Journal of Thermal Analysis, Vol. 36 (1990) 2417-2426

CRYSTALLIZATION KINETICS OF CHALCOGENIDE GLASS $Se_{0.8}Te_{0.2}$

M. M. Hafiz, N. Afify, M. A. Osman and M. Dongol*

PHYS. DEPT., ASSIUT UNIV., EGYPT,
*PHYS. DEPT., FAC. OF SCI. (QENA), ASSIUT UNIV., EGYPT

(Received March 19, 1990)

The crystallization kinetics of the chalcogenide glass $Se_{0.8}Te_{0.2}$ was studied by means of differential scanning calorimetry. The variation in partial area (X) with temperature (T) revealed that the transition from the amorphous to the crystalline phase occurs in two dimensions.

Activation energies were determined for both the glass transition (E_t) and the crystallization (E_c). E_t was calculated from the variation in T_g with the heating rate (α). E_c was determined by three different methods: (i) variation in X with T, (ii) variation in T_p with α, and (iii) variation in T_c with α. E_t and E_c have values of 161.01 ± 2.75 and 84.75 ± 8.21 kJ/mol, respectively.

The chalcogenide glasses $Se_{1-x}Te_x$ have recently attracted great attention because of their use in various solid-state devices. Structural studies of these materials are very important for a better understanding of their transport mechanism [1-5].

The use of chalcogenide glasses as photographic materials has led to great achievements. The shortcomings of pure glassy selenium used for photographic drums were its short lifetime and low sensitivity; certain additives are usually added to improve these properties. The Se chain can be crossed with [3, 4] coordinate elements, which decreases the tendency to crystallization and increases the lifetime of a pure Se drum [6, 7].

Kinetic studies are always connected with the concept of 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 repre-

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

sentative of the overall crystallization process [8-10]. 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 [9, 11].

The present work is concerned with a study of the crystallization kinetics and evaluation of the activation energies under non-isothermal conditions.

Experimental

The bulk alloy $Se_{80}Te_{20}$ was prepared by heating a stoichiometric mixture (4:1) of the components selenium and tellurium with purities of 99.999% in a vacuum-sealed quartz tube at a temperature of 220° for three days and at 550° for one day, followed by quenching in water to room temperature. During heating of the sample, the tube was frequently shaken to homogenize the resulting alloy [3].

The thermal behaviour was investigated by using a Du Pont 1090 differential scanning calorimeter. The temperature and energy calibrations of the instrument were performed by using the well-known melting temperatures and melting enthalpy of the high-purity indium supplied with the instrument.

The crystallization thermograms were recorded as the temperature of the samples was increased at a uniform rate. Typically, 20 mg of the sample in powdered form was sealed in standard aluminium pans and was scanned (over a temperature range from room temperature to about 250°) at uniform heating rates (α) ranging from 2.0 deg/min to 60.0 deg/min in static air.

The fraction X crystallized at any temperature T is given as $X = (A_T/A)$, where A is the total area of the exotherm between the temperature T_i where crystallization just begins and the temperature T_f where the crystallization is completed (Fig. 1a); A_T is the area between T_i and T, as shown by the hatched portion in Fig. 1a.

An X-ray investigation of the powder $Se_{0.8}Te_{0.2}$ was performed with a Philips diffractometer (type 1710). The patterns were run with Cu as target and Ni as filter (λ = 1.54178 Å), at 40 kV and 30 mA, with a scanning speed of 3.6 deg/min.

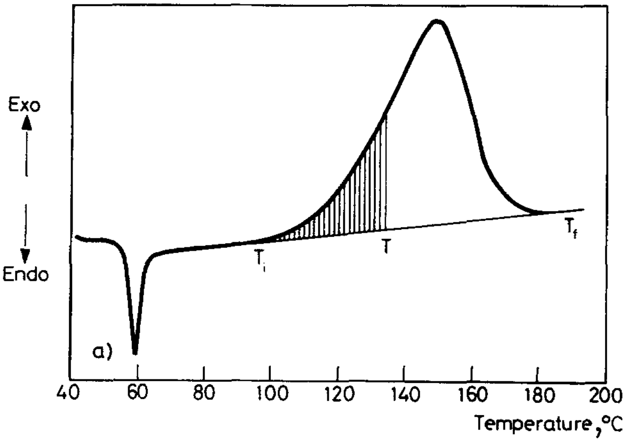

Fig. 1a Typical DSC trace of $Se_{0.8}Te_{0.2}$ glass at a heating rate 10 deg/min

All the experimental results were fitted by the least square method. The arithmetic average and the standard deviation were calculated for the activation energies.

