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The non-isothermal devitrification of lithium heptagermanate glass

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Abstract

The non-isothermal devitrification of $Li_2O \cdot 7GeO_2$ 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

The present study is part of a research programme in which the devitrification behaviour of lithium germanate glasses is investigated with the aid of differential thermal analysis (DTA) and X-ray diffraction (XRD).

The co-ordination number of germanium atoms in inorganic glasses has attracted much attention because Ge is a network forming cation which can be present in 4-co-ordination and 6-co-ordination states.

Occurrence of maxima on the curves showing the dependence of density, refractive index and viscosity [1,2] on the lithium oxide content in lithium germanate glasses can be explained by the change of the co-ordination number of Ge atoms from 4 to 6 with the addition Li_2O to GeO_2 glass.

Surface nucleation was observed to occur without exception on any GeO_2 glass specimen which had been cooled to room temperature for any length of time and then heated to a temperature in the crystallization range [3].

In contrast, a lithium germanate glass containing only 5 mol% of lithium oxide exhibits internal nucleation. This glass, when heated at constant rate during a DTA run, devitrifies in three steps. Metastable crystals are formed at 555 °C and are then converted at higher temperature (622 °C) into $Li_2Ge_7O_{15}$ crystals. These latter crystals act as nucleating agents for GeO_2 crystals, which grow at an even higher temperature (819 °C) [4].

In this study, the non-isothermal devitrification of $Li_2O \cdot 7GeO_2$ glass was investigated in order to evaluate the crystallization mechanism and kinetic parameters of crystal growth.

EXPERIMENTAL

The $Li_2O \cdot 7GeO_2$ glass was prepared using reagent grade lithium carbonate and germanium oxide in batches of a size to yield 2 g of glass. The glass was melted in a Pt crucible in an electric oven. The crucible containing the glass was weighed before removing the glass and again after removing the glass. The weight of glass agreed with that anticipated in the batch calculation. This result indicates that the actual glass composition is identical with that based on the formulation of the batch. The melts were cast at high cooling rate between two brass plates; although fracture of the glass resulted, pieces of sufficient size for the experimental measurements were obtained by this technique.

Differential thermal analysis (DTA) curves and their first derivative (DDTA) curves were recorded in air at different heating rates on bulk specimens of about 60 mg. Powdered Al_2O_3 was added to improve heat transfer between the bulk sample and the sample holder. A Netzsch high temperature DSC 404 thermoanalyser was used with Al_2O_3 as reference material.

The phases which crystallized during the DTA runs were identified by X-ray diffraction using a Philips diffractometer.

RESULTS AND DISCUSSION

Crystallizing phases

The DTA curve recorded for a bulk sample of the investigated glass shows a slope change at 491° C and two exothermic peaks at 560 and 628 ° C respectively (Fig. 1). The slope change can be attributed to the glass

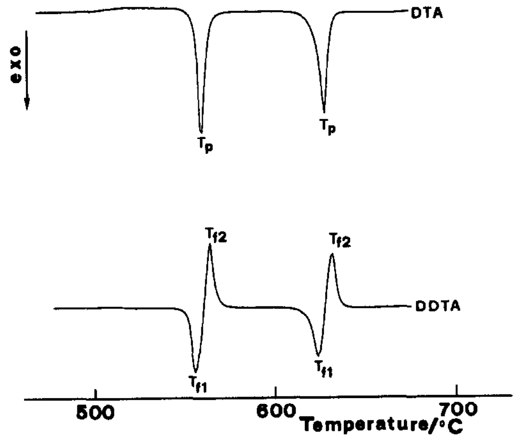

Fig. 1. DTA and DDTA curves recorded at 10 ° C min^{-1}.

