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KINETICS OF PHASE TRANSFORMATIONS OF $Se_{71}Te_{20}Ag_9$ GLASSY ALLOY

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$Se_{71}Te_{20}Ag_9$ glass has been prepared by melt quenching technique. The sample has been structurally characterized using X-ray diffraction (XRD) and the kinetics of phase transformation has been studied using differential scanning calorimetry (DSC). Kinetic parameters of phase transformations such as activation energy of glass transition, activation energies of crystallization, Avrami exponent (n), dimensionality of growth and frequency factor have been evaluated using Kissinger, Matusita -Sakka Gao –Wang and Augis-Bennet models.. The average value of m comes out to be one suggesting surface nucleation with one-dimensional growth.

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1. Introduction

Chalcogenide glasses containing S, Se or Te constitute a rich family of vitreous semiconductors and drawn a great deal of attention because of their use in various solid-state devices [1-3]. Among chalcogenide glasses, Se-Te glassy alloy are of interest because of their higher photosensitivity, greater hardness, higher crystallization temperature and smaller ageing effects as compared to pure Se glass for better applications. The addition of third element in Se-Te glass converts the glass into an interesting material and new promising properties of the material are expected [4]. With this point of view Ag has been added to Se-Te, which will create the compositional and configurational disorder in the material as compared to binary alloy. Generally these types of compounds are covalent in nature and the addition of third element will create iono-covalent bonds resulting in an increase in conductivity [5]. Se-Te-Ag chalcogenide glasses exhibit single glass transition temperature and single crystallization temperature, which is an important condition erasable phase-change optical recording [6-9]. It is difficult to write and erase if the amorphous-to-crystalline transformation rate is sufficiently high. For this reason, the study of crystallization is important for the development of new materials. Apart from the technical importance, the knowledge of the crystallization process is important for better understanding of the short-range order in these materials. Various thermal analysis techniques have been used to study the phase transformation of glasses. Differential Scanning Calorimetry (DSC) is one such technique, which is used for quantitative measurement of different kinetic parameter [10-14].

The aim of the present paper is to study the phase transformation and the crystallization kinetics of $Se_{71}Te_{20}Ag_9$ glassy alloy using differential scanning calorimetry (DSC). The study of kinetics is always connected with the concept of activation energy. The values of this energy are associated with nucleation and growth mechanism that dominate of the devitrification of most of glassy solids [15]. The activation energy of both the phase transformations (glass transition and

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crystallization) has been obtained using theoretical models [16] such as Kissinger, Matusita – Sakka, Gao –Wang and Augis-Bennet models.

2. Experimental details

$Se_{71}Te_{20}Ag_9$ glass has been prepared by melt quenching technique. The materials of high purity (99.999%) were weighed according to their atomic weight percentages into a quartz ampoule. The content of the ampoule was sealed in the vacuum of 10^{-6} Torr and heated in a furnace. The temperature of the furnace was raised at a rate of 3-4 K min^{-1} up to 925 K and kept around that temperature for 12 hours.

The ampoule was frequently rocked to ensure the homogeneity of the sample. The molten sample was then rapidly quenched in the ice-cooled water to get glassy state. The amorphous nature of the alloy was ascertained through X-ray diffraction pattern of the samples using Bragg-Brentanno geometry on analytical X'pert Pro diffractometer in 2θ range of $15\text{-}60^0$ with CuK_α radiation source (λ= 1.5406 Å). The X-ray tube was operated at 45kV and 40 mA. The thermal behavior of the samples has been investigated using differential scanning calorimetry (DSC) of Rigaku 8230. The accuracy of heat flow measurement is ±0.01 mW and the temperature precision as determined by the microprocessor of the thermal analyzer is ±0.1 K. DSC runs have been taken at five different heating rates, i.e. 10, 20, 30, 40 and 50 K min^{-1} on accurately weighed samples (10-15 mg) taken in aluminum (Al) pans under non-isothermal conditions. The temperature range covered in DSC was from room temperature (300K) to 433 K.

