Journal of Thermal Analysis, Vol. 46 (1996) 177-186

ACTIVATION ENERGY OF $Se_2Ge_{0.2}Sb_{0.8}$ CHALCOGENIDE GLASS BY DIFFERENTIAL SCANNING CALORIMETRY

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(Received January 20, 1995; in revised form July 24, 1995)

Abstract

Results of differential scanning calorimetry (DSC) at different heating rates on $Se_2Ge_{0.2}Sb_{0.8}$ chalcogenide glass are reported and discussed. As the heating rate (α) changed, also the glass transition temperature (T_g) and onset temperature of crystallization (T_c) changed. As the value of the transition activation energy E_t changed, the crystallization fraction (χ), heat flow (Δq) and the crystallization peak temperature (T_p) also changed. The value of the effective activation energy of crystallization E_c was calculated by means of six different methods. The $Se_2Ge_{0.2}Sb_{0.8}$ chalcogenide glass has two crystallization mechanisms, a one-dimensional and an other surface crystallization growth. The average value of E_t for $Se_2Ge_{0.2}Sb_{0.8}$ is equal to 194.95± 3.9 $kJ\cdot mol^{-1}$ and the average value of E_c is equal to 164±3.3 $kJ\cdot mol^{-1}$.

Keywords: activation energy, chalcogenide glass, DSC

Introduction

The physical properties of chalcogenide glasses have lately received a great deal of attention in many technical and scientific applications. The changes in these properties have been used to follow the phase transition from the amorphous to the crystalline state. The activation energy was used as a parameter for observing the steps of the crystallization process with sufficient accuracy [1]. In the present work crystallization studies were carried out under non-isothermal conditions with samples heated at various uniform rates. The glass transition temperature T_g and both the onset (T_c) and peak temperature (T_p) of crystallization are dependent on the heating rate (α). The glass transition activation energy E_t, and crystallization activation energy E_c were evaluated.

Experimental

The investigated samples of $Se_2Ge_{0.2}Sb_{0.8}$ were prepared from appropriate amounts of high purity (99.999%) chemicals put in a quartz glass ampoule

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(12 mm diameter) and sealed in a vacuum of 10^{-4} torr then heated in a rotary furnace at 950°C for 24 h. The melt was quenched in water at 0°C [2].

The thermal behavior of the product was investigated with a Shimadzu 50 differential scanning calorimeter. The temperature and energy calibrations of the instrument were performed using the well known melting temperature and melting enthalpy of high-purity indium metal. The calorimetric sensitivity is 10 W (0.008 mJ/s) and the temperature precision is ±0.1 K.

X-ray studies of $Se_2Ge_{0.2}Sb_{0.8}$ powder were performed with a Philips type 1710 diffractometer. The patterns were run with Cu as target and Ni as filter (λ=0.15417 nm), at 40 kV and 30 mA, at a scanning speed of 3.6 deg·min^{-1}.

The crystallization curves were recorded while the temperature of the sample was increased at a uniform rate. 10 mg of sample in powder form was placed in a standard aluminium cell and scanned over a temperature range from room temperature to 400°C at uniform heating rates ranging from 2 to 50 deg·min^{-1} in vacuum (10^{-2} Torr). The parameters T_g, T_c, T_p, χ, Δq were evaluated by the software of Shimadzu. Figure 1 shows the curve of the sample recorded at a heating rate of 30 deg·min^{-1}.

