Thermochimica Acta, 40 (1980) 397—403
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

SURFACE AND BULK CRYSTALLIZATION IN NON-ISOTHERMAL DEVITRIFICATION OF GLASSES

A. MAROTTA, A. BURI and F. BRANDA

Istituto di Chimica, Facolta di Ingegneria, Università di Napoli, 80125 Naples (Italy)

(Received 14 February 1980)

ABSTRACT

The surface and bulk crystallization of $Li_2O \cdot 2\ SiO_2$ glass has been studied by differential thermal analysis and the influence of the specific surface area of the sample and the nucleation heat treatment on the crystallization kinetics is pointed out. The kinetic parameters were also evaluated from the DTA curves and related to the crystallization mechanism . The results agree well with the isothermal data reported in the literature.

INTRODUCTION

Kinetic investigations on the crystallization of glass are of interest for elucidating the nature of crystal growth and for research on glass ceramic materials. Differential thermal analysis (DTA) has been extensively used to study the devitrification of glasses. Several methods have been proposed [1—6] to obtain kinetic data from DTA curves, but the role of the nature and number of nuclei has often been neglected.

In this paper, the influence of these parameters on (a) the temperature and shape of the DTA crystallization peak, and (b) the crystallization kinetics, has been studied. The crystallization of $Li_2O \cdot 2\ SiO_2$ glass has been investigated because the results can be compared with those obtained under isothermal conditions and recently reported in the literature [7,8].

EXPERIMENTAL

Samples of $Li_2O \cdot 2\ SiO_2$ glass were prepared by melting the pure reagents in a Pt crucible in an electric oven and casting them in Fe moulds at a high cooling rate.

The as-quenched glass was crushed in an agate mortar and then sieved in order to obtain fine (—240 + 350 mesh) and coarse (—30 + 52 mesh) particles. Small bulk samples suitable for the size of the sample holder of the DTA apparatus were also prepared. In this case, powdered Al_2O_3 was added to improve the heat transfer between the sample and sample holder.

Differential thermal analysis of ~90 mg of powdered or bulk glass was carried out in air at different heating rates (5, 10, and 20°C min^{-1}). Two sets of DTA curves were recorded. In the first set, the as-quenched samples were used. In the second, the samples were first kept for 14 h at the temperature of maximum nucleation rate (475°C) [9]. A Netzsch differential thermal analyzer model 404M was used and Al_2O_3 was used as reference material.

THEORETICAL CONSIDERATIONS

Glass devitrification is the result of two individual processes: nucleation and crystal growth.

Nucleation

The total number of nuclei per unit volume, N, is the sum of the surface nuclei, N_s, the bulk nuclei formed during the DTA run, N_B; and the bulk nuclei formed during the heat treatment of nucleation, N_B^0.

$$N = N_s + N_B + N_B^0 \tag{1}$$

N_s is proportional to the specific surface area, S, of the sample, i.e.

$$N_s \propto S \tag{2}$$

N_B is proportional to the reciprocal of the heating rate, β, i.e.

$$N_B \propto \frac{1}{\beta} \tag{3}$$

and N_B^0 is proportional to the time of heating, t_N, at the temperature of maximum nucleation rate, i.e.

$$N_B^0 \propto t_N \tag{4}$$

In the quenched samples, $N_B^0 = 0$ and in samples nucleated for a long time, $N_B^0 >> N_B$.

As a glass usually crystallizes at temperatures well above the temperatures of high nucleation rates, in all cases, the crystals grow from an almost fixed number of nuclei, N_0.