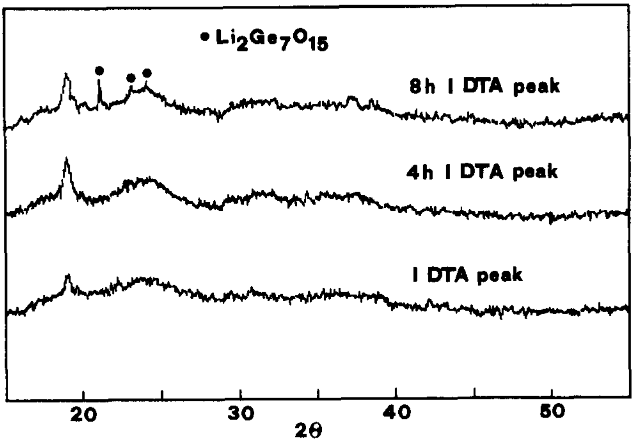

Fig. 2. X-ray diffraction patterns.

transition that occurs at a temperature of 491 ° C, markedly lower than that (551 ° C) of GeO_2 glass. The two exothermic peaks correspond to the crystallization of two crystalline phases. To identify these phases X-ray diffraction analysis was used. Only a sharp reflection at $2\theta = 19°$ (θ is the Bragg angle in degrees) can be detected on the XRD pattern of a glass sample heated in the DTA furnace up to the temperature (560 ° C) of the first exothermic peak; see Fig. 2. This result and the glassy look of the sample after the heat treatment, in spite of the strong thermal effect on the DTA curve, suggest the precipitation of a high number of very small crystals.

To enhance the size of these crystals, three glass samples were held in the DTA furnace at 560 ° C for 4, 8 and 16 h respectively. On the XRD pattern of the sample held for 4 h the intensity of the reflection at $2\theta = 19°$ is increased but no other reflection can be detected; see Fig. 2. The XRD pattern of the sample held for 8 h at 560 ° C exhibits the three stronger reflections of the $Li_2Ge_7O_{15}$, whereas the intensity of the reflection at $2\theta = 19°$ begins to decrease (Fig. 2).

Finally, the XRD pattern of the sample held for 16 h at 560 ° C exhibits the same reflection as the XRD pattern of the glass sample heated in the DTA furnace up to the temperature (628 ° C) of the second exothermic peak. All these reflections can be assigned to $Li_2Ge_7O_{15}$ crystals: see Fig. 3. On both these XRD patterns the reflection at $2\theta = 19°$ is not present.

The reflection at $2\theta = 19°$ corresponds to one of the stronger reflections ($hkl = 010$) of $Li_2Ge_4O_9$ crystals. This phase is not reported in the Li_2O–GeO_2 phase diagram [1] but was obtained [5] by reheating a glass of the same composition. The crystal structure of this compound contains chains of GeO_4 tetrahedra linked by GeO_6 octahedra, forming a three-dimensional network. This structure is quite similar to that of $Li_2Ge_7O_{15}$, which

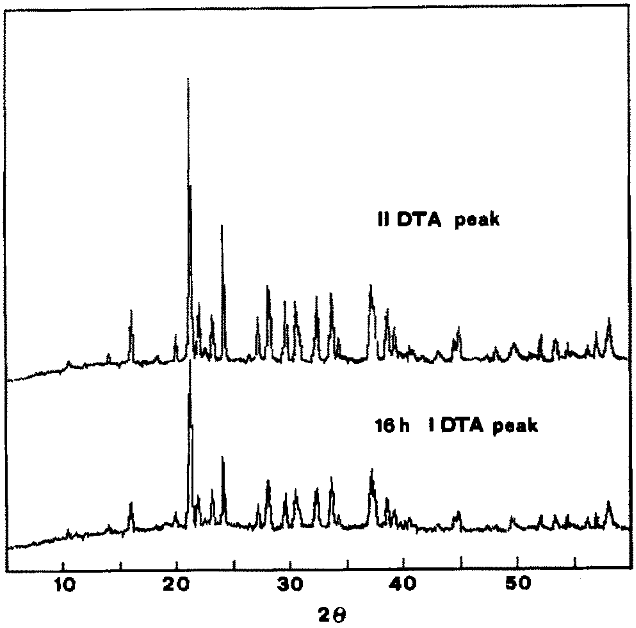

Fig. 3. X-ray diffraction patterns.