Results and discussion

A typical DSC trace of the prepared $Se_2Ge_{0.2}Sb_{0.8}$ glass obtained at a heating rate of 30 deg·min^{-1}, is shown in Fig. 1. Three characteristic phenomena are

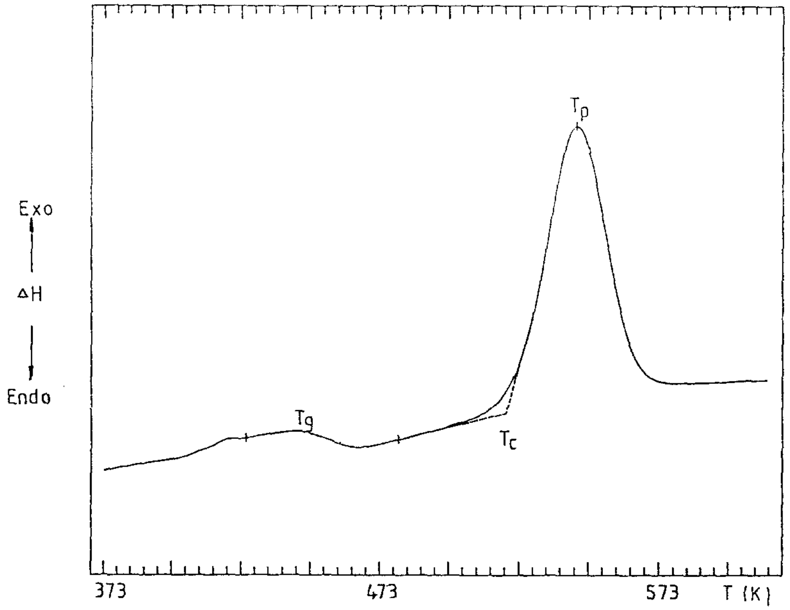

Fig. 1 Typical DSC trances at a heating rate of 30 deg·min^{-1} for $Se_2Ge_{0.2}Sb_{0.8}$ chalcogenide glass

observed in the studied temperature range. The first one T_g corresponds to the glass transition temperature, the second one T_c corresponds to the onset temperature of crystallization, and the last characteristic temperature T_p is the peak temperature of crystallization of $Se_2Ge_{0.2}Sb_{0.8}$ glass. The X-ray diffractogram also indicates that the as-prepared sample is amorphous (Fig. 2).

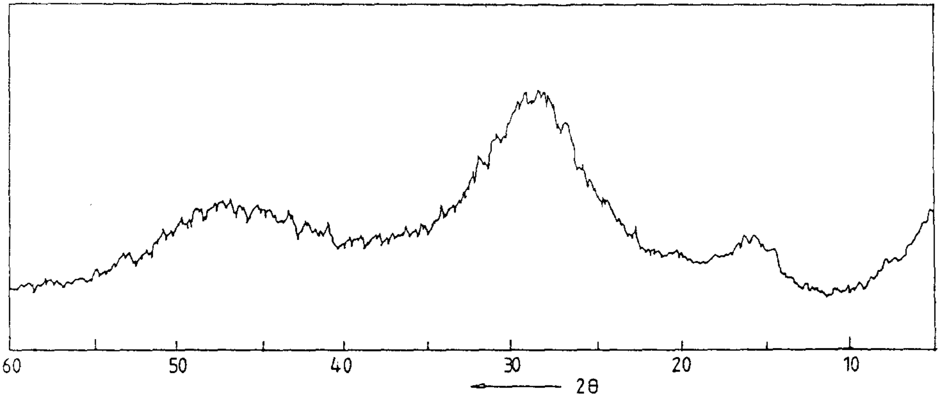

Fig. 2 The X-ray diffractograms of $Se_2Ge_{0.2}Sb_{0.8}$

From the Jonson-Mehl-Avrami equation [3], the activation energy of crystallization (E_c) is:

$$E_c = (E_N + mE_c)/n \tag{1}$$

where n is an integer of half integer which depends on the mechanism of growth and the dimensions of the crystal. E_N and E_G are the effective activation energies for nucleation and growth, respectively, $n=m$ for $I_v=0$ [4] and $n=m+1$ for $I_v\neq0$ [3], since I_v is the nucleation energy.

If E_N is negligible over the temperature range of concern in the thermoanalytical study [3], then

$$E_c \cong (m/n)\ E_G \tag{2}$$

Thus, the activation energy of growth (E_G) is

$$E_G \cong (nE_c\ /m) \tag{3}$$

There are six different methods for the determination of the effective activation energy of the crystallization process [5, 6]. Two methods Piloyan-Borchardt, and Coats-Redfern-Šesták were used for evaluation of E_G from one DSC trace, and four other methods Augis-Bennet, Takhor, Kissinger and Ozawa-Chen were used for the determination of E_G from different traces obtained at different heating rates.

