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The non-isothermal devitrification of $Li_2O{\cdot}TiO_2{\cdot}6GeO_2$ glass

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Abstract

The effect of a partial replacing of GeO_2 by TiO_2 structure and non-isothermal devitrification of lithium heptagermanate glass, examined by Fourier transform infrared spectra, differential thermal analysis and X-ray diffraction, is reported and discussed. The structure and the glass-transition temperature are not affected by the substitution of GeO_2 by TiO_2 but the investigated glass, unlike lithium heptagermanate glass, devitrifies only from the surface into a crystalline phase isomorphous with $Li_2Ge_7O_{15}$ crystals. The validity of the Arrhenius-type relationship between the rate constant of crystal growth and the absolute temperature is also discussed. © 1998 Elsevier Science B.V.

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1. Introduction

Kinetic investigations of the crystallization of glasses are of interest for elucidating the nature of crystal growth and for research into glass–ceramic materials. The present study is part of a research programme in which the devitrification behaviour of alkali germanate glasses is investigated with the aid of differential thermal analysis (DTA) and X-ray diffraction (XRD) [1–5]. In a previous paper [3], the non-isothermal devitrification of lithium heptagermanate glass has been investigated. The devitrification process occurs in two steps: metastable microcrystallites are formed initially and are then converted at higher temperatures into well-shaped $Li_2Ge_7O_{15}$ crystals. The activation energy of each step was found to be 531 and 523 kJ mol^{-1}, respectively.

In the present study, the effect of replacing the network forming Ge^{4+} ions by intermediate Ti^{4+} ions in the 1/7 molar ratio, on the structure and devitrification behaviour of lithium heptagermanate glass has been investigated.

2. Experimental

The glass was prepared using reagent-grade lithium carbonate, titanium and germanium oxide in a batch to yield 10 g of glass. The glass was melted 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 is 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 a fracture of the glass, pieces of

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sufficient size for the experimental measurements were obtained by this technique.

Differential thermal analyses (DTA) were carried out in air at heating rates of 2°, 5°, 10°, and 20°C min^{-1} on bulk or fine powdered specimens (ca. 50 mg) from room temperature to 800°C. Powdered Al_2O_3 was added to the bulk samples to improve heat transfer between bulk samples and sample holder. A Netzsch thermoanalyser high-temperature DSC 404 was used with Al_2O_3 as a reference material. The nucleation heat treatments were performed in the DTA furnace to eliminate temperature gradients.

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 $\mathrm{Cu}K_\alpha$ radiation was used.

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

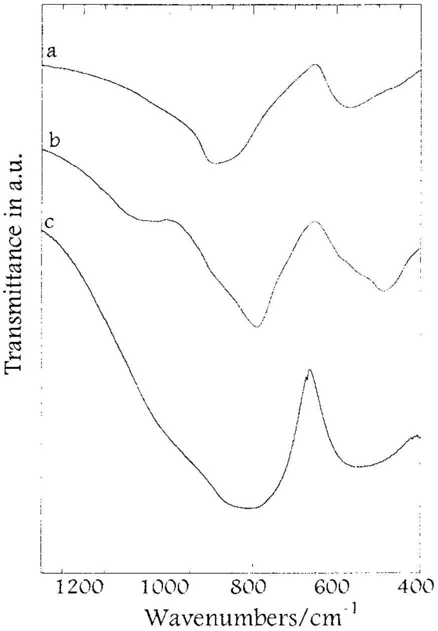

Fig. 1. FT-IR spectra of (a) GeO_2, (b) $Li_2O{\cdot}TiO_2{\cdot}6GeO_2$ and (c) $Li_2O{\cdot}7GeO_2$ glasses.

3. Results and discussion

The FTIR transmittance spectra of the $Li_2O{\cdot}TiO_2{\cdot}6GeO_2$ glass and lithium heptagermanate glass in the 400–1300 cm^{-1} range, where the Ge–O–Ge and O–Ge–O stretching and deformation modes are active, are shown in Fig. 1. These spectra exhibit broad bands, as expected for glassy systems. Both glasses exhibit the highest absorption band at ca. 790 cm^{-1}. From previous studies [6], it is known that in the infrared spectra of hexagonal and vitreous GeO_2, in which the coordination number of germanium is four, the absorption band at ca. 878 cm^{-1} is due to Ge–O–Ge stretching, while in tetragonal GeO_2, in which germanium assumes sixfold coordination, this band occurs at ca. 688 cm^{-1}. In alkali-germanate glasses [7], the maximum of the absorption band due to Ge–O–Ge stretching is shifted to lower wave numbers. This shift can be related to the change in the coordination number of Ge from four to six. The higher the number of octahedrally coordinated Ge ions the greater is the shift. In the transmittance spectra of the investigated glass, and of $Li_2O{\cdot}7GeO_2$ glass, the maximum of the absorption band due to Ge–O–Ge stretching shifts to lower wave numbers of about the same amount 90 cm^{-1}. This result suggests that the replacing of GeO_2 by TiO_2 does not change the GeO_6/GeO_4 molar ratio.