Crystal growth

As the crystallization proceeds in a glass, the heat of crystallization is evolved and an exothermic peak appears on the DTA curve, as shown in Fig. 1. The degree of crystallization, α, during the DTA peak can be described by the Johnson—Mehl—Avrami (JMA) equation [10,11]

$$-\ln(1-\alpha) = kt^n \tag{5}$$

The rate constant, k, is related to the absolute temperature, T, by an Arrhenius-type equation

$$k \propto N_0 \exp\left(-\frac{nE}{RT}\right) \tag{6}$$

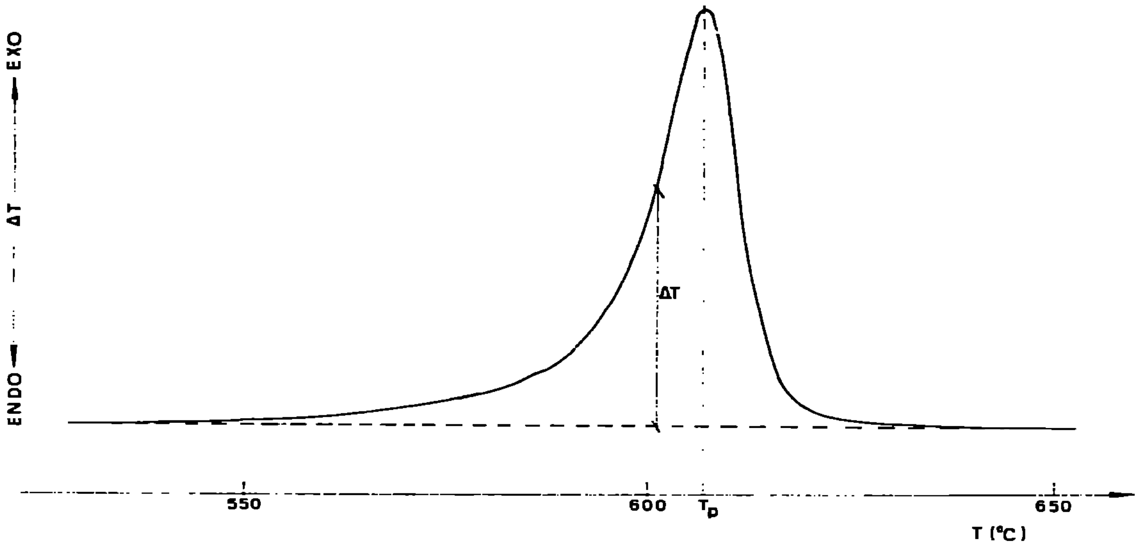

Fig. 1. A typical DTA curve. ΔT = Temperature difference between sample and reference; T_p = peak temperature.

where E is the activation energy for the crystal growth. The parameter n is related to the crystallization mechanism and the shape of the crystals [6] and its value determines the shape of the DTA peak. The higher the value of n, the narrower is the peak [12].

RESULTS AND DISCUSSION

In the devitrification of $Li_2O \cdot 2\,SiO_2$ glass, three crystallization mechanisms can occur [7,8], viz.

(a) $N_s >> N_B + N_B^0$. Surface nucleation is dominant. The crystals grow one-dimensionally from the surface to the inside of the glass and $n = 1$.

(b) $N_B + N_B^0 >> N_s$. Bulk nucleation is dominant. Each crystal grows three-dimensionally (spherulites) in the bulk and $n = 3$.

(c) N_s and $N_B + N_B^0$ are of the same order of magnitude. The crystals grow from the surface and in the bulk. The value of n ranges between 1 and 3 and can lead to a misinterpretation of the crystallization mechanism.

The DTA curves recorded at the same heating rate (5°C min^{-1}) on the as-quenched and nucleated samples are shown in Fig. 2. The shape of the peaks and the values of peak temperature, T_p, reported in Table 1 suggest the following points.

As-quenched glasses

In fine and coarse powdered samples, surface nucleation is dominant (large peak) due to the high specific surface of the samples and the short time (DTA run) of bulk nucleation. In the bulk sample, the small number of bulk nuclei is comparable with that of surface nuclei due to the very low