The method of Piloyan-Borchardt [7, 8] determines the variation of Δq (the heat flow difference between the sample and reference material) with temperature at constant heating rate. In this method the following equation is used:

$$\ln\,[T\Delta q/F(\chi)] = (-E_c\,/\,RT) + \text{const.} \tag{4}$$

where R is gas constant, $F(\chi)=(1-\chi)\,[-\ln(1-\chi)]^{\{(n-1)/n\}}$.

The Coats-Redfern-Šesták method [9] determines the influence of temperature on the crystallization fraction (χ) for one heating rate. In this method the following equation is used:

$$\ln[-\ln(1-\chi)/T^{2n}] = (-nE_c\,/RT) + \text{const.} \tag{5}$$

The methods of Augis-Bennett [10] and Takhor [11] use the relationship

$$\ln[\alpha/(T_p - T_o)] = (-E_c\,/RT_p) + \text{const.} \tag{6}$$

where T_o is the initial temperature, and if $T_p \gg T_o$, Eq. 6 becomes

$$\ln(\alpha/T_p) = (-E_c\,/RT_p) + \text{const.} \tag{7}$$

Kissinger's method [12, 13] is commonly used in analyzing crystallization data in DSC and DTA systems. This method applies the following equation for the determination of the activation energy of crystallization.

$$\ln(\alpha/T_p) = (-E_c\,/RT_p) + \text{const.} \tag{8}$$

The last method, that of Ozawa [14] and Chen [15], employs the relationship:

$$\ln(\alpha/T) = (-nE_c\,/RT) + \text{const.} \tag{9}$$

at constant volume fraction (χ).

Glass transition

The dependence of the glass transition temperature on the heating rate (α) was found to follow the formula [15]

$$\ln(\alpha/T_g^2) = (-E_t\,/RT_g) + \text{const.} \tag{10}$$

where E_t is the activation energy of glass transition. If the variation of T_g is small at different rates (α) Eq. 10 becomes

$$\ln(\alpha) = (-E_t\,/RT_g) + \text{const.} \tag{11}$$

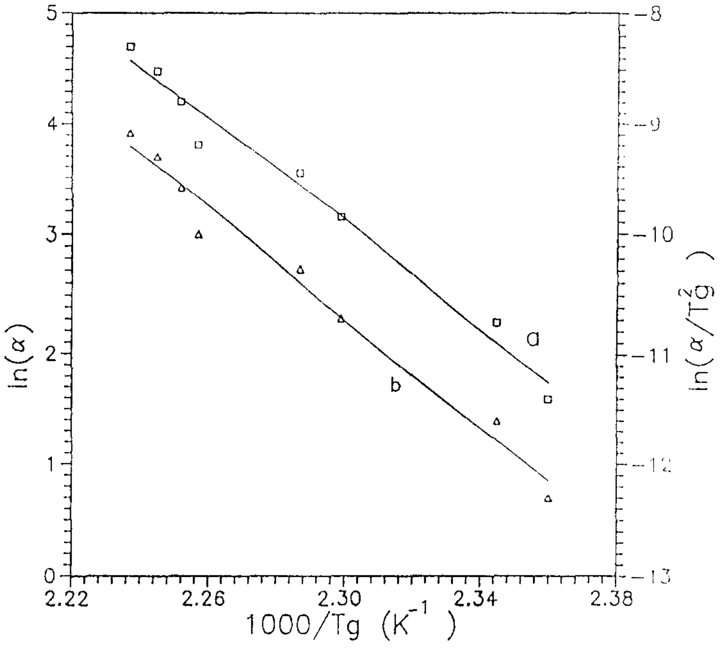

Fig.3 (a) Relationship between $\ln(\alpha/T_g^2)$ and $1000/T_g$ of $Se_2Ge_{0.2}Sb_{0.8}$ glass sample.
(b) relationship between $\ln(\alpha)$ with $1000/T_g$ of $Se_2Ge_{0.2}Sb_{0.8}$ glass sample

