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Study of the glass transition in amorphous Se by differential scanning calorimetry

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ABSTRACT

The activation energy (E) of the glass transition and the heating-rate dependence of the glass transition temperature (T_g) of Se glass were determined using differential scanning calorimetry (DSC) technique. Non-isothermal measurements were performed at different heating rates β (2–99 K/min). The heating-rate dependence of T_g was used to investigate the applicability of different theoretical models describing the glass transition. The application of Kissinger and Moynihan et al. models to the present data led to different values of E for different heating-rate regions. This behavior was attributed to the strong heating-rate dependence of the activation energy of the process. The activation energy of the glass transition was determined by analyzing the data using isoconversional methods: Kissinger–Akahira–Sunose (KAS), Friedman and Vyazovkin methods. A strong variation of the activation energy with the degree of transformation (α) was observed in the present sample indicating a complex transformation process of the glass transition.

1. Introduction

The nature of glass transition is a fundamental issue in the condensed matter physics [1,2]. In spite of extensive research devoted to understand the phenomenon of glass transition, there is no satisfactory description of this phenomenon and more work is needed to overcome this difficulty. The differential scanning calorimetry (DSC) technique is widely used to investigate the glass transformation in glassy materials. The kinetics of the glass transition as studied by the DSC method is important in investigating the nature the glass transformation process. The glass transition temperature, T_g, can be accurately determined by DSC measurements. Moreover, the kinetic aspect of the glass transition is evident from the strong dependence of T_g on the heating rate. This behavior can be used to identify different mechanisms involved in the transition process. One of the key kinetic parameters which can be determined by DSC measurements is the activation energy, E, of the glass transition. It has been assumed by many authors that E is constant during the glass transformation. To test this proposal, E was determined from the present measurements using different models. In particular, the isoconversional methods were used to evaluate the values of E at different stages of the transformation. In this study, the kinetics of the glass transition phenomenon in the amorphous Se chalcogenide is studied using DSC measurements. Pure selenium is the simplest glass-forming substance widely used for many practical applications. It is a major glass-forming component in many chalcogenide glasses and is an important material for opto-electronics [3,4]. It is well known that selenium consists of a wide variety cyclic molecules rings and chain polymers [5]. The objectives of this work are: (1) to investigate the effect of heating rate on the glass transition of the amorphous Se, (2) to investigate the variation of the activation energy of the glass transition and its dependence on extent of conversion and temperature and (3) to use the experimental data to test a number of theoretical models proposed to describe the glass transition.

2. Experimental

The Se chalcogenide glass was prepared using the standard melt–quench technique. High purity (99.999%) Se was sealed in a quartz ampoule (12 mm diameter) under a vacuum of 10^{-4} Torr. The content was heated at around 600 K for 24 h. The melt was quenched in ice to obtain the glassy state.

Thermal behavior was investigated using Shimadzu DSC-60 with sensitivity of $\pm 10\,\mu$W. The temperature accuracy is ± 0.1 K. Typically, 3 mg of sample in powder form was sealed in standard aluminum pans and heated at different heating rates 2–99 K/min under dry nitrogen supplied at the rate 50 ml/min. The starting temperature for all heating rates was 265 K. 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 were checked with indium at heating rate 10 K/min ($T_m = 156.6\,^\circ$C,

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$\Delta H_m = 28.55$ J/g) as standard material supplied by Shimadzu. We have checked this calibration at different heating rates. Only at heating rates higher than 40 K/min where small shift in temperature is detected. The procedure we followed in these measurements was to cool the samples with one cooling rate and then reheat with many heating rates.

3. Results and discussion

The DSC outputs showing the endothermic effect for Se chalcogenide glass obtained at different heating rates are shown in Fig. 1. In the inset of Fig. 1 the complete trace of the DSC thermogram at $\beta = 25$ K/min is shown. The transformation is characterized by two temperatures. The glass transition 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. As the output of the DSC during heating is proportional to the heat capacity, it is a straightforward and convenient method of detecting the glass transition and investigating its kinetics. For example, the heating-rate dependence of the glass transition temperature T_g can be used to determine the activation energy of the transition from glassy to liquid state [6,7]. In this work, the maximum point of the endothermic trace was used to define T_g. Other definitions for T_g were used by different workers. For instance, Moynihan et al. [6] used three different definitions of T_g that included the extrapolated onset, the inflection point and the maximum of the DSC output curve obtained on heating. Using these definitions of T_g the result of extracting the activation energy for three different glasses was found to be the same. The exothermic peak temperature T_p is used to identify the crystallization process. Both T_p and T_g shift to higher temperatures with increasing heating rate. The heating-rate dependence of T_g is clearly indicated in the main figure. The kinetic aspect of the glass transition is evident from the pronounced shift in T_g. It is worth observing that an order of magnitude increase in β causes a shift in T_g of 15 K.

