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Short communication

Effect of Y_2O_3 addition on viscosity and crystallization of the lithium aluminosilicate glasses

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Abstract

The melting and crystallization behaviors of lithium aluminosilicate (LAS) glasses containing Y_2O_3 were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis (DTA) and viscosity test. Effects of Y_2O_3 on the viscosity of LAS glasses were investigated from the softening point temperature to melting temperature. It was indicated that the introduction of yttria effectively decreased the melting temperature and viscosity of LAS glasses. The DTA and XRD results showed that yttria controlled the crystallization of LAS glasses by increasing the crystallization peak temperature (T_p) and activation energies (E), and the main crystalline phase of glass–ceramics was β-spodumene.

Keywords: Glass–ceramics; Viscosity; Crystallization

1. Introduction

Lithium aluminosilicate (LAS) glass–ceramics in the system $Li_2O–Al_2O_3–SiO_2$, containing β-spodumene ($Li_2O·Al_2O_3·4SiO_2$) and/or β-quartz solid solution, own low thermal expansion coefficient, good thermal and chemical stability, and so have been applied in many fields [1–6]. β-Spodumene-containing glass–ceramics also have the potential to meet the dielectric constant and thermal expansion requirements for integrated circuit substrates.

However, due to their high melting temperatures and viscosity in LAS glasses, it makes them difficulty to be prepared, so additions of fluxes such as B_2O_3, BaO, SrO, alkali oxides and alkali earth oxides have been used in LAS glass–ceramics to decrease the viscosity and melting temperature. But it would induce some problems like high thermal expansion coefficient and/or loss of transparency, and/or low mechanical properties at the same time [7–14].

Lanthanon metal oxides, such as Y_2O_3, have been introduced as nucleating agent in glass–ceramics. The introduction of 4 and 8.33 mol% Y_2O_3, respectively, the transformation temperature of β-quartz to β-spodumene increases from about 900 to 1000 °C and the melting temperature increases to 1650 °C [15]. However, the increase of melting temperature caused by too much addition of yttria in this research is not our expectant. So in order to lower viscosity and melting temperature, the addition of yttria must be appropriate because it plays a role of a kind of network-modifier. Besides, it could improve the crystallization of LAS glass–ceramics.

In this study, LAS glass–ceramics were prepared by adding small content of Y_2O_3 as flux, and the effects of Y_2O_3 introduction on the viscosity and crystallization were evaluated.

2. Experimental

The initial materials were reagent grades SiO_2, Al_2O_3, $MgCO_3$, Li_2CO_3, ZnO, Na_2CO_3, KNO_3, TiO_2, ZrO_2, Sb_2O_3 and Y_2O_3, in which Sb_2O_3 was used as refining agent and TiO_2 and ZrO_2 as composite nucleation agents. The detailed compositions were given in Table 1. The glasses were melted in an electric furnace for 4 h at 1600–1630 °C and moulded in a pre-heated die. The glasses were annealed at 550 °C for 1 h to eliminate internal stress.

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Table 1
Oxide composition (wt%) of LAS glass–ceramics

	Li_2O	Al_2O_3	SiO_2	ZnO	MgO	TiO_2	ZrO_2	Na_2O	K_2O	B_2O_3	Sb_2O_3	Y_2O_3
Y0	4.2	22.2	64.9	0.5	1.5	2.3	2	0.6	0.3	1	1.1	–
Y1	4.2	22.2	64.9	0.5	1.5	2.3	2	0.6	0.3	1	1.1	3.35
Y2	4.2	22.2	64.9	0.5	1.5	2.3	2	0.6	0.3	1	1.1	4.46

A mass of glass was selected and cut into pieces with the weight of about 10–50 g for each one. The samples were placed the correct quantity into the THETA Rheotronic II to measure viscosity of glass above the softening point. The glasses were heated to a temperature that the viscosity of glass was lowered sufficiently to allow trapped air bubbles to be released. This temperature should be below the original melting temperature to avoid reboil. The viscosity of glasses can be fitted to the Fulcher equation [16]:

$$\log_{10}\eta = A + [B/(T - T_0)]$$

where T is the temperature (°C) and A, B and T_0 are the adjustable constants.