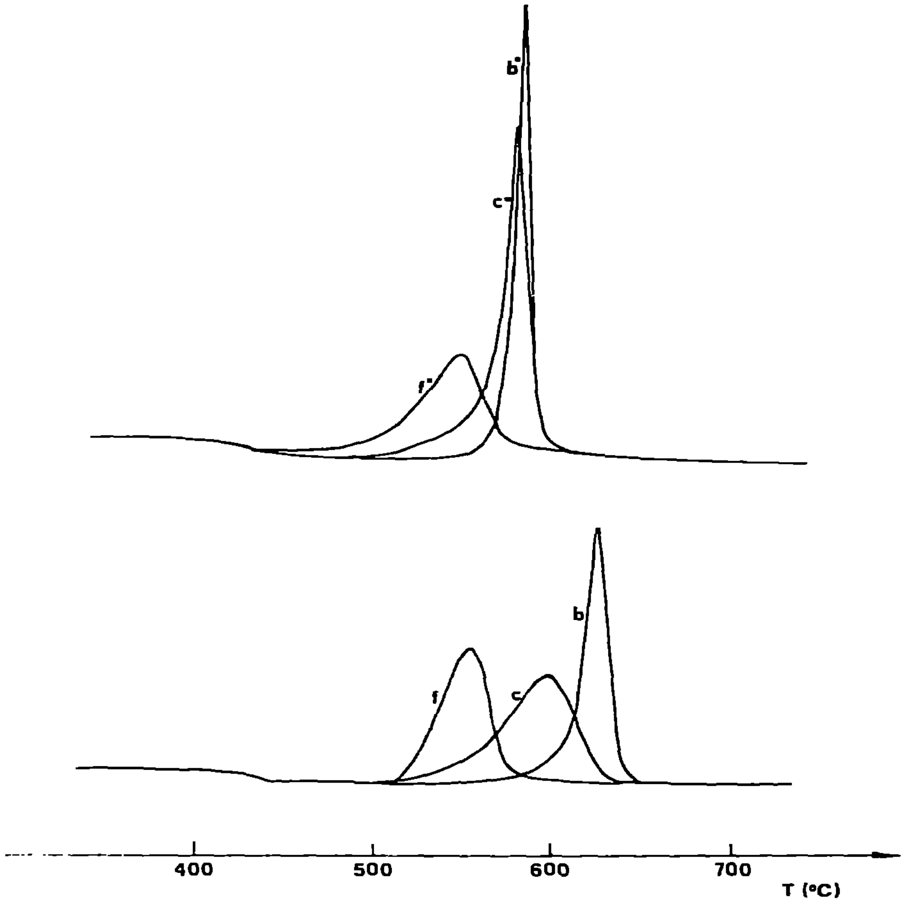

Fig. 2. DTA curves recorded at 5°C $\min^{-1}$. f = Fine powder; c = coarse powder; b = bulk; * = nucleated samples.

specific surface of the sample. The crystals grow from the surface and in the bulk from a small total number of nuclei, N_0. The DTA peak is therefore narrower and shifted, according to eqn. (6), towards higher temperatures than those of powdered glasses.

TABLE 1

DTA peak temperatures and kinetic parameters

Samples	Q			N		
	T_p	E	n	T_p	E	n
Fine powder	583	70	1.2	579	63	1.0
Coarse powder	620	61	1.0	609	72	2.7
Bulk	650	40	2.7	614	59	3.9

Q = as-Quenched samples; N = nucleated samples;
T_p = DTA (5°C $\min^{-1}$) peak temperature (°C).
E = activation energy (kcal mole^{-1}); n = JMA equation parameter.

Nucleated glasses

The high number of nuclei, formed during the long (14 h) heat treatment at the temperature of maximum nucleation rate, makes bulk nucleation dominant in the bulk sample and comparable with that of the surface in the coarse powdered sample. The DTA peaks are therefore narrower and shifted toward lower temperatures than those of the as-quenched samples. In the fine powdered samples, the shape and temperature, T_p, of the DTA peak are not changed by the heat treatment of nucleation; so the latter seems to be ineffective on crystallization mechanism and on number of nuclei.

The activation energy, E, has been evaluated from DTA curves by the following equation [2,5], based on the shift of the peak temperature, T_p, as the heating rate, β, is changed [13].

$$\log \beta = -\frac{E}{4.57}\frac{1}{T_p} + \text{cost} \tag{7}$$

Plotting $\log \beta$ vs. $1/T_p$ gives straight lines, as can be seen from Fig. 3. The values of E calculated from their slopes and given in Table 1 are all, except for the as-quenched bulk sample, in good agreement with the value 65 ± 10 kcal mole^{-1} obtained under isothermal conditions [7].