Results and discussion

A typical DSC trace of glassy $Se_{0.8}Te_{0.2}$, obtained at α = 10 deg/min, is shown in Fig. 1a. Three characteristic phenomena are clear in the studied temperature region. The first (T = 55.3°) corresponds to the glass transition temperature T_g, the second (T = 115.8°) to the onset crystallization temperature T_c, and the last (T = 133.4°) to the peak temperature of crystallization T_p of $Se_{0.8}Te_{0.2}$. Figure 1b shows DSC thermograms of $Se_{0.8}Te_{0.2}$ at different values of α. The values of T_g, T_c and T_p vary by 19.8, 51.2 and 50.1 deg, respectively, as α is varied from 2 deg/min to 60 deg/min.

Through the use of Kissinger's formula [12] to evaluate the activation energy for the glass transition E_t for homogeneous crystallization with spherical nuclei, it has been shown [13, 14] that the dependence of T_c on α is given by

$$\ln \alpha/T_c^2 = -E/RT_c + \text{const.} \qquad (1)$$

where E is the effective crystallization activation energy. Though originally derived for a crystallization process, it has been suggested that this expression is valid for glass transition [15] and it has often been used [13-16] to calculate E_t.

Plots of $\log(\alpha/T_g^2)$ *vs.* $1/T_g$ for the glass $Se_{0.8}Te_{0.2}$ (plot *a* in Fig. 2) indicated linearity up to $\alpha = 60$ deg/min.

It is common practice to determine E_g from the slope of the $\ln\alpha$ *vs.* $1/T_g$ plot itself [8]. In general, the variation in $\ln(1/T_g^2)$ with $\ln\alpha$ is much slower than that in $1/T_g$ with $\ln\alpha$ [8]. Kissinger's equation can be approximated by the form:

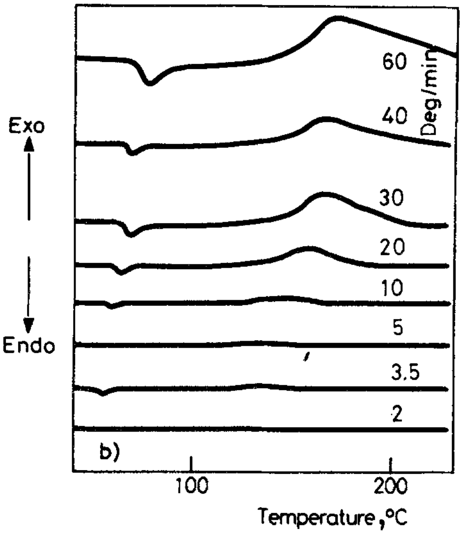

Fig. 1b DSC traces of $Se_{0.8}Te_{0.2}$ glass at different heating rates

$$\ln(\alpha) = -E_t/RT_g + \text{const.} \tag{2}$$

Plot *b* in Fig. 2 shows the $\ln(\alpha)$ *vs.* $1/T_g$ data for the chalcogenide glass $Se_{0.8}Te_{0.2}$. From relation *a* in Fig. 2, E_t for $Se_{0.8}Te_{0.2}$ was calculated to be 158.26 kJ/mol. E_t was also determined from relation *b* in Fig. 2, its value being 163.75 kJ/mol. It is evident that the two values are in good agreement with each other. This means that one can use either of the two relations to calculate E_t for $Se_{0.8}Te_{0.2}$.

The X-ray diffraction results indicate that the as-prepared sample has crystallization nuclei formed during the sample preparation. This result is very important as concerns an understanding of the mechanism of crystallization.

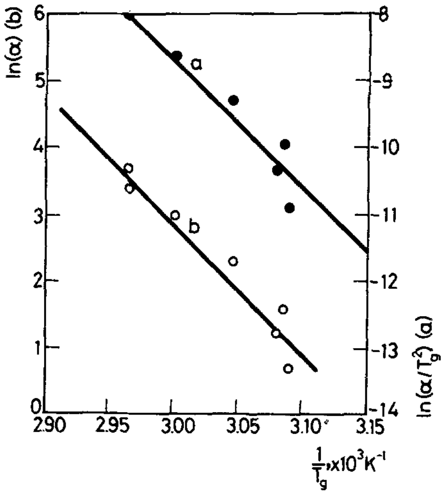

Fig. 2 a) Plot of ln (α/T_g^2) vs. 1000 $/T_g$ of $Se_{0.8}Te_{0.2}$ glass; b) Plot of ln(α) vs. 1000./T of $Se_{0.8}Te_{0.2}$ glass

Before the evaluation of E_c, some information concerning the crystallization kinetics is needed.