Differential thermal analysis (DTA) of annealed glass specimens was done using a Netzsch Sta 449C. 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 between 20 and 1000 °C with heating rate of 5–20 °C min^{-1}.

The heat-treatments of the annealed glass samples were carried out at 600–970 °C with the heating rate of 10 °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 step of 0.02°. Optical mount specimens were prepared by standard metallographic techniques using chemical etching in an HF solution (5%) for 1.5 min. Etched glass–ceramic samples were coated with a thin layer of gold, and scanning electron microscopy (SEM) was done with a JSM-5610LV.

3. Results and discussions

3.1. The viscosity of glasses

The viscosity of the glass specimens is plotted as a function of temperature in Fig. 1. The curves in Fig. 1 show that the viscosity of Y1 and Y2 are lower than Y0 during the temperature region of 1200–1650 °C. It is the natural behavior of glass for the decrease of viscosity as temperature increase; however, the decreasing rate can be lowered by more addition of yttria, which results in the higher viscosity of Y2 than Y1 in Fig. 1 as the temperature passing through 1540 °C.

The temperatures at different viscosity are shown in Table 2. The point temperature at the viscosity of 10 Pa s is referred to the melting temperature of glass, so the melting temperature of Y0, Y1 and Y2 are 1628, 1606 and 1623 °C, respectively. It indicates that yttria with appropriate content can lower melting temperature and decrease viscosity. For yttria, the big ionic radius (89 pm) and eight-coordinate of Y^{3+} make it impossible to enter into the glass network. As a result, the yttrium ions are located at network interspace. Therefore, small addition of yttria can decrease the viscosity in this glass system.

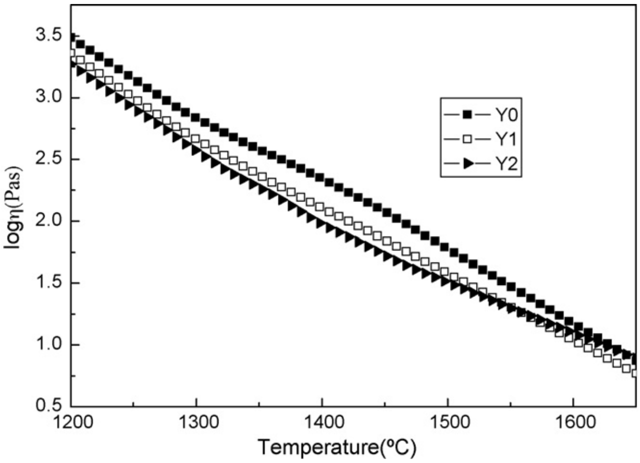

Fig. 1. Viscosity–temperature curves of Y0, Y1 and Y2.

3.2. Influence on crystallization

Fig. 2 shows the DTA curves of the LAS glasses. The DTA curve of Y0 specimen shows a small endothermic peak valley at 554 °C, a major peak at 820 °C and a shoulder peak at 910 °C. And the DTA trace of the Y1 specimen exhibits an endothermic peak valley at 740 °C, a major peak at 842 °C and a shoulder peak at 915 °C. The first peak implies the glass transition temperature (T_g), and the second and third peaks are attributed to the crystallization (T_p) or transformation of crystal structure. But the DTA trace of Y2 specimen has only an endothermic peak valley at 750 °C and an exothermic peak at 856 °C, without other peak, which indicates no crystallization transformation at higher temperature. The T_g and T_p of the LAS glasses shift to higher temperature as the yttria content increases. The crystallization peaks on the DTA curves imply that crystalline phase forms during the heat-treatment, which are also confirmed by XRD results.

