

Effect of K₂O on Crystallization of Li₂O–SiO₂ Glass

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Li₂O–SiO₂ 系ガラスの結晶化に及ぼす K₂O の効果

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The effect of a small amount of K₂O on the crystallization behavior of the system of Li₂O–SiO₂ glass was investigated. Lithium disilicate (Li₂O·2SiO₂; L·2S) and lithium metasilicate (Li₂O·SiO₂; L·S) crystals precipitate simultaneously, but only L·2S crystals grow upon further heat treatment in the glass without K₂O (Li glass). In the glass containing K₂O (K3 glass), only L·S crystals precipitate and grow. The stable crystalline phases are L·2S and SiO₂ crystals in both glasses. Phase separation was observed before crystallization; a Li₂O-rich phase formed an isolated droplet phase in Li glass and the continuous phase in K3 glass. The Li⁺–K⁺ ion exchange test confirmed these structures. [SEM–EDX] analysis confirmed that K₂O exists in the Li₂O rich phase after phase separation in K3 glass. Thus, K3 glass separates into two phases, one of which is a continuous phase rich in Li₂O and containing considerable amount of K₂O. The L·S crystal precipitates and grows in this phase upon further heat treatment. Consequently, K₂O suppresses the crystallization of L·2S and promotes the precipitation of L·S crystals.

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1. Introduction

It is well known that the Li₂O–SiO₂ system is a base glass for glass ceramics, and much research on the crystallization process has been carried out.^{1)–4)} According to the phase diagram of this system, the immiscible region is located between the Li₂O·2SiO₂ and SiO₂ end members, and the glass containing more SiO₂ than the Li₂O·2SiO₂ composition separates into two phases; one is an isolated droplet phase rich in SiO₂ and the other is a matrix phase close to the Li₂O·2SiO₂ composition. Li₂O·2SiO₂ crystals precipitate homogeneously in matrix phase upon the heat treatment.⁵⁾ Recently, Soares et al.⁴⁾ confirmed that both Li₂O·SiO₂ and Li₂O·2SiO₂ crystals precipitate simultaneously at first, but only Li₂O·2SiO₂ grows. Also Li₂O·SiO₂ disappears upon further heat treatment in glass with Li₂O·2SiO₂ composition.

From a practical point of view, high-hardness and high-fracture strength glass ceramics composed of lithium disilicate crystal can be obtained from modified Li₂O–SiO₂ glass. On the contrary, a modified Li₂O–SiO₂ glass containing a small percentage of K₂O has been applied as a chemically machinable photosensitive glass or glass ceramic.⁶⁾ In this case, Li₂O·SiO₂ crystal precipitates as a metastable initial phase and converts to Li₂O·2SiO₂ and quartz crystals upon heat treatment above 800°C. The solubility of Li₂O·SiO₂ crystal in HF solution is much higher than that of glass, and therefore, chemical machining can be achieved. Although the amount of K₂O added is usually 3–4 mass% and the SiO₂/Li₂O ratio is kept higher than 2.5, lithium metasilicate crystal precipitates as an initial phase. The Li₂O·2SiO₂ crystal should precipitate according to the phase diagram.⁷⁾ This behavior is well known, however, the reason behind it is not yet clear.

The author investigated the effect of K₂O on crystallization behavior of the system of Li₂O–SiO₂. The results are reported here.

2. Experimental

2.1 Sample preparation

Two types of glass were prepared, as shown in **Table 1**. Li₂O of 3 mol% was replaced by equimolar K₂O (K3 glass).

High-purity silica sand and alumina, and reagent-grade chemicals of Li₂CO₃, K₂CO₃, (NH₄)₂HPO₄ were used as raw materials. Batches corresponding to 150 g of glass were mixed thoroughly and precalcined at 300°C overnight to remove NH₃. They were melted in a 100 ml Pt/Rh10 crucible at 1450°C for 2 h in an electric furnace in air. The molten glasses were poured onto an iron plate and crushed, and melted again under the same conditions. They were then poured onto the iron plate and pressed by another iron plate. The glasses were heat treated for crystallization under various conditions after an initial heat treatment at 500°C for 15 h for nucleation.

2.2 TDA and DTA

Glass transition temperature (T_g), dilatometric softening point (Y_p) and thermal expansion coefficient of glasses were measured routinely using a fused silica single-push-rod dilatometer (Netzsch 402P) at the heating rate of 5°C/min. The differential thermal analysis (DTA) was carried out using a Perkin–Elmer DTA–7 at the heating rate of 10°C/min.

