Thermochimica Acta 485 (2009) 14–19

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Variation of the activation energy of crystallization in $Se_{81.5}Te_{16}Sb_{2.5}$ chalcogenide glass: Isoconversional analysis

A.A. Abu-Sehly*,[1]

Physics Department, Faculty of Science, Taibah University, PO Box 344, Madina, Saudi Arabia

ARTICLE INFO

Article history:
Received 9 July 2008
Received in revised form
22 November 2008
Accepted 3 December 2008
Available online 11 December 2008

PACS:
6470.P
6140
6140.D

Keywords:
DSC
Crystallization kinetics
Chalcogenide glass
Activation energy
Isoconversional methods

ABSTRACT

Differential scanning calorimetry (DSC) technique was used to investigate the kinetics of crystallization in $Se_{81.5}Te_{16}Sb_{2.5}$ chalcogenide glass. Non-isothermal measurements were performed at different heating rates (5–60 K/min). A strong heating rate dependence of the activation energy was observed when the data were analyzed using Matusita model. This variation of the activation energy was confirmed by the application of the isoconversional methods of Friedman, Kissinger–Akahira–Sunose (KAS) and Vyazovkin. These methods showed that the activation energy of crystallization is not constant but varies with the degree of conversion and hence with temperature. However, the values of the activation energy obtained from Friedman method are much lower compared with the values estimated from KAS and Vyazovkin methods. It is suggested that this disagreement was due to possible errors involved in the Friedman method.

1. Introduction

Chalcogenide glasses have drawn great attention because of their interesting semiconducting properties [1,2] that can be used in various solid-state devices and also due to their more recent importance in optical recording [3]. It has recently been pointed out that the addition of Se to Te improves its corrosion resistance [4]. Therefore, Se–Te alloys are thought to be promising media, which can be used for phase change (PC) between amorphous to crystalline state. These alloys are found to have some significant problems when used as a recording layer material in optical PC technique [5,6]. The two serious problems are the limited reversibility [7] and low glass transition and crystallization temperatures. These problems can be removed by adding a third element as a chemical modifier in Se–Te alloys. A lot of work has been done on ternary chalcogenide glasses having different compositions like Se–Te–Sb, Se–Te–Ge, and Se–Te–In [8–10]. Moreover, addition of a third element such as Sb to binary chalcogenide glass produces a higher stability [11].

The kinetics of crystallization is widely studied using differential scanning calorimetry (DSC) where important information regarding the transformation mechanisms can be obtained. For instance, different kinetic parameters (such as activation energy and reaction order) can be estimated using different methods. The methods commonly used for analyzing non-isothermal kinetics data are generally grouped into two categories: model-fitting and isoconversional (model-free) methods. Model fitting methods were widely used because of their ability to directly determine the kinetic triplet. These methods involve fitting different reaction models to experimental data leading to a simultaneous determination of the kinetic parameters. In model fitting methods the kinetic parameters are assumed constant. On the other hand, isoconversional (model-free) methods are becoming more popular because of their ability to determine the activation energy at progressive extent of conversion (α) without assuming any reaction model.

The variation of the activation energy with the degree of crystallization is an important issue in the kinetics of amorphous to crystalline transformation [12]. As pointed out by Vyazovkin [12], this variation of the activation energy with the degree of crystallization, and hence with temperature, can provide useful information about the different mechanisms involved in the transformation process. Liu et al. [13,14] have considered a generalization of the Johnson–Mehl–Avrami (JMA) model to account for the variation of

---

* Tel.: +966 508629110; fax: +966 48454770.
E-mail address: a.abusehly@hotmail.com.

[1] On leave from Physics Department, Assiut University, Assiut, Egypt.

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.12.006

the activation energy. In contrast to the original formalism of the JMA theory, where only nucleation site saturation or continuous nucleation was assumed, Liu et al. model predicts that the activation energy is not constant throughout the crystallization process when mixed nucleation (a combination of pre-existing nuclei and continuous nucleation modes, with site saturation and continuous nucleation as two extremes) is considered.

In order to reveal this variation of the activation energy of crystallization, two approaches are normally used [9]. The first approach is to use Matusita et al. [15] method to determine the kinetic parameters such as the activation energy E and the Avrami exponent n of the crystallization process. The variation of the activation energy can be further analyzed using isoconversional methods which were widely used by different authors to investigate different kinetic processes associated with this transformation [9,16–25].

