Thermochimica Acta, 46 (1981) 123—129
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

NUCLEATION AND CRYSTAL GROWTH IN $Na_2O \cdot 2\ CaO \cdot 3\ SiO_2$ GLASS: A DTA STUDY

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(Received 1 December 1980)

ABSTRACT

The non-isothermal devitrification of $Na_2O \cdot 2\ CaO \cdot 3\ SiO_2$ glass has been studied by differential thermal analysis in order to evaluate, from DTA curves, the temperature of maximum nucleation rate, T_m, and the activation energy values, E_c, for crystal growth.

The temperature, $T_m = 580°C$, is very close to the glass transition temperature, $T_g = 570°C$, and the value of $E_c = 78$ kcal mole^{-1} for the surface crystal growth is nearly the same as the value $E_c = 89$ kcal mole^{-1} for the bulk crystal growth; both are consistent with the activation energy for viscous flow. It is also pointed out that the nucleation rate—temperature curve and the crystallization rate—temperature curve are partially overlapped.

INTRODUCTION

In previous papers [1—3] the non-isothermal devitrification of $Li_2O \cdot 2\ SiO_2$ glass has been investigated by differential thermal analysis (DTA). Methods of evaluating the temperature of maximum nucleation rate [3], the activation energy of crystal growth [1], and the crystallization mechanism [1] from DTA curves were shown. The influence of the sample's specific surface on the experimental data was also pointed out [2].

It is of interest to verify the applicability of the proposed methods to a three-component $Na_2O \cdot 2\ CaO \cdot 3\ SiO_2$ glass which, like $Li_2O \cdot 2\ SiO_2$ glass, exhibits internal crystallization without the addition of any nucleating agent [4].

The complete procedure for obtaining all the parameters required to produce fine grained glass-ceramic materials from the above mentioned glass using DTA curves is shown in this paper, and the experimental results are compared with those obtained by other techniques.

EXPERIMENTAL

The $Na_2Ca_2Si_3O_9$ glass was prepared by melting analytical grade reagents at 1400°C for 6 h in a Pt crucible in an electric oven. The melts were cast at a high cooling rate by plunging the bottom of the crucible in cold water.

The as quenched glass was crushed or cut in order to obtain powdered samples (—170 +230 mesh) and small bulk samples (suitable for the size of the sample holder of the DTA apparatus), respectively.

The heat treatments of nucleation were performed in the DTA apparatus to eliminate temperature gradients. Nucleation times were measured on isothermal DTA curves from the time at which the samples, heated at 50°C min^{-1}, reached the selected temperature.

Differential thermal analysis curves of ~60 mg specimens at different heating rates (5—20°C min^{-1}) in air were recorded. Powdered Al_2O_3 was added to improve heat transfer between bulk samples and the sample holder. A Netzsch thermoanalyzer 404M was used and powdered Al_2O_3 was used as reference material.

THEORETICAL CONSIDERATIONS AND RESULTS

Kinetic equations

The non-isothermal devitrification of glass is the result of two individual processes: nucleation and crystal growth. The number of nuclei per unit volume is the sum of surface nuclei, N_s, bulk nuclei formed during the DTA run, N_h, and bulk nuclei formed during a previous heat treatment of nucleation, N_n.

$$N = N_s + N_h + N_n \tag{1}$$

The values of N_s, N_h and N_n are proportional to the sample's specific surface, S, the reciprocal of DTA heating rate, β, and the time, t_n, of the nucleation heat treatment, respectively. As a glass crystallizes at temperatures well above the temperatures of high nucleation rates, the number of nuclei already present in the glass cannot appreciably increase during the crystallization, so the crystals grow from a nearly fixed number of nuclei [5].

The process of crystal growth in a glass is well described by a Johnson—Mehl—Avrami equation [6,7]

$$-\ln(1 - \alpha) = (kt)^n \tag{2}$$

where α is the volume fraction of crystallized phase at time t, and n is a parameter related to the mechanism of the process ($n = 1$, surface crystallization; $n = 3$, bulk crystallization).

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

$$k = AN \exp\left(-\frac{E_c}{RT}\right) \tag{3}$$

where E_c is the activation energy for the crystal's growth, N is the number of nuclei, and A is a constant.

