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Crystallization study of $Bi_5Ge_{20}Se_{75}$ glass

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Results of thermal analysis performed at different heating rates on the composition $Bi_5Ge_{20}Se_{75}$ are reported and discussed. The values of crystallization temperature (T_c) and the peak temperature of the crystallization (T_p) were found to be dependent on the heating rates. The activation energy of crystallization E_c was evaluated by five different methods. The average value of E_c is equal to 119.64 ± 6.97 kJ mol^{-1}.

The crystallization data are examined in terms of recent analysis developed for non-isothermal conditions. The results indicate a two-dimensional crystal growth for the investigated composition.

1. Introduction

Chalcogenide glasses have been attracting much attention in the fields of electronics as well as infrared optics since they exhibit several peculiar phenomena which are applicable for devices such as electrical switches and or memory image storage and photoresistors [1–3]. It is generally admitted that most of the chalcogenide glasses show *p*-type conduction and their electrical conductivity is very slightly affected by doping. The insensitivity to impurities is due to the presence of charged defects which pin the fermi level near the midband gap [4, 5]. Tohge and co-workers [6, 7] were the first to point out the role of Bi in the appearance of *n*-type conduction in chalcogenide glasses for the $Ge_{20}Bi_xSe_{80-x}$ system. The structural studies of these materials are very important for better understanding for their transport mechanism [8, 9]. Different techniques were used to study crystallization of chalcogenide glasses (e.g. electrical resistivity, electron microscopy, X-ray diffraction and scanning calorimetry [10–12].

Studies of the crystallization of a glass upon heating can be performed in several ways. In calometric measurements two basic methods can be used, isothermal and non-isothermal. 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 at a constant temperature is recorded as a function of time. In the non-isothermal method the sample is heated at a fixed rate (α) and the heat evolved is recorded as a function of temperature or time. The results of crystallization process can be interpreted in terms of several theoretical models [13–15].

The present work is concerned with the study of crystallization kinetics for the composition $Bi_5Ge_{20}Se_{75}$ chalcogenide glass. The evaluation of the activation energy for crystallization was conducted using five different techniques under non-isothermal conditions. Applying a recent analysis developed for non isothermal crystallization studies useful information about some aspects of the crystallization process have been obtained.

2. Experimental procedure

As discussed by Ibrahim *et al.* [16] homogeneous glasses are usually prepared by melting a mixture of appropriate amounts of pure Bi, Ge and Se at 1100 °C for about 15 h, followed by quenching in an ice–water mixture.

The electrical conductivity, thermoelectric power and the dielectric parameters of the investigated glasses were measured in the temperature range 298–500 K using procedures described elsewhere [16–19].

Thermal differential analyses (DTA) were carried out using a Dupont 1090 instrument. Typically 20 mg of the samples were sealed in aluminium pans and scanned over a temperature range from room temperature to about 650 °C at uniform heating rates (α) ranging from 7.5 to 40 °C min^{-1} in static air.

X-ray investigation of $Bi_5Ge_{20}Se_{75}$ powder (particle size 54 μm) was performed using a Philips diffractometer type 1710 with Ni-filtered CuK_α source ($\lambda = 0.154$ nm).

3. Theoretical basis

The theoretical basis for interpreting the DTA or DSC data is provided by the formal theory of transforming kinetics given by Johnsen–Mehl–Avrami formula [15]

$$\chi = 1 - \exp[1 - (kt)n] \tag{1}$$

where χ is the volume fraction crystallized, n is an integer or half an integer depends on both the growth mechanism and the crystal dimensions; K is defined as the effective overall reaction rate which is usually assigned an Arrhenian temperature dependence as follows

$$K = K_0 \exp\frac{-E}{RT} \tag{2}$$

where E is the effective activation energy describing the overall crystallization process. At the same time E can be approximated as follows

