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Short communication

Crystallization and microstructure of Li_2O–Al_2O_3–SiO_2 glass containing complex nucleating agent

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Abstract

The crystallization and microstructure of Li_2O–Al_2O_3–SiO_2 (LAS) glass ceramic with complex nucleating agents ($TiO_2 + ZrO_2 + P_2O_5$ +/or F^-) are investigated by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM), and the effects of P_2O_5 and F^- on the crystallization of LAS glass are also analyzed. The introduction of both P_2O_5 and F^- promotes the crystallization of LAS glass by decreasing the crystallization temperature and adjusting the crystallization kinetic parameters, allows a direct formation of β-spodumene without the transformation of $LiAl(SiO_3)_2$ into β-spodumene and as a result, increases the crystal size and crystallinity of LAS glass ceramic.

Keywords: Glass ceramic; Crystal size; Crystallization; Microstructure

1. Introduction

Li_2O–Al_2O_3–SiO_2 (LAS) system glass ceramics has been extensively investigated because of its low, zero or even negative thermal expansion coefficient as well as high thermal shock resistance and long chemical durability [1–4]. The most popular nucleating agents of LAS glass are TiO_2, ZrO_2, etc., and fluorine (F) has recently been introduced as a nucleating agent to accelerate the nucleation and crystallization of LAS glass [5–8]. P_2O_5 has also been used as nucleation agent in a wide category of glass ceramic including Li_2O–SiO_2, Li_2O–Al_2O_3–SiO_2, Li_2O–MgO–SiO_2, MgO–Al_2O_3–SiO_2 [9,10] and apatite glass ceramics [11].

The present study on the LAS glass ceramics is mainly concentrated on the crystallization mechanism of LAS glass containing one or two nucleating agents, such as TiO_2 +/or ZrO_2 +/or F^-. In this paper, the complex nucleating agent consisting of TiO_2, ZrO_2, P_2O_5 and/or F^- was used in the LAS system, and the crystallization behavior and microstructure development were monitored and analyzed by DTA, XRD, IR and TEM.

2. Experimental

Acid washed quartz sand and high purity Li_2CO_3, Al_2O_3, MgO, ZnO, ZrO_2, TiO_2, P_2O_5, F^- and other minor additives were used to produce two glass batches, G-P and G-PF (Table 1), the main difference of which is without and with F^-. ZrO_2, TiO_2, P_2O_5 and F^- were employed as a complex nucleating agent. The raw materials all together were melted at 1600–1650 °C and moulded in a pre-heated die. The glass was then annealed at 580 °C for 1 h to eliminate internal stress.

Differential thermal analysis (DTA) of the annealed glass samples was carried out on a differential thermal analyzer (NETZSCH STA 409 PC Luxx, Germany) with alumina as the reference. The sample was heated at 5–20 °C min^{-1} from 20 to 1100 °C, during which DTA trace was recorded. Phases of the samples were analyzed by the X-ray diffraction (XRD) method on a XJ10-60 X-ray diffractometer using nickel filtered Cu Kα radiation in the range of $2\theta = 10$–80° with a scanning speed of 2° min^{-1}. The surface of the samples was finished and eroded by HF (2 wt%) for 30–40 s for the morphology observation on the scanning electron microscopy (SEM, FEI SIRION).

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Table 1
Oxide composition (mass%) of G-P and G-PF LAS glass specimens

Compounds	G-P	G-PF
Li_2O	4.0	4.0
Al_2O_3	19.5	19.5
SiO_2	67	67
ZnO	0.7	0.7
MgO	0.6	0.6
BaO	0.4	0.4
Na_2O	1.0	1.0
K_2O	1.0	1.0
TiO_2	2.5	2.2
ZrO_2	2.0	1.8
F^-	–	0.5
P_2O_5	0.5	0.5

3. Results and discussions

3.1. Crystalline phases

Fig. 1 shows the DTA curves obtained from as-cast LAS glass. The DTA trace for G-P specimen shows a small endothermic dip at 820 °C, a major peak at 849 °C and a shoulder peak at 1020 °C. The first peak implies the glass transition temperature (T_g), and the second and third peaks are attributed to the crystallization (T_p) and transformation of crystal structure. The DTA trace of G-PF specimen exhibits only an endothermic dip at 755 °C and an exothermic peak at 837 °C, but no other peak, i.e. no crystallization transformation at higher temperature. As compared to G-P specimen, T_g and T_p of G-PF specimen are relatively low, suggesting that fluorine can improve the crystallization of LAS glass, which is in agreement with our previous studies [8].