When a glass crystallizes during a DTA run the heat of crystallization is evolved and an exothermic peak appears on the DTA curve (Fig. 1). The ΔT deflection from the baseline of the DTA curve is, at each temperature T,

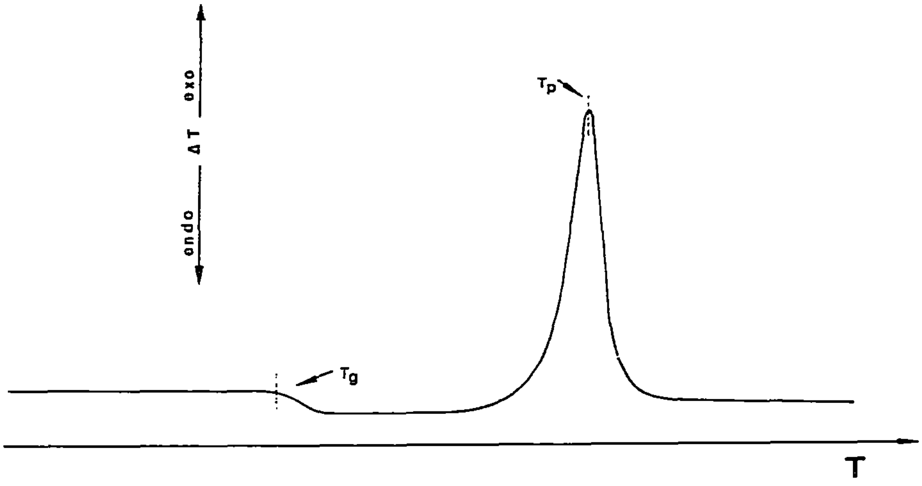

Fig. 1. Typical DTA crystallization curve.

proportional to the instantaneous reaction rate $d\alpha/dt$ [8]

$$\Delta T = k^n t^{n-1} (1 - \alpha) \tag{4}$$

The condition that at the crystallization peak temperature T_p

$$\frac{d\,\Delta T}{dT} = \frac{d}{dT}\left(\frac{d\alpha}{dt}\right) = 0 \tag{5}$$

leads to [1,9]

$$kt = 1 \tag{6}$$

Taking into account eqn. (3) and assuming that the time of heating is proportional to the reciprocal of the DTA heating rate, β, if the latter is constant [10], the logarithms of eqn. (6) lead to the following equation

$$\ln N - \ln \beta = \frac{E_c}{R}\,\frac{1}{T_p} + \text{const.} \tag{7}$$

Temperature of maximum nucleation rate

If the DTA runs are carried out on samples of the same specific surface S at the same heating rate β, the sum N_0 of surface nuclei, N_s, and bulk nuclei formed during the DTA run, N_h, is constant, and eqn. (7) becomes for a previously nucleated sample

$$\ln(N_0 + N_n) = \frac{E_c}{R}\,\frac{1}{T_p} + \text{const.} \tag{8}$$

and for an as quenched sample ($N_n = 0$)

$$\ln N_0 = \frac{E_c}{R}\,\frac{1}{T_p^0} + \text{const.} \tag{9}$$

From eqns. (8) and (9) the following equation can be drawn

$$\ln \frac{N_0 + N_n}{N_0} = \frac{E_c}{R}\left(\frac{1}{T_p} - \frac{1}{T_p^0}\right) \tag{10}$$

If bulk samples (low specific surface) are used, the DTA runs are carried out at a high heating rate (20°C min^{-1}) and the samples are long nucleated ($t_n = 2$ h)

$$N_n >> N_0 \tag{11}$$

As the number of nuclei N_n is related to the time t_n of nucleation heat treatment by

$$N_n = It_n^b \tag{12}$$

where I is the kinetic rate constant of nucleation, and b is a parameter related to the nucleation mechanism, if the samples are held the same time t_n at each temperature T_n of the heat treatment, the following approximated equation can be drawn from eqn. (10)

$$\ln I = \frac{E_c}{R}\left(\frac{1}{T_p} - \frac{1}{T_p^0}\right) + \text{const.} \tag{13}$$

By plotting $[(1/T_p) - (1/T_p^0)]$ vs. the temperature T_n of the nucleation heat treatment a nucleation rate—temperature like curve is obtained (Fig. 2) that shows a maximum at 580°C, which is in very good agreement with the value reported in the literature [4].

