

Calorimetric Studies of the Crystallization Growth Process in Glassy $\text{Se}_{70}\text{Te}_{30-x}\text{Ag}_x$ Alloys

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Abstract

Differential Scanning Calorimetry (DSC) is performed at different heating rates under non-isothermal conditions to study the crystallization kinetics of $\text{Se}_{70}\text{Te}_{26}\text{Ag}_{04}$ and $\text{Se}_{70}\text{Te}_{24}\text{Ag}_{06}$ chalcogenide glasses in terms of the activation energy of nucleation and growth process. To understand the nucleation and growth process, the values of the growth morphology parameter n and the numerical factor m of crystallization mechanism have been evaluated using different non-isothermal methods. The values of n and m have been found to be nearly equal, indicating that the present glasses have sufficient nuclei before DSC experiment and the activation energy for nucleation process E_N is zero. Hence, the effective activation energy for overall crystallization E_c is equal to the activation energy for growth process E_G .

Key Words: Chalcogenide glasses, Differential Scanning Calorimetry, Crystallization Kinetics.

1. Introduction

Recently, Ag-doped chalcogenide glasses have become attractive materials for fundamental research into their structure, properties and preparation [1–5]. They have many current and potential applications in optics and optoelectronics, such as photo doping, optical imaging, photo lithography and phase change (PC) optical recording [6–16].

In PC optical recording, the storage of information is based on writing and erasing of amorphous marks in a crystallization layer of a phase change material with the help of a laser beam. Since the optical properties of the amorphous phases are different from those of the crystallized phase, the written mark can be read out as a contrast in the reflectance. Besides sufficient optical contrast between the crystalline and amorphous state, the crystallization behavior at various temperatures is one of the most important features in developing phase-change materials.

The optical properties and photostructural changes of Ag-doped chalcogenide glasses have been studied by various workers [6–10]. Thin films of chalcogenide glasses containing Ag have found application in erasable PC optical recording [11–16]. Different Ag doped chalcogenide alloys have been developed as recording layer and their good practical performance has been reported [11–16]. In case of Ag-doped glasses, much attention has been devoted to optical properties [6–10], but only a few studies have been performed on crystallization kinetics [17–19].

The crystallization kinetics in chalcogenide glasses can be investigated using either isothermal or non-isothermal methods [20–22]. In the isothermal method, the sample is brought near to the crystallization

temperature very quickly and then any physical quantity which changes drastically is measured as a function of time. In the non-isothermal method, the sample is heated at a fixed rate and the physical parameter is recorded as a function of temperature. A disadvantage of the isothermal method is the impossibility of reaching a test temperature instantaneously and during the time which the system needs to stabilize, no measurements are possible. On the other hand, measurements can be achieved in a relatively rapid and precise manner by the non-isothermal technique.

Various theoretical methods have been suggested to determine the activation energy of crystallization from the non-isothermal DSC data. It is, therefore, interesting to use different methods for studying the crystallization kinetics using the same experimental data of a particular chalcogenide glassy alloy.

With the above points of view, different methods of analysis have been used to study the crystallization kinetics of two Ag-doped chalcogenide glasses $\text{Se}_{.70}\text{Te}_{.24}\text{Ag}_{.06}$ and $\text{Se}_{.70}\text{Te}_{.26}\text{Ag}_{.04}$ under non-isothermal conditions.

2. Theoretical Basis

The theoretical basis for interpreting DSC data is provided by the classical Johnson-Mehl-Avrami (JMA) model [23–25] in which the crystallized fraction α can be described as a function of time t according to the formula

$$\alpha(t) = 1 - \exp[-(Kt)^n]. \quad (1)$$

Here, K is defined as the effective overall reaction rate, which is usually assigned by an Arrhenian temperature dependence [26]:

$$K = K_o \exp(-E_c/RT), \quad (2)$$

where, R is the universal gas constant, E_c is the effective activation energy describing the overall crystallization process and K_o is a constant.

