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Crystallization and microstructure changes in fluorine-containing Li_2O–Al_2O_3–SiO_2 glasses

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Abstract

The nucleation and crystallization of Li_2O–Al_2O_3–SiO_2 glasses doped with 0, 0.4, 0.8 and 1.2 wt.% F^- were investigated. With increasing fluoride content, the transformations from glass to β-quartz solid solution (β-quartz) and β-quartz to β-spodumene solid solution (β-spodumene) appeared at lower temperatures. The crystallization peak temperature (T_p) and activation energies (E) decreased, the Avrami exponent (n) and pre-exponential factor (ν) increased. The results suggest that fluoride promotes the initial crystallization and diffusion in the glass.

Keywords: Glass; Glass-ceramics; Nucleation; Crystallization

1. Introduction

Lithium aluminum silicate (LAS) glass-ceramics have low thermal expansion coefficients as well as excellent thermal and chemical durability, and have achieved great industrial and economic importance [1–6]. Fluorine plays an important role in LAS glass-ceramics. Holland and Gulati [10] realized that around 0.2 wt.% fluorine caused the exterior lattice volume of LAS glass-ceramics to be 0.4% greater than that of the interior. This volume difference is believed to be the cause of a compression layer that is responsible for higher strength. Duan et al. [7], Tian et al. [8] and Griggs et al. [9] concluded that fluoride promoted nucleation and growth of glass-ceramics by the ingression of F^- ions into the glass network to replace non-bridging oxygen ions and decrease the extent of aggregation of the glass network. But the effect of fluorine on crystallization in LAS glass has not previously been discussed. The purpose of this study is to characterize the crystallization kinetics of fluorine-containing Li_2O–Al_2O_3–SiO_2 glasses and the effect of fluorine on the microstructure of the system.

2. Experimental procedures

The initial materials were analytical grade reagents (Table 1): SiO_2, Al_2O_3, Li_2CO_3, MgO, ZnO, TiO_2, ZrO_2, and MgF_2. An excess of fluoride was added to compensate for volatilization during melting, and the concentration of fluoride was determined by dispersive X-ray spectrometry (EDX). The detailed compositions of these glasses are given in Table 1. Glass batches were well mixed by dry ball-milling for 12 h, and thereafter melted in Pt crucibles at 1873 K in an electric furnace for 3 h. The melts were poured onto 600 °C steel plates, transferred to an annealing furnace, and held for 1 h followed by slow cooling to room temperature.

Differential thermal analysis (DTA) of annealed glass specimens was done in a Dupont 2100 Thermal Analyzer. After crushing annealed glasses to about 100–200 μm, non-isothermal experiments were performed by heating 30 mg samples in a Pt crucible with Al_2O_3 as the reference material in the temperature range between 20 and 1200 °C at heating rates of 5–20 °C min^{-1}.

X-ray diffraction (XRD) investigations were done with a D-max-RB diffractometer with Cu Kα radiation in the 2θ range from 10 to 70° at 0.02° steps.

Scanning electron microscopy (SEM) was done with an H-800. Optical mount specimens were prepared with standard metallographic techniques followed by chemical

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Table 1
Chemical composition of the glasses (in wt.%)

Sample no.	Li_2O	Al_2O_3	SiO_2	MgO	ZnO	TiO_2	ZrO_2	F^-
1	4.0	21.0	67.0	2.0	1.0	4	1.0	0
2	4.0	20.9	66.7	2.0	1.0	4	1.0	0.4
3	4.0	20.8	66.4	2.0	1.0	4	1.0	0.8
4	4.0	20.7	66.1	2.0	1.0	4	1.0	1.2

etching in an HF solution (5%) for 1.5 min. Etched glass-ceramic samples were coated with a thin layer of gold.

3. Results and discussion

DTA curves for the four glass samples at a heating rate of 10 K/min are shown in Fig. 1. Only one exotherm was observed in each curve, the same as in previous investigations [1–5]. The glass transition temperature (T_g) and glass crystallization peak temperature (T_p) shifted to lower temperature as the fluoride content increased.