Fig. 3 shows the diffraction patterns of samples treated at different temperatures for 2 h according to their DTA curves. After Y0 specimen was treated at 820 °C, β-spodumene

Table 2
The temperature of all specimens at different viscosity (log η = 1, 2, 3)

Samples	log η = 1	log η = 2	log η = 3
Y0 (°C)	1628	1463	1268
Y1 (°C)	1606	1420	1245
Y2 (°C)	1623	1397	1233

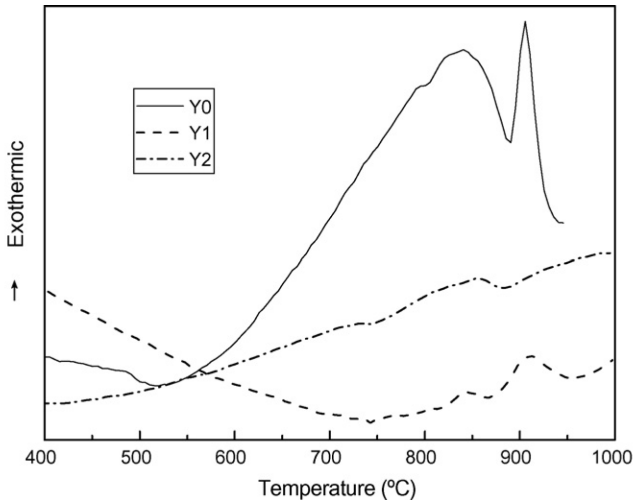

Fig. 2. DTA curves for glass samples with various Y_2O_3 content at 10 °C min^{-1}.

($Li_2O·Al_2O_3·4SiO_2$, JCPDS-PDF 73-2336, $a = b = 5.217$, $c = 5.464$) is observed directly without transformation from β-quartz to β-spodumene. As the temperature increases from 820 to 970 °C, the content of β-spodumene increases gradually.

XRD patterns of Y1 and Y2 specimens after treated at 820 °C show a board scattering spectrum and the main phase is still amorphous glass. After heated at higher temperatures, 842 and 856 °C, the broad scattering spectrum disappears and β-spodumene precipitates. As the heated temperature increases to 920 °C, β-spodumene is still the main phase, and the specimens become opaque due to the increase of grain size and crystallinity.

3.3. Microstructure analysis

Figs. 4–6 show the microstructure of Y0, Y1 and Y2 samples heat-treated for 2 h at several temperatures at and above 820 °C. The crystal grain of the Y0 specimen is sphere-shaped with the size of 0.5–1.5 μm after treated at 820–920 °C. There are not any crystal phase in Y2 and Y3 after treated at 820 °C. The crystal shape of Y1 and Y2 specimens is sphere-shaped particle or block, and its size is about 500 nm and 50–200 nm after heat-treated at and above 842 and 856 °C, respectively.

It can be seen that the grain size of the three samples increases at higher crystallization temperature. But the Y2 specimen has the lowest crystallinity at the same heated temperature, which is in accordance with the result of DTA curves and powder XRD patterns.

The transparency and strength of the glass–ceramics would become worse due to the over-growth of crystal. In this glass system, the crystal size and crystallinity decrease with the increase of yttria addition. The crystal particles of Y1 treated at 920 °C for 2 h is about 100–250 nm and the content of