Over a sufficient limited range of temperature (such as the range of crystallization peaks in DSC experiment), the nucleation frequency per unit volume (I_v) and the crystal growth rate (u) can be expressed according to [26]

$$I_v = (I_v)_o \exp(-E_N/RT) \quad (3)$$

$$u = u_o \exp(-E_G/RT), \quad (4)$$

where E_N and E_G are the effective activation energies for nucleation and growth, respectively.

The overall effective activation energy for crystallization is expressed according to [26]:

$$E_c \approx (E_N + mE_G)/n, \quad (5)$$

where m is an integer or non-integer, depending on the mechanism of growth, and n is a numerical factor depending on the nucleation processes. When $I_v = 0$, then $n = m + 1$; and when $I_v \neq 0$ [26], then $n = m$ [27].

Various theoretical methods have been suggested to understand the nucleation and growth process using the non-isothermal DSC data. It is, therefore, interesting to use different methods for studying the nucleation and growth process. The details of these methods are described as follows.

(i) The volume fraction of crystallites α precipitated in a glass heated at constant rate β is related to the activation energy for crystallization E_c through the relation [28]

$$\ln[\ln(1 - \alpha)^{-1}] = -n \ln \beta - (1.052mE_c)/RT + \text{constant} \quad (6)$$

For a quenched glass containing no nuclei $n = m + 1$, and for a glass which has sufficiently large nuclei before the DSC experiment, $n = m$ [28].

(ii) The value of E_c is also calculated using the variation of onset crystallization temperature T_o with the heating rate β according to the following relations [29, 30]:

$$\ln \beta/T_o^2 = -(m/n)(E_c/RT_o) + \text{constant}; \quad (7)$$

$$\ln \beta = -(m/n)(E_c/RT_o) + \text{constant}. \quad (8)$$

(iii) For the evaluation of E_c , another useful relation is the modified Kissinger's relation, which is given by

$$\ln(\beta^n/T_c^2) = -mE_c/RT_c + \ln K. \quad (9)$$

(iv) Bansal et al. [31] have developed a method for non-isothermal analysis of devitrification. The final expression is

$$\ln \beta/T_c^2 = -E_c/RT_c + \ln K_o - \ln(E_c/R). \quad (10)$$

(v) In non-isothermal crystallization, the relation between the sample temperature T and the heating rate β can be written as

$$T = T_i + \beta t, \quad (11)$$

where T_i is the initial temperature.

As in the most crystallization processes, $E_c / RT_c \gg 1$. Takhor [32–34] obtained the following relation:

$$\ln \beta/(T_c - T_i) = -E_c/RT_c + \ln K_o. \quad (12)$$

(vi) For $T_i \ll T_c$, Augis and Bennett [35] developed an approximation method of the form

$$\ln(\beta/T_c) = -E_c/RT_c + \ln K_o. \quad (13)$$

3. Experimental

Glassy alloys of $\text{Se}_{.70}\text{Te}_{.30-x}\text{Ag}_x$ ($x = 0.04$ and 0.06) were prepared by the quenching technique. High purity materials (5N pure) were weighed according to their atomic percentages and were sealed in quartz ampoules under a vacuum of 10^{-5} Torr. Each ampoule was heated at a rate $3\text{--}4$ °C /min. and kept inside the furnace at a maximum temperature. To make the melt homogeneous, the ampoules were shaken frequently over the 10 hrs where they were kept in the furnace at the maximum temperature. The ampoules were quenched in ice water; and the glassy nature of the alloys was examined by x-ray diffraction technique.

The glasses were then ground to a fine powder for examination in a differential scanning calorimeter (DSC). 10 to 20 mg of samples were used in the DSC studies, and heated at four different rates: 5, 10, 15 and 20 °C/min.

