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EFFECT OF NUCLEATING AGENTS ON THE CRYSTALLIZATION OF Li_2O–Al_2O_3–SiO_2 SYSTEM GLASS

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Abstract

The processes of nucleation of Li_2O–Al_2O_3–SiO_2 glasses with TiO_2 and TiO_2+ZrO_2 as nucleating agents were discussed. The DTA peak temperature and DTA peak height shown a strong dependence on the nucleation temperature in the glass with TiO_2, while in the glass with TiO_2+ZrO_2, this tendency was small. The optimum nucleation temperatures were 745 and 760°C for two glasses. It suggested that with TiO_2+ZrO_2 as nucleating agents, the crystallization had lower sensitivity for nucleation temperature, and the glass had higher nucleation efficiency than with TiO_2.

Keywords: crystallization, differential thermal analysis, glass-ceramics, nucleation

Introduction

Lithium aluminumsilicate glass-ceramics (Li_2O–Al_2O_3–SiO_2), whose major crystalline phases are h-quartz solid solution (h-quartz$_{ss}$) and β-spodumene, have low thermal expansion coefficient as well as excellent thermal and chemical durability, and have achieved great industrial and economical importance [1–6]. In LAS glass-ceramics, the most important nucleating agents were TiO_2 and ZrO_2 or a combination of both [1–6]. Doherty [3] showed that phase separation occurred on cooling from the melt and subsequent heating caused the formation of a large number of aluminium titanate crystals approximately 5.0 nm in diameter. These crystals acted as sites for heterogeneous nucleation. As contrast, Maier [4] observed the formation of $ZrTiO_4$ crystallites which acted as precursor nuclei for subsequent crystallization in glass containing TiO_2+ZrO_2. Sack and Schiffner [5, 6] thought that with TiO_2+ZrO_2 as nucleating agents, the LAS glass had higher nucleation efficiency than that with TiO_2. But effect of the two nucleating agents on process of nucleation had not been discussed.

The nucleation process is usually investigated by differential thermal analysis (DTA) [7–10]. Recently a new technique using differential thermal analysis (DTA) has been proposed [11, 12]. Because the formation of a consistent number of nuclei

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shifts the exothermic peak to low temperature, the nucleation can obtain by DTA technique therefore an evaluation of nucleation can be obtained by comparing the position of the exothermic peak and nucleation peak height in samples nucleated with a different thermal schedule.

In present paper, the nucleation and crystallization behavior of Li_2O–Al_2O_3–SiO_2 glasses with TiO_2 and TiO_2+ZrO_2 as nucleating agents were investigated, the optimum nucleation temperature was determined, and effect of the two nucleating agents on process of nucleation have been discussed.

Experimental

The starting materials were analytical grade reagents: SiO_2, Al_2O_3, Li_2CO_3, MgO, ZnO, $BaCO_3$, P_2O_5, TiO_2, ZrO_2. The starting materials were analytical grade reagents: SiO_2, Al_2O_3, Li_2CO_3, MgO, ZnO, $BaCO_3$, P_2O_5, TiO_2 and ZrO_2. The detailed compositions of these glasses were given in Table 1. Glass batches were hand-mixed for 20 min using an alumina mortar and pestle and thereafter melted in alumina crucibles at 1500–1600°C for 2 h for complete glass melting. The as-cast glass samples were annealed at 500°C for 1 h followed by slow cooling to the room temperature.

Table 1 Chemical composition of the glass (mass%)

No.	LiO_2	Al_2O_3	SiO_2	MgO	ZnO	P_2O_5	BaO	TiO_2	ZrO_2
1	3.9	21.5	65.4	2.0	1.2	1	1.0	4	0
2	3.9	21.5	65.4	2.0	1.2	1	1.0	2	2

Differential thermal analysis (DTA) scans of annealed glass specimens were carried out in a DuPont 2100 Thermal Analyzer. After crushing annealed glasses to the size of about 100–200 μm, non-isothermal experiments were performed by heating 30 mg glass samples in a Pt crucible and using Al_2O_3 as the reference material. In order to determine the optimal nucleation temperature, DTA runs were carried out as follows: during each DTA run, a glass sample was heated at a rate of 10°C min^{-1} to nucleation temperature, 600, 660, 700, 740, 780°C respectively for 2 h and subsequently heated to 1200°C at the rate of 10°C min^{-1}.

The X-ray diffraction (XRD) investigations were carried out in a D-max-RB Model diffractometer using CuK_α radiation at 40 kV and 40 mV settings in the 2θ range from 10 to 70 at 0.02° step size. The crystallized phases were identified by comparing the peak positions and intensified with those in the JCPDS (Joint Committee on Powder Diffraction Standards) data files.