$$E \cong \frac{E_N + E_G}{n} \tag{3}$$

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where E_N and E_G are the effective activation energies for nucleation and growth respectively and $n = m$ for the nucleation frequency I_v equal to zero [12] and $n \not\equiv m$ for $I_v \not\equiv 0$ [20]. If the nucleation frequency is negligible over the temperature range of concern in the thermoanalytical study [15], then

$$E \cong E_G \tag{4}$$

3.1. Piloyan–Borchardt method

In non-isothermal crystallization, it is assumed that there is a constant heating rate (α) in the DTA and DSC experiments. The relation between the sample temperature and the heating rate (α) can be written in the form

$$T = T_0 + \alpha t \tag{5}$$

where T_0 is the initial temperature. Differentiating Equation 1 results in the following expression

$$\dot{\chi} = (1 - \chi)nK^n t^{n-1}\left(1 + \frac{t}{K}\dot{K}\right) \tag{6}$$

where $\chi = \mathrm{d}\chi/\mathrm{d}t$ and $\dot{K} = \mathrm{d}K/\mathrm{d}t$. The derivative of k with respect to time is obtained from Equations 2 and 5

$$\dot{k} = (\mathrm{d}k/\mathrm{d}T)(\mathrm{d}T/\mathrm{d}t) = \frac{\alpha E}{RT^2}K \tag{7}$$

Substituting 7 into Equation 6 yields

$$\dot{\chi} = (1 - \chi)nk^n t^{n-1}(1 + at) \tag{8}$$

where $a = \dfrac{\alpha E}{RT^2}$

In the Piloyan–Borchardt method [21, 22] the term (αt) was negligible in comparison to unity assuming that $E/RT \ll 1$. This assumption can cause a non-acceptable error in most studies because for most crystallization reactions E/RT is greater than unity, ($E/RT \geqq 25$ typically). A better approach seems reasonable, if T_0 in Equation 5 is much smaller than T. The term at $\simeq E/RT$, and Equation 8 becomes

$$\dot{\chi} = (1 - \chi)nk^n t^{n-1}\frac{E}{RT} \tag{9}$$

Combining Equation 9 with the concept stated by Borchardt [22] that, at least for $\chi < 0.5$, the reaction rate $\dot{\chi}$ at a particular temperature T is proportional to the temperature difference measured in DTA at that temperature between the crystallizing sample and the inert reference. Thus for DTA

$$\dot{\chi} = c\Delta T \tag{10}$$

The following relationship can be obtained by the following operations: (i) expressing t in terms of χ from Equation 1; (ii) substituting for t in Equation 9; (iii) combining Equations 2, 9 and 10; (iv) taking the logarithm of the resulting expression, the result is

$$\ln \Delta T = \ln f(\chi) + \ln K_0 n - \frac{E}{RT} \tag{11}$$

where the function $f(\chi)$ is defined as follows

$$f(\chi) = (1 - \chi)[-\ln(1 - \chi)]^{(n-1)/n} \tag{12}$$

for small values of χ and for values close to 1; ln $[f(\chi)]$ changes rapidly with χ. However for $0.25 \leqq \chi \leqq 0.75$ the function may be considered as constant [21]. Plotting ln ΔT versus $1/T$ yields a straight line with a slope equal to E/R, where E is the activation energy of crystal growth.

3.2. Dependence of $\dot{\chi}$ on χ and T

Before discussing the other analytical methods, it is useful to re-examine the parametric dependence of the reaction rate ($\mathrm{d}\chi/\mathrm{d}t$) . Any operations on Equation 8 such as differentiation or integration of $\mathrm{d}\chi/\mathrm{d}t$ is greatly simplified if $\mathrm{d}\chi/\mathrm{d}t$ can be expressed as [15]

$$\dot{\chi} = g(\chi)h(T) \tag{13}$$

i.e. if the dependence of $\dot{\chi}$ on temperature can be separated from its dependence on χ. There are a number of ways in which $g(x)$ and $h(T)$ can be formulated since both χ and T are functions of time [15]. There are different methods of defining $g(\chi)$ and $h(T)$. The time t in Equation 8 can be expressed either in terms of χ as in Equation 1 or in terms of T by using Equation 5 to give

$$t = \frac{T - T_0}{\alpha} \tag{14}$$

It should be noted that the use of Equation 13 and the separation of variables' approximation introduces an additional assumption into the analysis.