The Johnson-Mehl-Arvami (JMA) equation for isothermal crystallization processes [17-19] can be extended to include non-isothermal processes, because the chalcogenide glass $Se_{0.8}Te_{0.2}$ satisfied the condition for this extension or generalization [8, 20, 21].

The volume fraction X of crystals formed in the glass at temperature T during heating at uniform α is related to E_c by the expression [8, 21]:

$$\ln[-\ln(1-X)] = -n \ln \alpha - 1.052\, mE_c/RT + \text{constant} \qquad (3)$$

where n and m are constants having values between 1 and 4, depending on the morphology of the growth. For the case of nuclei formed during the sample preparation, the values of *n* and *m* are equal [8]. Table 1 shows the values of *n* and *m* for various crystallization mechanisms [8, 22].

Table 1 Values of *n* and *m* for various crystallisation mechanism [8, 22]

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

Figure 3a shows plots of ln[–ln(1–*X*)] *vs.* 1/*T* for different values of α. These plots are found to be linear over most of the temperature range. At high temperature or in regions of large crystallization fraction, a break in the linearity or rather a lowering of the initial slope is seen for all α; this result is in good agreement with the results of Mohadevan *et al.* [8].

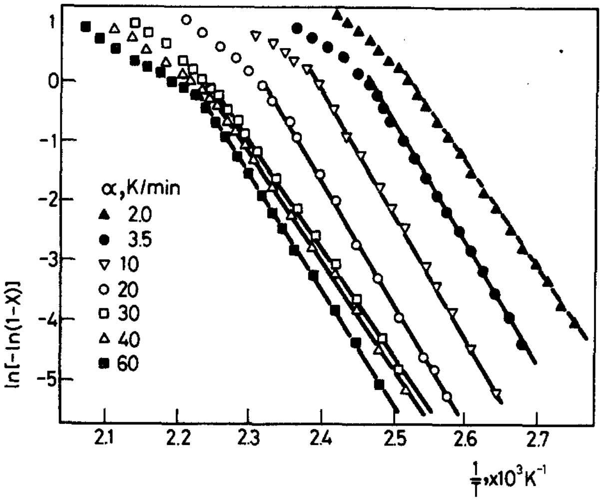

Fig. 3a ln [–ln (1–*X*)] *vs.* 1/*T* of $Se_{0.8}Te_{0.2}$ glass at different heating rates

Figure 3b gives the relation between ln[–ln(1–*X*)] and ln α at constant temperature (127°), deduced from Fig. 3a. From this relation, the value of *n* for the crystallization of $Se_{0.8}Te_{0.2}$ was deduced as 1.740. The calculated value of *n* is not at integer. This means that the crystallization process occurs with different mechanisms, and that the predominant one is the process in which $n = 2$ [8, 10]. Therefore, from Table 1, the value of m is equal to 2, which means that the crystallization of $Se_{0.8}Te_{0.2}$ is a two-dimensional crystallization process. From the values of m and the slopes in Fig. 3a, the average value of E_c for $Se_{0.8}Te_{0.2}$ is 75.30±4.86 kJ/mol.

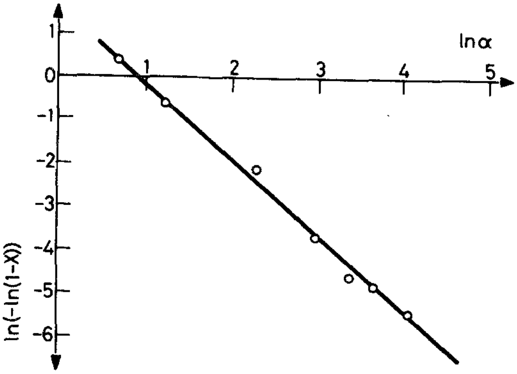

Fig. 3b ln [–ln (1–X)] *vs.* ln (α) of $Se_{0.8}Te_{0.2}$ glass at T=300 K (127°C)

For the evaluation of E_c from the variation in T_p with α, Kissinger's equation

$$\ln(\alpha/T_p^2) = -(E_c/RT_p) + \text{constant} \tag{4}$$

derived for the rate equation of an n–th order chemical reaction, is generally used [9, 12, 13, 23-26]. However, this equation has recently been modified [21, 22, 27-31] to the form

$$\ln(\alpha^n/T_p^2) + \ln K = -mE_c/RT_p \tag{5}$$

where K is a constant containing factors depending on the thermal history of the sample [8].