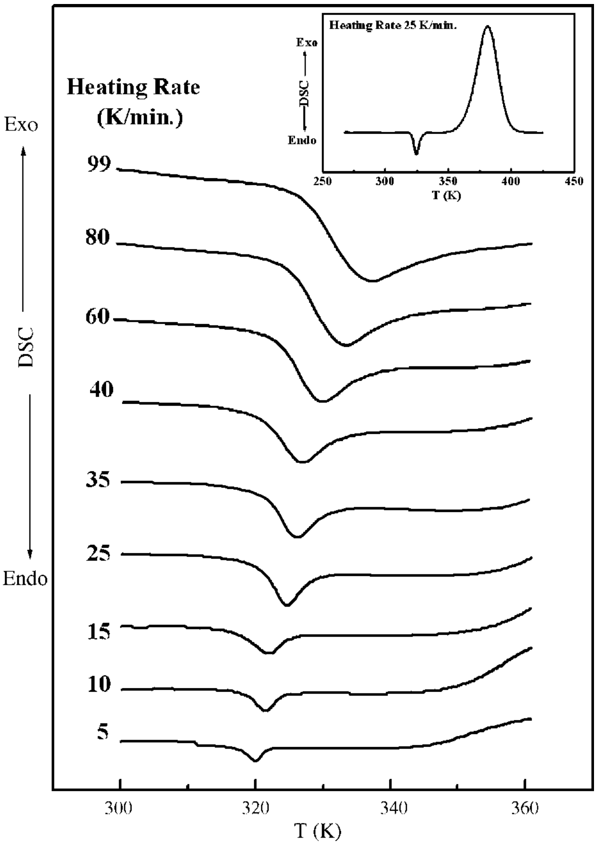

Fig. 1. DSC curves of the Se chalcogenide glass at different heating rates. Only endothermic outputs are shown in the main figure. In the inset the (endothermic) glass transition and (exothermic) crystallization effects for $\beta = 25$ K/min are shown.

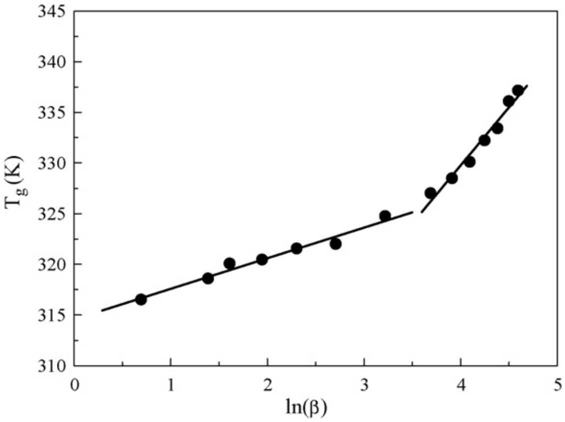

Fig. 2. The glass transition temperature T_g is plotted against $\ln\beta$. The solid lines represent fit to Eq. (1).

It has been widely observed that the dependence of the T_g on the heating-rate β follows Lasocka's relationship [8]:

$$T_g = a + b \ln\beta \tag{1}$$

where a and b are constants for a given glass composition. In order to see if Eq. (1) describes the heating-rate dependence of T_g, the T_g is plotted against $\ln\beta$ as shown in Fig. 2. As evident from this figure, the present data cannot be fitted to Eq. (1) for the whole range of β. The figure shows that the $T_g(\beta)$ behavior can be described by Eq. (1) for $\beta < 25$ K/min. In this range the values of the constants a and b are 314.6 K and 3.04 min, respectively. Above this heating rate, the least square fit to Eq. (1) gives $a = 283.9$ K and $b = 11.45$ min. As pointed out by Mehta et al. [9], the value of b is sensitive to the cooling rate of the melt. This behavior indicates that the physical significance of b is related to the nature of the structural relaxation within the glass transition region. The different values of b obtained in present work may be related to a change in the transformation processes involved in the glass transition.