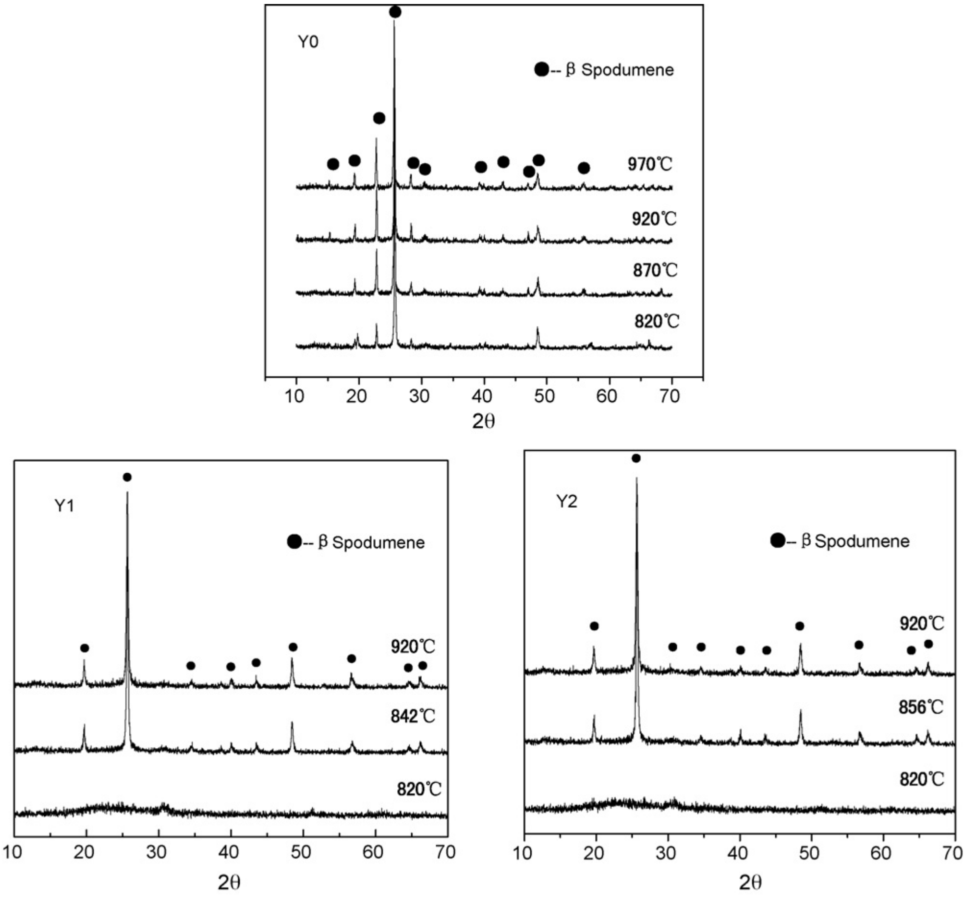

Fig. 3. XRD patterns of the three samples: Y0, Y1 and Y2.

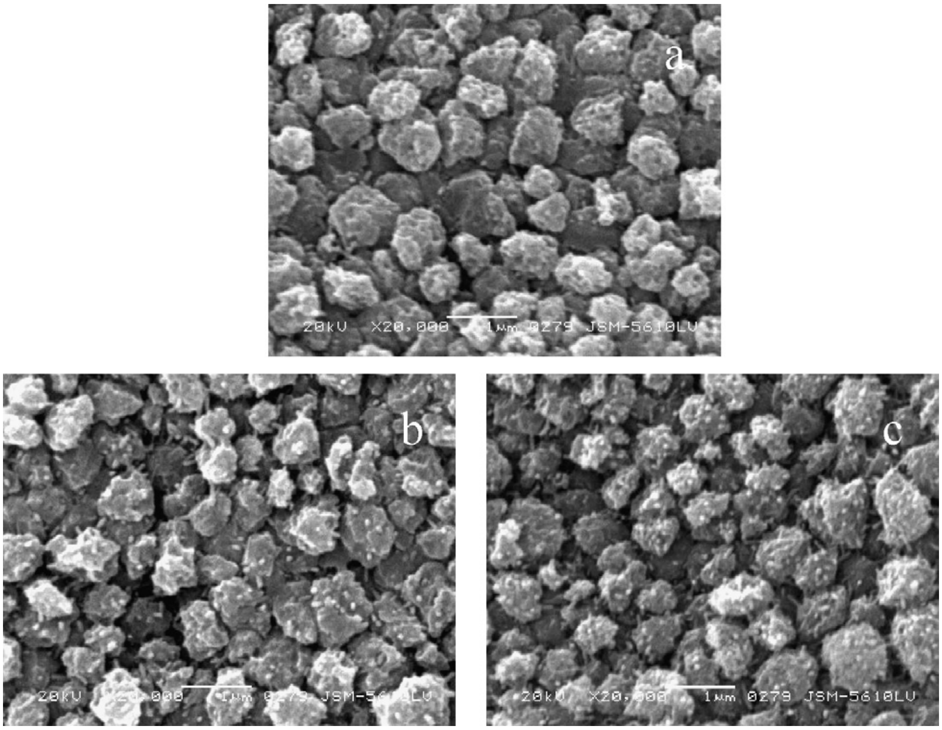

Fig. 4. SEM photos of Y0 specimen heat-treated for 2 h at different crystallization temperature: (a) 820 °C, (b) 870 °C and (c) 920 °C.

crystalline phase is appropriate, which would result in excellent mechanical properties and thermal properties.