It is common practice also to infer $(m/n)E_c$ from the slope of the ln α *vs.* $1/T_p$ plot itself; in general, the variation in $\ln(1/T_p)$ with ln α is much slower than that in $1/T_p$ with ln α [8]. Plot b in Fig. 4 shows the ln α *vs.* $1/T_p$ data for the chalcogenide glass $Se_{0.8}Te_{0.2}$. The value of E_c is 97.25 kJ/mol

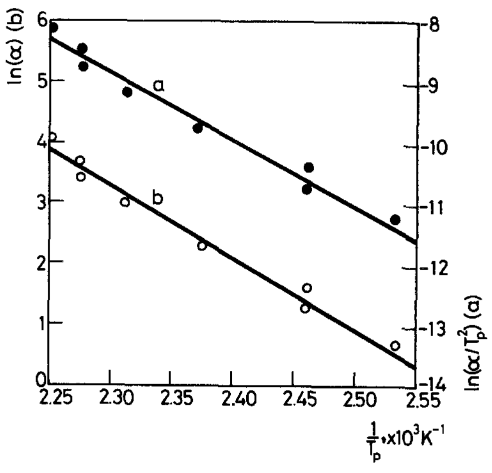

Fig. 4 a) Plot ln (α/T_p^2) *vs.* 1000 /T_p of $Se_{0.8}Te_{0.2}$ glass; b) Plot of ln (α) *vs.* 1000 /T_p of $Se_{0.8}Te_{0.2}$ glass

Many authors have used the relation $\ln(\alpha/T_p^2)$ *vs.* $1/T_p$ [9, 32] (plot *a* in Fig. 4). From its linearity and the deduced E_c value (90.33 kJ/mol), it is clear that this relation is valid for the present study. Moreover, this E_c value is much closer to that deduced from the partial crystallization data (Fig. 3a) than that deduced from the ln α *vs.* $1/T_p$ relation (plot *b* in Fig. 4).

E_c is also calculated by using the variation in T_c with α for $Se_{0.8}Te_{0.2}$. By using relations similar to those in Eqs (1) and (2), E_c can be calculated from the two (α, T_c) relations. The relations used can be written in the form:

$$\ln\alpha = -(m/n)(E_c/RT_c) + \text{constant} \qquad (6)$$

and

$$\ln(\alpha/T_c^2) = -(m/n)(E_c/T_c) + \text{constant} \qquad (7)$$

These relations were plotted as shown in Fig. 5, and the deduced E_c values for $Se_{0.8}Te_{0.2}$ crystallization averaged 80.36±3.28 kJ/mol, in good agreement with the above results.

The activation energy for $Se_{0.8}Te_{0.2}$ crystallization, calculated by different methods, has an average value of 84.72±8.21 kJ/mol.

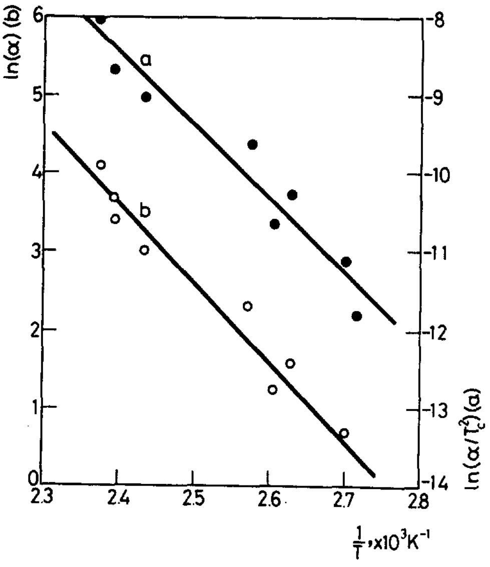

Fig. 5 a) Plot ln (α/T_c^2) vs. 1000 $/T_c$ of $Se_{0.8}Te_{0.2}$ glass; b) Plot ln (α) vs. 1000 $/T_c$ of $Se_{0.8}Te_{0.2}$ glass

Conclusions

The modified JMA equation indicates that the crystallization mechanism of $Se_{0.8}Te_{0.2}$ involves a two-dimension process.

The glass transition activation energy E_t can be determined from two different forms of Kissinger's equation. The crystallization activation energy E_c can be determined from the JMA equation and two different forms of Kissinger's equation.

