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Differential scanning calorimetric study of $Bi_{10}Se_{80}In_{10}$ chalcogenide glass

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Results of differential scanning calorimetry under isothermal and non-isothermal conditions on $Bi_{10}Se_{80}In_{10}$ glass are reported and discussed. By using the Johnson–Mehl–Avrami equation the activation energies for crystal growth have been evaluated and the crystallization mechanism has been studied. The results indicate that the crystallization process is a two-dimensional growth. The average calculated value of activation energy is 330.2 kJ mol^{-1} for $Bi_{10}Se_{80}In_{10}$ chalcogenide.

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 applicable for devices such as electrical switches and/or memories [1], image storage [2] and photoresist [3]. It was generally accepted that most of the chalcogenide glasses show p-type conduction and that their electrical conductivity is only very slightly affected by doping. This insensitivity to impurities is due to the presence of charged defects which pin the Fermi level near the mid-bandgab [4, 5]. Tohge *et al.* [6, 7] were the first to point out the role of Bi in the appearance of n-type conduction in chalcogenide glasses. Structural studies of these materials are very important for a better understanding of their transport mechanisms [8–12]. Different techniques have been used to study the crystallization of chalcogenide glasses, e.g. electrical resistivity [13, 14], electron microscopy [15], X-ray diffraction [16] and scanning calorimetry [12].

Studies of the crystallization of a glass upon heating can be performed in several different ways. In calorimetric 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 isothermal crystallization data are usually interpreted in terms of the Johnson–Mehl–Avrami transformation equation [17–20].

The present work was concerned with the study of the crystallization kinetics for $Bi_{10}Se_{80}In_{10}$ chalcogenide glass and the evaluation of the activation energy for crystal growth by using the isothermal and non-isothermal techniques.

2. Theoretical

The theoretical basis for interpreting differential scanning calorimetry (DSC) data is provided by the formal theory of transformation kinetics as developed by Johnson and Mehl [21] and Avrami [22–24]. A similar approach was also adopted by Kolomogoroff [25] and by Erofeev and Mitzkevich [26]. By using the Johnson–Mehl–Avrami equation [17], the volume fraction, X, crystallized in time t can be written as

$$X = 1 - \exp[-(Kt^n)] \tag{1}$$

where n is an integer or half-integer which depends on the mechanism of growth and the dimensionality of the growing crystals [17, 27]. K is defined as the effective overall reaction rate, which is usually assigned an Arrhenian temperature dependence

$$K = K_0 \exp(-E/RT) \tag{2}$$

where E is the effective activation energy describing the overall crystallization process, R is the universal gas constant and T is the absolute temperature.

The overall effective activation energy for crystallization, E, is expressed as

$$E = (E_N + mE_G)/n \tag{3}$$

where E_N and E_G are the effective activation energies for nucleation and growth, respectively. When the nucleation frequency, I_v, [28] is equal to zero [5] $n = m$ whereas $n = m + 1$ for $I_v \neq 0$ [17].

If the nucleation frequency is negligible over the temperature range of concern in the thermo-analytical study [17], then

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

2.1. The Piloyan–Borchardt method

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

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

where T_0 is the initial temperature. Differentiating

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Equation 1 gives

$$\dot{X} = (1 - X)nK^n t^{n-1}[1 + (t/K)\dot{K}] \qquad (6)$$

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

$$\dot{K} = \frac{\mathrm{d}K}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{\alpha EK}{RT^2} \qquad (7)$$

Thus Equation 6 becomes

$$\dot{X} = (1 - X)nK^n t^{n-1}(1 + at) \qquad (8)$$

where $a = \alpha E/RT^2$.