The fraction α crystallized at any temperature T is given as $\alpha = A_T / A$, where A is the total area of the exothermic peak between the temperature T_b , where the peak begins, i.e. the crystallization starts, and the temperature T_e , where the peak ends, i.e. the crystallization completes. A_T is the partial area of the exothermic peak between the temperatures T_b and T .

4. Results

Figure 1 shows typical DSC thermograms for $\text{Se}_{.70}\text{Te}_{.30-x}\text{Ag}_x$ alloys ($x = 0.04$ and 0.06) heated at 10 K/min. Similar thermograms were obtained for other heating rates also (not shown here). The values associated with the peak crystallization temperature T_c and onset crystallization temperature T_o at different heating rates for glassy $\text{Se}_{.70}\text{Te}_{.26}\text{Ag}_{.04}$ and $\text{Se}_{.70}\text{Te}_{.24}\text{Ag}_{.06}$ alloys are given in Table 1.

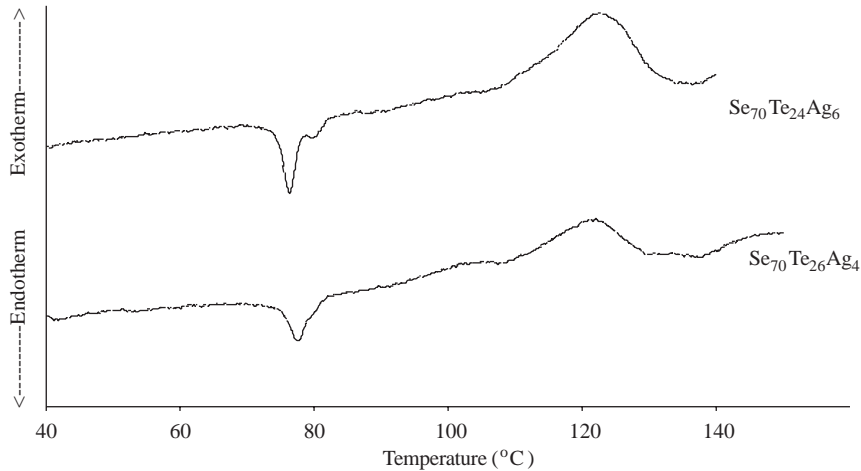


Figure 1. DSC thermograms for the $\text{Se}_{.70}\text{Te}_{.26}\text{Ag}_{.04}$ and the $\text{Se}_{.70}\text{Te}_{.24}\text{Ag}_{.06}$ alloys at a heating rate of 10 K/min.

Table 1. Values of peak crystallization temperature T_c and onset crystallization temperature T_o of glassy $\text{Se}_{.70}\text{Te}_{.26}\text{Ag}_{.04}$ and $\text{Se}_{.70}\text{Te}_{.24}\text{Ag}_{.06}$ alloys.

Heating Rate β (K/min)	Peak crystallization temperature T_c (K)		Onset crystallization temperature T_o (K)	
	$\text{Se}_{.70}\text{Te}_{.26}\text{Ag}_{.04}$	$\text{Se}_{.70}\text{Te}_{.24}\text{Ag}_{.06}$	$\text{Se}_{.70}\text{Te}_{.26}\text{Ag}_{.04}$	$\text{Se}_{.70}\text{Te}_{.24}\text{Ag}_{.06}$
5	388.8	389.0	376.0	375.7
10	394.0	395.6	380.9	380.2
15	397.5	399.1	382.4	382.6
20	401.1	401.4	386.8	386.6

The crystallization mechanism of chalcogenide glasses is controlled by the nucleation and growth process, which is characterized by the overall effective activation energy of crystallization E_c , the Avrami index, or growth morphology parameter n and the numerical factor of the crystallization mechanism m . From the values of E_c , n and m , the kinetics of nucleation and growth process can be understood.