3.4. Crystallization kinetics

The crystallization kinetic characteristics of LAS glass can be determined as following by Arrhenius [17], Kissinger [18] and Augis–Bennet [19], which are, respectively, expressed as

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

$$\ln\left(\frac{T_{\mathrm{p}}^{2}}{\alpha}\right) = \frac{E}{RT_{\mathrm{p}}} + \ln\frac{E}{R} - \ln\upsilon \tag{2}$$

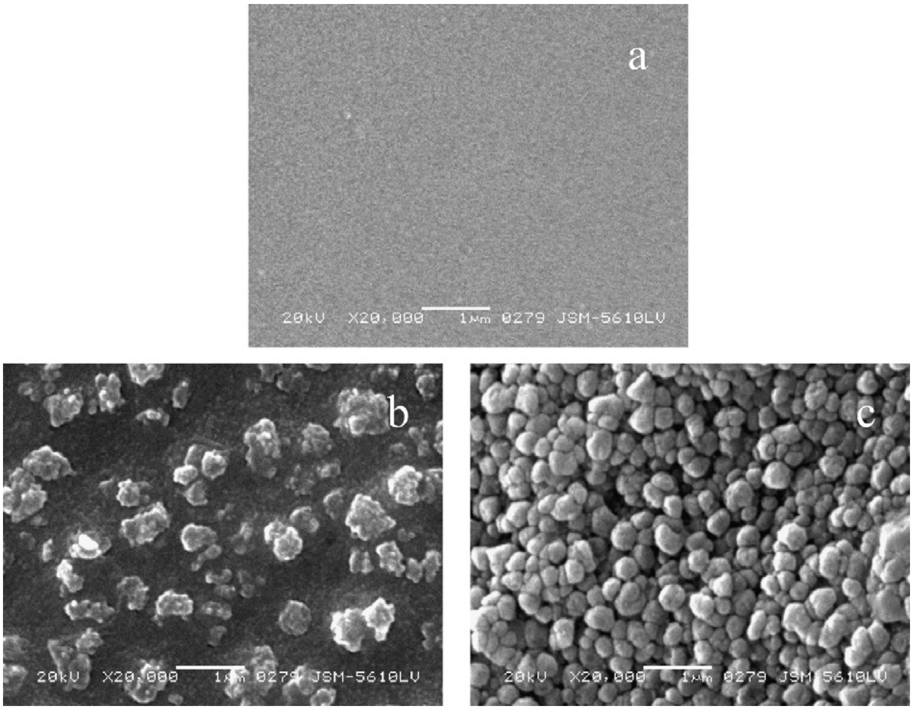

Fig. 5. SEM photos of Y1 specimen heat-treated for 2 h at different crystallization temperature: (a) 820 °C, (b) 842 °C and (c) 920 °C.