contains layers of GeO_4, tetrahedra linked by GeO_6 octahedra to form a three-dimensional network [6]. The two structures can be characterized by the formulae $Li_2[Ge(GeO_3)_3]$ for lithium tetragermanate and $Li_2[Ge(Ge_2O_5)_3]$ for lithium heptagermanate. The oxygen atoms occurring in both the networks are either bridging atoms between two tetrahedrally co-ordinated Ge atoms or bridging atoms between one tetrahedrally and one octahedrally co-ordinated Ge atom. The $Li_2Ge_4O_9$ crystals have a simpler (and therefore kinetically favoured) structure than that of the $Li_2Ge_7O_{15}$ crystals, but similar enough to allow a rapid conversion of the former into the latter, which are thermodynamically stable. Unfortunately, all heat treatments aimed at obtaining a more detailed XRD pattern of these metastable crystals lead to their conversion into the stable $Li_2Ge_7O_{15}$ crystals.

These results suggest that the non-isothermal devitrification occurs in two steps. First, a high number of very small crystals of one metastable phase are formed, and these are then converted at higher temperature into $Li_2Ge_7O_{15}$ crystals.

Kinetic parameters for crystal growth

The non-isothermal devitrification of glasses is well described by the equation proposed by Matusita and Sakka [7]

$$-\ln(1-\alpha) = C(N/\beta^n)\exp(-nE/RT) \qquad (1)$$

where α is the volume fraction crystallized at temperature T, β is the DTA heating rate, N is the number of nuclei per unit volume, E is the activation energy for crystal growth, n is a parameter related to crystal shape, and C is a constant.

Assuming that the deflection ΔT from the baseline is proportional, at each temperature T, to the instantaneous reaction rate [8], the conditions that at the peak temperature T_p

$$\mathrm{d}\Delta T/\mathrm{d}T = 0$$

and at the inflection point temperature T_f

$$\mathrm{d}^2\Delta T/\mathrm{d}T^2 = 0$$

are satisfied, respectively, by [9,10]

$$x = 1 \tag{2}$$

$$x^2 - 3x + 1 = 0 \tag{3}$$

where

$$x = C(N/\beta^n)\exp(-nE/RT) \tag{4}$$

Assuming that the crystals grow in the bulk material from the same fixed number of nuclei at each heating rate, and taking into account eqn. (4), the logarithms of eqn. (2) lead to

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

Moreover, from the two solutions of the quadratic eqn. (3), the following relationship between nE and the two inflection point temperatures T_{f1} and T_{f2} can be derived [10]

$$nE = 1.92/(1/T_{f1} - 1/T_{f2}) \tag{6}$$

By plotting $\ln\beta$ vs. $1/T_p$, straight lines were obtained for each crystalline phase. The values of the activation energy E, as calculated from their slopes, and the values of the product nE, as calculated by eqn. (6) from the two inflection point temperatures detected on the DDTA curve of Fig. 1, are reported in Table 1.

The values of kinetic parameters are consistent with the proposed devitrification mechanism. The two crystalline phases have almost the same

TABLE 1

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

Crystallized phase	E	nE	n
1st peak	531	1266	2.4
2nd peak	523	1668	3.2

structure but the $Li_2Ge_4O_9$ crystals (chains of tetrahedra) have a lower polymerization degree than $Li_2Ge_7O_{15}$ crystals (layers of tetrahedra).

CONCLUSIONS

From the experimental results the following conclusions can be drawn.

(a) The lithium heptagermanate glass heated at constant heating rate during a DTA run devitrifies in two steps. $Li_2Ge_4O_9$ crystals are formed initially and are then converted at higher temperature into $Li_2Ge_7O_{15}$ crystals.

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

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