3.3. Ozawa–Chen method

The method proposed by Ozawa [23] and Chen [24] can be applied to Equation 8. Inserting in Equation 8 the expression for t from Equation 14 one obtains

$$\dot{\chi} = (1 - \chi)nk^n\left(\frac{T - T_0}{\alpha}\right)^n \frac{\alpha E}{RT^2} \tag{15}$$

Rearranging and taking the integral leads to

$$\begin{aligned} G(\dot{\chi}) &= \int_0^{\dot{\chi}} \frac{\mathrm{d}\dot{\chi}}{1 - \chi} \\ &= nK_0^n\left(\frac{E}{R\alpha^n}\right)\int_0^T \exp\frac{-nE}{RT}(T - T_0)^n(\alpha/T^2)\mathrm{d}t \end{aligned} \tag{16}$$

setting $\alpha \mathrm{d}t = \mathrm{d}T$ and assuming $T_0 \leqq T$, one obtains

$$G(\chi) = nK_0^n\left(\frac{E}{R\alpha^n}\right)\int_0^T \exp\left(\frac{-nE}{RT}\right)T^{n-2}\mathrm{d}T \tag{17}$$

for $E/RT \gg 1$ the solution of Equation 17 can be written in the form [15]

$$\ln g(\dot{\chi}) = n \ln \frac{K_0 T^2}{\alpha} - \frac{nE}{RT} \tag{18}$$

E can be determined from the relation between ln α/T^2 and $1/T$ at constant χ.

3.4. Method of Takhor

If $T_0 \ll T$ and $E/RT \ll 0$ Equation 8 becomes

$$\dot{\chi} = (1 - \chi) n K^n t^{n-1} \tag{19}$$

The method of Takhor [25] is based on twice differentiating Equation 19. It will be recalled that Equation 19 does not take proper account of the change of K with time (and temperature); and Takhor's method makes the same inappropriate assumption of ignoring the time dependence of K in the second differentiation. Assuming that $K \neq K(t)$ and the maximum rate of crystallization occurs at the peak of the exotherm at time t_p and temperature T_p [15] the differentiation of Equation 19 with respect to time yields

$$\ddot{\chi} = nK^n t^{n-2}[(n-1) - nK^n t^n] = 0 \tag{20}$$

where $\ddot{\chi} = d^2\chi/dt^2$. Then

$$(n-1) = n(K_0 t_p)^n \exp(-nE/RT_p) \tag{21}$$

Equation 14 is then invoked to convert the time t_p to temperature T_p, yielding

$$\ln\left(\frac{\alpha}{T_p - T_0}\right) = \frac{1}{n}\ln\left[\frac{n}{n-1}\right] + \ln K_0 - \frac{E}{RT_p} \tag{22}$$

by plotting $\ln \dfrac{\alpha}{T_p - T_0}$ versus $1/T_p$ the activation energy of the crystallization process can be obtained.

3.5. The Kissinger method

The method which is commonly used in analysing crystallization data in DSC and DTA experiments was developed by Kissinger [26]. By using Equation 19 and substituting for t from Equation 1 the rate of reaction is expressed as

$$\dot{\chi} = nK(1 - \chi)[-\ln(1-\chi)]^{(n-1)/n} \tag{23}$$

The temperature at the peak of the exotherm is identified as in Takhor's method, as the temperature of maximum crystallization rate, i.e. $\ddot{\chi} = 0$. In taking the derivative of Equation 23 with respect to time it is convenient to assume that near the peak $[-\ln(1-\chi)]^{(n-1)/n}$ is a constant, denoted A. Taking the derivative of Equation 23 with respect to time, one obtains

$$\ddot{\chi} = AK_0\left[\frac{E}{RT_p^2} - \frac{AK_0}{\alpha}\exp\left(\frac{-E}{RT}\right)\right] \alpha(1 - \chi_p)\exp(-E/RT_p) = 0 \tag{24}$$

i.e.

$$\alpha/T_p^2 = \frac{ARK_0}{E}\exp(-E/RT_p) \tag{25}$$

The value of E can be obtained from the relation between $\ln(\alpha/T^2\text{p})$ and $1/T_p$.

