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The non-isothermal devitrification of $Li_2TiGe_3O_9$ glass

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Abstract

The non-isothermal devitrification of a lithium titanium germanate glass of stoichiometry $Li_2TiGe_3O_9$ has been studied by differential thermal analysis. The temperature of maximum nucleation rate and the value of activation energy for crystal growth were evaluated from DTA curves. The influence on the crystallization process of the specific surface area of the samples and of the heat treatments of nucleation is emphasized. The investigated glass exhibited the same molar ratio of GeO_6/GeO_4 groups and the same T_g as lithium tetragermanate glass. © 1998 Elsevier Science B.V.

Keywords: Crystallization; DTA; FTIR; $Li_2TiGe_3O_9$ glass; Nucleation

1. Introduction

Kinetic investigations on glass devitrification are of interest to elucidate the nature of crystal growth and for researches on glass ceramic materials. This work is part of a more general research program on the devitrification behaviour of germanate glasses. In a previous paper [1], the non-isothermal devitrification of lithium tetragermanate glass was investigated. The devitrification process occurs in two steps. $Li_2Ge_4O_9$ microcrystallites were formed initially and were then converted at higher temperatures into well-shaped $Li_2Ge_4O_9$ crystals. The activation energy of each step was 698 and 502 kJ mol^{-1}, respectively.

In the present study, the effect of replacing 25% of the mole of network of former ions Ge^{4+} by intermediate ions Ti^{4+} on structure and devitrification behaviour of lithium tetragermanate glass has been investigated.

2. Experimental

The glass was prepared using reagent grade lithium carbonate, titanium and germanium oxide in a batch sized to yield 10 g of glass. The glass was melted at 1200°C in a Pt crucible in an electric oven. The crucible containing the glass was weighed both before and after the glass was removed. The weight of the glass agreed with that anticipated from the batch calculation. This result indicates that the actual glass composition was identical to that based on the glass batch. The melt was cast at a high cooling rate between two brass plates. Although this resulted in fracture of the glass, pieces of sufficient size for experimental measurements were obtained by this technique.

Differential thermal analysis (DTA) curves were recorded in air at heating rates of 2, 5, 10, 20°C min^{-1} on bulk specimens (ca. 50 mg) from room temperature to 800°C. Powdered Al_2O_3 was added to improve the heat transfer between bulk samples and sample holder. A Netzsch High Temperature DSC 404 thermoanalyser was used with Al_2O_3 as a reference material.

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The nucleation heat treatments were performed in the DTA furnace 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.

The amorphous nature of the as-quenched glass and the nature of the crystallizing phases during the DTA run were ascertained by X-ray diffraction (XRD). A Guinier-de Wolfe camera using CuK_α radiation was used.

Fourier transfer infrared (FTIR) absorbance spectra were measured in the 400–1300 cm^{-1} region using a Matson 5020 system with a resolution of 2 cm^{-1}. KBr palletized disks were fabricated containing 0.5 mg of the sample and 100 mg KBr.

3. Results and discussion

The FTIR absorbance spectra of the as-quenched glass, recorded in the 400–1400 cm^{-1} range, Fig. 1, exhibit the highest absorption band at ca. 790 cm^{-1}. In alkali-germanate glasses, the maximum of the absorption band due to Ge–O–Ge stretching is shifted to lower wavenumbers than vitreous GeO_2 in which the maximum is at ca. 895 cm^{-1}. This shift can be related to the change in the coordination number of Ge from 4 to 6. The higher the number of octahedrally-coordinated Ge ions the greater is the shift [2]. In the absorbance spectra of the lithium tetragermanate glass, the maximum of the absorption band due to Ge–O–Ge stretching shifted to lower wavenumbers of about the same amount, 90 cm^{-1}, of the investigated glass. This result suggests that the replacing of GeO_2 by TiO_2 did not change the GeO_6/GeO_4 molar ratio. However, the structure of the glass appeared not to be affected by the long heat treatment at 540°C.

Fig. 2 shows DTA curves recorded on an as-quenched bulk sample, a previously nucleated bulk sample and an as-quenched powdered sample of the investigated glass. All curves exhibited a slope change

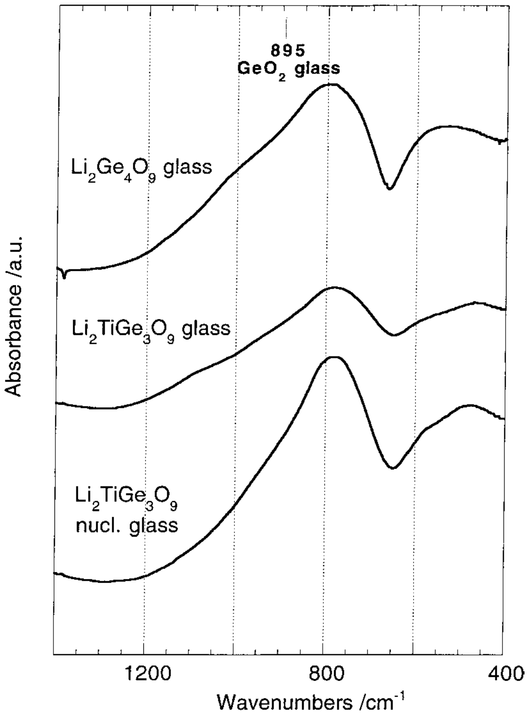

Fig. 1. FTIR absorbance spectra of $Li_2TiGe_3O_9$ and of lithium tetragermanate glasses.

