Thermochimica Acta, 140 (1989) 191–195
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE NON-ISOTHERMAL DEVITRIFICATION OF LITHIUM METASILICATE GLASS

A. MAROTTA, A. ARONNE, P. PERNICE and F. BRANDA

Department of Materials and Production Engineering, University of Naples (Italy)

(Received 8 April 1988)

ABSTRACT

The non-isothermal devitrification of lithium metasilicate glass was studied using differential thermal analysis and X-ray diffraction. A crystallization mechanism in two steps is proposed. The kinetic parameters of each step 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 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.

The non-isothermal devitrification of several binary silicate glasses has been studied previously [1–4]. $Li_2Si_2O_5$, $BaSi_2O_3$ and Na_2SiO_3 glasses exhibit internal crystallization without the addition of any nucleating agent. In $Na_2Si_2O_5$ glass only surface crystallization occurs.

In this study the non-isothermal devitrification of lithium metasilicate glass was investigated in order to evaluate the crystallization mechanism and the kinetic parameters of crystal growth.

EXPERIMENTAL

The lithium metasilicate (Li_2SiO_3) glass was prepared by melting small quantities (2 g) of analytical grade reagents in a platinum crucible in an electric oven. The melts were cast at 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). Differen-

0040-6031/89/$03.50

tial thermal analysis curves of 50 mg specimens were recorded in air at different heating rates (2–20 °C min^{-1}). Powdered Al_2O_3 was added to improve the heat transfer between the bulk samples and the sample holder. A Netzsch thermoanalyser (model 404M) was used for the analyses, with powdered Al_2O_3 as reference material.

The phases which crystallized after the thermal treatment were identified by X-ray diffraction. A Guinier–de Wolff camera and Cu *Kα* radiation were used.

RESULTS AND DISCUSSION

Crystallization mechanism

The DTA curve of lithium metasilicate glass (Fig. 1) exhibits a slope change at 427 °C which can be attributed to the glass transition. An exothermic crystallization peak appears just above the glass transition. A second exothermic crystallization peak appears at about 100 °C above the temperature of the first exothermic peak.

The phases which crystallized during the DTA run were identified by X-ray diffraction. The XRD pattern of the sample heated in the DTA furnace until the temperature of the first exothermic peak shows a few reflections that can be attributed to Li_4SiO_4 crystals. These reflections disappear completely in the XRD pattern of the sample heated until the temperature of the second exothermic peak. All the reflections of this pattern can be assigned to Li_2SiO_3 crystals. These results suggest that lithium metasilicate glass devitrifies in two steps

$$\text{Glass} \rightarrow Li_4SiO_4 + \text{Glass residue} \rightarrow Li_2SiO_3$$

The proposed crystallization mechanism is consistent with the structure of the glass. Tatsumisago et al. [5] found SiO_4 tetrahedral units with different

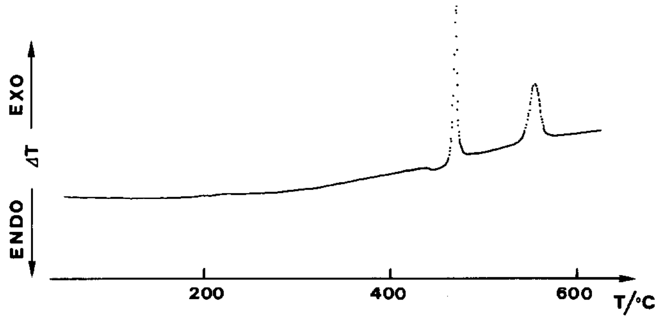

Fig. 1. DTA curve of Li_2SiO_3 glass recorded at 5 °C min^{-1}.

numbers of non-bridging oxygen atoms per silicon atom in lithium metasilicate glass. There are an appreciable number of SiO_4^{4-} ions in this glass. When lithium metasilicate glass is heated in the DTA apparatus the more simple Li_4SiO_4 crystals are formed initially. At higher temperature, where the decrease in the viscosity of the glass allows a more complicated rearrangement of the network, the Li_4SiO_4 crystals are converted into Li_2SiO_3 crystals whose composition is the same as that of the mother glass.