Activation energy and mechanism of crystal growth

In order to point out the influence of the sample's specific surface and its thermal history on the crystallization mechanism the following four types of samples have been studied:

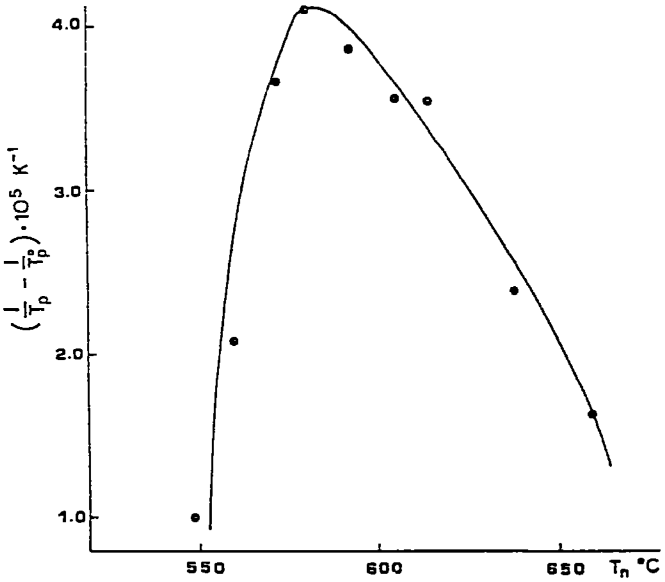

Fig. 2. Plot of $[(1/T_p) - (1/T_p^0)]$ vs the temperature T_n of heat treatment.

(A) as quenched powdered samples;
(B) as quenched bulk samples;
(C) bulk samples previously heated for 2 h at 580°C;
(D) bulk samples previously heated for 16 h at 600°C.

The kinetic parameter E_c and n were obtained by the following three equations derived [1,10] from eqns. (7) and (4), respectively

$$\ln\beta = -\frac{E_c}{R}\frac{1}{T_p} + \text{const.} \tag{14}$$

$$\ln\beta = -\frac{E_c}{2R}\cdot\frac{1}{T_p} + \text{const.} \tag{15}$$

$$\ln\Delta T = -\frac{nE}{R}\frac{1}{T} + \text{const.} \tag{16}$$

Equation (14) is based on the assumption that the number N_h of nuclei formed during the DTA run can be neglected so that the crystals grow at each heating rate β from the same number of nuclei; eqn. (15) is based on the assumption that the number N_h of nuclei formed during the DTA run is dominant so that the crystals grow at each heating rate β from a number of nuclei proportional to the reciprocal of β [11]; eqn. (16) is based on the assumption that in the initial part of the DTA crystallization peak the change in temperature has a much larger effect on the change in ΔT compared with the change in α [12].

Plots of ln β vs. $1/T_p$ (Fig. 3) and ln ΔT vs. $1/T$ (Fig. 4) gave straight lines in all cases.

The values of E_c, nE_c, and n for each type of sample calculated from their slopes are reported in Table 1. The value of n was calculated for the as