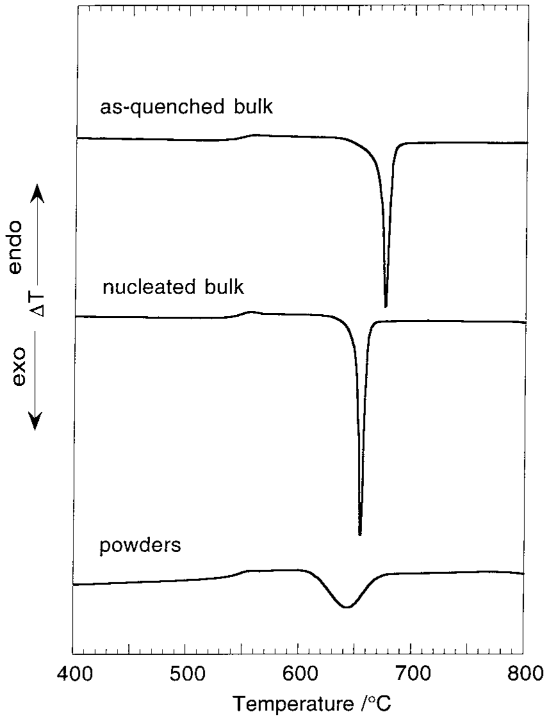

Fig. 2. DTA curves recorded at 10°C min^{-1} on as-quenched bulk powdered, nucleated bulk and as-quenched powdered samples of $Li_2TiGe_3O_9$ glass.

that may be attributed to the glass transition followed by an exothermic peak due to the heat evolved during the crystallization process. In this work, the temperature of the inflection point of the slope change, 535°C, was taken as T_g. This value is very close to that of 532°C for the lithium tetragermanate glass. The gap between the crystallization peak temperature and the glass-transition temperature rose from 30°C for lithium tetragermanate to 143°C for the investigated glass. This result indicates a lower tendency to devitrify $Li_2TiGe_3O_9$ glass.

The X-ray diffraction pattern of samples heated up to the temperature, T_p, of the exothermic peak shows several sharp lines that cannot be attributed to any known crystalline phase. However, the *d*-spacing of the strongest lines and their relative intensities were 3.01_{100}, 4.83_{60}, 4.15_{40} and 3.24_{40}.

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 and is observed in most compositions. It is often necessary to add nucleating agents to achieve internal crystal nucleation. However, certain glass systems nucleate internally without such additions. In non-isothermal devitrification process the number of nuclei, N, per unit volume is the sum of the number, N_s of surface nuclei, proportional to the specific surface area of the samples, the number, N_h, of bulk nuclei formed during the DTA run and of the number N_b bulk nuclei formed during a previous heat treatment of the sample [3]. The higher the number of N, the lower is the temperature of the DTA crystallization peak [4]. Moreover, the shape of the DTA crystallization peaks are strongly affected by the crystallization mechanism to surface and bulk crystallization correspond broad and sharp peaks, respectively [3]. In powdered samples, the great increase of the specific surface area led to an increase of the number of surface nuclei and made dominant surface crystallization. The DTA crystallization peak of powdered sample, Fig. 2, became therefore broader and occurred at a lower temperature than that of the bulk sample.

The temperature of maximum nucleation rate of the investigated glass was obtained using a DTA method described by Marotta et al. [4]. Bulk glass samples were isothermally heat treated at various nucleation temperatures in the DTA furnace, then DTA data were obtained using heating rates of 20°C min^{-1}. This fast heating rate reduced the chance of nuclei formation during the DTA run. Marotta et al. [4] derived an equation from the Johnson–Mehl–Avrami equation:

