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ISOTHERMAL DSC METHOD FOR EVALUATION OF THE KINETICS OF CRYSTALLIZATION IN THE Ge–Sb–S GLASSY SYSTEM

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The isothermal DSC method was used to study the crystallization kinetics of Sb_2S_3 in glassy $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$. The effective activation energy of crystallization (E_a/n) was evaluated from the DSC curves using the Johnson–Mehl–Avrami transition equation.

The value of the effective activation energy (E_a/n = 178.4 kJ/mol) found from the isothermal DSC curves was only slightly higher than that obtained previously with the non-isothermal DTA method (E_a/n = 166.4 kJ/mol). It turns out that both methods can be used in this case.

Studies of kinetics are always connected with the concept of the activation energy. The value of this in glass crystallization phenomena is associated with the nucleation and growth processes 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 have usually been combined into an activation energy representative of the overall crystallization process [1]. 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 continuous heating crystallization. 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 continuous heating method the sample is heated at a fixed rate β, 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 [2–4].

The present work is concerned with the evaluation of the effective activation energy of crystallization (E_a/n) of amorphous $(GeS_2)_x(Sb_2S_3)_{1-x}$, where $x = 0.3$,

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using the isothermal method. As some controversy has arisen about the correct interpretation of non-isothermal results [5, 6], the data were compared with those in our previous work [7].

Experimental

The bulk glassy sample $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ was prepared by direct synthesis from germanium, antimony (purity 5*N*) and purified sulphur (nearly DAB 6) in evacuated ($p \sim 10^{-3}$ Pa) quartz ampoules in a rotary furnace. After synthesis and homogenization (10 hours, $T = 1120$ K), the melt was rapidly cooled in water.

The glassy nature of the samples was confirmed by both X-ray diffraction and transmission microscopy.

DSC was carried out in a Perkin–Elmer DSC-2C on 10 mg samples (plates 0.6 mm high, $\sim 2 \times 2$ mm) in sealed Al pans, with an empty pan as the standard. The samples were heated to 50 deg below the required temperature, held at this temperature for about 30 s and then heated at a rate of 320 deg/min to the annealing temperature. This process is used to minimize the.non-stationary effects caused by the thermal delay in the DSC calorimeter. Isothermal curves were recorded at temperatures from 615 to 640 K. The fraction of crystallized material α at given time t was determined from the DSC scans as a ratio between the subtended area at time t and the area of the complete exothermic peak.

Results and discussion

A typical DSC trace of glassy $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$, obtained at a heating rate of 20 deg/min, is shown in Fig. 1. Two characteristic phenomena are clear in the

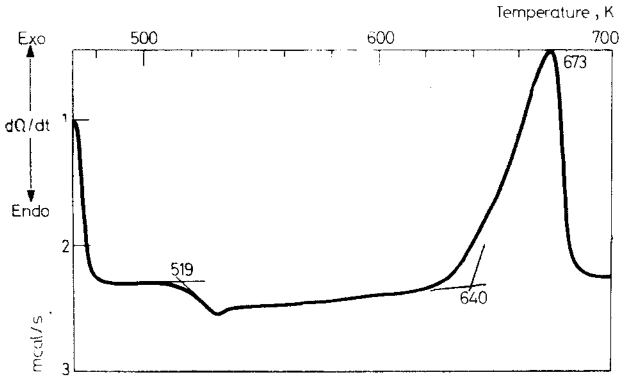

Fig. 1 Typical DSC trace of $(GeS_2)_x(Sb_2S_3)_{1-x}$ $x = 0.3$ at a heating rate 20 deg/min

studied temperature region. The first one ($T \sim 519$ K) corresponds to the glass transition temperature, and the second one ($T \sim 673$ K, exo) to the crystallization of Sb_2S_3. These rgsults are in good agreement with our previous data (see Ref. 7).

Under isothermal conditions, the relationship between the fraction crystallized (α) and the nucleation and growth rates is given by the Johnson–Mehl–Avrami transition equation:

$$\alpha(t) = 1 - \exp(-kt^n); \quad k \sim Iu^3 \tag{1}$$

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

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

Thus, a plot of $\ln[-\ln(1-\alpha)]$ as a function of $\ln t$ will yield the values of n and k.

Using partial peak area analysis of the isothermal DSC traces taken at 620 K, 625 K, 630 K and 635 K, the fraction of the crystallized material (Sb_2S_3) as a function of time is shown in Fig. 2. In Fig. 3 the $\alpha(t)$ function is shown 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.

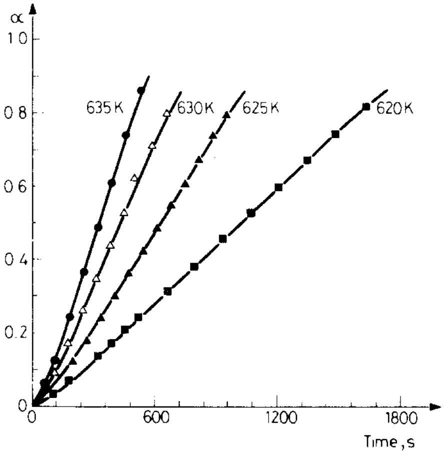

Fig. 2 Fraction crystallized obtained by the analysis of the partial peak area of the DSC curves