In the present work, the kinetics of crystallization of amorphous $Se_{81.5}Te_{16}Sb_{2.5}$ alloy is studied using the DSC technique at different constant heating rates. The DSC data are analyzed using different kinetics models to investigate the growth processes involved in the transformation. The heating rate dependence of the activation energy of crystallization is discussed.

2. Theoretical background

The kinetics of isothermal crystallization involving nucleation and growth is usually analyzed using Kolmogorov–Johnson–Mehl–Avrami (KJMA) model [26,27]. According to the KJMA model, the volume fraction of crystallites (α) is given by [28–30]:

$$\alpha = 1 - \exp(-kt^n) \tag{1}$$

where n is the Avrami exponent that is associated with the nucleation and growth mechanisms and k is the reaction rate constant. In this thermally activated process the rate constant is related to temperature T via the Arrhenius equation:

$$k = A \exp\left(\frac{-E}{RT}\right) \tag{2}$$

where E is the activation energy of crystallization, A is the pre-exponential factor and R is the gas constant. In the framework of KJMA model, the kinetic parameters n, A and E are assumed to be constant during the crystallization process.

2.1. Kissinger method

This method [31] is most commonly used in analyzing crystallization data in DSC. According to this method the activation energy can be evaluated using the following equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \text{Const.} - \frac{E}{RT_p} \tag{3}$$

where T_p is the crystallization peak temperature and β is the heating rate.

2.2. Matusita method

The crystallization kinetics can be obtained using a method suggested specifically for non-isothermal experiments by Matusita et al. [15]. The volume fraction of crystallites (α), precipitated in a glass heated at constant rate (β), is related to the activation energy for crystallization through the following expression [15]:

$$\ln[-\ln(1-\alpha)] = -n \ln\beta - 1.052\frac{mE}{RT} + \text{Const.} \tag{4}$$

where m is an 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 [32,33].

2.3. Isoconversional methods

The kinetics of crystallization in amorphous materials can be described by the following rate equation:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{5}$$

where $f(\alpha)$ is the reaction model. Under non-isothermal conditions with a constant heating rate $\beta = dT/dt$, Eq. (5) may be rewritten as

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\left(\frac{1}{\beta}\right) = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{6}$$

The integral form of the reaction model can be obtained by integrating Eq. (6) as follows:

$$g(\alpha) = \int_0^{\alpha}\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T}\exp\left(-\frac{E}{RT}\right)\,dT = \frac{A}{\beta}I(E,T) \tag{7}$$

Using an advanced isoconversional method developed by Vyazovkin [22], for a series of n experiments carried out at different heating rates the effective activation energy can be determined at any particular value of α by finding the value of E_α for which the objective function Ω is minimized, where:

$$\Omega = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{I(E_\alpha, T_{\alpha i})\beta_j}{I(E_\alpha, T_{\alpha j})\beta_i} \tag{8}$$

where the integral $I(E,T)$ is given by

$$I(E,T) = \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha}\exp\left(\frac{-E}{RT}\right)dT \tag{9}$$

The integral $I(E,T)$ was numerically evaluated using the trapezoidal method. The activation energy E_α is the value that minimizes Ω in Eq. (8) for a particular α.

The Kissinger–Akahira–Sunose method [34,31,35] (or the generalized Kissinger method as it is sometimes called) may be obtained through derivation of Eq. (7). Subsequent logarithm application and rearrangement yield:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right) = \text{Const.} - \frac{E_\alpha}{RT_{\alpha i}} \tag{10}$$

The subscript i denotes different heating rates. For each degree of the conversion, α, a corresponding $T_{\alpha i}$ and heating rate are used to plot $\ln(\beta_i/T_{\alpha i}^2)$ against $1/T_{\alpha i}$. The plot should be a straight line whose slope can be used to calculate the activation energy E_α.

The differential isoconversional method suggested by Friedman [36] is based on Eq. (7). For various heating rates, β_i, this method can be used directly from Eq. (7) at a specific crystallization fraction, α, as:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha i} = \text{Const.} - \frac{E_\alpha}{RT_{\alpha i}} \tag{11}$$

The parameter E_α at this specific value of α, is then estimated from a plot of $\ln(d\alpha/dt)_{\alpha i}$ versus $1/T_{\alpha i}$ across different heating rates. The procedure is repeated for many values of α, yielding continuous functions of α for E_α.