4.1. Calculation of n , m and E_c by the Matusita Theory

At constant temperature, equation (6) can be written as

$$\ln[\ln(1 - \alpha)^{-1}] = -n \ln \beta + \text{constant} \quad (14)$$

Figures 2 and 3 show the variation of $\ln [\ln (1-\alpha)^{-1}]$ with $\ln \beta$ for the present samples at three constant temperatures (116 °C, 118 °C, 120 °C). Using equation (14), the values of n have been determined from the slopes of these curves at each temperature and are given in Table 2 for both alloys. The average value of n is nearly equal to 2 for both alloys, indicating that only one crystallization mechanism (according to two-dimensional growth) is responsible for the amorphous to crystalline (a-c) transformation of both alloys.

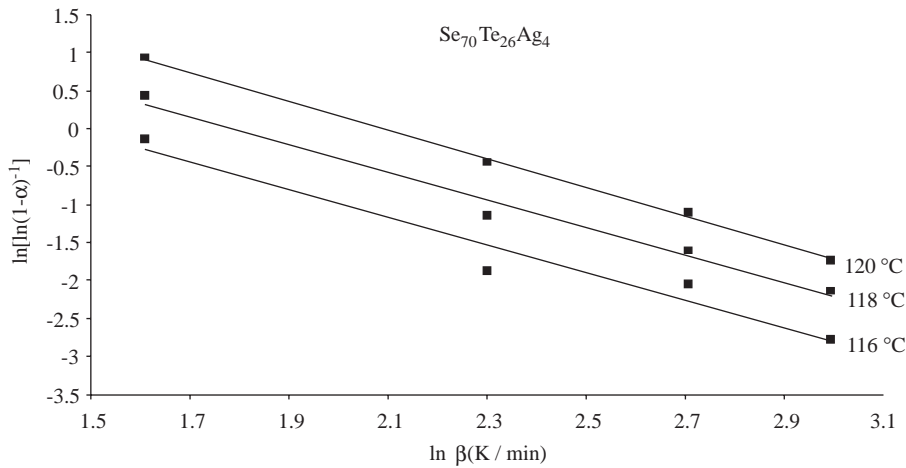


Figure 2. Plots of $\ln [\ln(1-\alpha)^{-1}]$ vs $\ln \beta$ for the $\text{Se}_{70}\text{Te}_{26}\text{Ag}_{04}$ alloy at different temperatures.

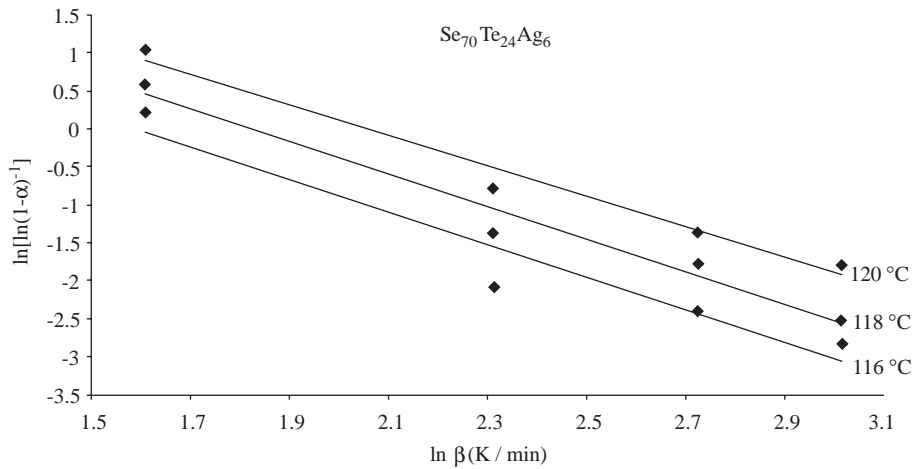


Figure 3. Plots of $\ln [\ln(1-\alpha)^{-1}]$ vs $\ln \beta$ for the $\text{Se}_{70}\text{Te}_{24}\text{Ag}_{06}$ alloy at different temperatures.

