the concept of nucleation and growth has not been included in Kissinger and the Ozawa equations. Augis and Bennett method is helpful in obtaining kinetic parameters such as frequency factor (K_0),

rate constant (K) along with activation energy of crystallization. The model developed by Gao and Wang for the calculation of the kinetics is preferred over all the other models. The advantage of the Gao and Wang model over other models is that it also allows calculating other kinetic parameters, i.e., the Avrami exponent, the rate constant and the frequency factor in addition to the activation energy, which in turn are used to understand the physics of the crystallization process. Table 4 gives the calculated values of glass transition activation energy E_g and crystallization activation energy E_c using different models for $Se_{90}In_8Sb_2$ glass.

Table 4: The calculated values of glass transition activation energy E_g and crystallization activation energy E_c using different models for $Se_{90}In_8Sb_2$ glass.

Glass transition activation energy (E_g) (kJ/mol)	Crystallization activation energy (E_c) kJ/mol			
	Kissinger's model	Augis- Bennett's model	Matusita and Sakka's model	Gao-Wang's model
181.33 ± 2.66	96.94±6.73	105.47±2.00	94.39±2.61	58.20±7.98

4. Conclusions

A systematic study of $Se_{90}In_8Sb_2$ chalcogenide glass leads to the following conclusions: -

1. Using different thermal stability parameters it is found that thermal stability of the sample increases with heating rate.
2. Difference in values of activation energy E_c using different theoretical models may be attributed to the different approximation used in the models.
3. The value of Avrami index n obtained from Matusita's model is 2.85 ± 0.25 , suggesting the two-dimensional nucleation growth during its amorphous to crystalline transformation.

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