From the Johnson–Mehl–Avrami (JMA) equation [11,12], non-isothermal crystallization kinetics of glass can be described by the Kissinger expression [13].

$$\ln\frac{T_p^2}{\alpha} = \frac{E}{RT_p} + \ln\frac{E}{R\nu} \qquad (1)$$

where T_p is the crystallization peak maximum temperature in a DTA curve, α the heating rate. T_p of four samples at different heating rates are given in Table 2. From Table 2, we can see that T_p increased with increased heating rate and decreased with increased F content. Values of E and

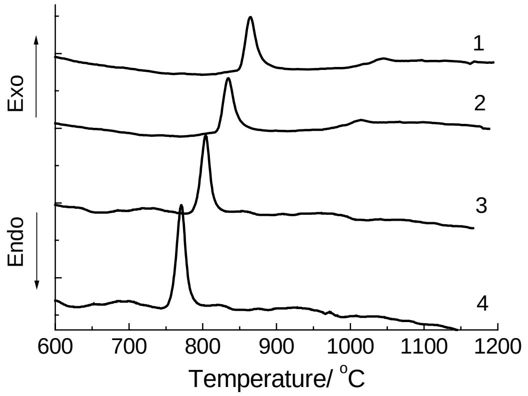

Fig. 1. DTA curves for glass samples with various F^- content at 10 K/min. (1) Parent glass; (2) $F^- = 0.4\%$; (3) $F^- = 0.8\%$; (4) $F^- = 1.2\%$.

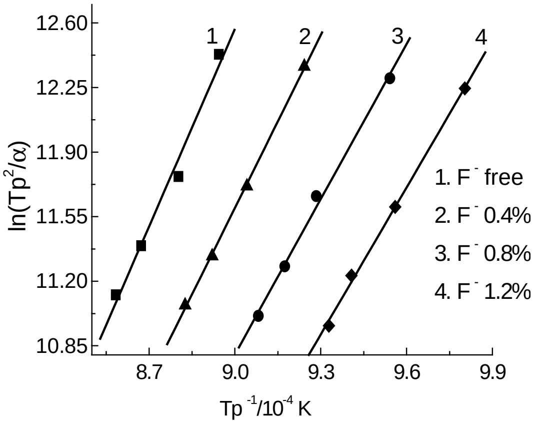

Fig. 2. Plots of $\ln(T_p^2/\alpha)$ vs. $1/T_p$ for the glasses.

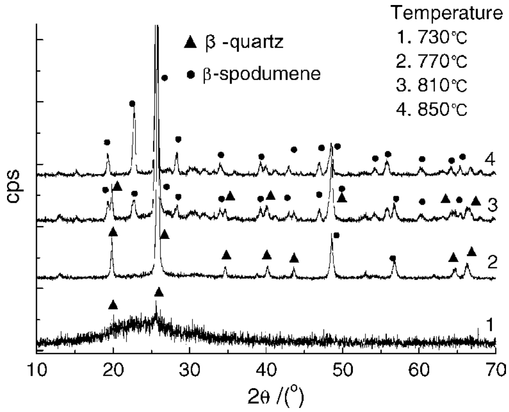

Fig. 3. XRD patterns of sample with 1.2% F^- content heated at 730, 770, 810 and 850 °C for 2 h.

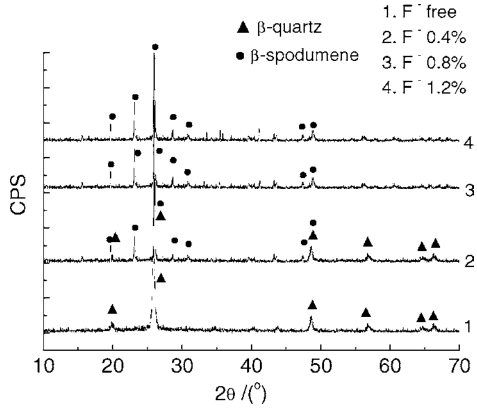

Fig. 4. XRD patterns of four samples with different F^- ion content heated at 850 °C for 2 h.

Table 2
T_p (K), E and ν of four samples

Sample no.	5 ($K\,min^{-1}$)	10 ($K\,min^{-1}$)	15 ($K\,min^{-1}$)	20 ($K\,min^{-1}$)	E ($kJ\,mol^{-1}$)	ν (min^{-1})
1	1118 ± 2	1136 ± 2	1153 ± 2	1165 ± 2	315 ± 3	$(3.1 \pm 0.2) \times 10^{11}$
2	1082 ± 2	1106 ± 2	1121 ± 2	1133 ± 2	284 ± 3	$(3.3 \pm 0.2) \times 10^{12}$
3	1048 ±2	1077 ±2	1090 ±2	1101 ±2	271 ± 3	$(4.3 \pm 0.3) \times 10^{13}$
4	1020 ± 2	1046 ± 2	1063 ± 2	1072 ± 2	242 ± 2	$(5.2 \pm 0.3) \times 10^{14}$

