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ISOTHERMAL CRYSTALLIZATION KINETICS OF THE CHALCOGENIDE GLASS $Bi_{10}Se_{70}In_{20}$

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Results of DSC under isothermal conditions on the chalcogenide glass $Bi_{10}Se_{70}In_{20}$ are reported and discussed. The Johnson-Mehl-Avrami equation was used to evaluate the crystallization activation energy (E_a) and the crystallization mechanism was studied. The results indicate that the crystallization mechanism involves one dimensional and surface processes for $Bi_{10}Se_{70}In_{20}$. The average calculated value of E_a for $Bi_{10}Se_{70}In_{20}$ is 34.38 ±1.46 kcal/mol.

Studies of kinetics are always connected with the concept of activation energy. The value of this in glass crystallization phenomena is associated with the nucleation and growth process that dominate the devitrification of most glassy solids. In general, separate activation energies must be identified with the individual nucleation and growth steps in a transformation, although they are usually combined into an activation energy representative of the overall crystallization process [1-4]. 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 crystallization process can be interpreted in terms of several theoretical models. The isothermal crystallization data are usually interpreted in terms of the Johnson-Mehl-Avrami transformation equation [4-7].

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The present work is concerned with a study of the crystallization kinetics and the evaluation of the activation energies for the chalcogenide glass $Bi_{10}Se_{70}In_{20}$ by using the isothermal method.

Experimental methods

High-purity (99.999%) Se, Bi and In (from Aldrich Co., UK) in appropriate at.% proportions were weighed into a quartz ampoule (12 mm diameter). The contents of the ampoule (15 g total) were sealed at 10^{-4} Torr and heated in a rotary furnace at around 550° for 24 hours. The melt was quenched in water at 0° to obtain the glasses.

The thermal behaviour was investigated by using a DuPont 1090 differential scanning calorimeter. The temperature and energy calibrations of the instrument were performed by using the well-known melting temperature and melting enthalpy of high-purity indium supplied with the instrument. The DSC curves were recorded by using typically 20 mg of sample in powdered form, sealed in standard aluminium pans.

The isothermal curves were recorded by heating the samples to 50 deg below the required temperature, holding them at this temperature for about 30 s and then heating them at a rate of 100 deg/min to the annealing temperature. This process was used to minimize the non-stationary effects caused by the thermal delay in the DSC calorimeter [3]. Isothermal curves were recorded at temperatures of from 95 to 115°. The fraction of crystallized material (x) at a given time (t) was determined from the DSC scans as the ratio of the subtended area at time t and the area of the complete exothermic peak.

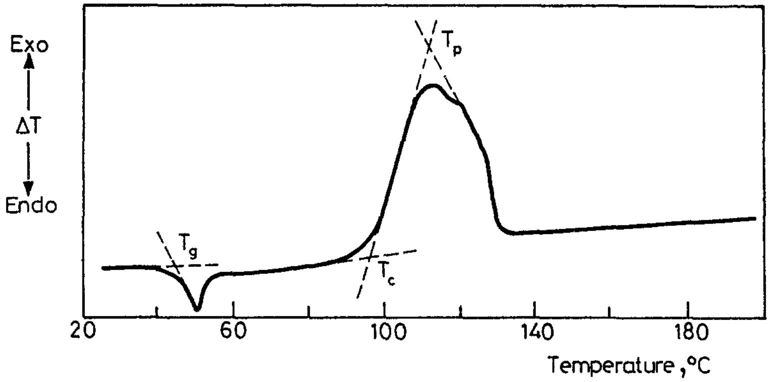

Fig. 1 Typical DSC traces at a heating rate 10 deg/min for $Bi_{10}Se_{70}In_{20}$ chalcogenide glass

The calorimetric sensitivity was 10 μW/cm and the temperature precision was ±0.1 deg.

The best fit for the results was calculated by the least squares method. The arithmetic mean and the standard deviation were calculated for the activation energies.

Results and discussion

A typical DSC trace of the chalcogenide glass $Bi_{10}Se_{70}In_{20}$ obtained at a heating rate of 10 deg/min, is shown in Fig. 1. Three characteristic phenomena are clear in the studied temperature region. The first one ($T = 40.0^o$) corresponds to the glass transition temperature (T_g) the second one ($T = 93.0^o$) to the crystallization onset temperature (T_c) and the last one ($T = 109.0^o$) to the peak of crystallization (T_p). The isothermal study was performed at temperatures above T_g and below T_c.