In the Piloyan–Borchardt method [29, 30] the term at was neglected with respect to unity, assuming that $E/RT \ll 1$. This assumption can cause a large error because, for most crystallization reactions, E/RT is greater than unity ($E/RT \approx 10$ typically). A better approach seems reasonable if T_0 in Equation 5 is much smaller than T. The term $at \approx E/RT$, and Equation 8 becomes

$$\dot{X} = (1 - X)nK^n t^{n-1}E/RT \qquad (9)$$

Combining this equation with the concept stated by Borchardt [30] that, at least for $X < 0.5$, the reaction rate, $\dot{X}$, at a particular temperature T is proportional to the heat flow difference between the sample and inert reference, Δq, for DSC

$$\dot{X} = C\Delta q \qquad (10)$$

In proceeding further, the following operations are performed: expressing t in terms of X from Equation 1; substituting for t in Equation 9; combining Equations 2, 9 and 10; and taking the logarithm and rearranging the resulting expression to give

$$\ln[T\Delta q)/F(X)] = \ln(nK_0/C) + \ln(E/R) - E/RT \qquad (11)$$

The function $F(X)$ is defined as

$$F(X) = (1 - X)[-\ln(1 - X)]^{n-1/n} \qquad (12)$$

A linear relationship should be obtained when $\ln[(T\Delta q)]$ is plotted as a function of $1/T$. However, for $0.25 \leqslant X \leqslant 0.75$ the function $F(X)$ may be considered constant [30]. The slope of this relationship yields the activation energy of crystal growth, E, if the assumptions of the analysis are valid.

3. Experimental procedure

High-purity (99.999%) Se, Bi and In (from Aldrich Co., UK) in appropriate atomic percentage proportions were weighed into a quartz glass ampoule (12 mm in diameter). The contents of the ampoule (15 g total) were sealed in a vacuum of 13.3 mPa (about 0.01 $\mathrm{N\,m^{-2}}$) and heated in a rotary furnace at around 825 K for 24 h. The ampoule with liquid was quenched in an ice–water mixture. The amorphous nature of the as-prepared samples was confirmed by X-ray diffraction, using a Philips 1710 diffractometer with Ni-filtered CuK_α radiation ($\lambda = 0.154$ nm).

The thermal behaviour was investigated using a Du Pont 1090 DSC. The temperature and energy calibrations of the instrument were performed using the well-known melting temperature and melting enthalpy of high-purity indium supplied with the instrument. The calorimetric sensitivity was 10 $\mu\mathrm{W\,cm^{-1}}$ and the temperature precision was ± 0.1 K.

The DSC thermogram measurements were carried out typically by using 20 mg sample in powdered form sealed in standard aluminium pans. The isothermal thermograms were carried out by heating the samples to 50 K below the required temperature, holding at this temperature for about 30 s and then heating at a rate of 100 $\mathrm{K\,min^{-1}}$ to the annealing temperature. This process was used to minimize the non-stationary effects caused by the thermal delay in the DSC calorimeter [31]. Isothermal curves were recorded at temperatures ranging from 354.3 to 363.3 K.

The values of the glass transition, T_g, the crystallization onset, T_c, and the crystallization peak, T_p, temperatures [12] were determined to an accuracy of ± 0.1 K by using the microprocessor of the thermal analyser.

Under isothermal conditions the fraction, X, crystallized at any time t (or temperature T in the non-isothermal experiment) is given as $X = (A_t/A)$ (or A_T/A for non-isothermal), where A is the total area of the exotherm between the time t_i (or temperature T_i) at which crystallization just begins and the time t_f (or temperature T_f) at which the crystallization is completed. A_t (or A_T) is the area between t_i (or T_i) and t [12, 31].

A best fit for the results was calculated by the least-squares method. The arithmetic mean as well as the standard deviation were used in the experimental results.

