

CRYSTAL NUCLEATION AND GROWTH IN AN LiNaSiO_3 GLASS

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ABSTRACT

The non-isothermal devitrification of LiNaSiO_3 glass was studied using differential thermal analysis and X-ray diffraction. A crystallisation mechanism in two steps was found. The temperature of maximum nucleation rate and the kinetic parameters of crystal growth were evaluated from the DTA curves.

INTRODUCTION

Nucleation in glass-forming systems can occur either in the volume or on the surface of the sample. In practice, surface crystal-nucleation occurs more easily than internal crystal-nucleation and it is observed in most compositions. To achieve internal crystal-nucleation, it is often necessary to add nucleating agents. However, certain glass systems nucleate internally without such additions.

Kinetic investigations on the crystallization of glasses are of interest for elucidating the nature of crystal nucleation and growth, and for research on glass-ceramic materials. The greater number of investigations in this field are devoted to the study of the devitrification behaviour of glasses containing much less than 50 mol% of network modifiers [1–3]. It is therefore of interest to study the kinetics of crystal nucleation and growth in glasses containing a high level of network modifiers. As melts containing high proportions of alkali oxides crystallize or devitrify during cooling, the glass selected for study has a composition LiNaSiO_3 , very close to the LiSiO_3 – NaSiO_3 pseudo-binary eutectic composition [4], which would be the one more likely to form a glass [5].

EXPERIMENTAL

The LiNaSiO_3 glass was prepared by melting small quantities (2 grams) of analytical grade reagents in a Pt crucible in an electric oven. The melts were

cast at a high cooling rate between two brass plates. The as-quenched glass was cut in order to obtain small bulk samples (suitable for the size of the sample holder of the DTA apparatus).

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 $50^\circ\text{C min}^{-1}$, reached the selected temperature.

Differential thermal analysis curves at different heating rates ($2\text{--}20^\circ\text{C min}^{-1}$) were recorded in air for specimens of about 60 mg. Powdered Al_2O_3 was added to improve heat transfer between bulk samples and the sample holder. A Netzsch thermoanalyser 404 M was used with powdered Al_2O_3 as reference material.

The phases which crystallised during the DTA runs were identified by X-ray diffraction. A Guinier–de Wolff camera and $\text{Cu } K\alpha$ radiation were used.

RESULTS AND DISCUSSION

The DTA curve of the studied glass shows a slope change at 355°C and an exothermic peak at 525°C , followed by two endothermic peaks at 759°C and 849°C respectively, see Fig. 1. The slope change can be attributed to the glass transition that occurs, owing to the mixed alkali effect, at a temperature 355°C lower than those of Li_2SiO_3 (427°C) and Na_2SiO_3 (420°C).

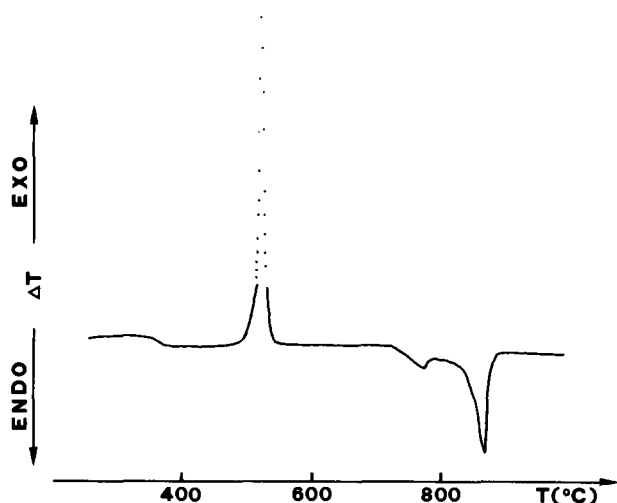


Fig. 1. DTA curve of LiNaSiO_3 recorded at $20^\circ\text{C min}^{-1}$.

TABLE 1
X-ray diffraction patterns

XRD pattern of a sample heated at the temperature of the exothermic peak		
LiNaSiO ₃ card 30-770		<i>d</i> -spacing observed
4.93		4.93
3.43		3.43
2.846		2.84
2.445		2.44
2.388		2.38
1.829		1.83
1.391		1.39
XRD pattern of a sample heated at the temperature of the first endothermic peak		
Li ₂ SiO ₃ card 24-829	Na ₂ SiO ₃ card 16-818	<i>d</i> -spacing observed
	5.26	5.24
4.70		4.71
	3.56	3.55
3.30		3.30
	3.04	3.02
2.71		2.70
	2.57	2.55
	2.41	2.40
2.34		2.33
2.33		2.32
	1.89	1.88
	1.756	1.75
		1.74
1.65		1.65
1.56		1.56
	1.42	1.41
1.29		1.29

The phases crystallising during the DTA runs were identified by X-ray diffraction. The XRD reflections of a sample heated in the DTA furnace up to the temperature of the exothermic peak were all assigned to LiNaSiO₃ crystals, Table 1. The reflections of the XRD pattern of a sample heated in the DTA furnace up to the temperature of the first endothermic peak suggest that the LiNaSiO₃ crystals are converted into a solid solution of Li₂SiO₃ and Na₂SiO₃ crystals. Finally, the second endothermic peak can be attributed to the fusion of these crystals.