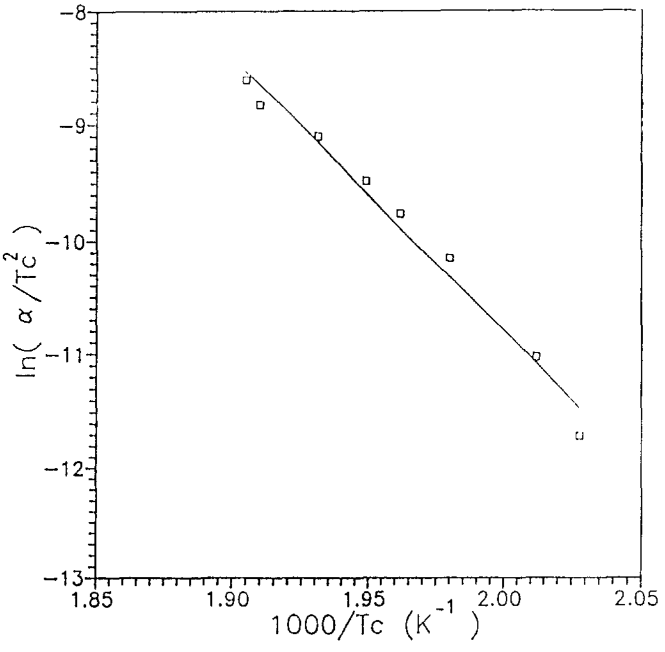

Fig. 4 Relationship between $\ln(\alpha/T_c^2)$ and $1000/T_c$ for $Se_2Ge_{0.2}Sb_{0.8}$ chalcogenide glass

To study and determine the activation energy of glass transition E_t by using two different methods, in the first one the glass transition temperature T_g and in the second one the onset temperature of crystallization, T_c was used.

In the first method relationships (10) and (11) were used. Figure 3 curve (a) shows the correlation between $\ln(\alpha/T_g^2)$ and $1/T_g$, and Fig. 3 curve (b) shows the relationship between $\ln(\alpha)$ and $1/T_g$. The values of E_t deduced were found to be 191.73±4.41 kJ·mol^{-1} and 199.18±4.38 kJ·mol^{-1}, respectively.

In the second method Kissinger's formula [12] was used which had been applied originally to crystallization studies. The dependence of T_c on α is given by

$$\ln(\alpha/T_c^2) + \text{const.} = -E_t/RT_c \qquad (12)$$

A plot of $\ln(\alpha/T_c^2)$ *vs.* $1/T_c$ for the $Se_2Ge_{0.2}Sb_{0.8}$ chalcogenide glass is shown in Fig. 4. The value of E_t was found to be 198.16±3.96 kJ·mol^{-1}.

Crystallization process

Before evaluation of the effective activation energy of crystallization E_c, the Ozawa method deduces the order of the crystallization reaction (n) using Eq. (5).