3. Experimental

The $Se_{81.5}Te_{16}Sb_{2.5}$ chalcogenide glass was prepared using the standard melt-quench technique. High purity (99.999%) Se, Te and Sb in appropriate atomic weight percentage were weighed and sealed in a quartz ampoule (12 mm diameter) under a vacuum of 10^{-4} Torr. The contents were heated at around 950 K for 24 h. During the melting process, the tube was frequently shaken to homogenize the resulting alloy. The melt was quenched in ice water to obtain the glassy state. The structure of the sample was examined using Shimadzu XRD-6000 X-ray diffractometer using Cu K_α radiation ($\lambda = 1.5418$ Å). The surface microstructure was revealed by SEM (Shimadzu Superscan SSX-550). The content of the alloy was checked by Energy Dispersive X-ray (EDX) using the scanning electron microscope (Shimadzu Superscan SSX-550). The composition of the elements (Se, Te and Sb) was determined by EDX at different locations of the sample and average values were used.

Thermal behavior was investigated using Shimadzu DSC-60. The calorimetric sensitivity is ±10 μW and the temperature accuracy is ±0.1 K. Typically, 3 mg of sample in powder form was sealed in standard pans and heated at different rates 5, 8, 12, 15, 17, 20, 25, 30, 40, 50 and 60 K/min under dry nitrogen supplied at the rate 35 ml/min. To minimize the temperature gradient the samples were well granulated to form uniform fine powder and spread as thinly as possible on the bottom of the sample pan. Temperature and enthalpy calibration was carried out with indium at heating rate 10 K/min ($T_m = 156.6\,^\circ$C and $\Delta H_m = 28.55$ J/g) as the standard material supplied by Shimadzu.

4. Results and discussion

The composition of as-prepared $Se_{81.5}Te_{16}Sb_{2.5}$ bulk was analyzed using EDX. Fig. 1(a) shows the spectral distribution of the constituent elements. The atomic percentage ratios of Se, Te and Sb were found to be 81.5, 16 and 2.5, respectively. The X-ray diffraction examination indicates the amorphous structure of the as-prepared specimen as shown in Fig. 1(b). Fig. 1(c) shows the SEM of a fractured as-prepared bulk specimen. Conchoidal contours of the fractured specimen indicate the glass structure.

DSC curves of the crystallization process of the $Se_{81.5}Te_{16}Sb_{2.5}$ chalcogenide glass obtained at different heating rates are shown in Fig. 2. The DSC thermograms are characterized by two temperatures. The glass temperature T_g as defined by the endothermic change in the DSC trace indicates a large change of viscosity, marking a transformation from amorphous solid phase to supercooled liquid state. The exothermic peak temperature T_p is used to identify the crystallization process. It is evident from this figure that both T_p and T_g shift to higher temperatures with increasing heating rate. The variation of the T_p at various heating rates is shown in Fig. 3. The shift of T_p arises from the dependence of the induction time, t_{in} associated with nucleation process. Crystallization is controlled by nucleation and there exist an induction time for nucleation. As the heating rate increases, the temperature at which t_{in} becomes zero increases leading to the observed shift of crystallization to higher temperatures.

The activation energy of the crystallization process is obtained using Kissinger equation (Eq. (3)). A straight line is obtained by plotting $\ln(\beta/T_p^2)$ versus $1/T_p$, as shown in Fig. 4. From the slope of the straight line, it is possible to derive the value of the activation energy of crystallization, yielding $E = 82.5 \pm 1.6$ kJ/mol. Because of the fact that the variation in $\ln(1/T_p^2)$ is much slower than $\ln(\beta)$, Kissinger equation was approximated by Mahadevan et al. [33] as

$$\ln(\beta) = \text{Const.} - \frac{E}{RT_p} \tag{12}$$

From the linear $\ln(\beta)$ versus $(1/T_p)$ plot, shown also in Fig. 4, the calculated value of E is equal to 76.2 ± 1.5 kJ/mol.

In order to investigate the heating rate dependence of the kinetic parameters, n and E, we analyzed the data using Matusita model (Eq. (4)). Fig. 5 shows the extent of crystallization (α) as a function of temperature at different heating rates. Using the data of Fig. 5, plots of $\ln[-\ln(1-\alpha)]$ against $1/T$ at different heating rates are obtained as shown in Fig. 6. The straight lines in this graph are linear fittings according to (Eq. (4)).