Based on structural relaxation models, the heating and cooling rate dependence of the glass transition temperature was investigated by many authors [6,10–13]. Moynihan et al. [6] have shown that the dependence of the glass transition temperature T_g on heating-rate β is given to a high degree of approximation by

$$\frac{d \ln\beta}{d(1/T_g)} = -\frac{E}{R} \tag{2}$$

where E is the activation energy for the structural relaxation associated with the glass transition and R is the gas constant. According to this model, a plot of $\ln(\beta)$ versus $1/T_g$ gives a straight line. The activation energy for the glass transition can be determined from the slope. The conditions necessary for the validity of this relation are that the structural relaxation be describable by a temperature-independent distribution of relaxation times and that the glass be cooled from a starting temperature well above the transition region and subsequently reheated at the same rate starting from a temperature well below the transition region. In Fig. 3, $\ln(\beta)$ was plotted against $1/T_g$. At least two regions can be identified in the plot for which the data fits to Moynihan et al. model. This leads to two different values for the activation energy. In the low-β region, the activation energy for the glass transition is 272.9 kJ/mole and in the

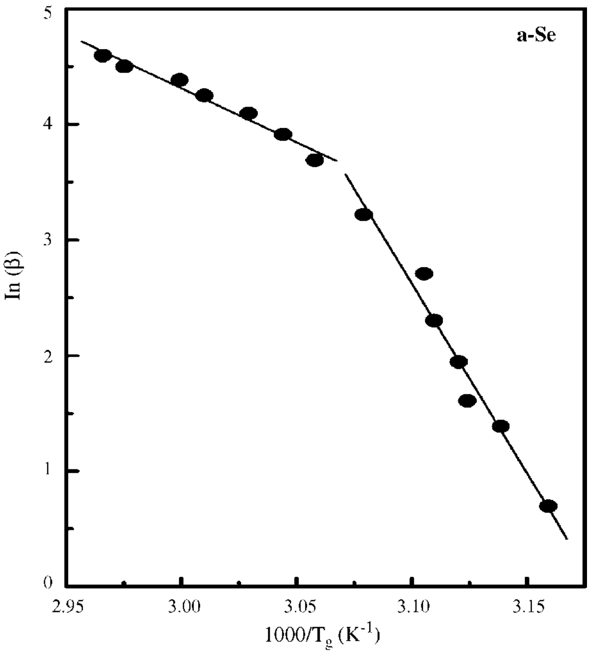

Fig. 3. ln(β) vs. 1/T_g. The straight lines are fit to Moynihan model (Eq. (2)).

high-β region the activation energy is 77.82 kJ/mole. This deviation from Moynihan et al. prediction shows that the glass transition process cannot be described by constant activation energy. As will be shown below this behavior is attributed to the rather strong heating-rate dependence of the activation energy in the present sample.

On the basis of the free volume model of glass transition, Ruitenberg [14] showed that the well-known Kissinger method for determining the activation energy for crystallization process can also be used to determine the glass activation energy. According to the Kissinger method, the glass activation energy can be obtained using the following equation:

$$\frac{\mathrm{d}\ln(\beta/T_g^2)}{\mathrm{d}(1/T_g)} = -\frac{E}{R} \tag{3}$$

A plot of $\ln(\beta/T_g^2)$ versus $1/T_g$ for the glass transition peak is shown in Fig. 4. It can be seen from this Kissinger plot that two regions are evident in the behavior of $\ln(\beta/T_g^2)$ versus $1/T_g$. The least square fitting of the data in the low-β and high-β regions gives E = 267.60 kJ/mole and E = 72.29 kJ/mole, respectively. It is worth mentioning that although Moynihan and Kissinger equations are based on different theoretical models, they both led to similar values of the activation energies in the low and high heating-rate regions. It should be mentioned here that the above analysis showed that even on the basis of Moynihan and Kissinger models, the process of glass transition cannot be described by single activation energy. A careful analysis of the data of Figs. 3 and 4 indicates that more than two heating-rate regions can be identified. As will be shown below this behavior was found to be a consequence of a strong heating-rate dependence of the activation energy. It is therefore tempting to investigate the dependence of the glass transition activation energy on the heating rates using the Matusita et al. method [15] that normally applied to non-isothermal amorphous to crystalline transformation. According to Matusita et al. method, the extent of transformation α is related to the effective activation energy for the glass transformation E through the following expression