3. Results and discussion

3.1 *Structural and Thermal analysis*

Fig. 1 shows the X-ray diffraction pattern of as-prepared $Se_{71}Te_{20}Ag_9$ glassy alloy at room temperature (293 K). The absence of any sharp peak confirms the amorphous nature of this alloy.

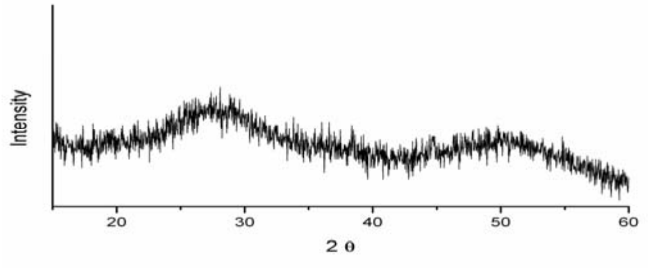

Fig.1 XRD pattern of $Se_{71}Te_{20}Ag_9$ *glass*

Fig. 1 shows a big halo from 25° to 35° of 2θ values, which is signature of polymeric nature of glass containing selenium and is also indicative of the fact that the material possesses only short-range order. The other halo from 45° to 60° of 2θ values is caused by broadening of diffraction peaks due the partially crystalline domains of the polymer network [17].

Fig. 2 shows the DSC thermograms of $Se_{71}Te_{20}Ag_9$ glass at five different heating rates i.e. 10, 20, 30, 40 and 50 K/min. Well defined single endothermic and exothermic region were observed corresponding to glass transition temperature (T_g) and crystallization temperature (T_c) respectively. The values of glass transition temperature (T_g) and onset crystallization temperature (T_c) have been obtained by extrapolating the transition elbows of glass transition and crystallization region respectively.

The values of glass transition temperature (T_g), onset crystallization temperature (T_c), peak glass transition temperature (T_{gp}) and peak crystallization temperature (T_p) at five different heating rates are given in Table 1.

Fig. 2. DSC thermogram of $Se_{71}Te_{20}Ag_9$ glass at five different heating rates.

Table 1. Values of glass transition temperature (T_g), peak glass transition temperature (T_{gp}), crystallization temperature (T_c) and peak crystallization temperature (T_p) for $Se_{71}Te_{20}Ag_9$ glass.

Heating rate α (K / min)	T_g (K)	T_{gp} K)	T_c (K)	T_p (K)
10	339.27	342.5	368.01	395.77
20	342.46	346.5	372.53	400.39
30	343.39	347.6	375.73	405.29
40	347.46	351.2	377.48	408.37
50	348.90	354.6	379.45	412.28

From the Fig. 2 and Table 1, it is clear that T_g and T_c both shift towards higher temperatures as the heating rate increases from 10 to 50 K/min.

3.2. *Kinetics of phase transformations*

Glass transition region

The glass transition region has been studied in terms of the glass transition temperature with heating rate. In addition to this, the activation energy of the glass transition (E_t) has also been evaluated. The glass transition temperature T_g represents the strength or rigidity of the glassy alloy. It is well known that the glass transition temperature T_g varies with the heating rate α [18-22].
The dependence of T_g on heating rate (α) can be discussed on the basis of two approaches. The first approach is the empirical relation suggested by Lasocka [23], which has the form

$$T_g = A + B \ln \alpha \qquad (1)$$

where A and B are constants for a given glass composition. The value of A depicts the value of the glass transition temperature (T_g) at heating rate of 1 K/min, while B is proportional to the time taken by the system to reduce its glass transition temperature (T_g), when its heating rate is lowered from 10 to 1 K/min. Fig.3 depicts the plot of T_g versus ln (α) for the investigated $Se_{71}Te_{20}Ag_9$ glassy alloy.