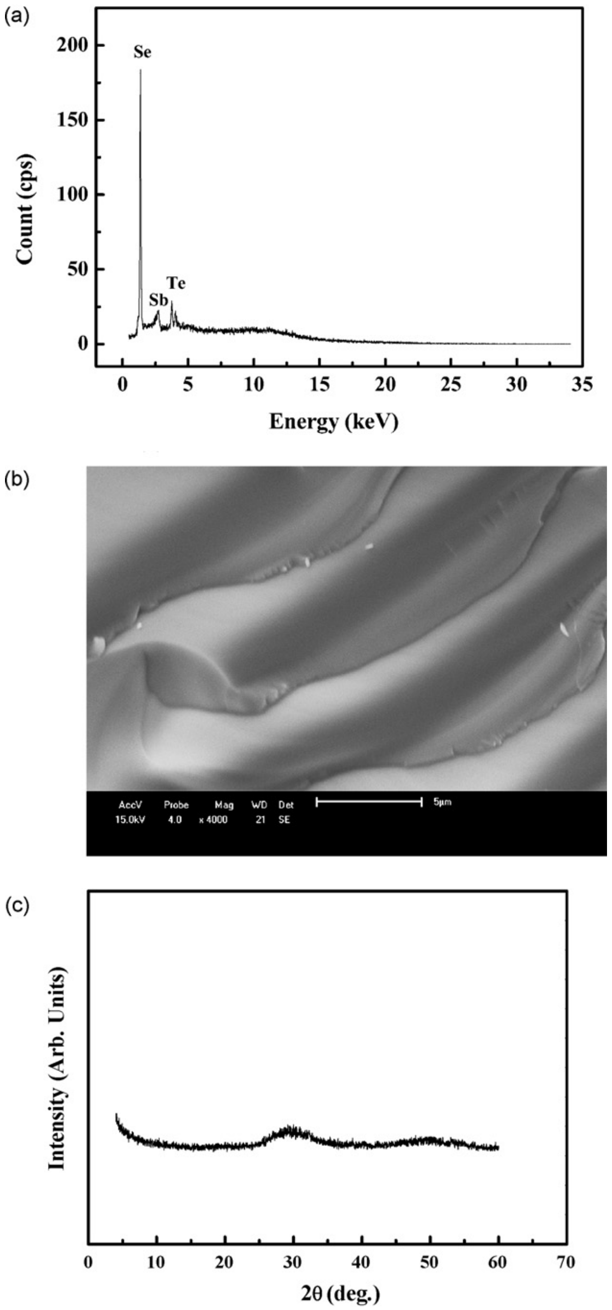

Fig. 1. (a) EDX results of the $Se_{81.5}Te_{16}Sb_{2.5}$ chalcogenide glass, (b) SEM micrograph and (c) X-ray diffractometer of as-prepared bulk specimen.

From the slope of each straight line shown in Fig. 6, mE value was determined. It is evident from this figure that different values of mE are obtained for different heating rates.

The Avrami exponent n can also be determined using Matusita equation (Eq. (4)) by plotting $\ln[-\ln(1-\alpha)]$ against $\ln(\beta)$ at different temperatures, as shown in Fig. 7. The slope of each line gives the value of n. It is clear from the figure that n is temperature independent and hence an average value can be calculated. The average value of n obtained from these results is 2.11 ± 0.02.

Once the value of n is obtained, the effective activation energy E can be evaluated at different heating rates. As the sample is pre-annealed for a period of time before each experimental run at

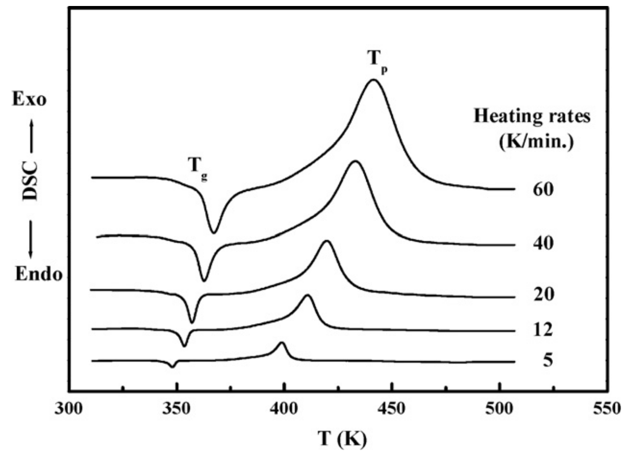

Fig. 2. DSC curves of the $Se_{81.5}Te_{16}Sb_{2.5}$ chalcogenide glass at different heating rates.