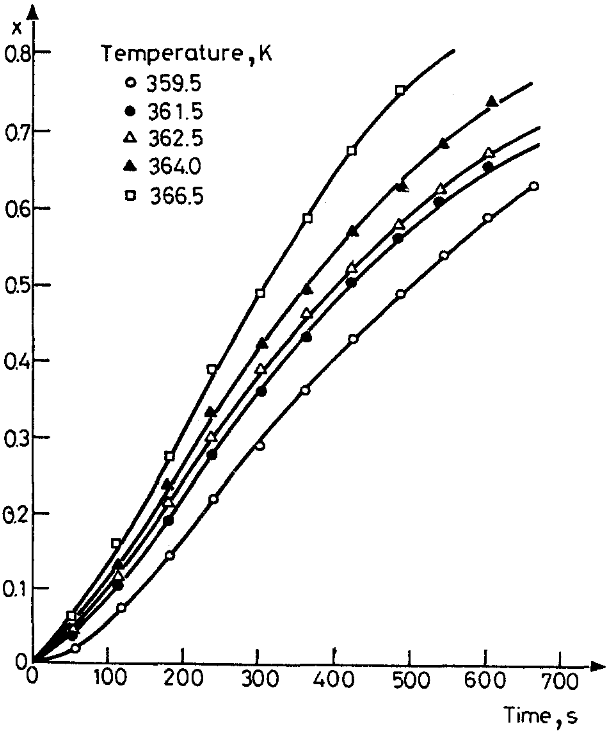

Fig. 2 Fraction crystallized (x) vs. the time for $Bi_{10}Se_{70}In_{20}$ chalcogenide glass

Under isothermal conditions, the relationship between the fraction crystallized (x) and the nucleation and growth rates is given by the Johnson-Mehl-Avrami transition equation [3, 4, 8-13]:

$$x(t) = 1 - \exp(-kt^n); \; k \approx \mathrm{l}u^3 \tag{1}$$

where x is the time-dependent fraction crystyallized after time t, k is the rate constant of the effect, n is a constant reflecting the nucleation and growth mechanism, l is the nucleation rate and u is the growth rate. Taking logarithms and rearranging:

$$\ln[-\ln(1-x)] = \ln k + n \ln t \tag{2}$$

A plot of ln [–ln (1–x)] as a function of ln (t) will yield the values of n and k.

Via partial peak area analysis of the isothermal DSC traces taken at 359.5, 361.5, 362.5, 364.0 and 366.5 K, the fraction of crystallized material as a function of time is shown in Fig. 2. In Fig. 3, the $x(t)$ function is depicted in the ln [–ln (1–x)] *vs.* ln (t) representation. It is evident that these data are well fitted by relation (2) for constant values of the growth mechanism; they are listed in Table 1. The mean value of n is 1.572 ±0.032.

Table 1 The values of n at different temperatures

T, K	359.5	361.5	362.5	364.0	366.5
n	1.635	1.554	1.558	1.545	1.570

According to the mean value of n (1.572), there are two mechanisms of crystallization: one-dimensional and surface crystallization [1, 4, 14].

The temperature-dependence of k is generally considered to demonstrate a single type of Arrhenius behaviour [3, 4]:

$$k = k_0 \exp(-E_a/RT) \tag{3}$$

where

k_0 is the preexponential constant,
E_a is the activation energy of crystallization and
R is the gas constant (1.98 $\mathrm{cal \cdot mol^{-1}\, deg^{-1}}$).

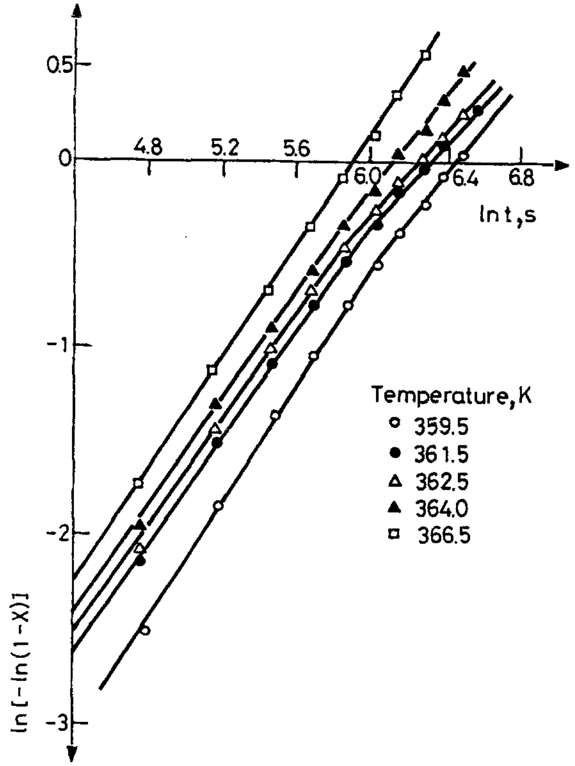

Fig. 3 Plot of ln [-ln(1-x)] *vs.* ln(t) for $Bi_{10}Se_{70}In_{20}$ chalcogenide glass

Equation (3) may be written as

$$\ln k = \ln k_0 - E_a/RT \tag{4}$$

values of ln k may be determined for successive temperatures from Eq. (2). From Eq. (4), a plot of ln k as a function of $1/T$ will yield the activation energy of crystallization as shown in Fig. 4. The obtained activation energy of crystallization (E_a) = 37.95 kcal/mol. The effective activation energy (E_a/n) is 21.14 kcal/mol.