The crystallization peaks on the DTA curves imply that crystal phase forms and then transforms during the heat treatment. This is confirmed by XRD results. Fig. 2 shows the diffraction patterns of G-P and G-PF samples, which were heat treated for 2 h at several temperatures above 830 and

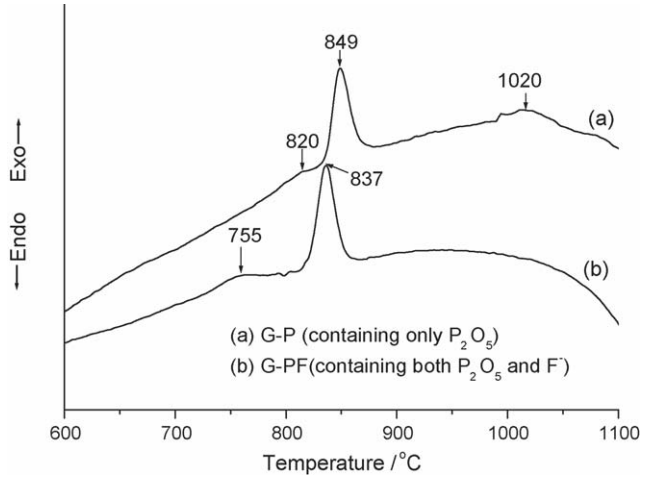

Fig. 1. DTA traces obtained from: (a) G-P (containing only P_2O_5) and (b) G-PF (containing both P_2O_5 and F^-) LAS glass powders.

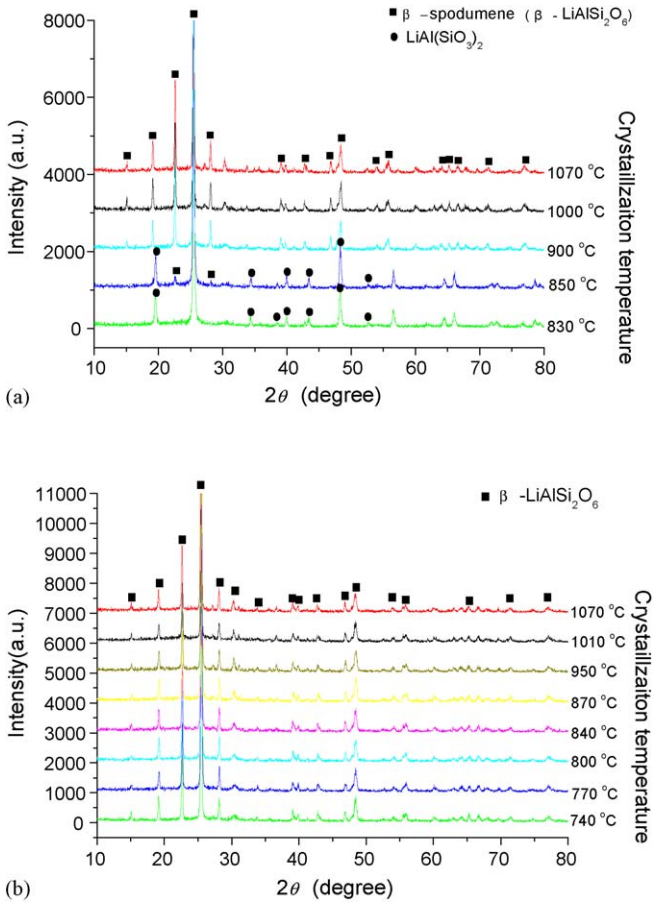

Fig. 2. XRD patterns of: (a) G-P and (b) G-PF LAS glass samples heat treated at different crystallization temperatures.