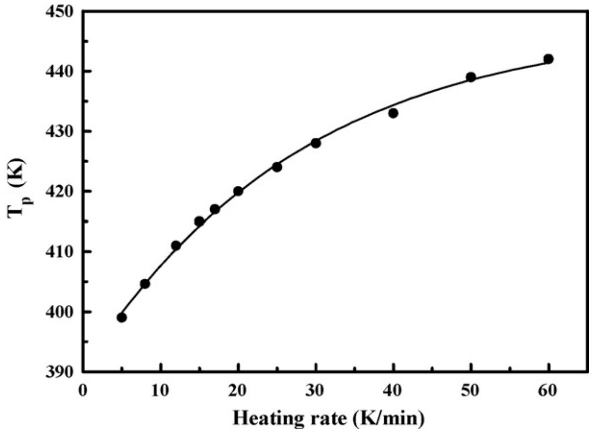

Fig. 3. The heating rate dependence of the crystallization peak temperature.

temperature below the glass transition temperature (T_g), the condition of site saturation could be fulfilled and hence we can assume $n = m$. Fig. 8 shows the variation of the effective activation energy with the heating rate showing a dramatic decrease in E as the heating rate increases from 5 to 40 K/min and then decreases slowly. A similar behavior was observed by [9]. The observed dependence of the effective activation energy on the heating rate can be attributed to the possible variation of E with temperature.

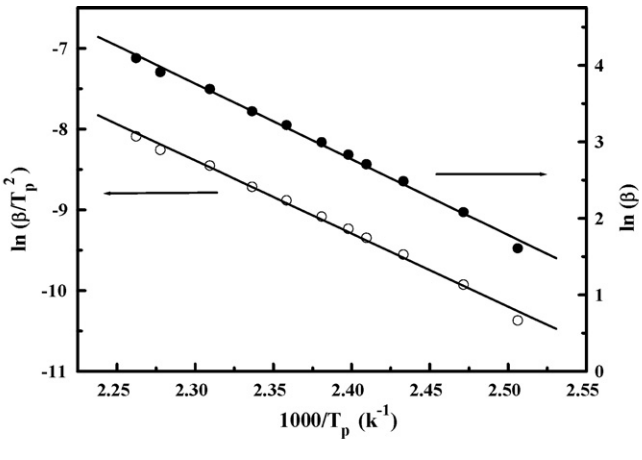

Fig. 4. $\ln(\beta/T_p^2)$ vs. $(1/T_\mathrm{p})$ plot (○), and $\ln(\beta)$ vs. $(1/T_\mathrm{p})$ plot (●) for $Se_{81.5}Te_{16}Sb_{2.5}$ chalcogenide glass.

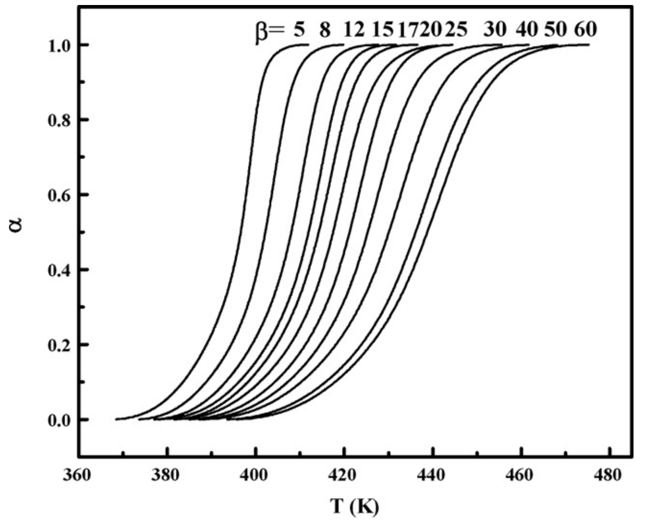

Fig. 5. Extent of crystallization, α, as a function of temperature at different heating rates.