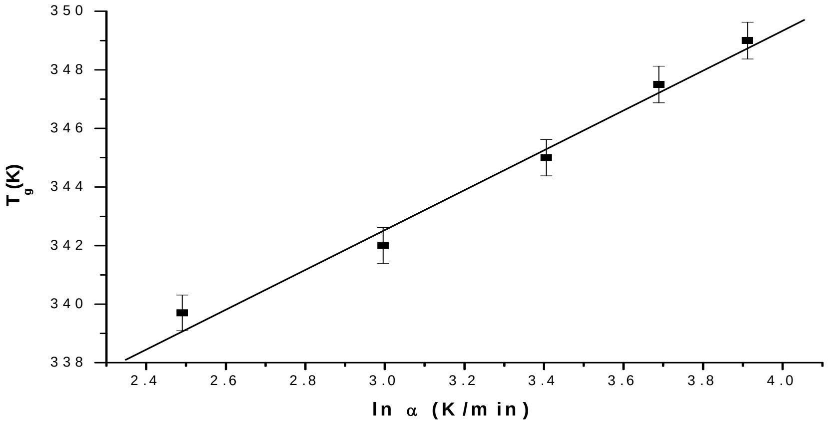

Fig 3. Variation of T_g *with ln (α) of* $Se_{71}Te_{20}Ag_9$ *glassy alloy.*

It is found that this equation holds good for the given sample. The values of A and B were found to be 330 K and 5.82 ± 1.2 min and the same has also been conformed from the DSC thermogram taken at 1 K/min, shown in the figure 4.

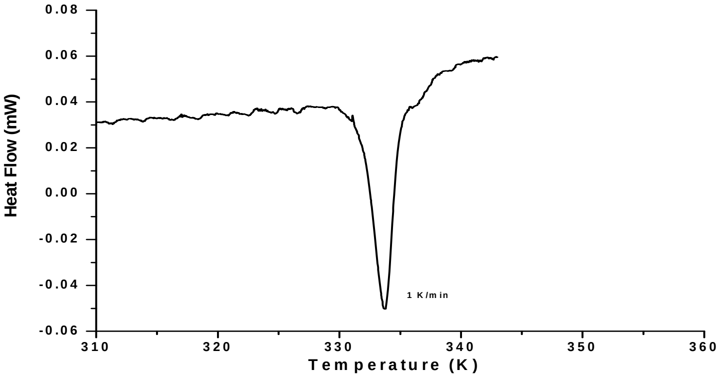

Fig. 4. DSC thermogram of $Se_{71}Te_{20}Ag_9$ *glass at 1K/min.*

The Kissinger [24] equation is another approach, which indirectly involves the dependence of T_g on heating rate (α). This equation is used for the evaluation of the activation energy for the amorphous glass-transition (E_t), inspite of the fact that this equation is used for the evaluation of the activation energy of the crystallization.

The Kissinger equation was originally developed for the peak temperatures and therefore may be written as:

$$\ln \alpha / T_{gp}^2 = - (E_t / RT_{gp}) + \text{constant} \qquad (2)$$

where E_t is the activation energy of the glass transition, T_{gp} is the peak glass transition temperature, α is the heating rate and R is the universal gas constant. Fig.5 shows the plot of ln (α / T_{gp}^2) versus 1000 / T_{gp} for the investigated glass.

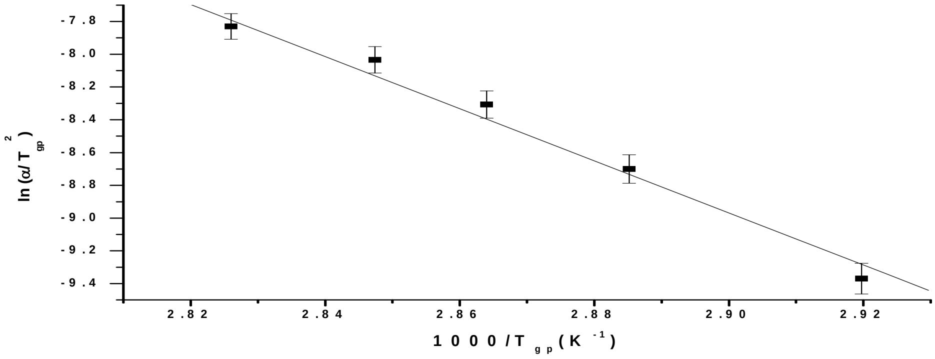

Fig. 5. Variation of ln (α / T_{gp}^2) with 1000/ T_{gp} of $Se_{71}Te_{20}Ag_9$ glassy alloy.