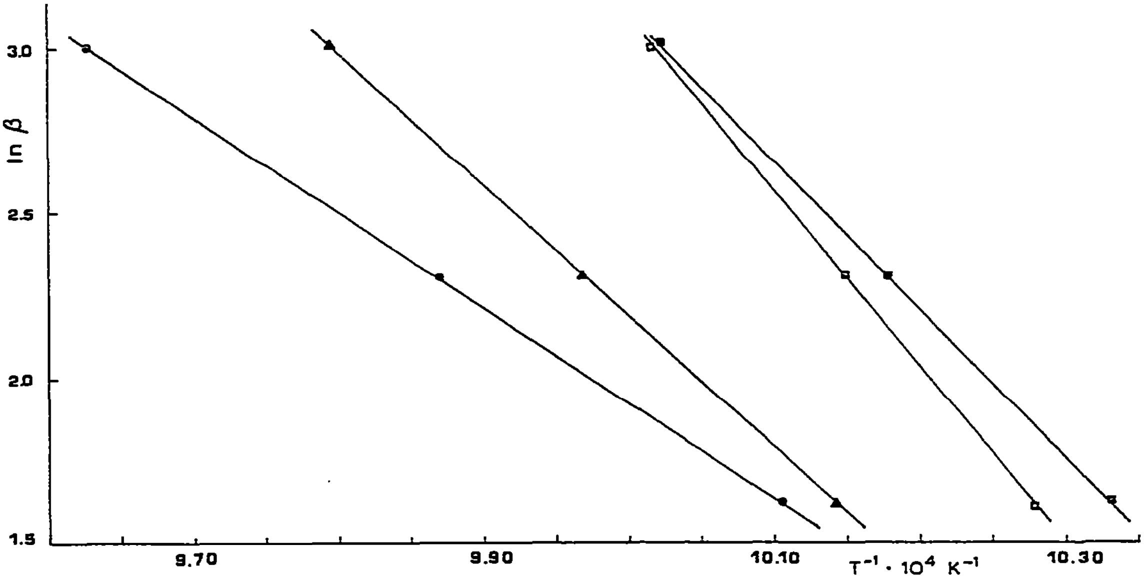

Fig. 3. Plot of ln β vs. $1/T_p$. ▲, As quenched powder sample; ●, as quenched bulk sample; ■, nucleated 2 h at 580°C bulk sample; □, nucleated 16 h at 600°C bulk sample.

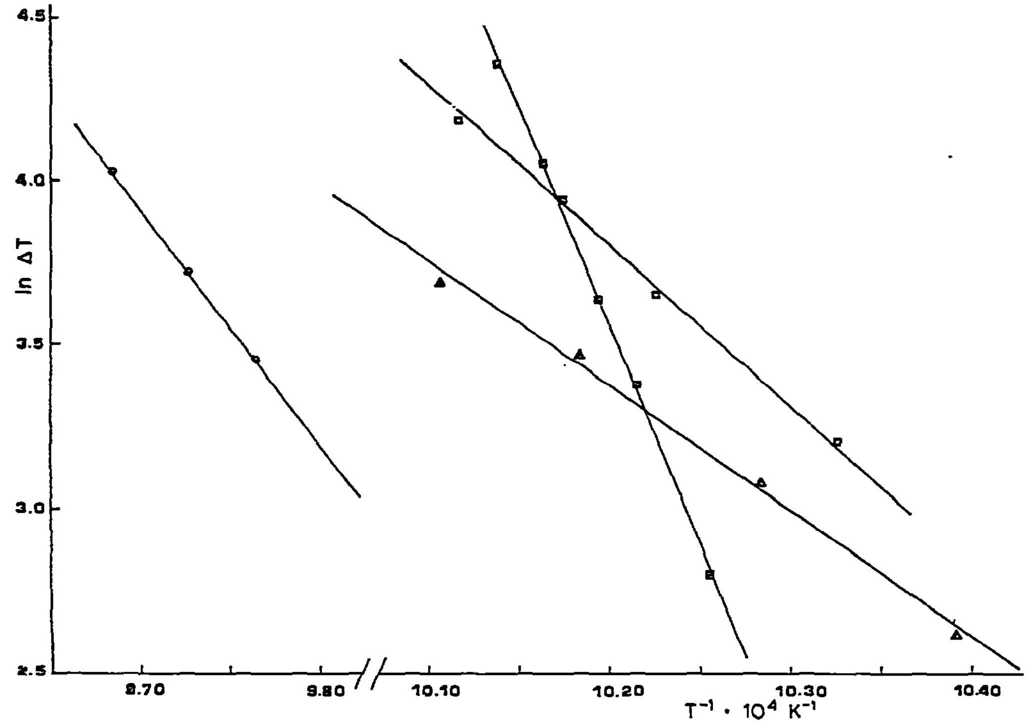

Fig. 4. Plot of ln ΔT vs. $1/T$. Symbols as in Fig. 3.

quenched bulk sample assuming a value of E_c = 85 kcal mole^{-1}. The values reported in Table 1 suggest the following.