The DTA curve of a bulk sample of the investigated glass is presented in the upper side of Fig. 2. There is a step change in the baseline followed by an exothermic peak.

The step change is attributed to the glass transition while the exothermic effect can be related to crystallization.

When a glass is heated, its heat capacity, together with other properties, changes abruptly in a narrow temperature range, called the glass transition [8]; this is the transformation temperature range at which the glass network acquires mobility, changing from a rigid to a plastic structure. In this work, the inflection point at the slope change temperature of the DTA curve was taken as the glass transition temperature, T_g=508°C, very close to the value of T_g=500°C for $Li_2O{\cdot}7GeO_2$ glass. This result is consistent with the results of FTIR measurements. It was reported [9] that the values of T_g in lithium germanate glasses are related to the values of the GeO_6/GeO_4 molar ratio.

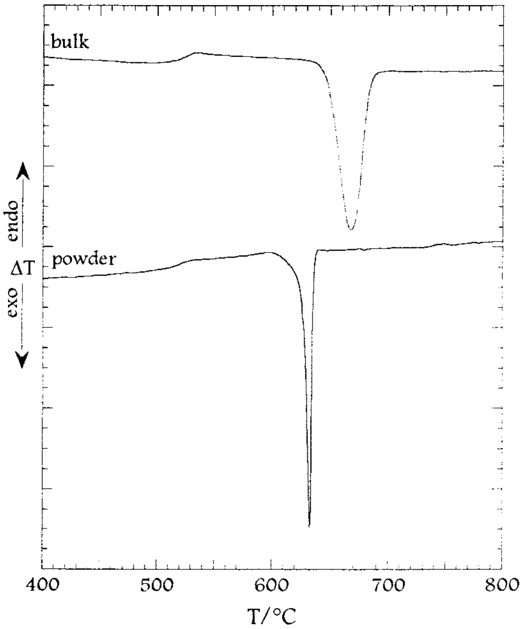

Fig. 2. DTA curves of bulk and powder samples of studied glass recorded at 10°C min^{-1}.

Table 1
ObservedXRD patterns, *d*-spacing in 10^{-10} m

$Li_2Ge_7O_{15}$ card 23-1180	DTA exo peak	
	bulk sample	powder sample
5.53_{30}	5.60_{20}	5.60_{20}
4.39_{40}	4.49_{20}	4.49_{20}
4.19_{100}	4.24_{100}	4.24_{100}
4.04_{30}	4.09_{30}	4.09_{20}
3.81_{30}	3.88_{40}	3.88_{30}
3.67_{70}	3.73_{90}	3.73_{60}
		3.43_{40}
3.26_{40}	3.31_{25}	3.31_{20}
3.16_{60}	3.20_{40}	3.20_{30}
3.00_{30}	3.05_{30}	3.05_{30}
2.91_{60}	2.97_{30}	2.97_{20}
2.75_{60}	2.79_{50}	2.79_{30}
2.65_{60}	2.69_{60}	2.69_{20}
2.41_{70}	2.44_{50}	2.44_{30}
2.33_{60}	2.36_{30}	2.36_{20}
2.29_{40}	2.32_{20}	2.29_{5}
2.21_{40}	2.24_{15}	2.24_{5}

When a glass crystallizes during a DTA run the heat of crystallization is evolved and an exothermic peak appears in the DTA curve. The XRD pattern obtained from a glass sample heated in the DTA furnace up to the temperature of crystallization peak are compared in Table 1 with those of $Li_2Ge_7O_{15}$. Usually, the unit cell expands if a small (0.053 nm) Ge^{4+} ion is being replaced by the larger (0.068 nm) Ti^{4+} one. From Bragg's law and the *d*-spacing formulae, an increase in the unit cell parameters leads to an increase in the *d*-spacing of powder lines, the whole pattern shifts as shown in Table 1 to lower values of 2Θ, although all the lines do not move by the same amount.

Glass devitrification is the result of two individual processes: nucleation and crystal growth. Nucleation in glass-forming systems can occur either in the volume or on the surface of the sample. In practice, surface crystal nucleation always occurs and it is the only one 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. In a non-isothermal devitrification process, the total number of nuclei per unit volume, N, is the sum of the number, N_s, of surface nuclei, the number, N_h, of bulk nuclei formed during the DTA run and of the number, N_b, of bulk nuclei formed during a previous heat treatment of the sample. The values of N_s, N_h and N_b are, respectively, proportional to the specific surface area of the samples, to the reciprocal of DTA heating rate and to the time of the nucleation heat treatment [10]. As a glass usually crystallizes at a temperature well above the temperatures of high nucleation rate, in all cases, the crystals grow from an almost fixed number of nuclei. For a given heating rate, the higher is the number N, the lower is the temperature of the DTA crystallization peak [11].