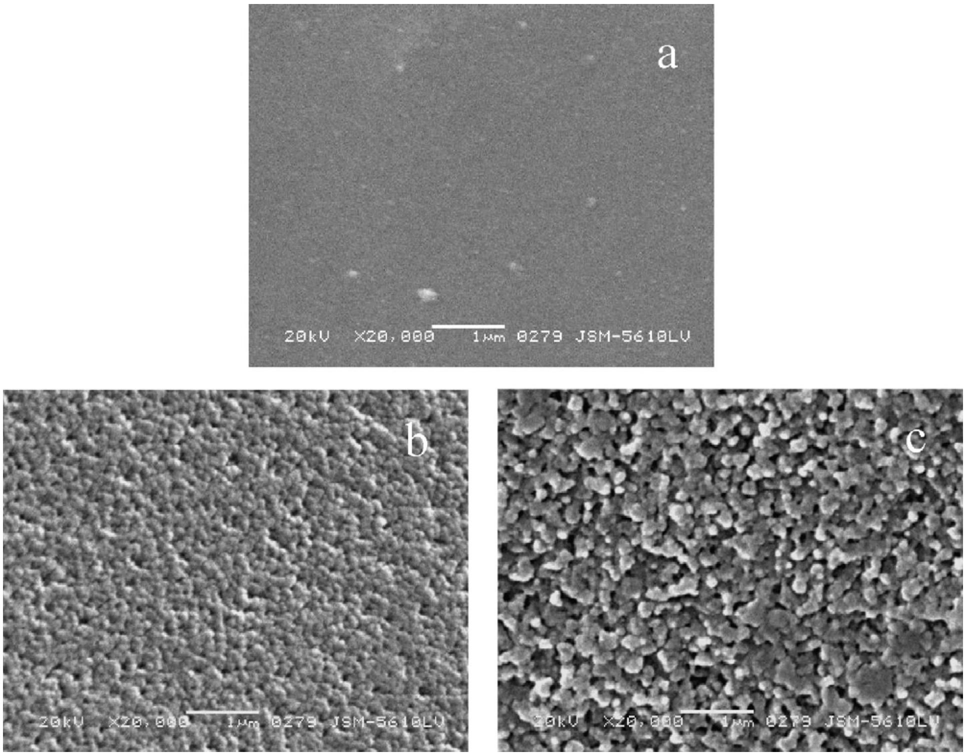

Fig. 6. SEM photos of Y2 specimen heat-reated for 2 h at different crystallization temperature: (a) 820 °C, (b) 856 °C and (c) 920 °C.

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

wherein E is the activation energy (kJ mol^{-1}), R the gas constant, υ the frequency factor, α the DTA heating rate (°C min^{-1}), k the reaction rate constant, which is related to the E and υ, 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), a lower E value and a higher υ value correspond to a higher k, indicating a higher crystallization rate. The crystallization index n is related to crystallization manner, the crystallization manner is surface crystallization when n value is close to 1, two-dimension crystallization when n is close to 2 and volumetric crystallization when n is close to 3 [20].

Table 3 shows the crystallizing peak temperatures (T_p) from DTA curves at different heating rates. The relationship between $\ln(T_p^2/\alpha)$ and $1/T_p$ is constructed (Fig. 7) to calculate the effective activation energy, frequency factor and crystallization index, as shown in Table 4. According to some literature, the activation energy of LAS glass without dopants is 427.5 kJ mol^{-1} [20] and 315.0 kJ mol^{-1}. [21] The calculated activation energy of the Y0 specimen without yttria is 398.6 kJ mol^{-1} and in good according with other researches, which shows that the calculated frequency factor and other crystallization index are appropriate.

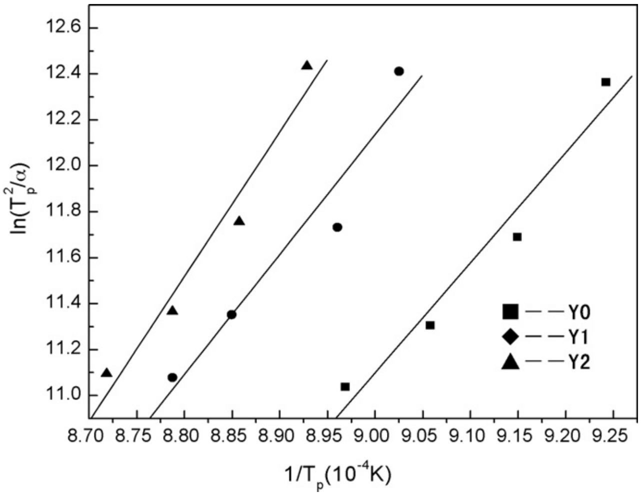

Fig. 7. Relationship between $\ln(T_p^2/\alpha)$ and $1/T_p$.

Table 3
T_p (K) values from DTA curve of LAS glass samples at different heating rates

Sample no.	$\alpha = 5$ (K min^{-1})	$\alpha = 10$ (K min^{-1})	$\alpha = 15$ (K min^{-1})	$\alpha = 20$ (K min^{-1})
Y0	1082 ± 2	1093 ± 2	1104 ± 2	1115 ± 2
Y1	1108 ± 2	1115 ± 2	1129 ± 2	1137 ± 2
Y2	1120 ± 2	1129 ± 2	1140 ± 2	1147 ± 2

Table 4
E, υ, n and k crystallization values of the LAS glass samples

Crystallization parameter	Y0	Y1	Y2
E (kJ mol^{-1})	398.6	434.1	511.8
n (min^{-1})	4.1×10^{18}	7.1×10^{19}	7.4×10^{23}
n	2.87	2.38	2.04
k ($\alpha = 5$ K min^{-1})	0.2223	0.2485	1.258