3.6. Method of Augis and Bennett

Augis and Bennett [27] developed a method based on Equation 8, which stands in contrast to all other investigations mentioned above which used the inaccurate Equation 19. Augis and Bennett substituted u (the crystal growth rate) for Kt and wrote Equation 8 as

$$\dot{\chi} = n\dot{u}u^{n-1}(1 - \chi) \tag{26}$$

where $\dot{u} = du/dt$. Differentiating Equation 26 leads to

$$\ddot{\chi} = [\ddot{u}u - (\dot{u})^2(nu^n - n + 1)]\, nu^{n-2}(1 - \chi) = 0 \tag{27}$$

where $\ddot{u} = d^2u/dt^2$. If $u = kt$ it can be shown that

$$\dot{u} = u\left(\frac{1}{t} + a\right) \tag{28}$$

where a is defined as $\alpha E/RT^2$

$$\ddot{u} = \dot{u}\left(\frac{1}{t} + a\right) + u\left(\frac{-1}{t^2} + a\right) \tag{29}$$

but $$\dot{a} = \frac{2\alpha^2 E}{RT^2} = \frac{-2\alpha a}{T} \tag{30}$$

then

$$\ddot{u} = u\left[\left(\frac{1}{t} + a\right)^2 - \left(\frac{1}{t^2} + \frac{2\alpha a}{T}\right)\right] \tag{31}$$

and also

$$\alpha/T = \frac{1}{t} - \frac{T_0}{Tt} \tag{32}$$

then

$$\ddot{u} = a^2 u - \frac{2aT_0}{Tt} \tag{33}$$

The last term in Equation 33 was omitted in the original derivation of ref [27] ($T_0 \ll T$). Its omission permits Equation 33 to be simplified

$$\ddot{u} = a^2 u \tag{34}$$

Substituting Equations 28 and 34 into Equation 27, the following expression is obtained

$$nu^n - n + 1 = \left(\frac{at}{1 + at}\right)^2 \tag{35}$$

For $E/RT \gg 1$, Equation 35 becomes

$$u = Kt = K_0\left[\exp\left(\frac{-E}{RT}\right)\frac{T_p - T_0}{\alpha}\right] \simeq 1 \tag{36}$$

or in logarithmic form

$$\ln\left(\frac{\alpha}{T_p - T_0}\right) \simeq \ln K_0 - \frac{E}{T_p} \tag{37}$$

by plotting $\ln\left(\dfrac{\alpha}{T_p - T_0}\right)$ versus $1/T_p$ one can obtain the activation energy E of the crystallization process.

4. Experimental results

A typical DTA thermogram of the composition $Bi_5Ge_{20}Se_{75}$ obtained at heating rates (α) ranging from 7.5 to 40 K min^{-1} is shown in Fig. 1. The thermograms give one exothermic peak, The temperature at which crystallization begins (T_c) and that corresponding to the maximum crystallization rate (T_p) increases with the heating rate.

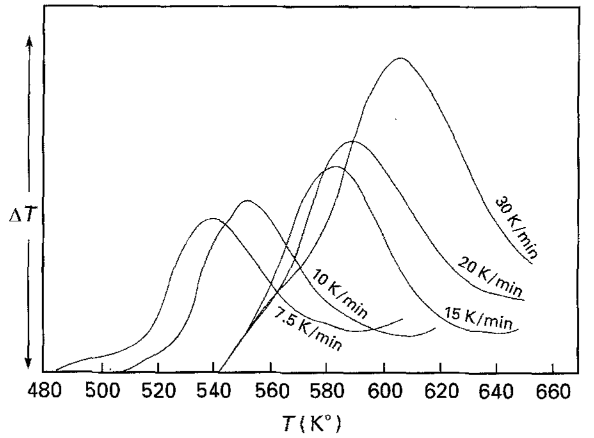

Figure 1 Typical DTA traces for $Bi_5Ge_{20}Se_{75}$ at different heating rates.