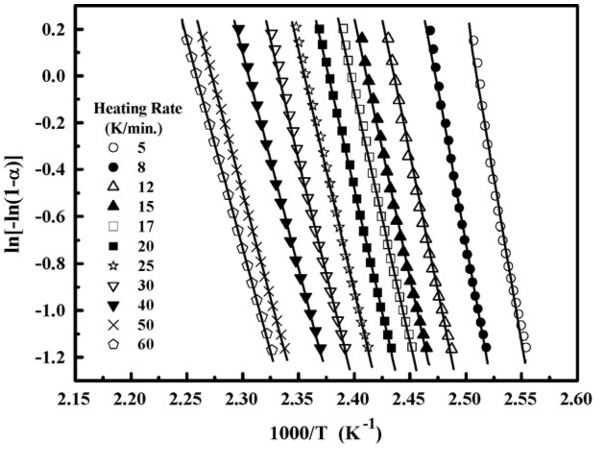

Fig. 6. $\ln[-\ln(1-\alpha)]$ vs. $1/T$ plots at different heating rates for the $Se_{81.5}Te_{16}Sb_{2.5}$ chalcogenide glass.

In order to investigate the variation of the activation energy with extent of conversion and hence with temperature, Vyazovkin, KAS, and Friedman isoconversional methods were used. Using the experimental data shown in Fig. 5, the three isoconversional methods are

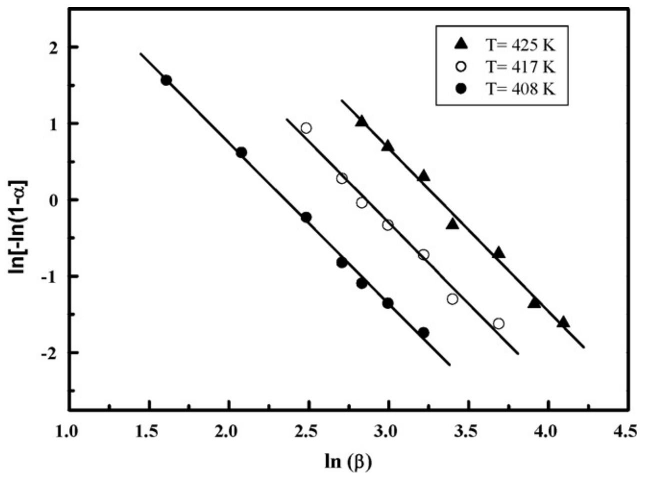

Fig. 7. $\ln[-\ln(1-\alpha)]$ vs. $\ln(\beta)$ plots at different temperatures for the $Se_{81.5}Te_{16}Sb_{2.5}$ chalcogenide glass.

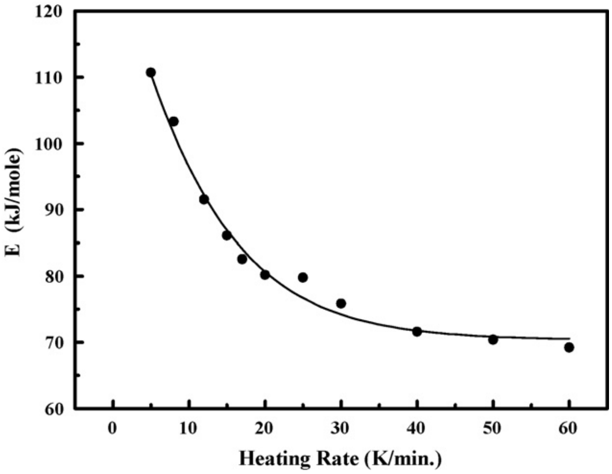

Fig. 8. Effective activation energy (E) as a function of heating rate for the $Se_{81.5}Te_{16}Sb_{2.5}$ chalcogenide glass.

used to evaluate the activation energies at different values of α. As shown in Fig. 9 a pronounced variation in the effective activation energy, E, as a function of the degree of conversion α is observed in the three methods. The temperature dependence of E can be extracted from Fig. 9 by replacing α with an average T using α versus T curve for the heating rate 20 K/min [19]. As indicated in Fig. 10, the three methods show a gradual decrease in E as the temperature increases. Vyazovkin and KAS methods give similar behavior of the dependence of E with temperature. However, a small difference in the values of the activation energies is observed (Fig. 10). In contrast to the Vyazovkin and KAS methods, Friedman method shows quite different behavior. A similar observation was reported for $Sb_{9.1}Te_{20.1}Se_{70.8}$ [16] glasses. It was also reported by Su et al. [37] that the activation energy calculated by KAS method at different α are higher than those obtained by Friedman method. It is possible that this disagreement is due to the fact that the systematic errors which arise from the numerical differentiation of the experimental data involved in Friedman method can lead to smaller values of E [38].