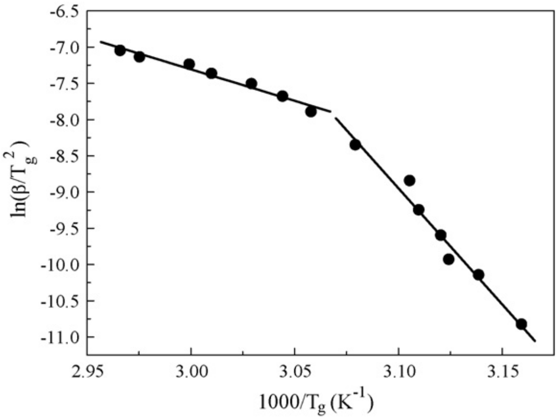

Fig. 4. A plot of $\ln(\beta/T_g^2)$ vs. $1/T_g$. The straight lines are fit to Kissinger equation.

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

where m and n are numerical factors depending on the transformation process. In order to investigate the heating-rate dependence of the kinetic parameters, n and E we analyzed the data using Matusita model. Fig. 5 shows the extent of transformation 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). 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. This heating-rate dependence of mE is presented in Fig. 7. It is evident from this figure that if m is assumed to be constant, the activation energy for glass transition strongly depends on the heating rate. The parameter n can also be determined using Matusita Eq. (4) by plotting $\ln[-\ln(1-\alpha)]$ against $\ln(\beta)$ at different temperatures, as shown in Fig. 8. The slope of each line gives the value of n. Different values for n was obtained at different temperature. This temperature dependence of n is shown in Fig. 9.

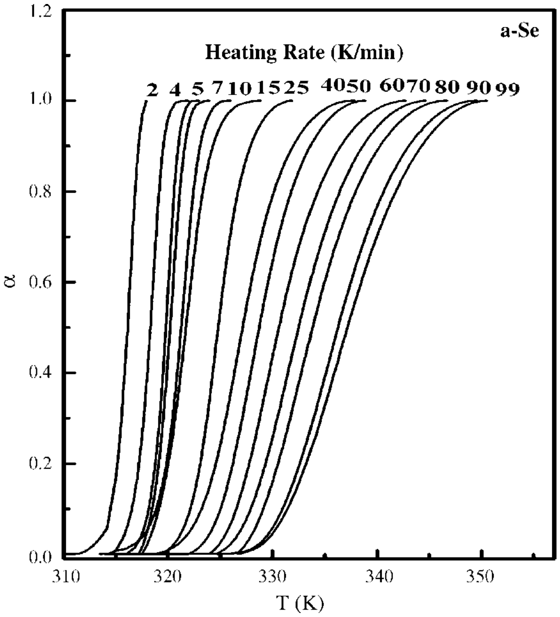

Fig. 5. Degree of transformation α as a function of temperature at different heating rates.

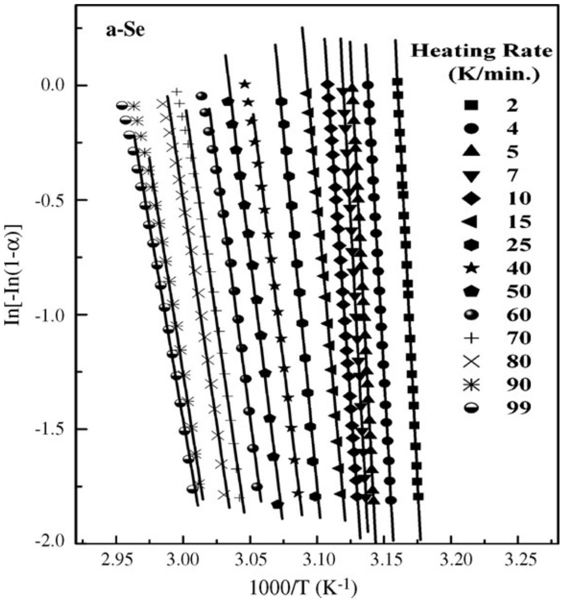

Fig. 6. $\ln[-\ln(1-\alpha)]$ vs. $1/T$ plots at different heating rates for the Se chalcogenide glass.