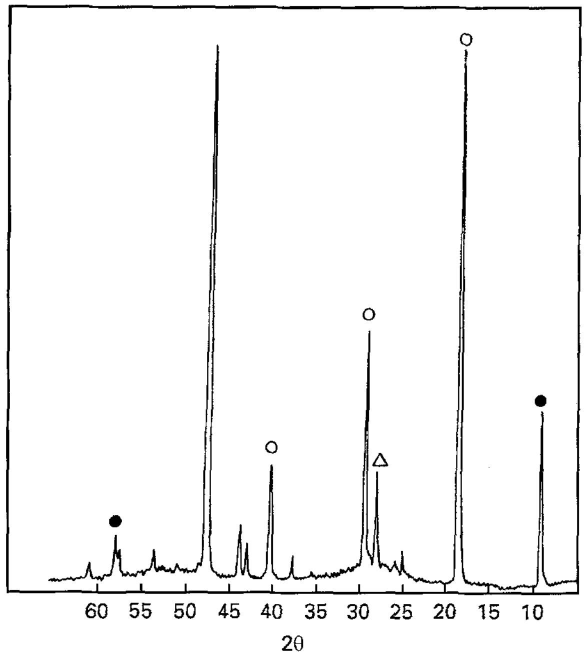

Figure 2 X-ray diffractogram of $Bi_5Ge_{20}Se_{75}$ sample annealed at 573 K for 1/h. ○ Bi_2Se_3; Δ Se; ● unidentified.

In order to identify the crystallization phase observed in DTA thermograms for the investigated glass, X-ray diffraction was made on the sample annealed at 300 °C for 1/h. Analysis of the X-ray diffraction pattern shown in Fig. 2 reveals the formation of the crystalline phases B_2Se_3. This indicates that the crystallization of $Bi_5Ge_{20}Se_{75}$ glass results in a multiphase structure.

Five different models were used for the calculation of the activation energy of crystallization E_c from the DTA thermograms. The first model (Piloyan–Borchardt), E_c was evaluated from one DTA thermogram, and for the other four models (Augis–Bennett, Takhor, Kissinger and Ozawa–Chen) different thermograms taken at different heating rates (α) were used.

5. Discussion

5.1. Piloyan–Borchardt method

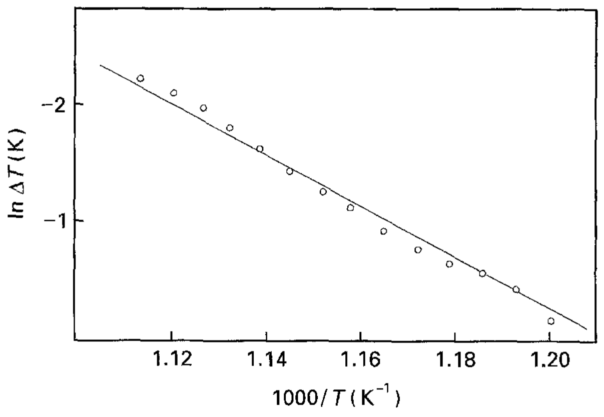

Figure 3 ln ΔT versus 1000/T for $Bi_5Ge_{20}Se_{75}$ chalcogenide glass at heating rates of 30 K min^{-1}.