From the slope of the straight line, the value of E_t is found to be 128.457 ± 2.59 kJ / mol.

Crystallization:

The Kinetic analysis of crystallization reaction is related to the knowledge of the reaction rate constant as a function of temperature. The activation energies to be considered in an amorphous-crystalline transformation process are the activation energy for nucleation (E_n) and activation energy for growth (E_g). The activation energy for the whole process is called the activation energy of crystallization and is denoted by (E_c). The thermal analysis methods enable the determination of E_c [25-27].

The activation energy of crystallization (E_c) for $Se_{71}Te_{20}Ag_9$ glassy alloy has been estimated using the following methods.

Kissinger Model:

The activation energy of crystallization (E_c) for $Se_{71}Te_{20}Ag_9$ glassy alloy is derived using the following equation proposed by Kissinger [24].

$$\ln \alpha / T_p^2 = -(E_c / RT_p) + \text{constant} \qquad (3)$$

where T_p is the peak crystallization temperature. Figure 6 shows the plot of ln α / T_p^2 against 1000/T_p for $Se_{71}Te_{20}Ag_9$ glassy alloy. The slope of straight line gives the activation energy of crystallization (E_c). The value of E_c has been given in table 2.

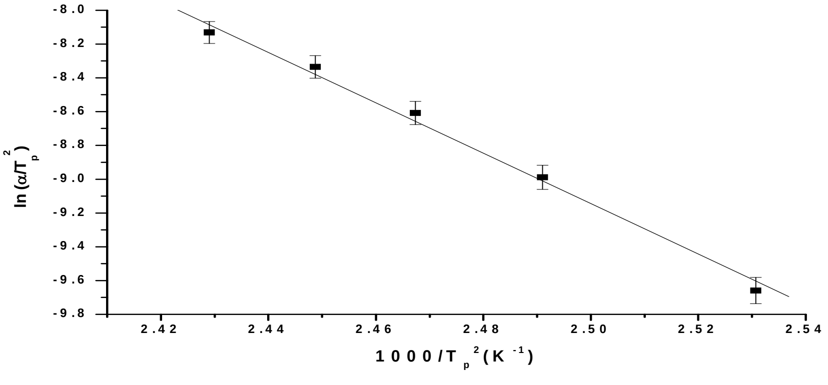

Fig. 6. Variation of ln (α / T_p^2) with 1000/ T_g of $Se_{71}Te_{20}Ag_9$ glassy alloy.

Matusita and Sakka Model:

Crystallization kinetics has also been studied using a method suggested specially for non-isothermal experiments by Matusita et al. [28]. The value of fraction crystallized (x), precipitated in glass heated at constant heating rate (α) is related to the effective activation energy of amorphous-crystalline transformation (E_c), through the following expression:

$$\ln [-\ln (1-x)] = -n \ln \alpha - 1.502mE_c / RT + \text{Constant} \qquad (4)$$

where m is a integer which depends on the dimensionality of the crystal, and n being a numerical factor depending on the nucleation process. When the nuclei formed during the heating at a constant rate are dominant, n is equal to (m+1) and when nuclei formed during any previous heat treatment prior to thermal analysis are dominant, n is equal to m [29]. In order to investigate the heating rate dependence of the kinetic parameters, n and E_c, the data obtained using Matusita model have been used. Fig.7 shows the plot of ln [-ln (1-x)] against 1000/T at five different heating rates 10, 20, 30, 40 and 50 K/min for $Se_{71}Te_{20}Ag_9$ glass.