4. Results

A typical DSC trace of the $\mathrm{Bi_{10}Se_{80}In_{10}}$ glass obtained at a heating rate of 20 $\mathrm{K\,min^{-1}}$ is shown in Fig. 1. In the figure three characteristic phenomena are clear in the temperature region studied. The first one ($T = 320$ K) corresponds to the glass transition temperature, T_g, the second ($T = 379$ K) to the onset crystallization at temperature, T_c, and the last

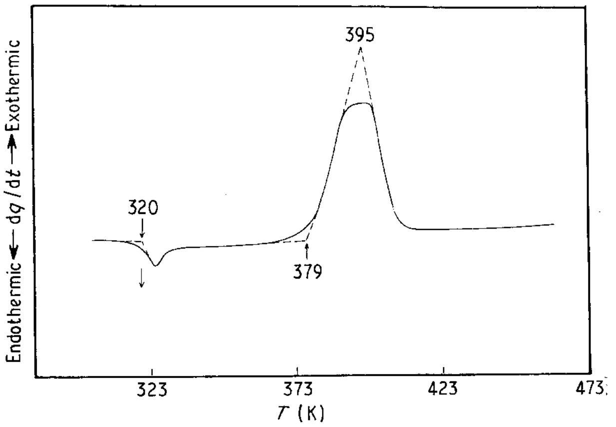

Figure 1 Typical DSC traces at a heating rate of 20 $\mathrm{K\,min^{-1}}$ for $\mathrm{Bi_{10}Se_{80}In_{10}}$ chalcogenide glass.