The Y0 specimen has the lower E and υ than Y1 and Y2 specimens. It is suggested that yttria can increase the activation energy and frequency factor. This is also confirmed by the k values. At the heating rate of 5 °C min^{-1}, the k values of LAS glass containing yttria of 3.35 and 4.46 wt%, are 0.2485 and 1.258, respectively, but the one without yttria is only 0.2223. It is proved that the introduction of yttria not only increases the activation energy and the frequency factor, but also increases the k values, which restrains the crystallization of LAS glass.

The n values, which are calculated by using Eq. (3), are also given in Table 4. The fact that n values is near 3 indicates that crystallization manner of LAS glass is volumetric crystallization. The n values of Y1 and Y2 specimens are 2.38 and 2.04, respectively, and lower than that of Y0 specimen, suggested that the crystallization mechanism changes from volumetric crystallization to two-dimension crystallization.

4. Conclusions

LAS glass–ceramics with the introduction of yttria were prepared and their viscosity, crystallization mechanism and microstructure were investigated. The viscosity and melting temperature decreased with the introduction of yttria, but the crystallization temperature and crystallizing activation energy of the resulting glass increased. And the kinetic and phase structure analysis indicated that yttria played an important role in adjusting the crystallization kinetic parameters and controlling the crystal size and crystallinity. The main crystalline phase of all specimens after the crystallization treatments was β-spodumene, which was formed directly without the transformation from β-quartz into β-spodumene.

References

[1] G.H. Beall, L.R. Pinckney, J. Am. Ceram. Soc. 82 (1999) 5–16.
[2] L. Arnault, M. Gerland, A. Riviere, J. Mater. Sci. 35 (2000) 2331–2345.
[3] P. Riello, P. Canto, N. Comelato, et al., J. Non-Cryst. Solids 288 (2001) 127–133.
[4] L. Barbieri, C. Leonelli, T. Manfredini, et al., J. Am. Ceram. Soc. 80 (1997) 3077–3083.
[5] J.Y. Hsu, R.F. Speyer, J. Am. Ceram. Soc. 73 (1990) 3585–3593.
[6] V. Maier, G. Mueller, J. Am. Ceram. Soc. 70 (1987) C176–C178.
[7] M.C. Wang, M.H. Hon, F.S. Yen, J. Cryst. Growth 91 (1988) 155–162.
[8] M.C. Wang, M.H. Hon, J. Ceram. Soc. Jpn. 100 (1992) 1285–1291.
[9] C. Leonelli, T. Manfredini, M. Paganelli, et al., J. Am. Ceram. Soc. 74 (1991) 983–987.
[10] L. Barbieri, A.B. Corradi, C. Leonelli, et al., Mater. Res. Bull. 32 (1997) 637–648.
[11] J.M. Rincon, M. Romero, J. Marco, V. Caballer, Mater. Res. Bull. 33 (1998) 1159–1164.
[12] A.W.A. Elshennawi, E.M.A. Hamzawy, G.A. Khater, Ceram. Int. 27 (2001) 725–730.
[13] J.J. Shyu, M.T. Chiang, J. Am. Ceram. Soc. 83 (2000) 635–639.
[14] K. Davkova, S. Zafirovski, S. Pocev, V. Zlatanovic, Glass Technol. 41 (2000) 197–198.
[15] J.J. Shyu, C.S. Hwang, J. Mater. Sci. 31 (1996) 2631–2639.
[16] J.E. Shelby, Introduction to Glass Science and Technology (Section edition), RSC, New York, 2005, pp. 120–122.
[17] M. Avrami, J. Chem. Phys. 7 (1939) 177.
[18] H.E. Kissinger, J. Res. Nar., Burton Stand 57 (1956) 217–221.
[19] J.A. Augis, J.E. Bennett, J. Therm. Anal. 13 (1978) 283–292.
[20] X.Z. Guo, H. Yang, et al., Thermochim. Acta 444 (2006) 201–205.
[21] A.M. Hu, K.M. Liang, et al., Thermochim. Acta 413 (2004) 53–55.