The observed dependence of the effective activation energy on the heating rate can be attributed to the possible variation of E with temperature. Isoconversional methods were used to investigate the variation of the effective activation energy with extent of transformation and hence with temperature. Using the experimental data shown in Fig. 5, three isoconversional methods are used to investigate this variation.

- On the basis of the Kissinger–Akahira–Sunose (KAS) method [16–18] (or the generalized Kissinger method as it is sometimes called), the E_α can be determined for each α using the following

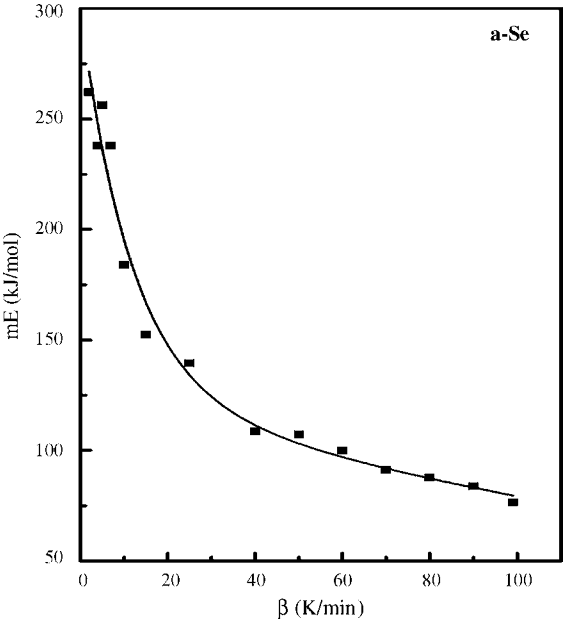

Fig. 7. mE as a function of heating rate for the Se chalcogenide glass.

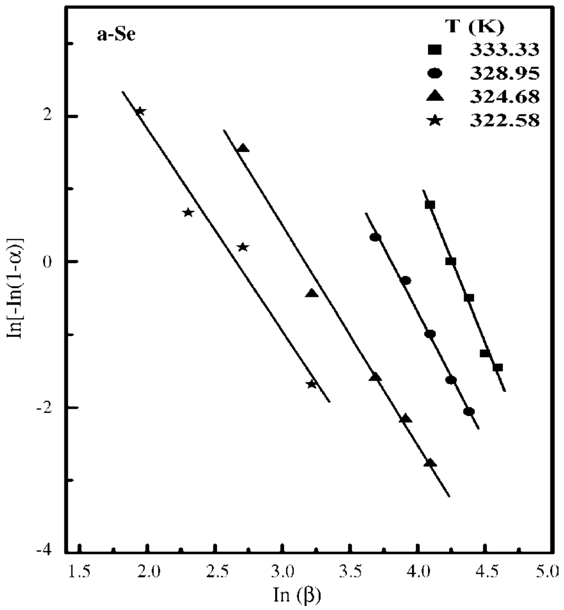

Fig. 8. $\ln[-\ln(1-\alpha)]$ vs. $\ln(\beta)$ at different temperatures for the Se chalcogenide glass.

expression:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{Constant} - \frac{E_\alpha}{RT_{\alpha,i}} \tag{5}$$

- For various heating rates, β_i, the Friedman method [19] can be used at a specific transformation fraction, α, as

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \text{Constant} - \frac{E_\alpha}{RT_{\alpha,i}} \tag{6}$$

- The third method is based on the advanced isoconversional method developed by Vyazovkin [20]. 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

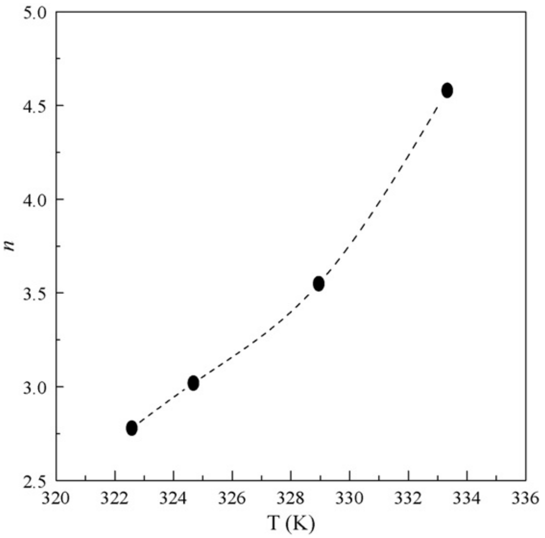

Fig. 9. Variation of the exponent n with temperature.