From the isothermal DSC traces, an effective activation energy (E_a/n) may be determined according to Marseglia [15]. From Eqs (2) and (4):

$$\ln [-\ln (1-x)] = \ln k_0 - E_a/RT + n \ln t \tag{5}$$

or

$$\ln t = 1/n \{\ln[-\ln(1-x)] - \ln k_o\} + -E_a/nRT \qquad (6)$$

but at constant x

$$d(\ln t)/d(1/T) = E_a/nR \qquad (7)$$

A plot of ln t as a function of $1/T$ at constant x will give the effective activation energy E_a/n. With the isothermal hold method, the plot of ln t as a function of $1/T$ at constant x is given in Fig. 5. The average value of the crystallization activation energy for $Bi_{10}Se_{70}In_{20}$, deduced from the ln t *vs*. $1/T$ plot at constant x, is 34.80 ±1.40 kcal/mol.

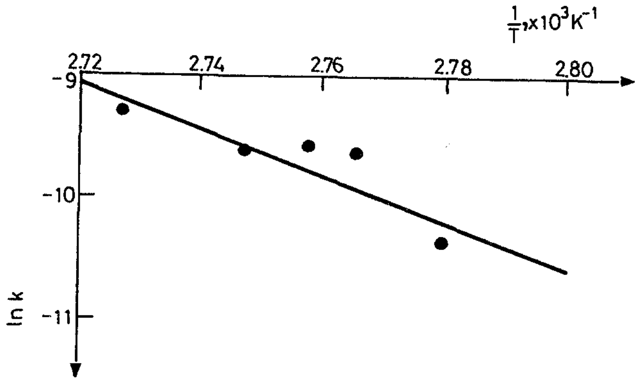

Fig. 4 ln(K) *vs.* 1000/T for $Bi_{10}Se_{70}In_{20}$ chalcogenide glass

From the two methods, the average crystallization activation energy is 36.38 ±1.46 kcal/mol.

The deduced value of the effective crystallization activation energy is in good agreement with the results obtained by the non-isothermal method [16]. This means that both methods (isothermal and non-isothermal) can be used for this glass to study the crystallization mechanism and to evaluate the effective crystallization activation energies.

Conclusion

From an analysis with the Johnson-Mehl-Avrami kinetic equation of the fraction crystallized under isothermal conditions, the activation energy of crystallization (E_a) was determined. The crystallization takes place by two

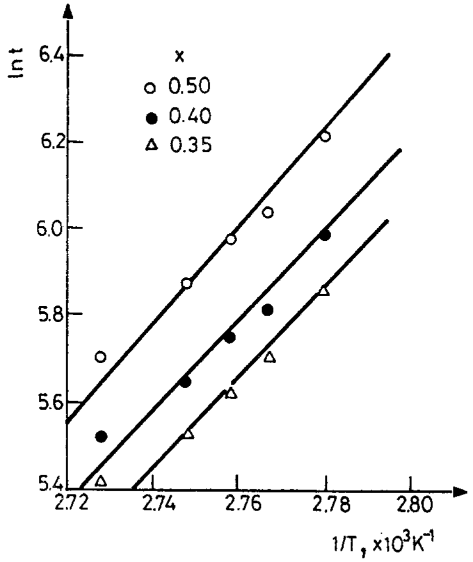

Fig. 5 ln(t) *vs.* 1000/T at different x for $Bi_{10}Se_{70}In_{20}$ chalcogenide glass

mechanisms: one-dimensional and surface crystallization. The average value of E_a (36.38 ± 1.46 kcal/mol) for the chalcogenide glass $Bi_{10}Se_{70}In_{20}$ was found to be in good agreement with that obtained with the non-isothermal method. This result means that both methods (isothermal and non-isothermal) are suitable for study of the crystallization mechanism and effective activation energy.

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Zusammenfassung — Die Ergebnisse von isothermen DSC-Untersuchungen an dem Chalkogenglas $Bi_{10}Se_{70}In_{20}$ wurden beschrieben und diskutiert. Die Aktivierungsenergie E_a der Kristallisierung wurde mit Hilfe der Johnson-Mehl-Avrami-Gleichung ermittelt und der Kristallisierungsmechanismus untersucht. Die Ergebnisse zeigen, daß der Kristallisierungsmechanismus von $Bi_{10}Se_{70}In_{20}$ eindimensionale und Oberflächenvorgänge beinhaltet. Der errechnete mittlere Wert von E_a beträgt für $Bi_{10}Se_{70}In_{20}$ 34.38 ±1.46 kcal/mol.