E_t for $Se_{0.8}Te_{0.2}$ is 161.0.1±2.75 kJ/mol, and E_c is 84.72±8.21 kJ/mol

* * *

This work was partly supported by a Grant-in-Aid for Scientific Research from the GTZ GmbH and DAAD, W. Germany.

References

1 A. K. Agnihotri, A. Kumar and A. N. Nigam, J. Non-Cryst. Solids, 101 (1988) 127.
2 L. Cheung, G. M. T. Foley, D. Fornia and B. E. Springett, Photogr. Sci. Eng. (USA), 26 (1982) 251.
3 V. Damodara Das and P. J. Lakshmi, Phys. Rev. B., 37 (1988) 720.
4 J. S. Vermak and J. Petruzzello, J. Appl. Phys., 53 (1982) 6809.
5 V. Damodara Das and P. J. Lakshmi, J. Appl. Phys., 62 (1987) 2376.
6 G. Pfister, J. Elect. Mat. 8 (1979) 789.
7 H. Yang, W. Wang and S. Min, J. Non-Cryst. Solids, 80 (1986) 503.
8 S. Mahadevan, A. Giridhar and A. K. Singh, J. Non-Cryst. Solids, 88 (1986) 11.
9 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
10 N. Rysavá, T. Spasev and L. Tichy, J. Thermal Anal., 32 (1987) 1015.
11 H. Yinnon and D. R. Uhlman, J. Non-Cryst. Solids, 54 (1983) 253.
12 H. E. Kissinger, J. Res. Not. Bur. Stand. 57 (1956) 217.
13 H. S. Chen, J. Non-Cryst. Solids, 27 (1978) 257.
14 J. E. Shelby, J. Non-Cryst. Solids, 34 (1979) 111.
15 J. Colemenero and J. M. Barandiaran, J. Non-Cryst. Solids, 30 (1978) 263.
16 J. A. Macmillan, J. Phys. Chem., 42 (1965) 3497.
17 B. G. Bagley and E. M. Vogel, J. Non-Cryst. Solids, 18 (1975) 29.
18 M. G. Scott, J. Mat. Sci., 13 (1978) 291.
19 V. R. V. Raman and G. E. Fish, J. Appl. Phys., 53 (1982) 2273.
20 D. W. Henderson, J. Non-Cryst. Solids, 30 (1970) 301.
21 K. Matusita, T. Konatsu and R. Yokota, J. Mat. Sci., 19 (1984) 291.
22 K. Matusita and S. Sakka, Phys. Chem. Glasses, 20 (1979) 81.
23 D. D. Thornburg and R. I. Johnson, J. Non-Cryst. Solids, 17 (1975) 2.
24 H. Yinnon and D. R. Uhlman, J. Non-Cryst. Solids, 54 (1983) 253.
25 R. Frahn, J. Non-Cryst. Solids, 56 (1983) 255.
26 M. Cadergren and G. Backstrom, J. Non-Cryst. Solids, 37 (1980) 213.
27 D. R. Macfarlane, M. Matecki and M. Poulain, J. Non-Cryst. Solids, 64 (1984) 351.
28 K. Matusita and S. Sakka, J. Non-Cryst. Solids, 38-39 (1980) 741.
29 K. Matusita and S. Sakka, Bull. Inst. Chem. Res. Kyoto Univ., 59 (1981) 159.
30 A. Morotta, S. Saiello and A. Buri, J. Non-Cryst. Solids, 57 (1983) 473.
31 K. Matusita and S. Sakka, Thermochim. Acta, 33 (1979) 351.
32 S. H. Kandil, M. E. Kassem, M. A. El-Gamal and E. F. El-Wahidy, J. Mater. Sci. Let., 5 (1986) 112.

Zusammenfassung — Mittels DSC wurde die Kristallisierungskinetik des Chalkogenidglases $Se_{0.8}Te_{0.2}$ untersucht. Eine Änderung partieller Gebiete (X) mit der Temperatur (T) zeigte, daß der Übergang von der amorphen zur kristallinen Phase zweidimensional verläuft.

Es wurde die Aktivierungsenergie sowohl für den Glasübergang (E_t) als auch für die Kristallisierung (E_c) bestimmt. E_t wurde mittels der Abhängigkeit von T_g von der Aufheizgeschwindigkeit (α) ermittelt. E_c wurde auf drei verschiedene Wege bestimmt: (i) Änderung von X in Abhängigkeit von T, (ii) Änderung von T_p in Abhängigkeit von α und (iii) Änderung von T_c in Abhängigkeit von α. Die Werte von E_t und E_c betragen 161.01±2.75 bzw. 84.75±8.21 kJ/mol.