It is evident from the observed temperature dependence of the activation energy in the present system that the amorphous to crystalline transformation cannot be described by a single-step mechanism. The transformation demonstrates complex multi-step reactions involving several processes of growth with different activation energies and mechanisms. The observed decrease of the activation energy with temperature demonstrates that the rate constant of crystallization is in fact determined by the rates of two processes, nucleation and diffusion. Because these two mechanisms are likely to have different activation energies, the effective activation energy of the transformation will vary with temperature [12]. This interpretation is based on the nucleation theory proposed by Fisher and Turnbull [39]. According to this theory, the temperature dependence of the crystallization rate r is given by

$$r = r_0 \exp\left(\frac{-E_D}{k_B T}\right) \exp\left(\frac{-\Delta F}{k_B T}\right) \quad (13)$$

where r_0 is the pre-exponential factor, k_B is the Boltzmann constant, E_D is the activation energy for diffusion and ΔF is the maximum free energy necessary for nucleus formation.

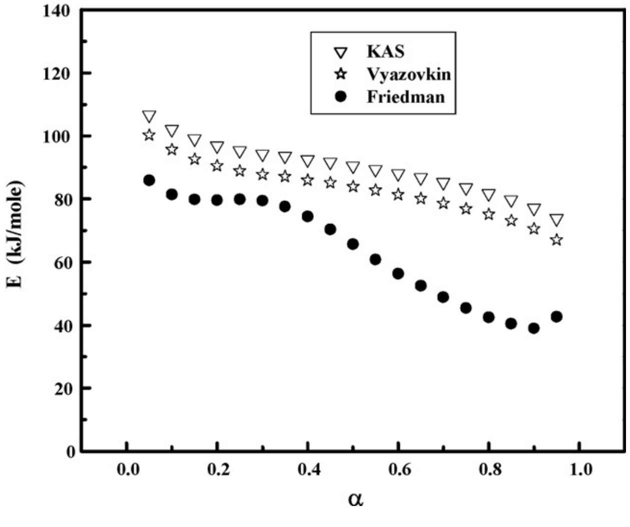

Fig. 9. The effective activation energy as a function of α as determined using different isoconversional methods.

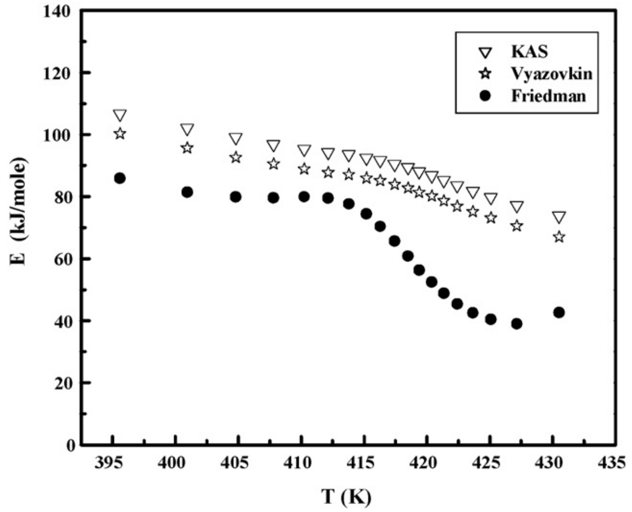

Fig. 10. The temperature dependence of the effective activation energy.

The simplified kinetic analysis in which the activation energy is assumed constant is not appropriate to describe the present data. The present findings also indicate that since the effective energy is not constant during the transformation, Matusita et al. model cannot be used to extract accurate values of the kinetic parameters E and n for the transformation.

5. Conclusions

The kinetics of transformation from amorphous to crystalline phase in $Se_{81.5}Te_{16}Sb_{2.5}$ is studied using DSC technique. The present findings showed the limitation of Kissinger and Mahedvan et al. methods in describing the kinetics of transformation as they both lead to a single activation energy for the whole crystallization process. The activation energy as determined from three isoconversional methods was found to vary with the extent of conversion and hence with temperature. All the three isoconversional methods showed that the activation energy decreases with temperature. The present work shows that the transformation from amorphous to crystalline phase in $Se_{81.5}Te_{16}Sb_{2.5}$ is a complex process involving different mechanisms of nucleation and growth.