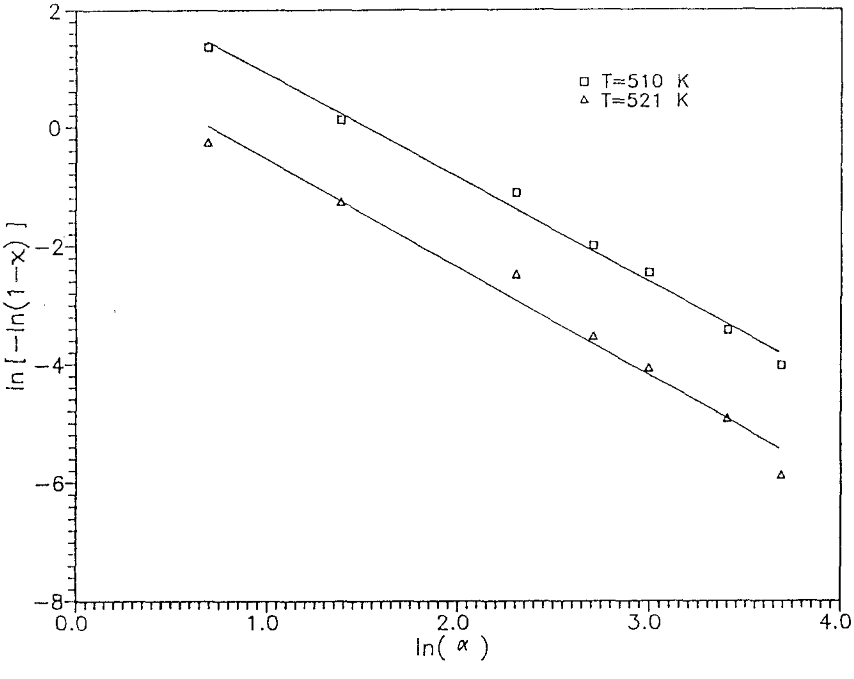

Fig. 5 Relationship between $\ln[-\ln(1-\chi)]$ and $\ln(\alpha)$ at temperature of 510 K and 521 K for $Se_2Ge_{0.2}Sb_{0.8}$ glass

$$d\{\ln[-\ln(1-\chi)]\} / d\{\ln(\alpha)\} = -n$$

where α is the heating rate.

On this basis, $\ln[-\ln(1-\chi)]$ is plotted *vs.* ln α, at the same temperature. The value of n for different heating rates was calculated. Figure 5 shows the relationships at temperatures of 510 and 521 K.

The average slope was 1.8, which means that $n=2$ and $m=1$, and the crystallization occurs by two different mechanisms, surface nucleation and bulk nucleation [one-dimensional growth].

The activation energy of crystallization was calculated by means of the Piloyan-Borchardt method form Eq. (4) by plotting $\ln[T\Delta q/F(\chi)]$ *vs.* $1/T$. Figure 6 shows this relationship at a rate of 10 deg·min^{-1}, the slope being $-E_c/RT$, thus $E_c=142.27$ kJ·mol^{-1}.

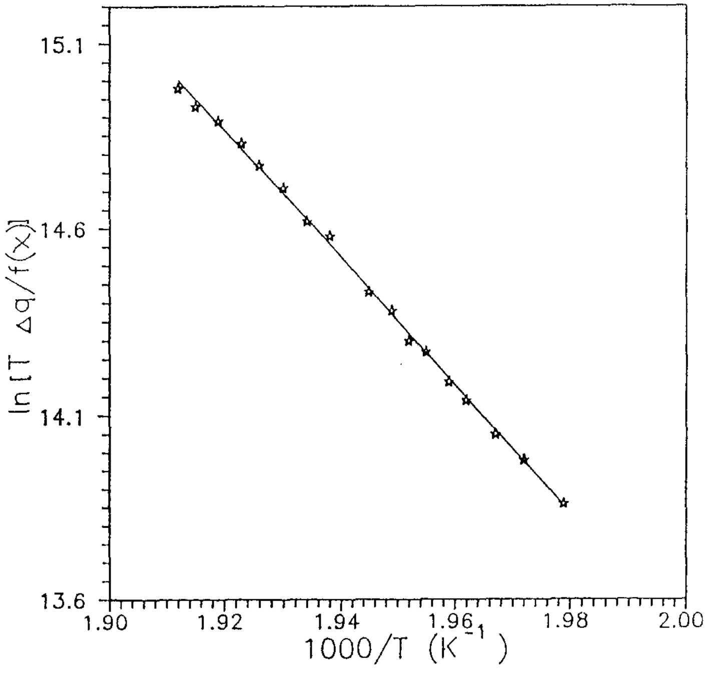

Fig. 6 Relationship between $\ln[T\Delta q/F(\chi)]$ and (1000/T) at a heating rate of 10 deg·min^{-1} for $Se_2Ge_{0.2}Sb_{0.8}$ glass

E_c was evaluated by means of the Coats-Redfern-Šesták method, using Eq. (5),, by plotting $\ln[-\ln(1-\chi)/T^4]$ *vs.* $1/T$, at different heating rates ($n=2$). Figure 7 shows the average slope to be equal to nE_c/R, thus $E_c=163.77+23.4$ kJ·mol^{-1}.