740 °C, respectively. The G-P specimen heat treated at 830 °C is clear with $LiAl(SiO_3)_2$ crystal (JCPDS-PDF 31-0706), similar to α-spodumene. For the G-P specimen heat treated at 850 °C, some β-spodumene occurred coexisting with the $LiAl(SiO_3)_2$. The relative amount of β-spodumene increases with increasing heat-treatment temperature, indicating a transformation of $LiAl(SiO_3)_2$ into β-spodumene, which was completed in the specimen heat treated at 1000 °C, at the same time, the specimen became opaque due to the increase of crystallinity.

In G-PF specimen, however, even heat treatment at 740 °C, β-spodumene started to be observed. β-Spodumene as the main crystallization phase was kept up to heat treated at 1070 °C. It is confirmed that fluorine addition allows a direct formation of β-spodumene without the transformation of $LiAl(SiO_3)_2$ into β-spodumene.

3.2. Crystallization kinetics

The crystallization kinetic characteristics of LAS glass can be decided as follows by Arrhenius [12], Kissinger [13] and Augis–Bennett [14], which are, respectively, expressed as

$$k = \nu \exp\left(-\frac{E}{RT}\right) \quad (1)$$

Table 2
T_p (K) values from DTA curve of LAS glass samples at different heating rates

Heating rates (°C min^{-1})	G-P	G-PF
5	1084	1106
10	1100	1121
15	1120	1130
20	1129	1139

$$\ln\left(\frac{T_p^2}{a}\right) = \frac{E}{RT_p} + \ln\frac{E}{R} - \ln\nu \quad (2)$$

$$n = \frac{2.5}{\Delta T} \times \frac{RT_p^2}{E} \quad (3)$$

wherein E is the activation energy (kJ mol^{-1}), R the gas constant, ν the frequency factor, a the DTA heating rate (°C min^{-1}), k the reaction rate constant, which is related to the E and ν, n the crystallization index, i.e. Avrami exponent, depending upon the morphology or directionality of crystal growth and ΔT is the half-height temperature wideness of the maximum exothermical peak of DTA. According to Eqs. (1)–(3), low E value and high ν lead to high k, indicating high crystallization rate and crystallinity. Crystallization index n is related to crystallization manner, $n \approx 1$, surface crystallization and $n \approx 3$, volumetric crystallization.

Table 2 shows the crystallizing peak temperatures (T_p) from DTA curves at different heating rates. The relationship between $\ln(T_p^2/a)$ and $1/T_p$ is constructed (Fig. 3) to calculate the effective activation energy, frequency factor and crystallization index, as shown in Table 3. The G-PF specimen has a lower E and a lower ν than G-P specimen. It is suggested that fluorine can lower the activation energy and P_2O_5 can enhance frequency factor, and both benefit the crystallization of LAS glass. This is also confirmed by the k values. At the heating rate of 5 °C min^{-1}, the k values of G-P and G-PF specimens are 0.223 and 0.159, respectively. It should be noted that in our previous studies, the k value of LAS glass containing F^- (without P_2O_5) is 0.135 and the one without both F^- and P_2O_5 is only 0.126 [8]. It is

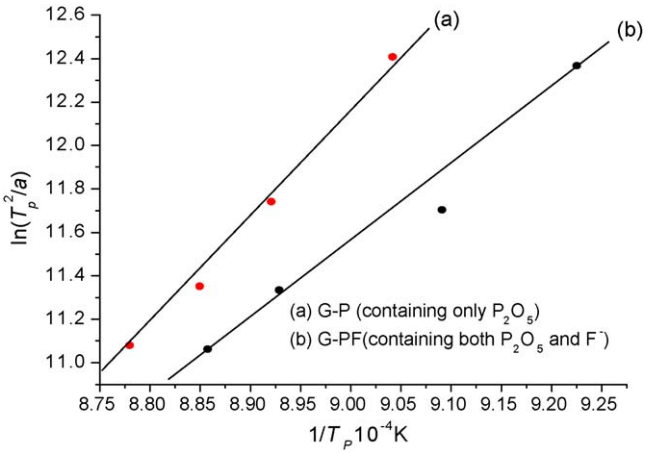

Fig. 3. Relationship between $\ln(T_p^2/a)$ and $1/T_p$: (a) G-P (containing only P_2O_5) and (b) G-PF (containing both P_2O_5 and F^-).