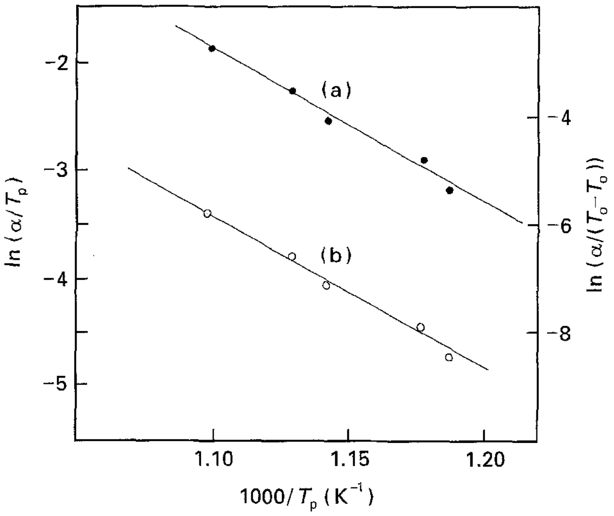

Figure 4 (a) ln [(α(T_p − T_0)] versus 1000/T_p for $Bi_5Ge_{20}Se_{75}$ chalcogenide glass. (b) −ln(α/T_p) versus 1000/T_p for $Bi_5Ge_{20}Se_{75}$ chalcogenide glass.

This method depends mainly on Equation 11 for the calculation of the activation energy of crystallization E_c. An example of ln ΔT versus $1/T$ at heating rate 30 K min^{-1} is shown in Fig. 3. This relationship is linear in the range $0.25 \ll \chi \ll 0.75$ for the investigated composition. The value of E_c calculated from this relation was 154.46 kJ mol^{-1}.

5.2. Augis–Bennett method

The activation energy (E_c) of the amorphous–crystalline transformation was calculated by applying Equation 37 derived by Augis and Bennett [27]. The plot of ln $\alpha/(T_p - T_0)$ versus $1/T_p$ results in a straight line as shown in Fig. 4(a). The value of E_c calculated from the slope of the straight line is 117.28 ± 7.479 kJ mol^{-1}.

By assuming that $T_0 \leqslant T_p$ the relation of ln (α/T_p) versus $1/T_p$ is also a linear relationship as shown in Fig. 4(b). The calculated value of E_c for this relationship is 117.64 ± 7.52 kJ mol^{-1}.

5.3. Takhor's method

Takhor assumed that ln $(T_p - T_0)$ is a function that changes slowly with the heating rate than $1/T_p$ (see Eq. 22). The value of E_c deduced from the slope

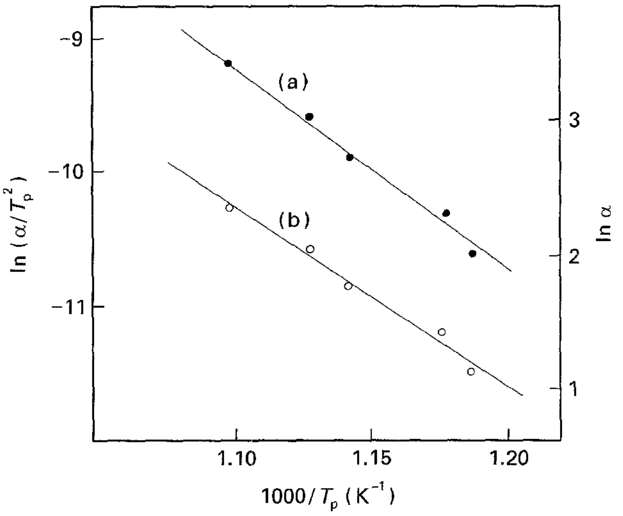

Figure 5 (a) ln α versus $1000/T_p$ for $Bi_5Ge_{20}Se_{75}$ chalcogenide glass. (b) ln (α/T_p^2) versus $1000/T_p$ for $Bi_5Ge_{20}Se_{75}$ chalcogenide glass.