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

treatment of nucleation N_n .

$$N = N_s + N_h + N_n \quad (1)$$

The values of N_s , N_h and N_n are respectively proportional to the sample specific surface S , to the reciprocal of the DTA heating rate β and to the time t_n of the nucleation heat treatment. Because a glass crystallises at temperatures well above the temperatures of high nucleation rates, the number of nuclei already present in the glass cannot appreciably increase during the crystallisation so that the crystals grow from a nearly fixed number of nuclei [6]. The process of crystal growth can be described by the following equation [7]

$$-\ln(1 - \alpha) = A(N/\beta^n) \exp(-nE/RT) \quad (2)$$

where α is the volume fraction crystallised at temperature T , E is the activation energy for crystal growth, n is a parameter related to the crystal shape (rod-like, $n = 1$; plate-like, $n = 2$; three dimensional, $n = 3$), β is the DTA heating rate and A is a constant.

Assuming that the ΔT deflection from the baseline is proportional, at each temperature T , to the instantaneous reaction rate [8], the temperature T_p of the crystallisation peak can be obtained by setting

$$(d(\Delta T)/dT) = (d^2\alpha/dT^2) = 0 \quad (3)$$

and solving for T_p .

Taking into account eqn. (1), the following equations can be derived from eqn. (3) [9,10]

$$\ln N = (nE/R)(1/T_p) + \text{const.} \quad (\beta = \text{const.}) \quad (4)$$

$$\ln \beta = (-E/R)(1/T_p) + \text{const.} \quad (N = \text{const.}) \quad (5)$$

If the DTA runs are carried out on samples of the same specific surface, S , at the same heating rate, β , the sum, N_o , of surface nuclei, N_s , and bulk nuclei formed during the DTA run, N_h , is constant and eqn. (4) for a previously nucleated sample becomes

$$\ln(N_o + N_n) = (nE/R)(1/T_p) + \text{const.} \quad (6)$$

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

$$\ln N_o = (nE/R)(1/T_p^\circ) + \text{const.} \quad (7)$$

From eqns. (6) and (7), the following equation can be derived

$$\ln[(N_o + N_n)/N_o] = (nE/R)\left[(1/T_p) - (1/T_p^\circ)\right] \quad (8)$$

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

$$N_n \gg N_o \quad (9)$$

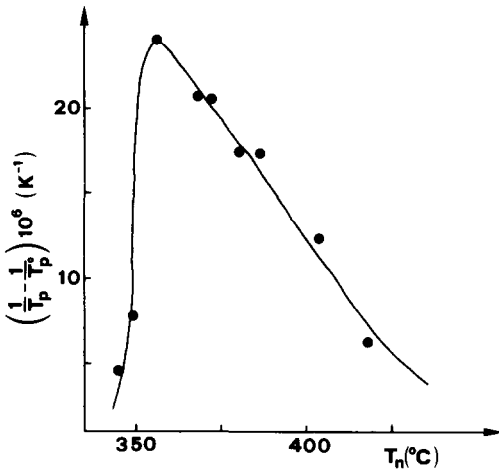


Fig. 2. Nucleation rate-temperature-like curve.

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

$$N_n = It_n^b \quad (10)$$

where I is the kinetic rate constant of nucleation and b a parameter related to the nucleation mechanism; if the samples are kept for the same time t_n at each temperature T_n of the heat treatment, the following approximated equation can be derived from eqn. (8)

$$\ln I = (nE/R) \left[(1/T_p) - (1/T_p^\circ) \right] + \text{const.} \quad (11)$$

By plotting $(1/T_p - 1/T_p^\circ)$ against the temperature T_n of the nucleation heat treatment, a nucleation rate-temperature-like curve is obtained, Fig. 2, that shows a maximum at a temperature very close to the glass transition temperature detected on the DTA curve. The kinetic parameters E and n were obtained using eqn. (5) and

$$\ln \Delta T = -(nE/R)/(1/T) + \text{const.} \quad (12)$$

Equation (5) is based on the assumption that the number of nuclei formed during the DTA run, N_h , can be neglected so that at each heating rate, β , the crystals grow from the same number of nuclei; eqn. (12) is based on the assumption that in the initial part of the DTA crystallisation peak the change in temperature has a much larger effect on the change in the ΔT deflection from the baseline compared with the change in α [11].

To evaluate the kinetic parameters E and n for bulk crystal growth using eqns. (5) and (12), the condition $N = N_h = \text{const.}$ is required. Therefore, bulk samples (low specific surface) were used which had been previously nucleated for the same time (12 h) at a temperature of high nucleation rate (350°C). In this way, the number of surface nuclei, N_s , and the number of

bulk nuclei N_h formed during the DTA run can be neglected with respect to the high number of bulk nuclei formed during the heat treatment, N_n .

By carrying out multiple DTA runs at different heating rates, β , a value of $E = 322 \text{ kJ mol}^{-1}$ for the activation energy of the crystal growth was calculated from the slope of the straight line obtained by plotting $\ln \beta$ against $1/T_p$.

A value of $nE = 811 \text{ kJ mol}^{-1}$ was calculated from the slope of the straight line obtained by plotting $\ln \Delta T$ against $1/T$. The value $n = 2.5$, obtained from the values of E and nE , agrees well with the rounded lath-shape of LiNaSiO_3 crystals as reported by West [12].

CONCLUSIONS

From the experimental results the following conclusions can be drawn.

(a) The LiNaSiO_3 glass, heated at constant heating rate during a DTA run, devitrifies in two steps. LiNaSiO_3 crystals are formed initially and are then converted at a higher temperature into Li_2SiO_3 and Na_2SiO_3 crystals.

(b) The studied glass exhibits internal crystal-nucleation, without the addition of any nucleating agent, with a maximum rate at 356°C .

(c) The values of the kinetic parameters are consistent with the crystal shape.

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