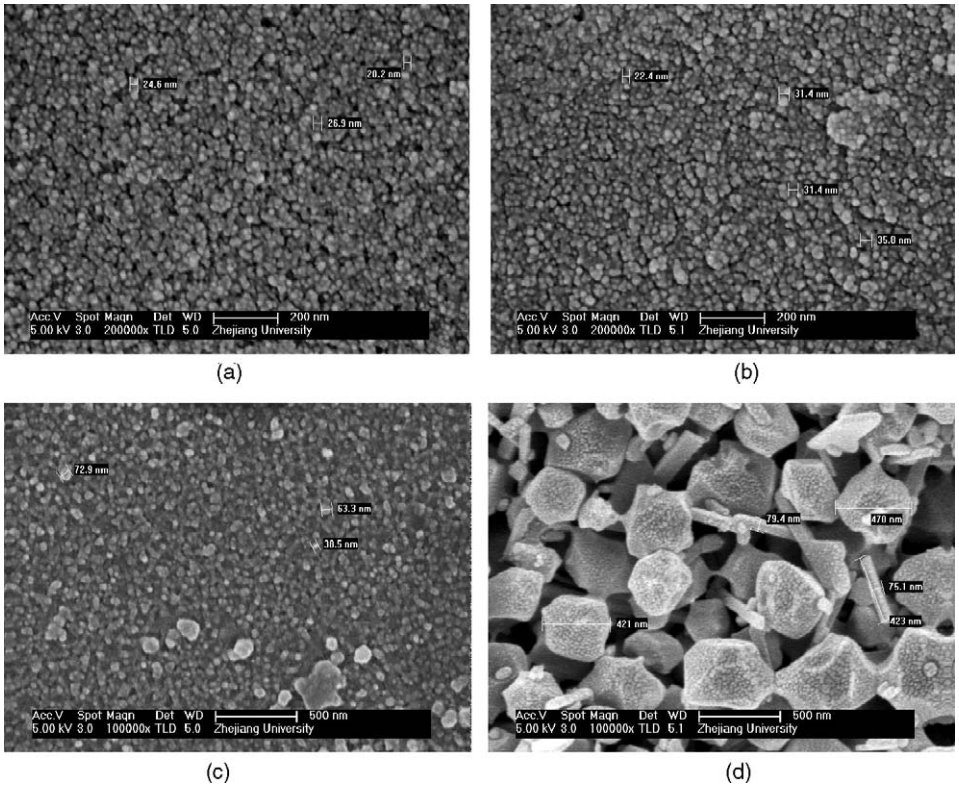

Fig. 4. SEM photos of G-P LAS glass samples (containing only P_2O_5) heat treated for 2 h at different crystallization temperatures: (a) 830 °C, (b) 850 °C, (c) 900 °C and (d) 1070 °C.

Table 3
E, *ν*, *n* and *k* crystallization values of the LAS glass samples

Crystallization parameter	G-P	G-PF
E (kJ mol^{-1})	427.5	280.7
ν (min^{-1})	3.0×10^{19}	4.9×10^{12}
n	2.76	2.88
k ($a = 5\,^{\circ}$C min^{-1})	0.223	0.159

proved that the coexistence of F^- and P_2O_5 not only decreases the activation energy, but also increases the frequency factor, which improves the crystallization of LAS glass.

The n values, which are calculated by using Eq. (3), are also given in Table 3. The fact that n value is near 3 indicates that crystallization manner of LAS glass is volumetric crystallization. The n value of G-P specimen is lower than that of G-PF specimen, suggesting that the G-P specimen has a slower crystal growth rate and consequently finer crystal structure.

3.3. Microstructure of LAS glass ceramics

Figs. 4 and 5 show the microstructure of G-P and G-PF samples heat treated for 2 h at several temperatures above 830 and 740 °C, respectively. It can be seen that the grain size of both G-P and G-PF samples increases with the crystallization temperatures, and the G-P specimen has smaller grain size and slower crystallinity than the G-PF specimen, which is in accordance with the result of crystallization index. The crystal grain of the G-P specimen is sphere-shaped with the size of 20–80 nm after heat treated at 830–900 °C, and becomes hexahedron or needle with the size of 300–450 nm at 1070 °C. The crystal shape of G-PF specimen is of block or particle, and its size is about 50 nm after heat treated at 740 °C and increases to 300–500 nm at 1070 °C. It indicates that the addition of P_2O_5 and/or fluorine can control the grain size, crystal shape and crystallinity of LAS glass ceramics.