Table 2. Temperature dependence of the growth morphology factor n .

Se ₇₀ Te ₂₆ Ag ₀₄		Se ₇₀ Te ₂₄ Ag ₀₆	
Temperature (K)	n	Temperature (K)	n
116.0	1.90	116.0	2.00
118.0	1.82	118.0	2.14
120.0	1.81	120.0	2.14

For a given heating rate, the equation (6) takes the form

$$\ln[\ln(1 - \alpha)^{-1}] = -(1.052mE_c)/RT + constant \tag{15}$$

Using (15), the values of mE_c have been evaluated at two heating rates (10 K/min and 15 K/min) from the plots of $\ln [\ln (1-\alpha)^{-1}]$ against $10^3/T$ (see Figures 4 and 5); the results are given in Table 3.

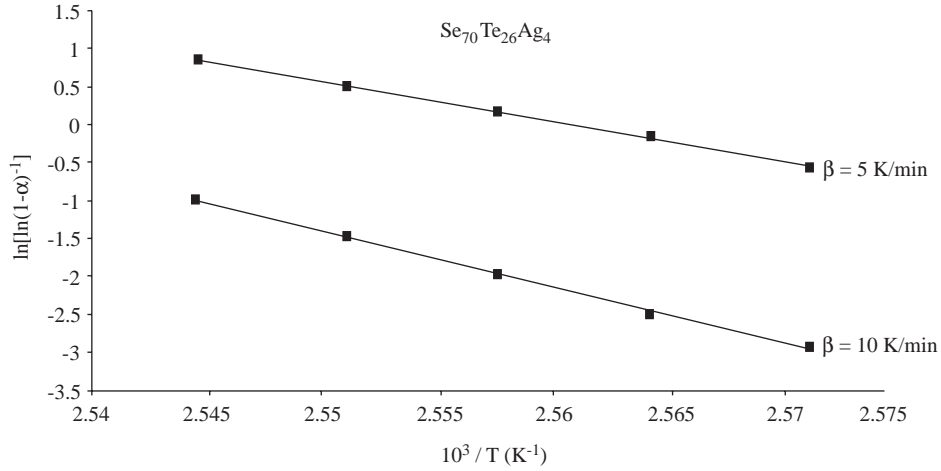


Figure 4. Plots of $\ln [\ln (1-\alpha)^{-1}]$ vs $10^3/T$ for the Se₇₀Te₂₆Ag₀₄ alloy at two different heating rates.

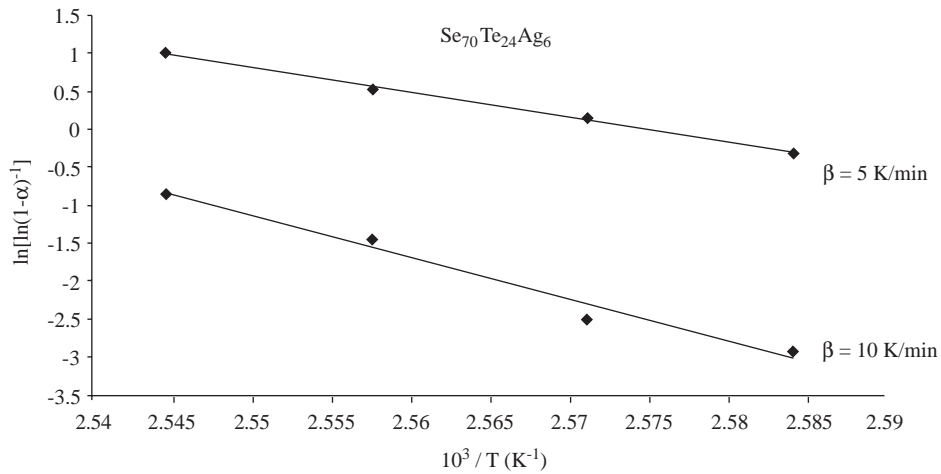


Figure 5. Plots of $\ln [\ln (1-\alpha)^{-1}]$ vs $10^3/T$ for the Se₇₀Te₂₄Ag₀₆ alloy at two different heating rates.