Kinetic parameters of crystal growth

The non-isothermal devitrification of glass is the result of two individual processes: nucleation and crystal growth. The number of nuclei N in unit volume of an as-quenched glass is the sum of surface nuclei N_s (proportional to the specific surface S of the sample) and bulk nuclei N_b (formed during the DTA run and proportional to the reciprocal of the DTA heating rate β [6]). If bulk samples (as in this work) are examined the surface nuclei can be neglected so that

$$N = N_b = A/\beta$$

where A is a constant.

The non-isothermal crystal growth in a glass can be well described in this case by the following equation [7]

$$-\ln(1-\alpha) = -\frac{B}{\beta^{n+1}}\exp(-nE/RT) \qquad (1)$$

where α is the degree of crystallization at each temperature T, β is the DTA heating rate, E is the activation energy of crystal growth and B is a constant. The Avrami parameter n is related to the crystal shape and ranges between $n = 3$ for three-dimensional crystals and $n = 1$ for rod-like crystals [7].

The kinetic parameters E and n can be evaluated from the DTA curves by the two equations

$$\ln\beta = -\frac{nE}{(n+1)R}\frac{1}{T_p} + \text{constant} \qquad (2)$$

$$\ln\Delta T = -\frac{nE}{R}\frac{1}{T} + \text{constant} \qquad (3)$$

Equation (2) is based on the assumption [8] that at the peak temperature T_p the degree of crystallization α reaches the same specific value and is not dependent on the heating rate β. Equation (3) is based on the assumption that in the initial part of the DTA crystallization peak the change in temperature T has a much larger effect on the ΔT deflection from the baseline than on the degree of crystallization α [9].

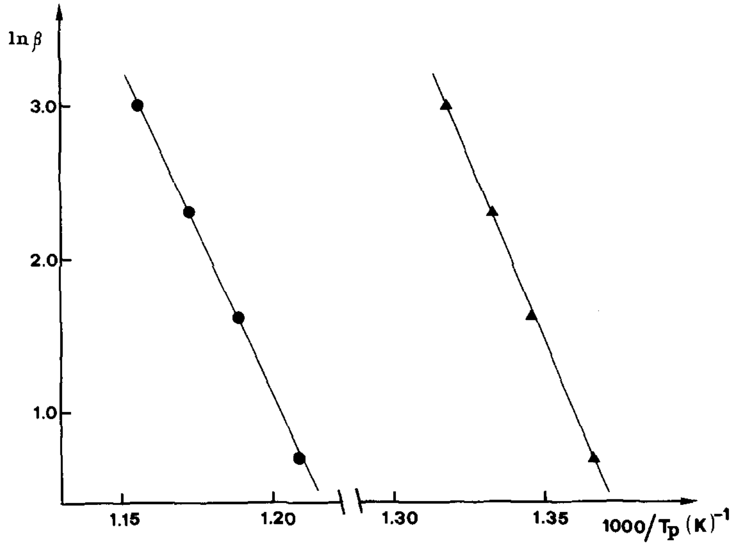

Fig. 2. Plot of ln β vs. $1/T_p$ (triangles, first DTA peak; circles, second DTA peak).

TABLE 1

Kinetic parameters E (kcal mol^{-1}) and n

Crystallized phase	$(nE)/(n+1)$	nE	E	n
Li_4SiO_4, 1st peak	95	388	128	3
Li_2SiO_3, 2nd peak	86	168	170	1