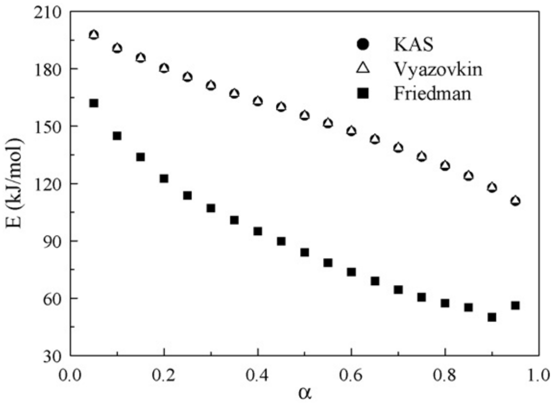

Fig. 10. The glass activation energy as a function of α as determined using different isoconversional methods.

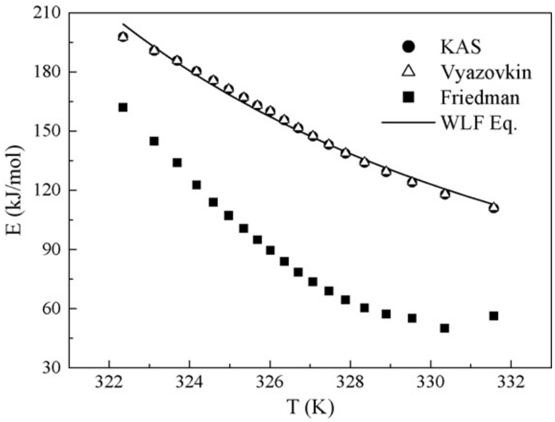

Fig. 11. Variation of the glass activation energy with temperature. Full line is the fit to WLF equation.

minimized where:

$$\Omega = \sum_{i=1}^{n}\sum_{j\neq i}^{n} \frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i} \tag{7}$$

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

$$I(E,\ T) = \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} \exp\left(\frac{-E}{RT}\right) \mathrm{d}T \tag{8}$$

The integral $I(E, T)$ was numerically evaluated using trapezoidal method. The activation energy E_α is the value that minimizes Ω in Eq. (7) for a particular α.

Fig. 10 shows the variation of the glass activation energy, E, as a function of the degree of conversion α according to the above three isoconversional methods. The temperature dependence of E can be extracted from Fig. 10 by replacing α with an average T using α versus T curve for the heating rate 50 K/min (from Fig. 5) [21]. All methods show a variation in E with α. KAS and Vyazovkin methods agree very well while the decrease of E with α according to Friedman method is more pronounced. This close agreement between KAS and Vyazovkin isoconversional methods was also reported by Joraid [22], Elabbar et al. [23] and Jankovic et al. [24]. These authors also found that Friedman method led to substantially different values of E compared to KAS and Vyazovkin isoconversional methods. It is possible that this disagreement between Friedman method and KAS and Vyazovkin maybe attributed to the systematic errors which arise from the numerical differentiation of the experimental data involved in Friedman method [20,25].

The observed decrease of the activation energy with increasing temperature is consistent with prediction of the free volume model of the glass transition. According to this model, the activation energy of the process E depends on the amount of the free volume in the sample. More free volume is related to lower activation energy. The amount of the free volume is assumed to vary linearly with temperature according to the following equation:

$$f = f_0 + a(T - T_0) \tag{9}$$

where f is the free volume fraction, f_0 is a free volume fraction at a reference temperature T_0 and a is a constant. Based on this free volume model, it can be shown that the temperature dependence of the activation energy of the glass transformation is given by the Williams–Landel–Ferry (WLF) equation [26]

$$E = 2.303\,R \frac{c_1 c_2 T^2}{(c_2 + T - T_0)^2} \tag{10}$$

where c_1 and c_2 are constants. The solid line in Fig. 11 is obtained from non-linear regression analysis of Eq. (10) with KAS $E(T)$ data using c_1 and c_2 as adjustable parameters. Using $T_0 = 320$ K as a reference temperature, the values of c_1 and c_2 obtained from the best fit are 2.7 and 22, respectively. These values are substantially different from the universal values ($c_1 = 17.44$ and $c_2 = 51.6$) normally assigned to these constants. With the universal values of c_1 and c_2, the temperature dependence of the activation energy was badly predicted. Sopade et al. [27] reported different values of c_1 and c_2 in their investigation for the applicability of the WLF model. It is evident from Fig. 11 that the WLF model can account for the variation of the activation energy with temperature as obtained using KAS and Vyazovkin methods [28].