Scanning electron microscopy (SEM) investigations were conducted in JEM-2010F operated at 25 kV. For the SEM investigations, optical mount specimens were prepared using standard metallographic techniques followed by chemical etching them in a HF solution (5%) for 1.5 min. The etched glass–ceramic samples were coated with a thin layer of gold.

Results and discussion

Figures 1a and b show the DTA curves of No.1 and No. 2 glass samples heat-treated at different temperatures for 2 h. The DTA curve of the sample heat-treated at 600°C for 2 h is the same as that of parent glass. Only one exothermic peak is formed during the DTA run, it is the same as other reports [2–6]. Crystallization peak temperatures (T_p) change as nucleation temperatures (T_n) vary, but glass transition temperatures (T_g) have little change, for No. 1 glass, T_g was about 662°C, and for the No. 2 glass, T_g was about 678°C. Crystallization peak temperature T_p *vs*. nucleation temperature T_n is show in Fig. 2. From Fig. 2, T_p decreased with increasing nucleation temperature at first, and showed a minimum temperature, then increased. After polynomial simulation, the minimum T_p of No. 1 glass samples appeared at 745°C, while the minimum T_p of No. 2 glass sample appeared at 760°C. According to Ray and Day [11, 12], the plot of crystallization peak temperature *vs*. nucleation temperature displays minimum, which represents the temperature of maximum nucleation rate, T_{max}.

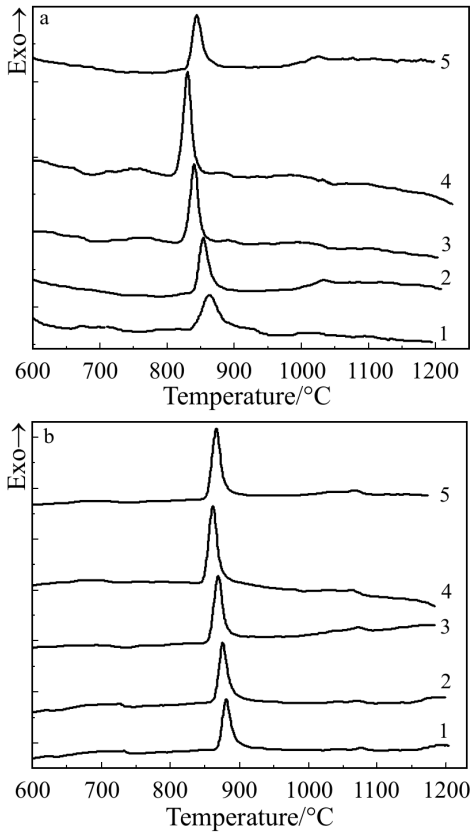

Fig. 1 The DTA curves of a – No. 1 and b – No. 2 glass samples, α=10°C min^{-1}. 1 – parent glass and 600°C; 2 – 660°C; 3 – 700°C; 4 – 740°C; 5 – 780°C

From Fig. 2, we can also see that when the nucleation temperature change from 600 to 780°C, the change of crystallization peak temperature in No. 1 glass samples is 34°C, while in No. 2 glass samples, the change of T_p is 16°C. Especially when the nucleation temperature is between 700 and 780°C, the variation of T_p is 14°C in No. 1 glass samples, which is 3°C in No. 2 glass sample.

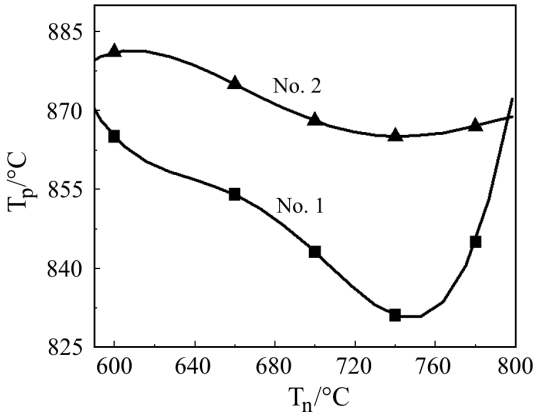

Fig. 2 Crystallization peak temperature (T_p) *vs.* nucleation temperature (T_n)