The activation energy of crystallization was determined by means of the methods of Augis-Bennett and Takhor using Eq. (7), since $T<<T$ in this work.

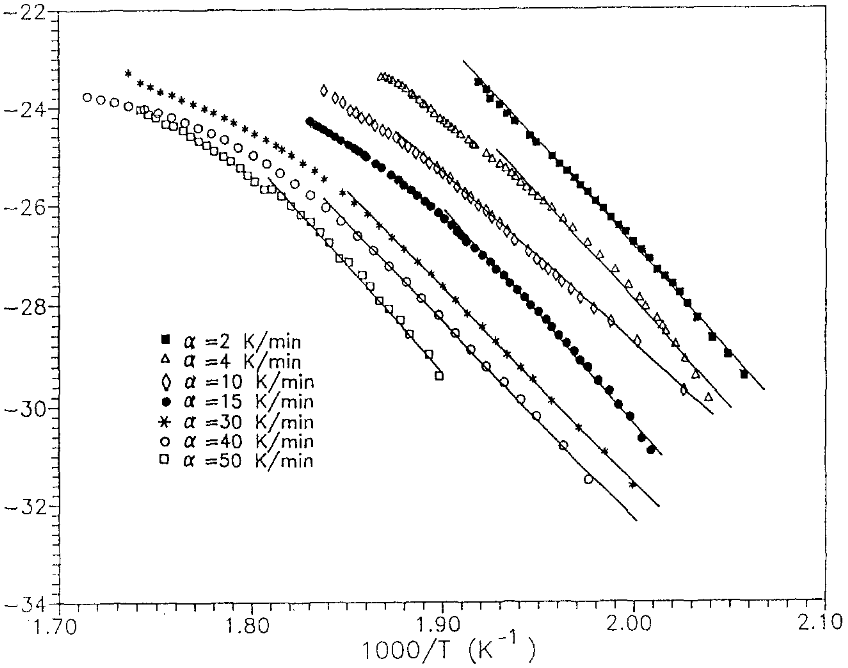

Fig. 7 Relationship between $\ln[-\ln(1-\chi)/T^4]$ and $(1000/T)$ for $Se_2Ge_{0.2}Sb_{0.8}$ glass

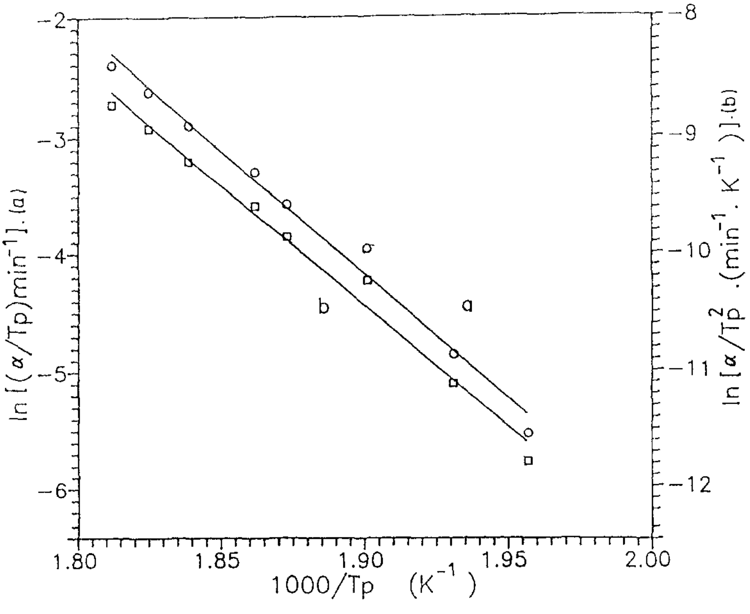

Fig. 8 (a) variation of $\ln[\alpha/T_p)\mathrm{min}^{-1}]$ and $1000/T_p$, (b) variation of $\ln[\alpha/T_p^2(\mathrm{min}^{-1}\cdot K^{-1})]$ with $1000/T_p$ for $Se_2Ge_{0.2}Sb_{0.8}$ glass