The observed temperature dependence of the activation energy in the present system shows that the glass transition cannot be described by a single step mechanism. The glass transition demonstrates complex multi-step reactions involving relaxational processes with different activation energies and mechanisms. The simplified analysis in which the activation energy is assumed constant is not appropriate to describe the present data.

4. Conclusions

Investigation of heating-rate dependence of the glass transition temperature in Se chalcogenide glass was carried out using DSC technique. The observed dependence was discussed in terms of different theoretical models describing glass transition. It was shown in this work that the transition process cannot be described in terms of single activation energy. Three different isoconversional methods were used to calculate the effective activation energy of the glass transition in Se chalcogenide glass. The activation energy was found to vary with extent of conversion (and with temperature), which explains the observed strong heating-rate dependence of the activation energy. The present work shows that the assumption that the glass activation energy does not vary during the glass transition process is not valid. The transformation from amorphous to supercooled liquid phase in Se is a complex process involving different mechanisms of transformation.

References

[1] S.R. Elliott, Physics of Amorphous Materials, 2nd edition, Longman Scientific & Technical, Essex, UK, 1990.
[2] G.W. Scherer, Relaxation in Glasses and Composites, John Wiley and Sons Inc., New York, 1986.
[3] E. Gerlach, P. Grosse (Eds.), The Physics of Selenium and Tellurium, Springer, Berlin/New York, 1979.
[4] S.G. Bishop, U. Strom, P.C. Taylor, Phys. Rev. Lett. 34 (1975) 1346.
[5] J. Donohue, The Structure of the Elements, Wiley, New York, 1974.
[6] C.T. Moynihan, A.J. Easteal, J. Wilder, J. Tucker, J. Phys. Chem. 78 (1974) 2673.
[7] S. Vyazovkin, N. Sbirrazzuoli, I. Dranca, Macromol. Rapid Commun. 25 (2004) 1708.
[8] M. Lasocka, Mater. Sci. 23 (1976) 173.
[9] N. Mehta, R.K. Shukla, A. Kumar, Chalcogenide Lett. 1 (2004) 131.
[10] H. Ritland, J. Am. Ceram. Soc. 39 (1956) 403.
[11] I. Avramov, Thermochim. Acta 280 (1996) 363.
[12] I. Avramov, N. Avramova, J. Non-Cryst. Solids 260 (1999) 15.
[13] Y. Yue, J. Chem. Phys. 120 (2004) 8053.
[14] G. Ruitenberg, Thermochim. Acta 404 (2003) 207.
[15] K. Matusita, T. Konatsu, R. Yokota, J. Mater. Sci. 19 (1984) 291.
[16] H.E. Kissinger, J. Res. Nat. Bur. Stand. 57 (1956) 217.
[17] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[18] T. Akahira, T. Sunose, Res. Rep. Chiba Inst. Technol. 16 (1971) 22.
[19] H.L. Friedman, J. Polym. Sci. C 6 (1964) 183.
[20] S. Vyazovkin, J. Comput. Chem. 22 (2001) 178.
[21] S. Vyazovkin, I. Dranca, Macromol. Chem. Phys. 207 (2006) 20.
[22] A.A. Joraid, Thermochim. Acta 456 (2007) 1.
[23] A.A. Elabbar, M. Abu El-Oyoun, A.A. Abu-Sehly, S.N. Alamri, J. Phys. Chem. Solids, submitted for publication.
[24] B. Jankovic, B. Adnadevic, J. Jovanovic, Thermochim. Acta 452 (2007) 106.
[25] N. Sbirrazzuoli, Macromol. Chem. Phys. 208 (2007) 1592.
[26] M.L. Williams, R.F. Landel, J.D. Ferry, J. Am. Chem. Soc. 77 (1955) 3701.
[27] P.A. Sopade, P. Halley, B. Bhandari, B. D'Arcy, C. Doebler, N. Caffin, J. Food Eng. 56 (2002) 67.
[28] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Rapid Commun. 27 (2006) 1515.