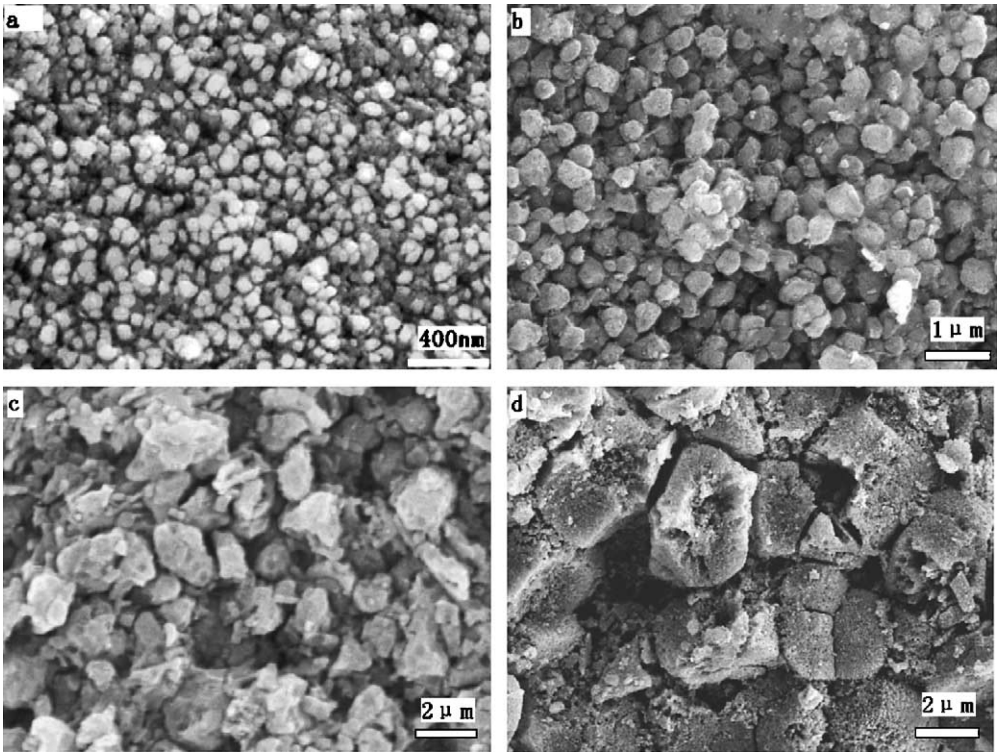

Fig. 5. SEM pictures showing the microstructure of four samples with different F^- ion content heated at 850° C for 2 h. (a) F^- ion free; (b) 0.4% F^-; (c) 0.8% F^-; (d) 1.2% F^-.

ν derived from the plots of $\ln(T_p^2/\alpha)$ versus $1/T_p$ in Fig. 2 are also given in Table 3. E decreased and ν increased with increasing F^-.

Powder XRD patterns of 1.2% fluoride glasses heated at 730, 770, 810 and 850 °C for 2 h are shown in Fig. 3. After being heated at 730 °C, the samples showed a broad scattering spectrum, and small amounts of high-quartz solid solution formed. For the glass samples being heated at higher temperature, 770 °C, the intensity of β-quartz increased and the broad scattering spectrum disappeared, indicating near completion of crystallization. β-spodumene appeared and β-quartz decreased after being heated at 810 °C, β-spodumene increased and β-quartz disappeared as the heating temperature increased to 850 °C.

Powder XRD patterns of 0–1.2% fluoride containing glasses heated at 850 °C for 2 h is shown in Fig. 4. For glasses without fluoride, only β-quartz precipitated. As the content of fluoride increased, the β-spodumene increased gradually. In the samples doped with 0.8% F^- and heated at 850 °C, β-quartz disappeared. From Figs. 3 and 4, we can see that fluoride ion not only promotes the transformation of glass to β-quartz, but also accelerates the transformation β-quartz to β-spodumene.

The microstructure of the four different glasses heated at 850 °C for 2 h is shown in Fig. 5(a–d).The grain sizes increased with increasing fluoride content. The samples without fluoride heated at 850 °C have grain size about 50–100 nm, which are the same as other reports [1–4].

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