Table 3. Data on n , m and E_c values obtained from different non-isothermal methods.

Se ₇₀ Te ₂₆ Ag ₀₄				Se ₇₀ Te ₂₄ Ag ₀₆			
m E_c (eV)		m E_c / n (eV)		mE_c (eV)		mE_c / n (eV)	
Eqn. (9)	Eqn. (15)	Eqn. (7)	Eqn. (8)	Eqn. (9)	Eqn. (15)	Eqn. (7)	Eqn. (8)
3.05	3.88	1.59	1.66	2.93	3.50	1.57	1.64

4.2. Calculation of $m E_c / n$ using the method of Afify et al.

As equations (7) and (8) can be used to calculate mE_c/n , $\ln \beta/T_o^2$ and $\ln \beta$ are plotted against $10^3/T_o$ in Figures 6 and 7 for both alloys. From this data mE_c/n is computed and is presented in Table 3.

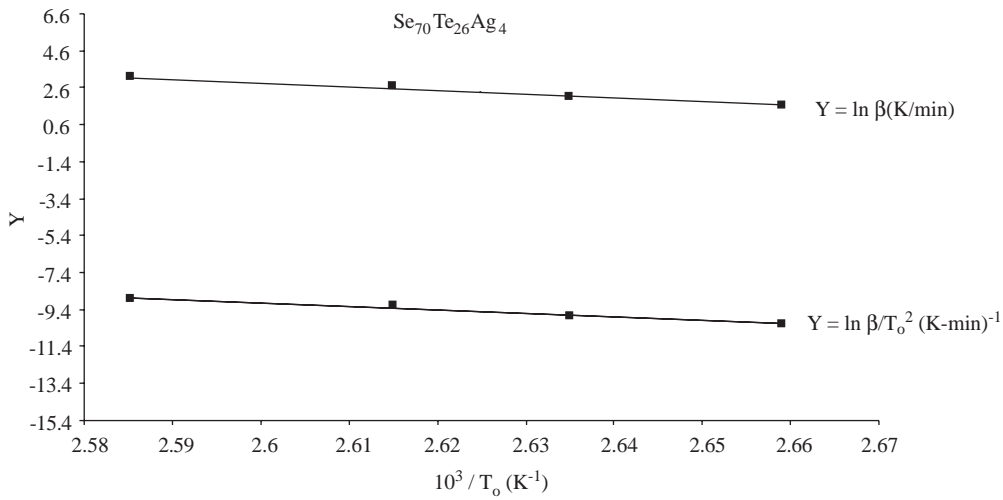


Figure 6. Plots of $\ln \beta/T_o^2$ and $\ln \beta$ against $10^3/T_o$ for the Se₇₀Te₂₆Ag₀₄ alloy.