References

[1] K. Tanaka, Y. Osaka, M. Sugi, S. Iizima, M. Kikuchi, J. Non-Cryst. Sol. 12 (1973) 100.
[2] E.R. Shaabam, Physica B 373 (2006) 211.
[3] Y. Sugiyama, R. Chiba, S. Fugimori, N. Funakoski, J. Non-Cryst. Sol. 122 (1990) 83.
[4] R. Chiba, N. Funakoshi, J. Non-Cryst. Sol. 105 (1988) 149.

[5] K. Weiser, R.J. Gambino, J.A. Reinhold, Appl. Phys. Lett. 22 (1973) 48.
[6] B.R. Brown, Appl. Opt. 13 (1974) 761.
[7] A.W. Smith, Appl. Opt. 13 (1974) 795.
[8] P. Agarwal, S. Goel, J.S.P. Rai, A. Kumar, Phys. Stat. Sol. (A) 127 (1991) 363.
[9] A.A. Abu-Sehly, A.A. Elabbar, Physica B 390 (2007) 196.
[10] N. Mehta, A. Kumar, J. Therm. Anal. Calorim. 83 (2006) 669.
[11] M. Mehdi, G. Brun, J.C. Tedenac, J. Mater. Sci. 30 (1995) 5259.
[12] S. Vyazovkin, New J. Chem. 24 (2000) 913.
[13] F. Liu, F. Sommer, C. Bos, E.J. Mittemeijer, Int. Mater. Rev. 53 (2007) 192.
[14] F. Liu, C. Yang, G. Yang, Y. Zhou, Acta Mater. 55 (2007) 5255.
[15] K. Matusita, T. Konatsu, R. Yokota, J. Mater. Sci. 19 (1984) 291.
[16] A.A. Joraid, Thermochim. Acta 436 (2005) 78.
[17] A.A. Joraid, Physica B 390 (2007) 263.
[18] M.J. Starink, Thermochim. Acta 404 (2003) 163.
[19] S. Vyazovkin, I. Dranca, Macromol. Chem. Phys. 207 (2006) 20.
[20] S. Vyazovkin, Int. Rev. Phys. Chem. 19 (2000) 45.
[21] S. Vyazovkin, Thermochim. Acta 397 (2003) 269.
[22] S. Vyazovkin, J. Comput. Chem. 22 (2001) 178.
[23] B. Jankovic, B. Adnadevic, J. Jovanovic, Thermochim. Acta 452 (2007) 106.
[24] B. Saha, A.K. Maiti, A.K. Ghoshal, Thermochim. Acta 444 (2006) 50.
[25] A. Khawam, D.R. Flanagan, Thermochim. Acta 436 (2005) 101.
[26] A.N. Kolmogorov, Bull. Acad. Sci. USSR. Phys. Ser. 3 (1937) 555.
[27] W.A. Johnson, P.A. Mehl, Trans. Am. Inst. Min. Metall. Eng. 135 (1939) 416.
[28] M. Avrami, J. Chem. Phys. 7 (1939) 1103.
[29] M. Avrami, J. Chem. Phys. 8 (1940) 212.
[30] M. Avrami, J. Chem. Phys. 9 (1941) 177.
[31] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[32] A.A. Abu-Sehly, Physica B 325 (2003) 372–379.
[33] S. Mahadevan, A. Giridhar, A.K. Singh, J. Non-Cryst. Sol. 81 (1986) 11.
[34] H.E. Kissinger, J. Res. Nat. Bureau Stand. 57 (1956) 217.
[35] T. Akahira, T. Sunose, Res. Rep. Chiba Inst. Technol. 16 (1971) 22.
[36] H.L. Friedman, J. Polym. Sci. C 6 (1963) 183.
[37] T. Su, H. Jiange, H.T. Sunose, Res. Rep. Chiba Inst. Technol. 16 (1971) 22.
[38] N. Sbirrazzuoli, Macromol. Chem. Phys. 208 (2007) 1592.
[39] J.C. Fisher, D. Turnbull, J. Chem. Phys. 17 (1949) 71.