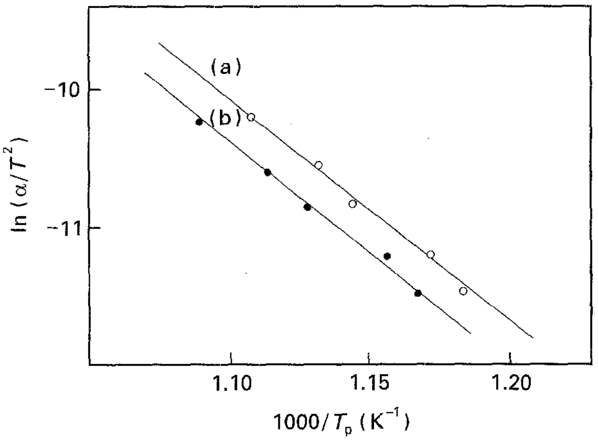

Figure 6 ln (α/T^2) versus $1000/T$ for $Bi_5Ge_{20}Se_{75}$ chalcogenide glass at (a) $\chi = 0.4$ and (b) $\chi = 0.6$.

of the ln α versus $1/T_p$ relationship (Fig. 4(a)) is 125.06 ± 7.57 kJ mol^{-1}.

5.4. Kissinger's method

For evaluation of the activation energy E_c for crystallization from the variation of T_p with respect to α, Equation 25 can be used. Fig. 5(b) shows the relation between ln (α/T_p^2) and $1/T_p$. The value of E_c calculated from this relation is equal to 110.439 ± 7.52 kJ mol^{-1}.

5.5. Ozawa–Chen method

The final method was used by Ozawa and Chen for obtaining the activation energy E_c from the heating rates dependence of temperature Equation 18. The relationship between ln (α/T^2) and $1/T$ at different crystallization fractions χ is shown in Fig. 6: The calculated E_c has the value 127.8 ± 4.81 kJ mol^{-1}.

The comparison between the calculated values of E_c using the above described methods shows that the E_c value deduced by the Piloyan–Borchardt model is higher than all the other E_c values. This deviation can be attributed to the approximation suggested by Piloyan *et al.* [21], that ln $f(x)$ is constant between $\chi = 0.25$ and 0.5. Sestak [28] has examined the validity of this approximation and he found that in the range $0.2 < \chi < 0.4$, the results produces an error of about 7% in the estimated slope. Therefore the value of E_c calculated by this method can be excluded from the calculated average value. The average value of E_c deduced by the other methods is 119.64 kJ mol^{-1}.

5.6. The kinetics of crystallization

The Johnson–Mehl–Avrami (JMA) equation concerning the kinetics of the amorphous–crystalline transformation involving nucleation and growth under isothermal conditions is generally used to analyse the crystallization process. For applicability of this equation to the non-isothermal crystallization process, several conditions will have to be satisfied [12, 29].

For non-isothermal crystallization the volume fraction χ of crystals precipitated in a glass heated at uniform rate is related to the E_c as follows

$$\ln[-\ln(1-\chi)] = -n\ln\alpha - 1.052\, mE_c/RT + \text{constant} \qquad (38)$$

where *m* and *n* are integers having values between 1 and 4 depending on the morphology of the growth. When nuclei formed during heating at constant rate α, *n* is equal to *m* + 1 [12]. Table I shows the values of *n* and *m* for various crystallization mechanisms. Fig. 7 shows the relation between ln $[-\ln(1-\chi)]$ and $1/T$ at various heating rates (α). The relationships are found to be linear over most of the temperature range. At high temperatue, or in regions of large crystallization, a break in the linearity or rather a lowering of the initial slope is observed for all the heating rates (Fig. 7). Generally this break in slope is attributed to

TABLE I Values of *n* and *m* for various crystallization mechanisms [12]

Mechanism	*n*	*m*
Three dimensional growth	3	3
Two dimensional growth	2	2
One dimensional growth	1	1