In the as-quenched bulk sample, the number of bulk nuclei, N_B, formed during the DTA run cannot, as in the other cases, be neglected. The crystals, according to eqn. (3) grow at each heating rate from a different number of nuclei so that the peak temperature is shifted not only by the change in the heating rate, but also by the change in the number of nuclei. Therefore, in this case, the decrease in activation energy is not real. It must finally be remarked that surface and bulk crystallization have the same activation energy value [7].

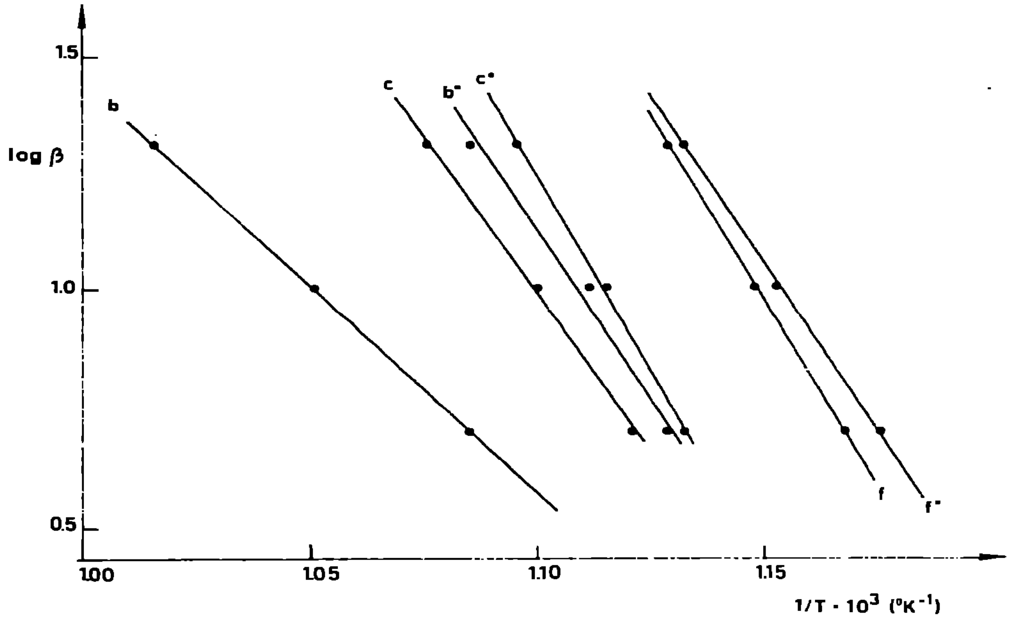

Fig. 3. Plot of $\log \beta$ vs. $1/T_p$. Symbols as in Fig. 2.