Table 1

T, K	615	620	625	630	635	640
n	1.34	1.38	1.58	1.53	1.68	1.7

The mean value of n is close to 1.54

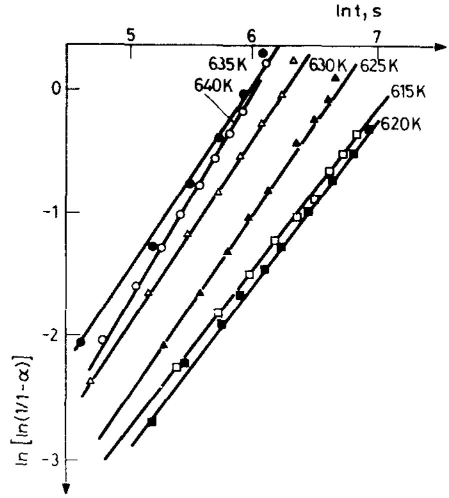

Fig. 3 Plot of $\ln[-\ln(1-\alpha)]$ against $\ln t$ for determination of values n and k

The temperature-dependence of k is generally considered to demonstrate a single type of Arrhenius behaviour:

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

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

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. Values of $\ln k$ as a function of $1/T$ are plotted in Fig. 4. Multiplying the slope of the least squares line through the points in Fig. 4 by R gives an activation energy of crystallization of $E_a = 65.8$ kJ/mol. With the average value of $n = 1.54$, the ratio $E_a/n = 178.4$ kJ/mol.

From the isothermal DSC traces, an effective activation energy (E_a/n) may be determined according to Marseglia [8]. From the curves in Fig. 3, n and $\ln k$ are obtained. By rearranging Eq. (1) for $\alpha = 1/2$ and taking logarithms, the expression for $t_{1/2}$ is obtained:

$$t_{1/2} = 1 - \exp(-kt^n_{1/2})$$

$$\ln t_{1/2} = 1/n\,[\ln(\ln 2) - \ln k]$$

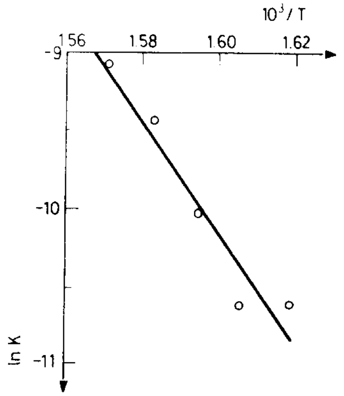

Fig. 4 Arrhenius plot for determination of the activation energy of crystallization

From the expression

$$d(\ln t_{1/2})/d(1/T) = E_a/nR$$

a plot of ln $t_{1/2}$ as a function of $1/T$ will give the effective activation energy E_a/n. With the isothermal hold method, the plot of ln $t_{1/2}$ as a function of $1/T$ is given in Fig. 5. Multiplying R by the slope of the least squares line yields an effective activation energy of E_a/n = 40.45 kcal/mol.

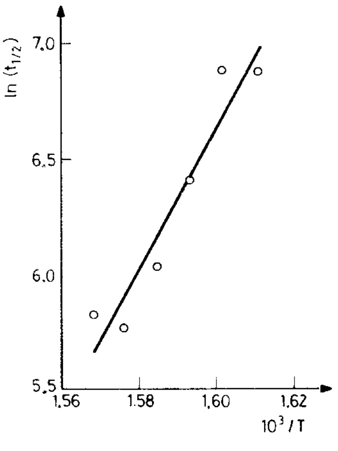

Fig. 5 Plot of ln $t_{1/2}$ against $1/T$ to determine effective activation energy

Conclusions

From an analysis with the Avrami kinetic equation of the fraction crystallized, the effective activation energy of crystallization E_a/n was determined. This value (178.4 kJ/mol) was found to be in good agreement with that found for the $t_{1/2}$ temperature-dependence (169.1 kJ/mol). Both values are only slightly higher than the value found with the heating rate method (166.4 kJ/mol) [7].

Comparison of the E_a/n values for the crystallization of $(GeS_2)_x(Sb_2S_3)_{1-x}$ ($x = 0.3$) glass indicates that the isothermal and the heating rate methods give the same results. Differences can be attributed to the various approximations in the two methods.

The value of n reflects the nucleation and growth mechanism. The non-integral number indicates that the mechanism involves several complex processes. One of them prevails with dependence on time. In our case, where n shows the temperature-dependence (see Table 1), the following processes can be taken into account:

(i) the one-dimensional growth of nucleation particles for small values of n at lower temperature, and

(ii) the two-dimensional growth of nucleation particles when n approaches 2.

The average value of $n = 1.58$ was used to evaluate the effective activation energy, only to simplify the calculation. We are aware of the inaccuracy caused by using the average value of n.

The good agreement between the values of the activation energy obtained from the isothermal and heating rate methods suggests that the heating rate method is also suitable for evaluation of the activation energy of crystallization of this glassy system.

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Zusammenfassung — Die isotherme DSC wurde zur Untersuchung der Kristallisationskinetik von Sb_2S_3 in glasigem $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ herangezogen. Die effective Aktivierungsenergie der Kristallisation (E_a/n) wurde aus den DSC-Kurven nach der Johnson–Mehl–Avrami-Gleichung ermittelt. Der Wert der aus isothermen DSC-Kurven bestimmten effektiven Aktivierungsenergie (178.4 kJ/mol) liegt nur wenig über den früher durch nicht-isotherme DTA erhaltenen Wert (166.4 kJ/mol). Es stellt sich heraus, daß in diesem Fall beide Methoden angewandt werden können.

Резюме — Изотермический метод ДСК был использован для изучения кинетики кристаллизации Sb_2S_3 в стеклообразном соединении $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$. Используя переходное уравнение Джонсона–Мехл–Аврами была определена эффективная энергия активации (E_a/n) процесса кристаллизации, равная 178,4 ккал/моль. Полученное значение было только немного выше такового, полученного из неизотермического метода ДТА (166,4 ккал/моль). Это показывает, что в данном случае оба метода могут быть использованы.