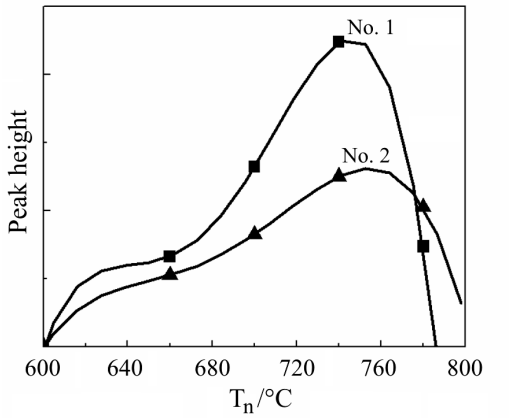

Fig. 3 Crystallization peak height *vs*. nucleation temperature (T_n)

The temperature of maximum nucleation rate, T_{max}, can also be determined by plotting the crystallization peak height *vs*. the nucleation temperatures (T_n), which is shown in Fig. 3. These results are the same as crystallization peak temperature T_p *vs*. the nucleation temperature T_n. With increasing nucleation temperature, crystallization peak height decreased at first, and showed a minimum temperature, then increased [11, 12]. After polynomial simulation, the minimum T_p of No. 1 glass samples appeared at 745°C, while the minimum T_p of No. 2 glass samples appeared at 760°C.

In Figs 2 and 3, the DTA peak temperature and DTA peak height show a strong dependence for the nucleation temperature as with TiO_2 as nucleating agents, while in glass with TiO_2+ZrO_2 as nucleating agents, this tendency is decreasing. especially when the nucleation temperature is between 700 and 780°C, nucleation often occurs in this range. This means that the process of nucleation strongly depends on the nucleation temperature in the glass with TiO_2 as nucleating agents. So in producing the LAS glass-ceramics, it is favorable to adopt TiO_2+ZrO_2 as nucleation agents.

TiO_2 and TiO_2+ZrO_2 are two of the most effective nucleating agents in promoting the crystallization of Li_2O–Al_2O_3–SiO_2 glasses [1–6, 13–15], but the mechanism of nucleation is different. Doherty [3] showed that phase separation occurred on cooling from the melt and subsequent heating caused the formation of a large number of aluminium titanate crystals. These crystals acted as sites for heterogeneous nucleation and allowed crystallization of the remaining glass to proceed as nucleation temperature increasing, the aluminium titanate crystals grew. Nordmann [13] showed that small crystallites of h-quartz$_{ss}$ formed at 725°C, 2 h, a further increment to 4 h and 750°C resulted in growth of h-quartz, the nuclei growing as time and temperature increasing. These mean that when TiO_2 served as nucleating agents, nuclei can grow with time and temperature and h-quartz$_{ss}$ can also appear in the range of nucleation temperature. As contrast, Maier [4] studied a lithium aluminosilicate glass containing TiO_2+ZrO_2. They observed the formation of $ZrTiO_4$ crystallites which acted as precursor nuclei for subsequent crystallization. Riello [14] showed that the average sizes of the crystalline nuclei of $ZrTiO_4$ were 4.3, 4.0, 4.8 nm for the samples crystallized at 750°C for 0.5, 1.5, 3.5 h, respectively. Arnault [15] also showed $ZrTiO_4$ crystallites were stable in LAS glass. The different stability of nuclei in two glass maybe why the process of nucleation strongly depends on the nucleation temperature in the glass with TiO_2, and glass with TiO_2·ZrO_2 is more favor than that of the glass with TiO_2 as nucleating agents. This maybe why that with TiO_2·ZrO_2 as nucleating agents, the LAS glass had higher nucleation efficiency than that with TiO_2 as nucleating agents.

In order to obtain the relationship between the crystallization peak temperature and the optimal nucleation time, the T_p *vs*. the nucleation time (t_n) was plotted in Fig. 4. At the heating rate is 10°C min^{-1}, the nucleation temperature were 745°C for No. 1 glass samples and 760°C for No. 2 glass samples, the nucleation time are 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 h. From the Fig. 4, T_p decreased rapidly at first with heat treatment and then its decreasing rate is slow down. When nucleating 2 h at the given temperatures, the variation of T_p is small, so the efficient nucleation time of the two glasses was 2 h.