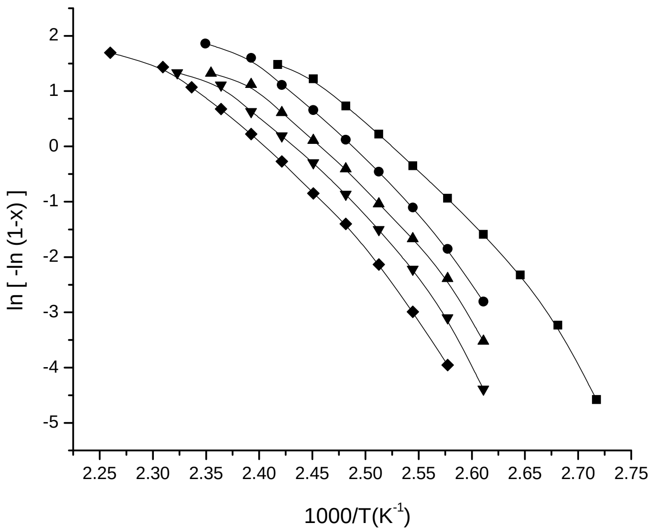

Fig 7. Variation of ln [-ln (1-x)] with 1000/ T at different heating rates for $Se_{71}Te_{20}Ag_9$ glassy alloy.

The straight lines in these curves are linear fit, according to equation 4. The plots are found to be linear over most of the selected temperature range but show a break at higher temperatures, which is attributed to the saturation of nucleation sites in the final stages of crystallization [30] or to the restriction of crystal growth by the small size of the particles [31]. The values of E_c for exothermic peak at different heating rates can be obtained from the slopes of Fig.7 and seemed to be independent of the heating rates. Therefore, an average of E_c were calculated by considering all the heating rates. The value of E_c obtained from Matusita and Sakka model has been given in Table 2.

The Avrami exponent (n) can also be determined using Matusita equation (eq. 4) by plotting ln [-ln (1-x)] against ln(α) at different temperatures. Figure.8 shows, the plot ln [-ln (1-x)] against ln (α) at three different temperatures for $Se_{71}Te_{20}Ag_9$ glassy alloy.

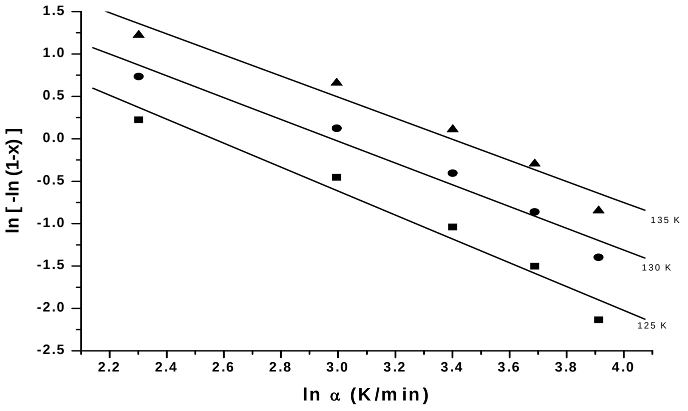

Fig. 8. Variation of ln [-ln (1-x)] with ln α of $Se_{71}Te_{20}Ag_9$ *glassy alloy.*

It is clear from the Fig.8 that n is the temperature independent and hence an average value can be calculated from the slopes of the straight lines fit for these relations. As no heat treatment was performed prior to DSC scans to nucleate the sample, therefore, n is considered to be equal to (m+1). The calculated value for n is found to be 1.32. The value of the corresponding *m* is equal to 1.The result indicates that the crystallization process is carried out by surface crystallization in one dimension.

Gao and Wang model:

Gao and Wang [32] proposed a slightly different method to analyze DSC thermograms in terms of the activation energy E_c, the dimensionality m, the rate constant in atomic diffusion, the microstructure of amorphous alloy K, the frequency factor K_o etc, during the crystallization process. This theory is based on the same fundamental assumption imposed on the Johnson-Mehl-Avrami ((JMA) transformation equation. It assumes that the nucleation is randomly distributed and that the growth rate of the new phase depends on the temperature and not on time. The theory provides the relationship between the maximum crystallization rate and peak crystallization temperature, which is given by:

$$\ln(dx/dt)_p = -E/RT_p + \text{Constant} \qquad (5)$$

where $(dx/dt)_p$ is the rate of volume fraction crystallized at the temperature corresponding to peak of crystallization T_p, which is proportional to the exothermic peak height. Fig. 9 shows the plot of $(dx/dt)_p$ against temperature (T) at different heating rates for $Se_{71}Te_{20}Ag_9$ glass.