(1) In as quenched (N_n = 0) powdered samples surface crystallization is dominant according to the high value of the sample's specific surface ($N_s >> N_h$). The crystals grow one-dimensionally (n = 1) from the surface to the inside of the glass. The value of E_c = 78 kcal mole^{-1} agrees well with that reported in the literature [4].

(2) In the bulk sample previously heated for 2 h at 580°C the high number, N_n, of nuclei formed during the heat treatment at the temperature of maximum nucleation rate makes dominant the bulk crystallization as $N_n >> N_s + N_h$. Each crystal grows three-dimensionally (spherulites; n = 3) in the bulk of the glass. The value of E_c = 89 kcal mole^{-1} is very close to that of 78 kcal mole^{-1} calculated for the as quenched powdered sample.

(3) In as quenched (N_n = 0) bulk samples, both surface and bulk crystalli-

TABLE 1

Kinetic parameters (E_c = kcal mole^{-1})

Sample	E_c	$n\,E_c$	n
As quenched powder sample	78	85	1
As quenched bulk sample	57—114	171	2
Bulk sample nucleated for 2 h at 580°C	89	260	3
Bulk sample nucleated for 16 h at 600°C	106	95	1

zation ($n = 2$) occur according to the low value of the sample's specific surface ($N_s \simeq N_h$). Consequently, the value of $E_c = 57$ kcal mole^{-1}, calculated by eqn. (14) assuming a surface crystallization mechanism ($N_s >> N_h$), is lower than that of 78 kcal mole^{-1} calculated for powdered samples in which only surface crystallization occurs, and the value of $E_c = 114$ kcal mole^{-1} calculated by eqn. (15) assuming a bulk crystallization mechanism ($N_h >> N_s$), is higher than that of 89 kcal mole^{-1} calculated for samples in which the crystals grow mainly from bulk nuclei.

(4) Glass samples previously heated for 16 h at 600°C are partially crystallized after the heat treatment as the areas of the DTA crystallization peak of these samples are 60% less than those of the other ones. The value $n = 1$ is consistent with the later stages of crystal growth when the increase of the spherulites' surface can be neglected compared with the increase of their radius.

CONCLUSIONS

From the experimental results the following conclusions can be drawn.

(1) It is confirmed that the investigated glass exhibits internal crystallization without the addition of any nucleating agent.

(2) The temperature 580°C of maximum nucleation rate is very close to that of the glass transition ($T_g = 570$°C measured for an as quenched bulk sample on a DTA curve recorded at 10°C min^{-1}).

(3) The activation energy value for the crystal growth for surface and bulk crystallization is, as for $Li_2O \cdot 2\ SiO_2$ glass, nearly the same and is consistent with the activation energy value for viscous flow [13].

(4) As after a prolonged heat treatment at only 20°C above the temperature of maximum nucleation rate the samples are over 50% crystallized, the nucleation rate—temperature curve and the crystallization rate—temperature curve should be already overlapped at 600°C, so a very exact determination of the temperature of maximum nucleation rate is required to produce fine grained glass-ceramic materials.

REFERENCES

1 A. Marotta and A. Buri, Thermochim. Acta, 25 (1978) 155.
2 A. Marotta, A. Buri and F. Branda, Thermochim. Acta, 40 (1980) 397.
3 A. Marotta, A. Buri and F. Branda, J. Mater. Sci., to be published.
4 C.J.R. Gonzales-Oliver, P.S. Johnson and P.F. James, J. Mater, Sci., 14 (1979) 1159.
5 V. Komppa, Phys. Chem. Glasses, 20 (1979) 85.
6 W.A. Johnson and H.F. Mehl, Trans. Am. Ceram. Soc., 51 (1939) 416.
7 M. Avrami, J. Chem. Phys., 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
8 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
9 J.A. Augis and J.E. Bennett, J. Therm. Anal., 13 (1978) 283.
10 R.L. Thakur and S. Thiagarajan, Glass. Ceram. Res. Inst. Bull., 15 (1968) 67.
11 K. Matusita, S. Sakka and Y. Matsui, J. Mater. Sci., 10 (1975) 961.
12 F.O. Piloyan, I.V. Ryabchikov and O.S. Novikova, Nature (London), 212 (1966) 1229.
13 C.J.R. Gonzales-Oliver and P.F. James, J. Non-Cryst. Solids, 38/39 (1980) 699.