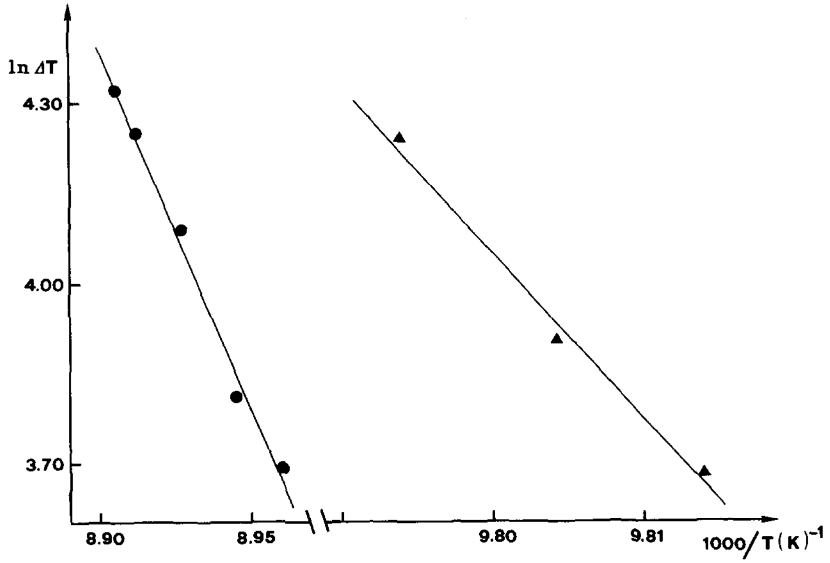

Fig. 3. Plot of ln ΔT vs. $1/T$ (symbols as in Fig. 2).

Multiple DTA runs were performed at different heating rates β and ln β vs. $1/T_p$ was plotted. A straight line was obtained for each of the two crystallization peaks (Fig. 2). The values of $nE/n+1$ calculated from their slopes are reported in the first column of Table 1. From the slopes of the plots of ln ΔT vs. $1/T$ for the two crystallization peaks (Fig. 3), two values of nE were calculated and these are reported in the second column of Table 1. The kinetic parameters E and n for each crystallization step were then derived and are reported in the third and fourth columns of Table 1.

The value $n = 3$ for the growth of Li_4SiO_4 crystals is consistent with the granular shape of these crystals [10]. The value $n = 1$ for the growth of Li_2SiO_3 crystals is consistent with the acicular shape of these crystals [10]. The higher value of activation energy for the second crystallization step can be attributed to the long-range diffusion of Li^+ ions required for the transformation of Li_4SiO_4 crystals into Li_2SiO_3 crystals.

CONCLUSIONS

From the experimental results the following conclusions can be drawn.

(a) The lithium metasilicate glass heated at constant heating rate during a DTA run devitrifies in two steps. Li_4SiO_4 crystals are formed initially and are then converted at higher temperature into Li_2SiO_3 crystals.

(b) The values of the kinetic parameters for each step are consistent with the crystal shapes and with the crystallization mechanism.

REFERENCES

1 A. Marotta and A. Buri, Thermochim. Acta, 25 (1978) 155.
2 F. Branda, A. Buri, A. Marotta and S. Saiello, Thermochim. Acta, 77 (1984) 13.
3 F. Branda, A. Buri, A. Marotta and S. Saiello, J. Mater. Sci. Lett., 3 (1984) 654.
4 F. Branda, A. Buri, A. Marotta and S. Saiello, Verres Refract., 38 (1984) 589.
5 M. Tatsumisago, T. Minami, N. Umesaki and N. Iawamoto, Chem. Lett., 8 (1986) 1371.
6 A. Marotta, A. Buri and F. Branda, Thermochim. Acta, 40 (1980) 397.
7 K. Matusita and S. Sakka, Bull. Inst. Chem. Res., Kyoto Univ., 59 (1981) 159.
8 T. Ozawa, Polymer, 12 (1971) 150.
9 F.O. Piloyan, I.V. Ryabchikov and O.S. Novikova, Nature (London), 212 (1966) 1229.
10 A.N. Winchell and H. Winchell, The Microscopical Characters of Artificial Inorganic Solid Substances: Optical Properties of Artificial Minerals, Academic Press, New York and London, 1964.