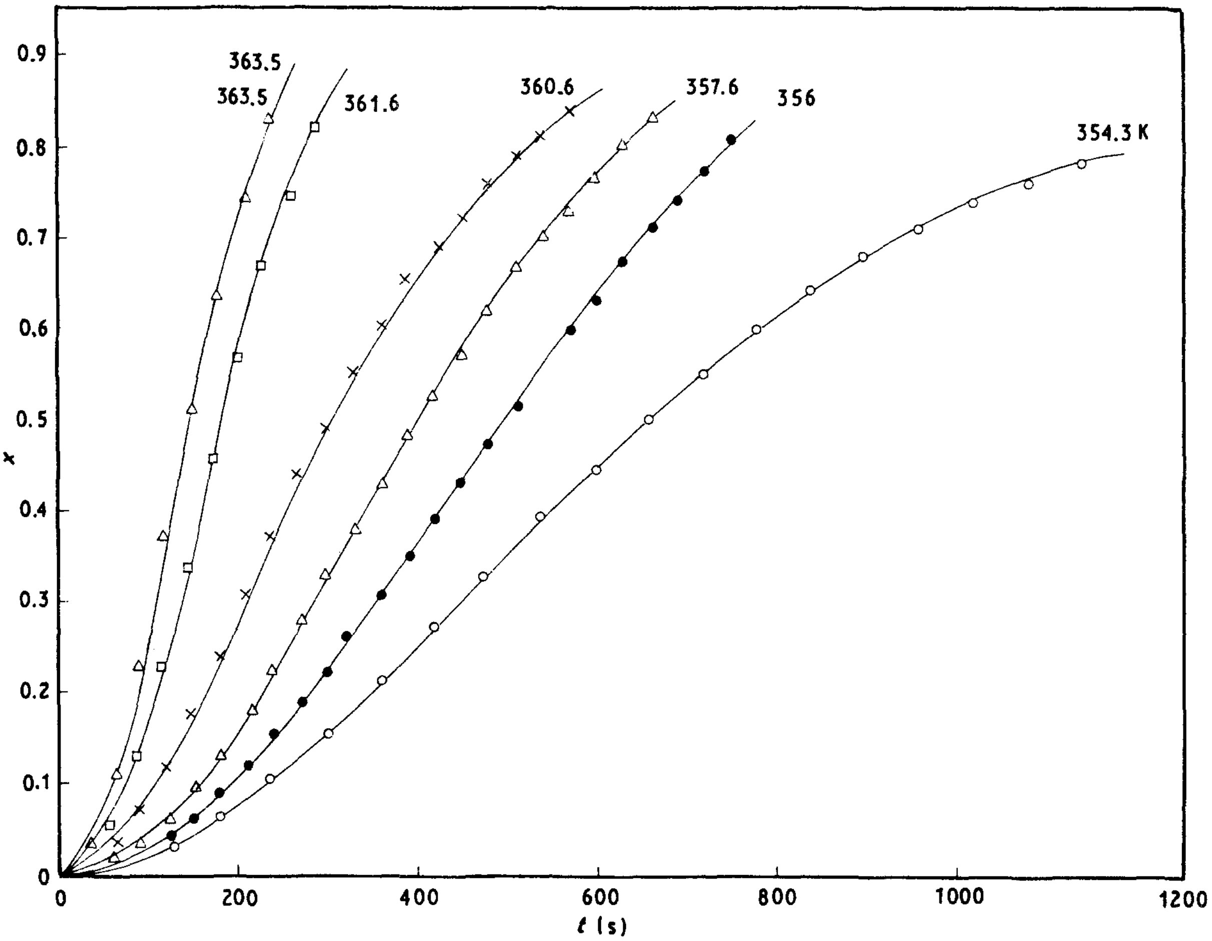

Figure 2 Fraction crystallized, X, versus time for $Bi_{10}Se_{80}In_{10}$ chalcogenide glass.

($T = 395$ K) to the peak of crystallization, T_p, of $Bi_{10}Se_{80}In_{10}$ glass.

The isothermal study was performed at a temperature between the glass transition temperature and the onset temperature (from 354.3 to 363.3 K). Using partial peak area analysis of the isothermal DSC traces taken at different temperatures [31], the fraction of the crystallized material, X, as a function of time, t, at different temperatures was plotted in Fig. 2.

5. Discussion

5.1. The isothermal method

Under isothermal conditions the relationship between the fraction crystallized, X, and the nucleation and the growth rates is obtained by Equation 1. Taking logarithms and rearranging Equation 1 gives

$$\ln[-\ln(1-X)] = \ln K + n \ln t \qquad (13)$$

A plot of $\ln[-\ln(1-X)]$ as a function of $\ln t$, as shown in Fig. 3, will yield the values of n and K. This relationship is found to be linear over most of the time range. At high values of t or for large crystallization fractions a deviation from linearity was observed for all isothermal curves. A similar behaviour was reported for other chalcogenide glasses [12, 26, 32], oxide glass [33] and metallic glasses [34, 35]. Generally, this deviation from the initial slope is attributed to the saturation of nucleation sites in the final stages of crystallization [32, 34] or to restriction of crystal growth by the small size of the particles [36]. In all of