To investigate the influence of the sample specific surface and of the heat treatments on devitrification mechanism, finely powdered glass samples and bulk samples previously heated for 4 h at T_g, as bulk nucleation rates are usually high in a temperature range near T_g were subjected to differential thermal analysis. The DTA crystallization peak of the powdered samples, as a consequence of the great increase in the number of surface nuclei, due to the increase in the specific surface area of the glass sample, is shifted to a lower temperature than the corresponding bulk samples, Fig. 3. The XRD pattern carried out on powdered samples heated to the crystallization temperature shows (Table 1) the presence of crystalline phase in bulk samples. The strongest reflection of

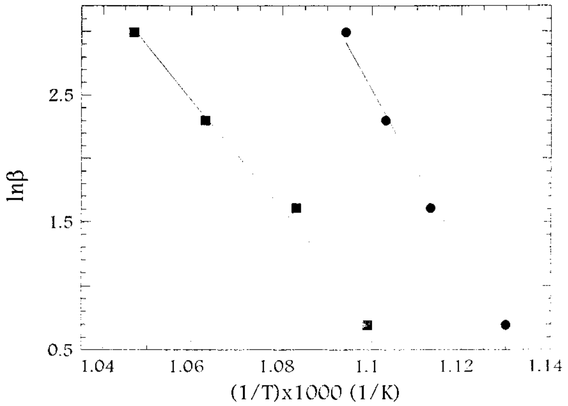

Fig. 3. Plots of ln β vs. $1/T_p$: (●) powder samples; and (n) bulk samples.

GeO_2 crystals were also found. The DTA crystallization peak of the heat-treated sample occurs at nearly the same temperature as that of the as-quenched bulk sample. These results suggest that only surface crystallization occurs during the DTA.

It is of interest to remark that, in spite of the same structure of the mother glasses and crystallizing phases, the investigated glass and lithium heptagermanate glass show two quite different devitrification mechanisms. Lithium heptagermanate glass devitrifies in two stages: the precipitation of a large number of $Li_2Ge_4O_9$ microcrystals occurs that act as bulk nuclei for the growth of $Li_2Ge_7O_{15}$ crystals [3]. The presence of Ti^{4+} ions in the network of the investigated glass hinders $Li_2Ge_4O_9$ microcrystals precipitation, and thus surface crystallization become dominant.

The activation energy for crystal growth, E, has been evaluated from a set of differential thermal analysis curves recorded at different heating rates, β, by the authors of Ref. [12]

$$\ln \beta = -E/RT_{\mathrm{p}} + \mathrm{const} \tag{1}$$

This equation is based on the following assumptions:

1. at the temperature, T_p, of the crystallization peak, the degree of crystallization attains the same specific value, independent of heating rate;
2. the crystals grow at each heating rate from the same number of nuclei, i.e. the bulk nuclei formed during the DTA run can be neglected; and
3. the rate constants are related to the absolute temperature, T, by an Arrhenius-type equation:

$$k = A \exp(-E/RT) \tag{2}$$

The values of E for bulk and powdered samples were calculated from the slopes of the straight lines obtained by plotting ln~β against $1/T_p$, Fig. 3, and are 357 and 520 kJ mol^{-1} for bulk and powdered samples, respectively. It can be noted that the value of E for fine powdered samples is ca. 30% higher than that of bulk sample. This difference can be attributed to the different crystallization temperature ranges (612–641°C) for powder samples and (637–683°C) for bulk samples. A similar discrepancy was already observed for lithium disilicate devitrification [13], where the activation energy for crystal growth rises from 301 kJ mol^{-1} in the (560–640°C) range to 366 kJ mol^{-1} in the (530–600°C) range.

As the crystallization is viscosity-controlled, the relationship between rate constants and absolute temperature is better described by a Vogel–Fulcher type equation:

$$k = B \exp[E'/R(T - T_0)] \tag{3}$$

The Arrhenius type equation holds only in a narrow temperature range leading to different values of activation energy for different crystallization temperature ranges [13].

4. Conclusions

From the experimental results the following conclusions can be drawn:

(a) $Li_2O{\cdot}TiO_2{\cdot}6GeO_2$ and $Li_2O{\cdot}7GeO_2$ glasses exhibit nearly the same values of GeO_6/GeO_4 group molar ratio and of the T_g.

(b) The investigated glass, unlike the $Li_2O{\cdot}7GeO_2$ glass, devitrifies from the surface during the DTA run in a single stage.

(c) The crystallizing phase seems to be isomorphous with $Li_2Ge_7O_{15}$ crystals.

(d) The rate constant of crystal growth can be related to the absolute temperature by an Arrhenius-type equation only in a narrow temperature range.

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