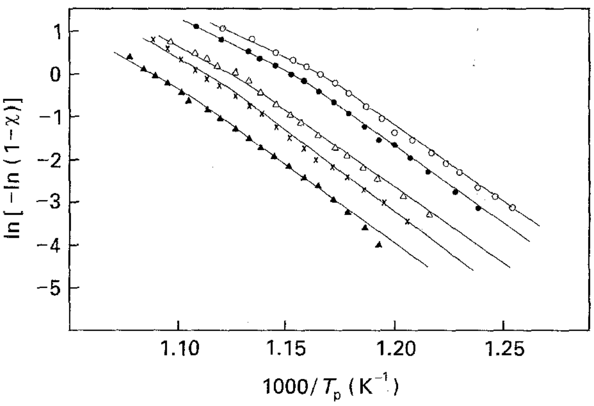

Figure 7 ln $[-\ln(1-\chi)]$ versus $1000/T$ for $Bi_5Ge_{20}Se_{75}$ at different heating rates. 0.75, ●10, Δ 15, X 20, and ▲30 kJ min^{-1}.

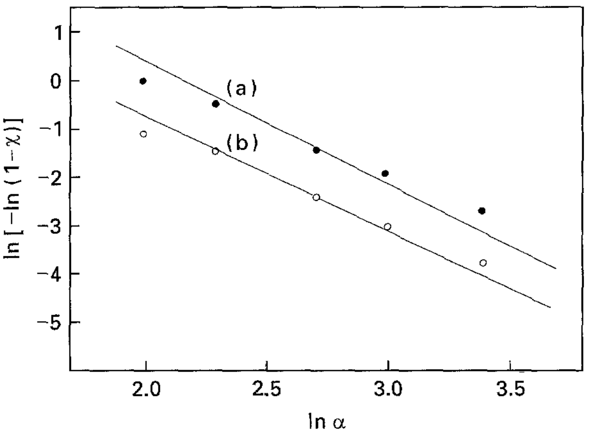

Figure 8 ln $[-\ln(1-\chi)]$ versus $1000/T$ for $Bi_5Ge_{20}Se_{75}$ at temperatures of (a) $T = 855$ K and (b) $T = 833$ K.

the saturation of nucleation sites in the final stages of crystallization [12, 30] or to restrictions of crystal growth by small size of the particles [31]. Plotting ln $[-\ln(1-\chi)]$ versus $1/T$ data, values of mE_c were calculated for all the heating rates. It is observable that mE_c is somewhat independent of the heating rate, and hence an average value of mE_c was calculated by considering all the heating rates. Then the average value of E_c was used for calculation of m. The calculated values of mE_c and m are 265.92 and 2.2 kJ mol^{-1}, respectively.

It is possible to evaluate ln $[-\ln(1-\chi)]$ as a function of ln α at any fixed temperature as indicated by Equation 38. Then n is obtained as the slope of the resulting line. Fig. 8 shows the plots of ln $[-\ln(1-\chi)]$ versus ln α at two different temperatures. From the slope of these linear relations the average value of n is not an integer. This means that the crystallization occurs with different mechanisms. This result is confirmed with the appearance of two phases (Bi_2Se_3 and Se) in the diffractogram. As the fraction is greater than 0.5, this means that the mechanism with a higher value of n is predominant. Therefore, from Table 1 the value of the corresponding m is equal to 2 which means that the overall crystallization mechanism of $Bi_5Ge_{20}Se_{75}$ chalcogenide glass is a two-dimensional growth. These results are in good agreement with those obtained by Tohge *et al.* [32].

6. Conclusions

The results from the DTA show that the crystallization temperature (T_c) and the peak temperature (T_p) depend on the heating rates for $Bi_5Ge_{20}Se_{75}$ composition. The crystallization kinetics were studied using the most recent analysis developed for the non-isothermal crystallization process and the results indicate that the crystallization takes place by a two-dimensional growth.

All the methods used to evaluate the activation energy (E_c) are used to explain the results of glass–crystalline transformation but with different accuracy. The average value of E_c for the investigated composition is equal to 119.64 ± 6.97 kJ mol^{-1}.

Acknowledgements

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