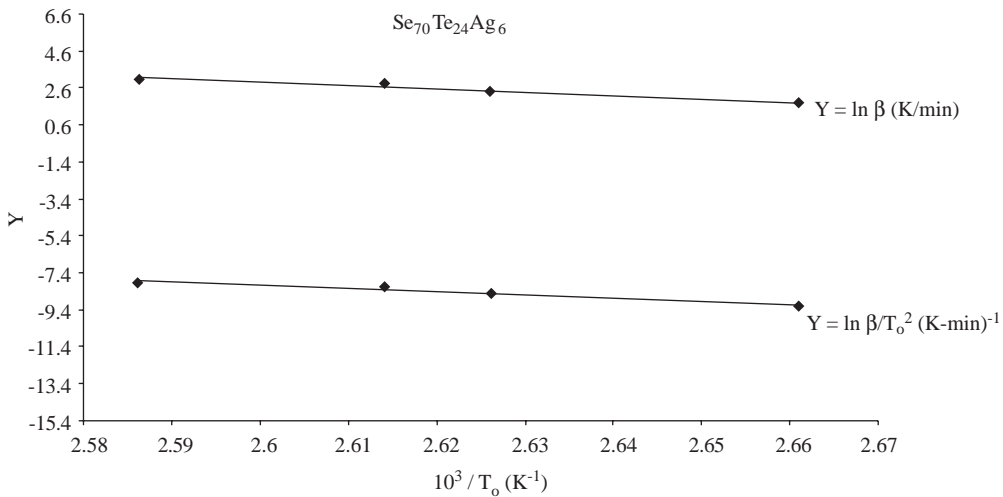


Figure 7. Plots of $\ln \beta/T_o^2$ and $\ln \beta$ against $10^3/T_o$ for the Se₇₀Te₂₄Ag₀₆ alloy.

4.3. Calculation of $m E_c$ using the Modified Kissinger Relation

The value of mE_c has been evaluated using equation (9) by plotting $\ln (\beta^n / T_c^2)$ against $10^3/T_c$. The plots are shown in Figures 8 and 9 for both alloys and the results are given in Table 3.

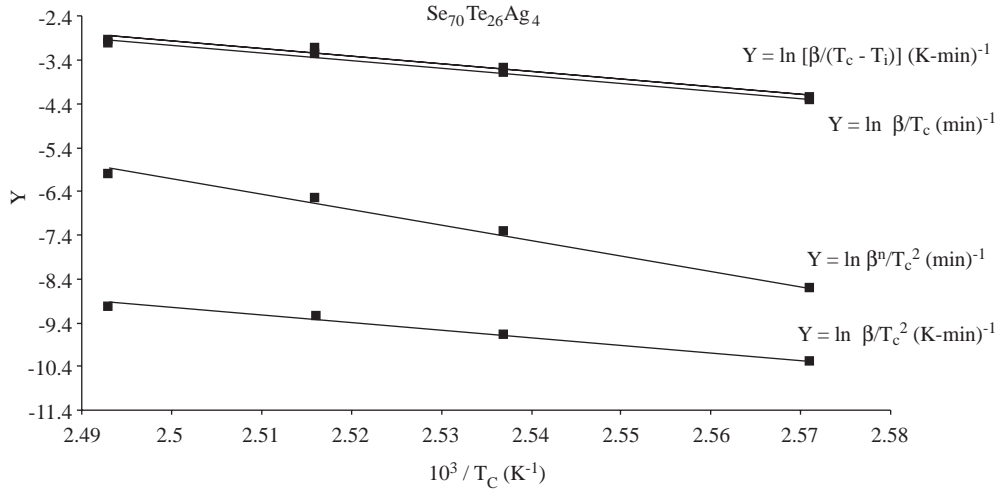


Figure 8. Plots of $\ln (\beta^n / T_c^2)$, $\ln (\beta / T_c^2)$, $\ln \beta / (T_c - T_i)$ and $\ln \beta / T_c$ against $10^3 / T_c$ for the $\text{Se}_{70}\text{Te}_{26}\text{Ag}_{04}$ alloy.