According to DTA curves, after the glass have been heated at the rate of 10°C min^{-1} and nucleated at 745°C for 2 h, the onset of crystallization temperature is about 795–805°C for No. 1 glass samples and 835–845°C for No. 2 glass samples, so the most appropriate nucleation and crystallization thermal cycles are nucleating 745°C for 2 h, crystallizing at 800°C for 2 h for No. 1 glass sample, and nucleating at 760°C for 2 h, crystallizing at 840°C for 2 h for No. 2 glass sample. After crystallization, only h-quartz$_{ss}$ ($Li_xAl_xSi_{1-x}O_2$) were formed as presented by Fig. 5 which shows the XRD patterns of the two glass ceramic systems. The microstructure of two

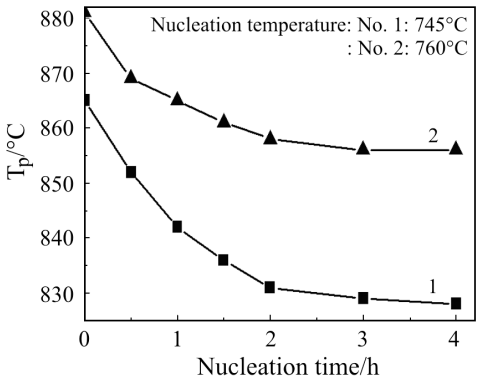

Fig. 4 Plot of the crystallization peak temperature (T_p) *vs*. the nucleation time

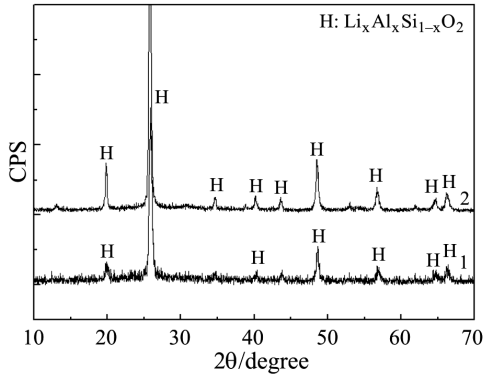

Fig. 5 XRD patterns of samples that have
1 – 4% TiO_2 as nucleating agents, heat treated at 745°C/2 h+800°C/2 h;
2 – 2% TiO_2+2%ZrO_2 as nucleating agents heat treated at 760°C/2 h+840°C/2 h

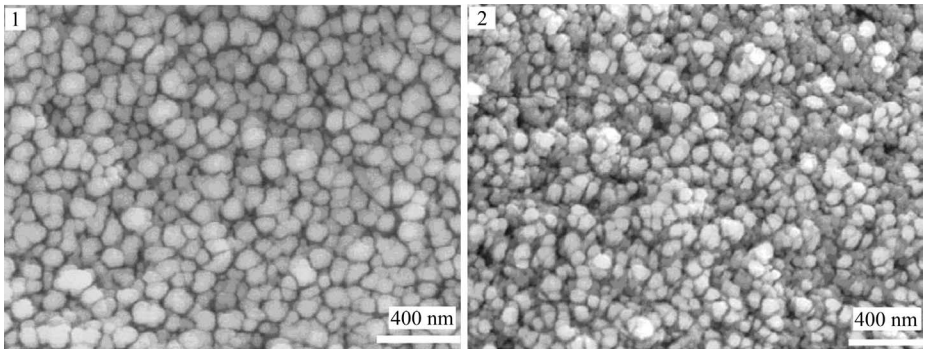

Fig. 6 SEM patterns of samples that have
1 – 4% TiO_2 as nucleating agents, heat treated at 745°C/2 h+800°C/2 h;
2 – 2% TiO_2+2%ZrO_2 as nucleating agents heat treated at 760°C/2 h+840°C/2 h

glass-ceramics was showed in Fig. 6. The two glass-ceramics all have very fine crystal grains, the glass ceramic with 4% TiO_2 is composed of small crystallites approximately 100–150 nm in diameter, while the glass ceramic with 2%TiO_2+2%ZrO_2 is composed of crystallites approximately 50–100 nm in diameter. It was the same as other literatures [1–6]. These mean that TiO_2+ZrO_2 as nucleating agents had higher nucleation efficiency than TiO_2.

Conclusions

The process of nucleation of Li_2O–Al_2O_3–SiO_2 glasses with TiO_2 and TiO_2+ZrO_2 as nucleating agents were discussed. The DTA peak temperature and height in the glass with TiO_2 more depended on the nucleation temperature than in the glass with TiO_2+ZrO_2. The optimum nucleation temperature were 745 and 760°C for two glasses. Only high-quartz solid solution crystals precipitated from the two glasses, in glass with small crystallites approximately 100–150 nm in diameter for TiO_2 doped glass, and 50–100 nm TiO_2+ZrO_2 doped glass. With TiO_2+ZrO_2 addition, the crystallization is less sensitive to nucleation temperature, and the glass has higher nucleation efficiency.

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