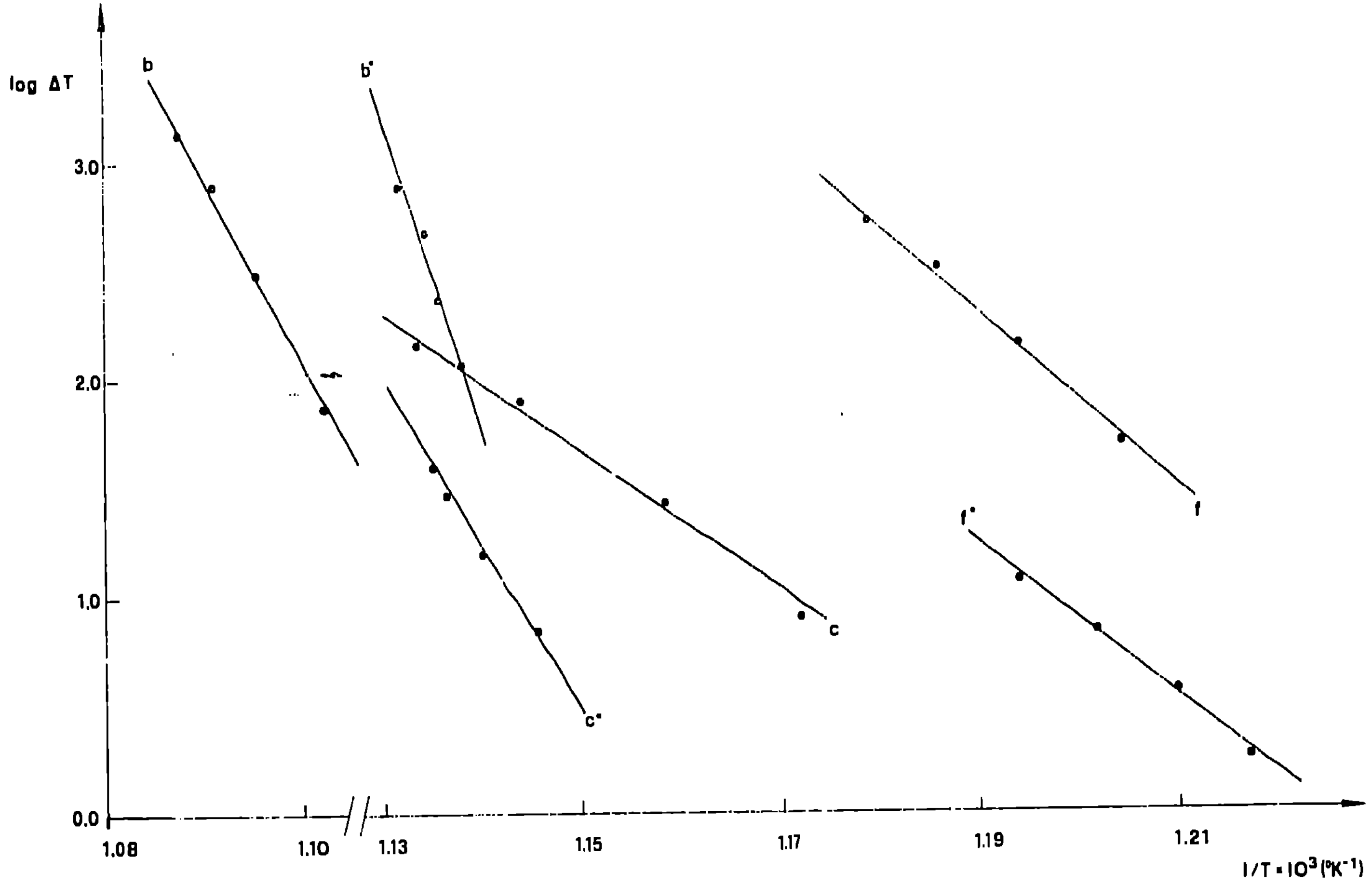

Fig. 4. Plot of log ΔT vs. $1/T$ (the values of ΔT and T are derived from DTA curves recorded at 5°C min^{-1}). Symbols as in Fig. 2.

A rough estimate of *n* has been obtained by the following oversimplified equation [5,14], based on the assumption [15] that the ΔT deflection from the baseline (Fig. 1) is proportional to the instantaneous reaction rate at each temperature

$$\log \Delta T = -\frac{nE}{4.57}\frac{1}{T} + \text{cost} \tag{8}$$

The *n* values were calculated from the slopes of the straight lines (Fig. 4) obtained by plotting log ΔT vs. $1/T$. A value of $E = 65$ kcal mole^{-1} was assumed.

The crystallization mechanisms suggested by the values of *n* reported in Table 1 agree well with those previously deduced from the shape of the DTA peaks.

CONCLUSIONS

From the above results, the following conclusions can be drawn.

(1) The shape and the temperature, T_p, of the DTA peaks suggest a good evaluation of the crystallization mechanism and of the effectiveness of nucleation heat treatment.

(2) To avoid misinterpretation of the kinetic parameters, surface and bulk crystallization must be studied separately, using as-quenched powdered samples and well nucleated bulk samples, respectively.

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