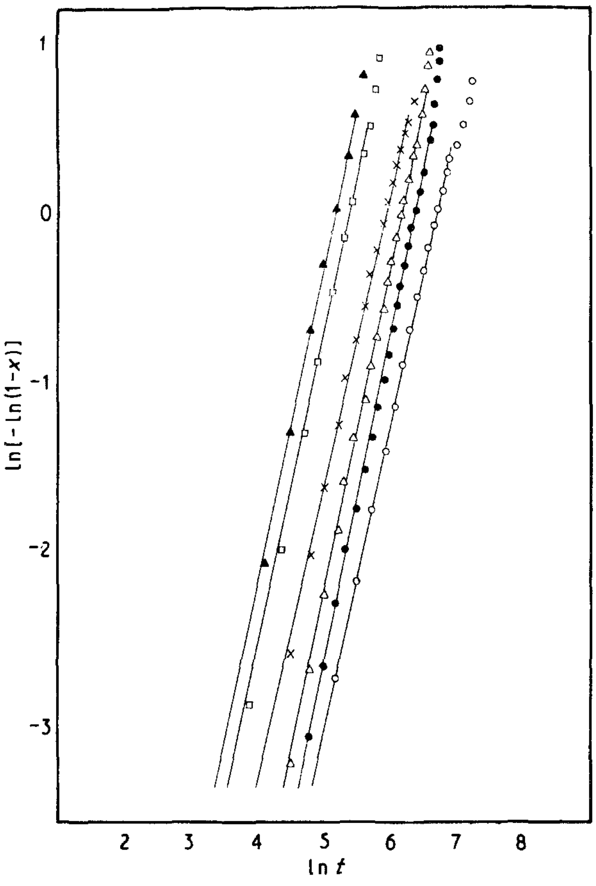

Figure 3 $\ln[-\ln(1-X)]$ versus $\ln t$ for $Bi_{10}Se_{80}In_{10}$ chalcogenide glass: (○) 354.3, (●) 356, (△) 357.6, (×) 360.6, (□) 361.6 and (▲) 363.5 K.

TABLE I Values of n and m for various crystallization mechanisms [12, 18]

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

these cases analysis is confined to the initial linear region, which extends over a larger range [12].

The average deduced value of n is 1.94 ± 0.33 for our $Bi_{10}Se_{80}In_{10}$ glass. This means that, according to Yinnon and Uhlman [17], Mahadevan *et al.* [12] and Matusita and Sakka [27], crystallization for this glass is two-dimensional growth (notice that the values of n and m correspond to the different crystallization mechanisms for $I_v = 0$ in Table I).

To calculate the activation energy, Equation 2 can be written in the form

$$\ln K = \ln K_0 - E/RT \tag{14}$$

Values of $\ln K$ were determined for successive temperatures from Fig. 3. A plot of $\ln K$ as a function of $1/T$ (Fig. 4) yields the activation energy of crystallization. According to Equation 4 the calculated activation energy is equal to the effective activation energy of crystal growth, E_g. The obtained activation energy of crystal growth was $332.4 \pm 0.2\ \mathrm{kJ\,mol^{-1}}$ for our $Bi_{10}Se_{80}In_{10}$ glass.

From the isothermal DSC traces the activation energy of crystallization, E, can be determined according to Marseglia [37]. By rearranging Equation 1 for $X = 1/2$ and taking logarithms, an expression for $t_{1/2}$ is obtained

$$X(1/2) = 1 - \exp(-Kt_{1/2}^{n}) \tag{15a}$$

$$\ln t_{1/2} = (1/n)[\ln(\ln 2) - \ln \mathrm{K}] \tag{15b}$$

from the expression

$$\mathrm{d}(t_{1/2})/\mathrm{d}(1/T) = E/nk \tag{16}$$

A plot of $\ln t_{1/2}$ as a function of $1/T$ will give the activation energy, E. With the isothermal hold method, the plot of $\ln t$ as a function of $1/T$ at $X = 1/2$ is shown in Fig. 5.

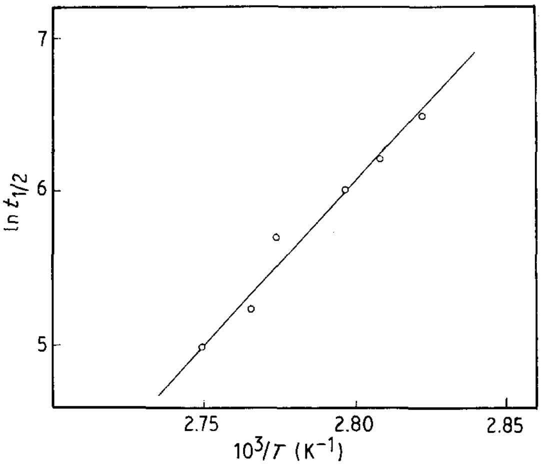

Figure 5 ln $t_{1/2}$ versus $1000/T$ for $Bi_{10}Se_{80}In_{10}$ chalcogenide glass.

The data are well fitted by a straight line and the calculated value of the activation energy is $E = 336.33 \pm 0.29\ \mathrm{kJ\,mol^{-1}}$.