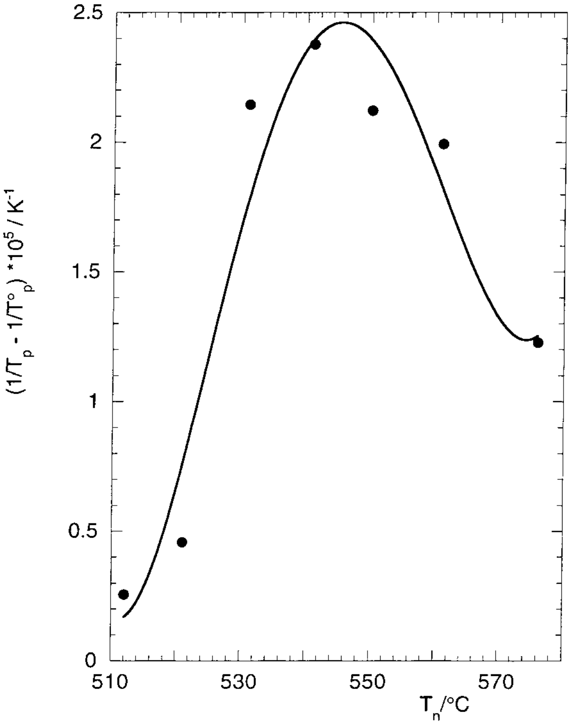

Fig. 3. Nucleation rate – temperature like curve.

$$\ln I = E_c/R(1/T_p - 1/T_p^0) + \text{const.}$$

where I is the kinetic rate constant of nucleation, E_c the activation energy for crystal growth, R the gas constant, T_p the crystallization peak in each DTA run for previously nucleated glass samples and T_p^0 the crystallization peak temperature for the as-quenched glass sample. The temperature of maximum nucleation rate occurs at the maximum (540°C) of $[(1/T_p - 1/T_p^0)]$ plotted as a function of the nucleation heat-treatment temperatures (Fig. 3).

The activation energies, E_c, of crystal growth in the as-quenched glass samples and in the long (16 h) nucleated glass samples were evaluated from a set of DTA curves recorded at different heating rates, β, by the following equation [5]:

$$\ln \beta = -E/RT_p + \text{const.}$$

For as-quenched bulk samples ($N_h \gg N_s + N_b$) E=3/4

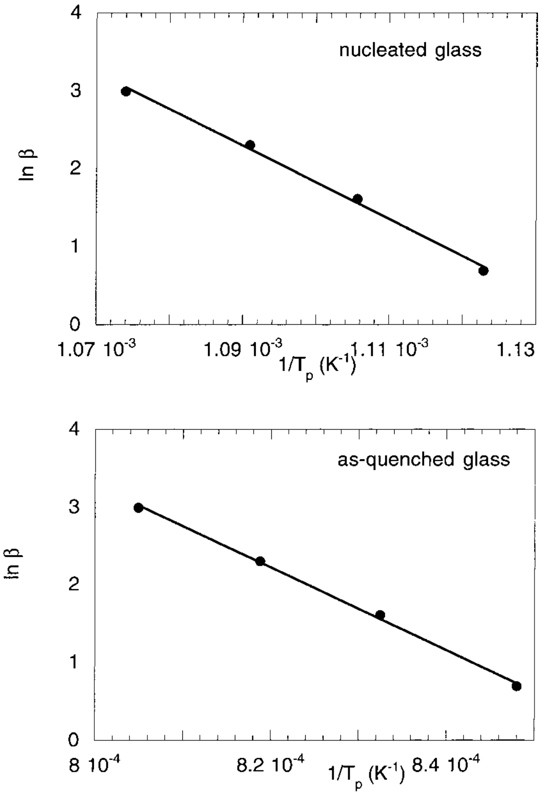

Fig. 4. Ozawa plots of as-quenched glass (upper side) and nucleated glass (lower side).

E_c and for nucleated bulk samples ($N_b \gg N_s + N_h$) $E = E_c$ [6]. By plotting ln β against $1/T_p$, straight lines in both cases were obtained (Fig. 4). The values of $E = 265 \pm 25$ and 391 ± 40 calculated from their slopes for as-quenched and nucleated glasses, respectively, led to two values of activation energies for crystal growth, $E_c = 353$ and 391 kJ mol^{-1}. The difference between these values is of the same order of magnitude, namely 10% of the experimental error. As the studied glass crystallizes at temperatures well above the temperatures of high nucleation rates, the number of nuclei already present in the glass cannot appreciably increases during the crystallization, so the crystals grow from a nearly fixed number of nuclei and the activation energy of crystallization should be equal to that of viscous flow [6]. The value of activation energy for crystallization in the studied glass is much lower than that in lithium tetragermanate where nucleation and crystal growth occur simultaneously [1].

4. Conclusions

The replacing of 25 mol% of Ge^{4+} ions by Ti^{4+} ions in lithium tetragermanate glass leads to a glass having the same GeO_6/GeO_4 molar ratio and the same glass-transition temperature but with a much lower tendency to devitrification. In powdered glass samples surface nucleation is dominant. Bulk glass samples exhibit internal homogeneous nucleation with a maximum nucleation rate at 540°C. The value of activation energy for the crystallization in the studied glass is much lower of that in lithium tetragermanate glass.

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