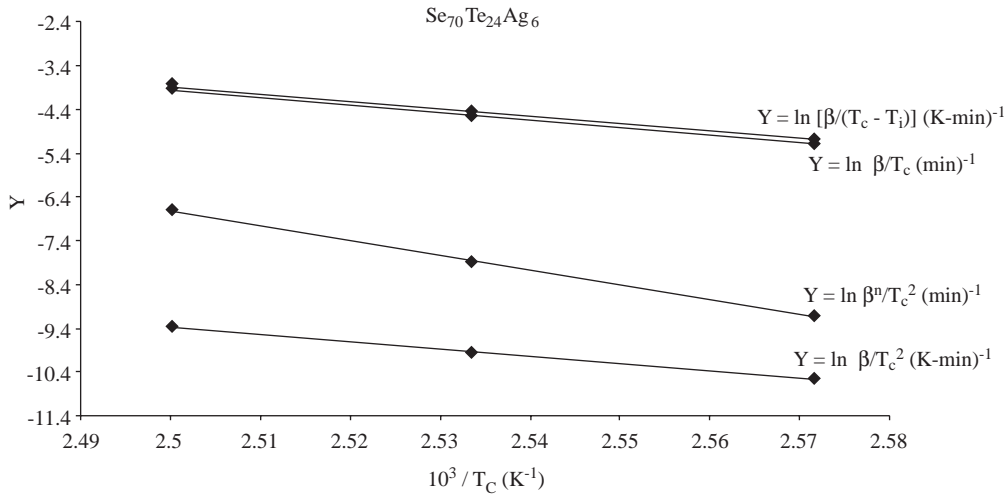


Figure 9. Plots of $\ln (\beta^n / T_c^2)$, $\ln (\beta / T_c^2)$, $\ln \beta / (T_c - T_i)$ and $\ln \beta / T_c$ against $10^3 / T_c$ for the $\text{Se}_{70}\text{Te}_{24}\text{Ag}_{06}$ alloy.

4.4. Calculation of E_c using different methods

Using the plots of $\ln (\beta / T_c^2)$, $\ln \beta / (T_c - T_i)$ and $\ln \beta / T_c$ against $10^3 / T_c$, shown in Figures. 8 and 9, and using equations (10), (12) and (13), the values of E_c have been calculated for both samples and are given in Table 4. It is evident from this table that the E_c values obtained from equations (10), (12) and (13) are in good agreement. This means, that, one can use any of the three equations to calculate the activation energy of crystallization.

5. Discussion

According to Table 3, $n \approx m$; this indicates that there is no contribution in overall effective activation energy E_c due to the nucleation process. It has been pointed out [36] that, in non-isothermal measurements, generally due to a rapid temperature rise and big differences in the latent heats of nucleation and growth,

the crystallization exotherm characterizes the growth of the crystalline phase from the amorphous matrix. Nucleation is more or less calorimetrically unobservable at temperatures below the crystallization exotherm, or it occurs very rapidly and immediately after overheating of the material in the initial stages of the crystallization exotherm. Therefore, the calorimetric analysis gives the value of the activation energy for crystal growth E_G . Based on this, the value of E_c (given in Table 4) can be taken to represent the activation energy for growth, E_G , in these glasses.

Table 4. Values of the activation energy of crystallization E_c calculated according to different non-isothermal methods.

Non-isothermal Method	Activation energy of crystallization E_c (eV)	
	Se ₇₀ Te ₂₆ Ag ₀₄	Se ₇₀ Te ₂₄ Ag ₀₆
Bansal's relation	1.50	1.43
Takhor's method	1.52	1.46
Augis and Bennett's approx.	1.52	1.46
Average value	1.51	1.45

6. Conclusions

The DSC experiment has been performed to understand the nucleation and growth process in Se₇₀Te₂₆Ag₀₄ and Se₇₀Te₂₄Ag₀₆ chalcogenide glasses. The average value of order parameter n is found to be nearly equal to 2 indicating that two dimensional growth occurs during the a-c transformation in both alloys.

The values of n and m have been found to be nearly the same for both alloys. This indicates that the nucleation rate is zero during the DSC experiment. Hence, the overall effective activation energy for crystallization E_c is equal to the activation energy for the growth process in the present chalcogenide glasses. The average values of the activation energy of crystallization of chalcogenide glasses Se₇₀Te₂₆Ag₀₄ and Se₇₀Te₂₄Ag₀₆ have been found equal to 1.51 eV and 1.45 eV, respectively.

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