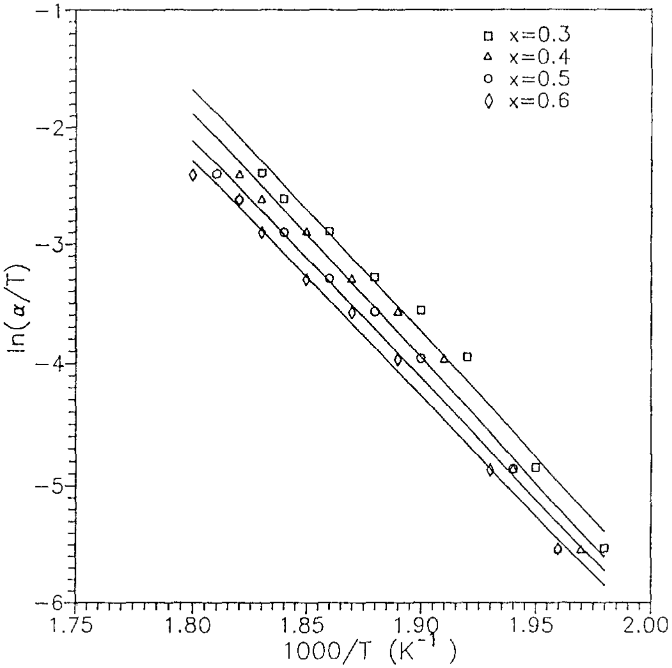

Fig. 9 Relationship between ln(α/*T*) and 1000/*T* at various volume fractions (χ=0.3, 0.4, 0.5, 0.6) for $Se_2Ge_{0.2}Sb_{0.8}$ glass

The relation between ln(a/T_p) and *vs.* $1/T_p$ is shown by curve (a) in Fig. 8 E_c was evaluated from the slope as E_c =176.93 kJ·mol^{-1}.

In Kissinger's method Eq. (8) was used ln(α/T_p^2) was plotted *vs.* $1/T_p$, as shown by curve (b) in Fig. 8. From the slope E_c was calculated as E_c=172.62 kJ·mol^{-1}.

In the last method, that of Ozawa and Chen, Eq. (9) was used. The relationship between ln(α/*T*) *vs.* 1/*T* for different volume fractions (χ=0.3, 0.4, 0.5, 0.6) is shown in Fig. 9. From the slope, the average value of the activation energy of crystallization was calculated (E_c=168.65 kJ·mol^{-1}). Table 1 shows E_c and E_G calculated by means of different methods.

Table 1

Methods used	E_c / kJ·mol^{-1}	E_G / kJ·mol^{-1}
Piloyan-Borchardt	142.27	284.54
Coats-Redfern-Šesták	163.77	327.54
Augis-Bennett & Takhor	176.93	353.80
Kissinger	172.62	345.24
Ozawa-Chen	168.65	337.30

Conclusion

The mean value of the effective activation energy of crystallization E_c is equal to 164±3.3 kJ·mol^{-1}, and the average value of the effective activation energy of crystal growth (E_G) for $Se_2Ge_{0.2}Sb_{0.8}$ glass obtained by means of six different methods under non-isothermal conditions is 328±6.6 kJ·mol^{-1}, and the average value of the transition activation energy E_t is 194±3.9 kJ·mol^{-1}. The crystallization mechanism for $Se_2Ge_{0.2}Sb_{0.8}$ glass is a two-dimensional growth.

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