5.2. The non-isothermal method

The non-isothermal study was carried out at a heating rate of $20\ \mathrm{K\,min^{-1}}$. A plot of $\ln(T\Delta q)$ versus $(1/T)$ is shown in Fig. 6. It is clear that the $\ln(T\Delta q)$ versus $1/T$ relationship is linear in the range $0.2 < X < 0.5$ and satisfies the conditions suggested by Borchardt [30]. From Equation 11 the slope yields the activation energy of crystal growth ($322 \pm 0.3\ \mathrm{kJ\,mol^{-1}}$).

From this study it is clear that both the isothermal and non-isothermal methods can be used to study the crystallization kinetics and to evaluate the crystallization activation energy for this glass.

6. Conclusion

The activation energies of crystal growth, E, for $Bi_{10}Se_{80}In_{10}$ chalcogenide glass obtained from the Johnson–Mehl–Avrami kinetic equation of the fraction crystallized under isothermal and non-isothermal

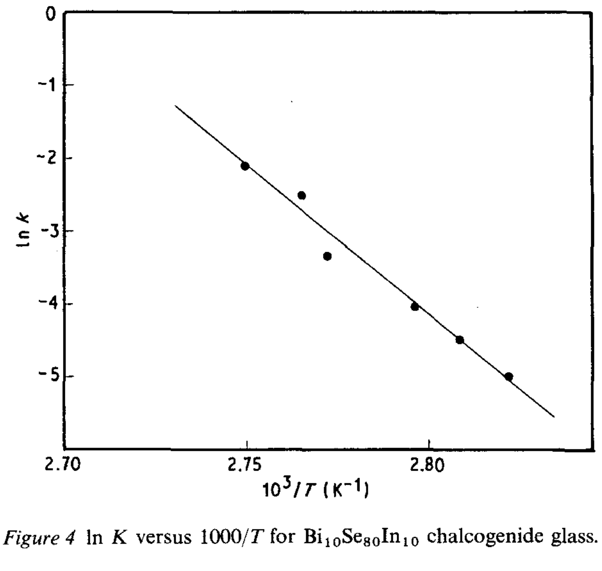

Figure 4 ln K versus $1000/T$ for $Bi_{10}Se_{80}In_{10}$ chalcogenide glass.

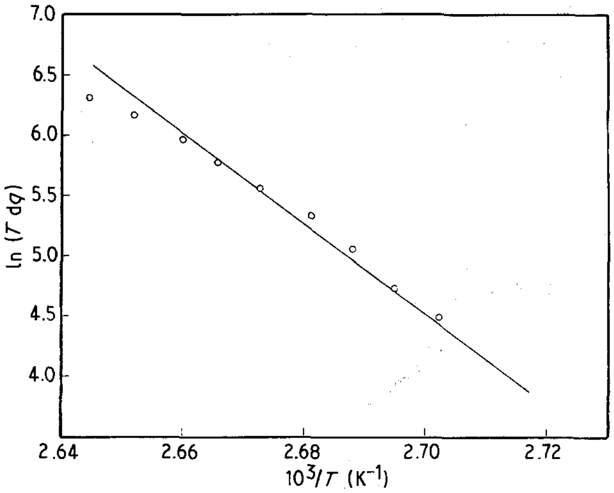

Figure 6 $\ln[(T\Delta q)]$ versus $1000/T$ at a heating rate of $20\ \mathrm{K\,min^{-1}}$ for $Bi_{10}Se_{80}In_{10}$ chalcogenide glass.

conditions are 332.4, 336.33 and 322 kJ mol^{-1}, respectively. The crystallization mechanism for $Bi_{10}Se_{80}In_{10}$ chalcogenide glass is two-dimensional growth.

This result means that both methods (isothermal and non-isothermal) are suitable for studying the crystallization kinetics and the activation energy for $Bi_{10}Se_{80}In_{10}$ chalcogenide glass.

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