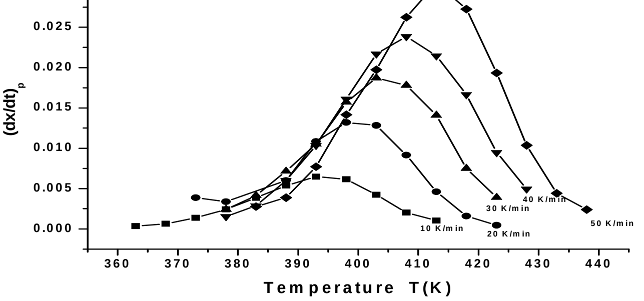

Fig. 9. Variation of $(dx/dt)_p$ *with temperature (T) at different heating rates for* $Se_{71}Te_{20}Ag_9$ *glassy alloy*

It is clear from the Figure 9 that the peak height increases and shifts towards higher temperature values with the increase in the heating rate. This is due to the fact that as the heating rate is increased from 10 to 50 K/min, the rate of crystallization increases and crystallization shifts towards higher temperatures hence, the peak shifts towards higher temperature values. Again we can say that with this increased rate of crystallization, a greater volume fraction is crystallized in a smaller time as compared to the low heating rate, which further signifies the increased peak height with increase in heating rate in these curves.

Gao and Wang plots (ln $(dx/dt)_p$ versus $1000/T_p$) for $Se_{71}Te_{20}Ag_9$ glass is shown in Fig.10 as a representative case. This plot is fitted to straight line and the slope of this straight line gives the activation energy of crystallization (E_c). The value of E_c has been given in Table 2.

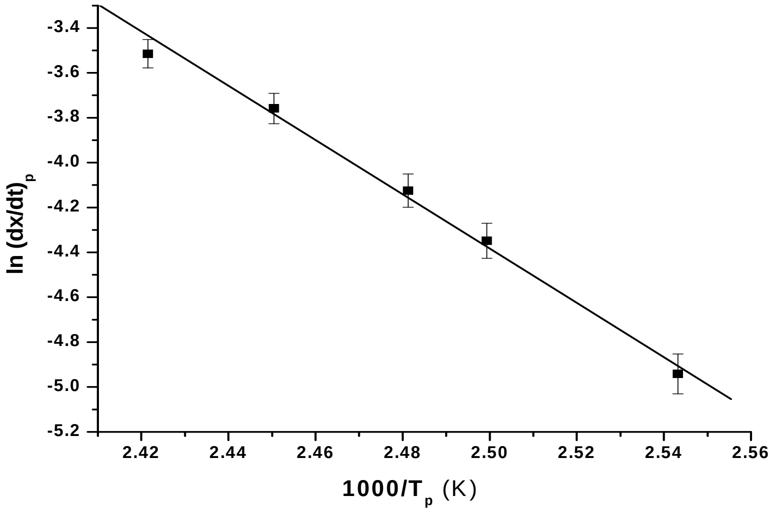

Fig 10. Variation of ln $(dx/dt)_p$ with 1000/T for $Se_{71}Te_{20}Ag_9$ glassy alloy

The Gao and Wang method is also used to evaluate the Avrami exponent using the following relations:

$$(\alpha E_c / RT^2)Kp = 1 \tag{6}$$

$$K_p = K_o \exp(-E_c/RT_p) \tag{7}$$

$$(dx/dt)_p = 0.37\, n\, Kp \tag{8}$$

The values of Avrami exponent (n) obtained using above relation is shown in found to be 1.34.

The value of the corresponding *m* is equal to 1.The result indicates that the crystallization process can be carried out by surface crystallization in one dimension.

The values of Avrami exponent (n) and dimensionality of growth (m) obtained from the Gao - Wang and Matusita models are in good agreement with each other.