In our previous work, it was reported that F^- can improve the nucleation and crystallization by weakening glass structure through substituting a couple Si–F for strength Si–O–Si [8]. Due to the existence of P_2O_5, phosphate group will be consequentially separated from the silicate glass, leading to a phase separation, which plays a role in the nucleation and the microstructure formation of the glass ceramic [4,9,10]. The coexistence of F^- and P_2O_5 affects the crystallization of LAS glass by "the mix-alkali" function, that is to say, complex nucleating agents can improve the crystallization of LAS glass by P_2O_5-inducing the phase separation and F^--modifying the glass structure.

4. Conclusions

The crystallization mechanism and microstructure of Li_2O–Al_2O_3–SiO_2 system glass ceramic containing complex nucleating agents ($TiO_2 + ZrO_2 + P_2O_5$ +/or F^-) are investigated. The introduction of both P_2O_5 and F^- decreases the

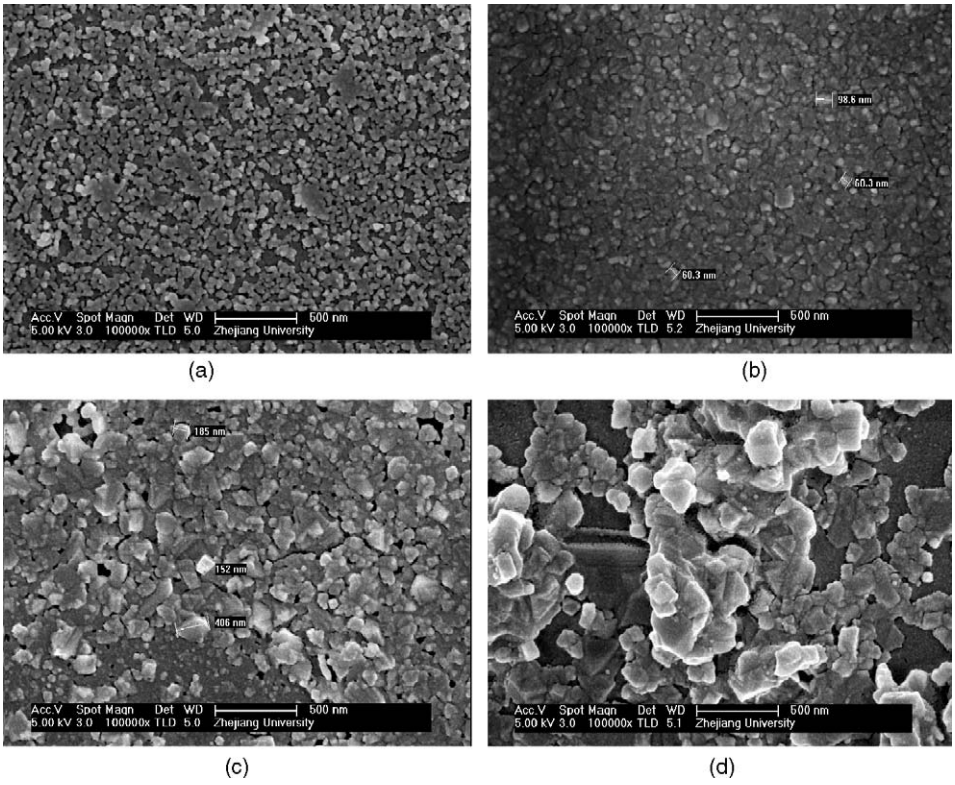

Fig. 5. SEM photos of G-PF LAS glass samples (containing both P_2O_5 and F^-) heat treated for 2 h at different crystallization temperatures: (a) 740 °C, (b) 800 °C, (c) 900 °C and (d) 1070 °C.

crystallization temperature of LAS glass, adjusts the crystallization kinetic parameters and obtains the crystalline phases of β-spodumene just formed directly without the transformation from $LiAl(SiO_3)_2$ into β-spodumene, while they increase the crystal size and crystallinity of LAS glass ceramic. The coexistence of P_2O_5 and F^- improves the crystallization of LAS glass by P_2O_5-inducing the phase separation and F^--modifying the glass structure.

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