Augis and Bennet Model:

The activation energy (E_c) of crystallization as well as frequency factor can also be determined by an approximation method developed by Augis and Bennet [33], which is given as follows:

$$\ln(\alpha/T_c) = -E_c/ RT_c + \ln K_o \tag{9}$$

where T_c is the temperature at which the crystallization just begins and K_o is the frequency factor (in s^{-1}). The relation between ln (α/T_c) and $1000/T_c$ for $Se_{71}Te_{20}Ag_9$ glassy alloy is shown in Figure 11. This plot is fitted to straight line and the slope of the straight line gives the activation energy of crystallization (E_c), which is shown in table 3.

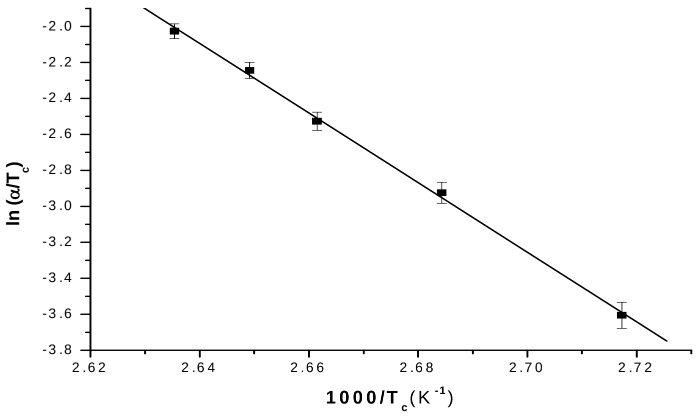

Fig 11. Variation of ln (α/T_c) with 1000/T_c for $Se_{71}Te_{20}Ag_9$ glassy alloy.

The value of K_o, which is defined as the number of attempts made by the nuclei per second to overcome the energy barrier, can be evaluated from the knowledge of ln K_o from the equation (9). This also provides the information for the calculation of nucleation sites present in the material for crystal growth. The calculated value for K_o comes out to be 1.85 x 10^{21}.

Table 3 lists the values of activation of crystallization (E_c) of $Se_{71}Te_{20}Ag_9$ glassy alloy using different theoretical models.

Table 3. Activation energy of crystallization (E_c) of $Se_{71}Te_{20}Ag_9$ glassy alloy using different theoretical models.

Models	Activation energy of crystallization (E_c) (kJ mol^{-1})
Kissinger model	124.06 ± 1.47
Matusita and Sakka model	132.005 ± 2.34
Gao and Wang model	100.6 ± 1.76
Augis and Bennet model	160.79 ± 0.44

From the above, we know that the activation energies of amorphous alloy calculated by means of the different theoretical models differ substantially from each other. This difference in the activation energies as calculated with the different models, 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 the Kissinger's method, the transformation under non-isothermal conditions is represented by the first order reaction. Moreover the concept of nucleation and growth has not been included in the Kissinger equation. Matusita et. al have develop a method on the basis of the fact that crystallization does not advance by an nth-order reaction but by a nucleation and growth process. They emphasized that crystallization mechanism such as bulk crystallization (bulk nucleation followed by two-or three-dimensional growth) or surface crystallization (bulk nucleation followed by linear growth) should be taken into account for obtaining E_c. In addition to the activation energy, Matusita's method provides information about the Avrami exponent and dimensionality of growth. The Augis and Bennet method is helpful in obtaining frequency factor along with activation energy of crystallization. and therefore preferred over the other models used for description of phase transformations.

4. Conclusions

The study of the activation energy, entropy difference and excess enthalpy of $Se_{71}Te_{20}Ag_9$ glassy alloy in glass transition region leads to the following conclusion:

1. The DSC thermograms exhibit a single glass transition and crystallization temperatures, which confirms the homogeneity of the sample.
2. The glass transition activation energy (E_t) has been calculated using Kissinger model and the activation energies of crystallization ($E_{c)}$ has been calculated using Kissinger, Matusita and Sakka, Augis-Bennet and Gao-Wang models Difference in values of activation energy ($E_{c)}$ may be attributed to the different approximations used in the models.
3. The average value of m comes out to be 1 suggesting surface nucleation with one-dimensional growth.

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