2.3 XRD and SEM

Crystalline phases were examined by powder X-ray diffraction analysis (XRD, Bruker, AXS Model 5005) under the condition of Cu K α radiation, 40 kV–40 mA, 0.01° step and 1 s/

Table 1. Glass Compositions (mol%) Studied

No.	SiO ₂	Al ₂ O ₃	Li ₂ O	Na ₂ O	K ₂ O	P ₂ O ₅	SiO ₂ /Li ₂ O
Li	73.0	2.15	23.7	-	-	1.15	3.08
K3	73.0	2.15	20.7	-	3.0	1.15	3.53

Table 2. Properties of Glasses Studied

Glass	Dilatometer			DTA				
	T _g (°C)	Y _p (°C)	α* (×10 ⁻⁷ /K)	T _g (°C)	T _{1onset} (°C)	T _{1peak} (°C)	T _{2onset} (°C)	T _{2peak} (°C)
Li	481	541	81.5	476	609	636	825	836
K3	476	536	88.5	470	592	614	819	830

*: mean thermal expansion coefficient, 30-300°C.

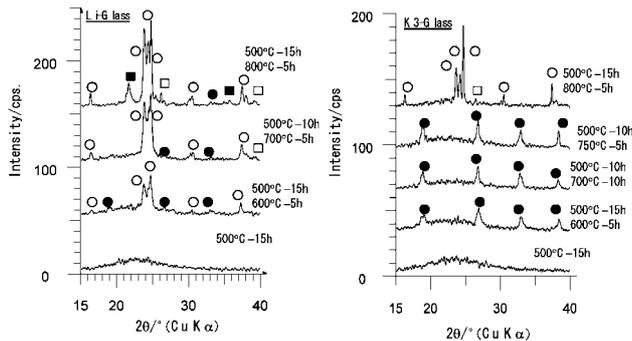


Fig. 1. XRD patterns of Li and K3 glass ceramics heat treated under various conditions.

○ Li₂O·2SiO₂, ● Li₂O·SiO₂, □ α-Quartz, ■ Cristobalite.

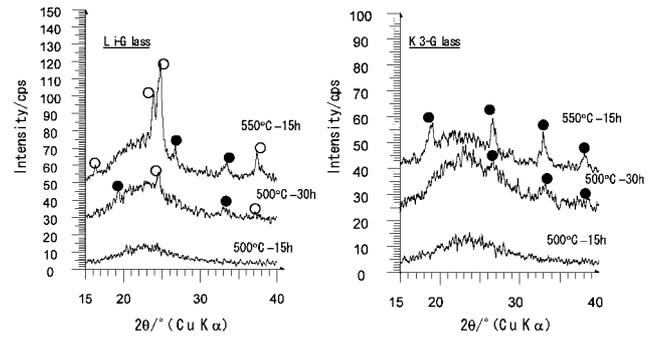


Fig. 2. XRD patterns of Li and K3 glasses in the initial stage of phase separation and crystallization.

○ Li₂O·2SiO₂, ● Li₂O·SiO₂.

step.

Crystalline size was calculated using Scherrer's equation,

$$d = 0.9\lambda / \beta \cdot \cos \theta, \quad (1)$$

where d is the crystalline size (nm), λ the wavelength of X-rays (0.154 nm), β the true half-width (radian) and θ the diffraction angle (degree). The true half-width was determined by the Jones method,⁸⁾ and α -quartz was used as a standard.

The structures of glasses and glass ceramics were observed using scanning electron microscope (SEM, JEOL JSM 6400). The fracture surface of glass and glass ceramics was etched by 1% HF solution for 2 min at room temperature.

2.4 Ion exchange

A rod about 5 mm in diameter was freshly drawn and cut into samples about 5 cm long. Samples were then heat treated at 500–550°C for 15–30 h. Ion exchange was carried out using KNO₃ molten salt at 400°C for 70 h under the condition of KNO₃/glass = 10 by weight. The weight change (mg/cm²) was measured after ion exchange.

3. Results and discussion

3.1 Crystallization behavior

Table 2 shows the properties of the glasses. The properties of the two types of glass are almost the same, but the crystallization starts at a lower temperature for K3 glass.

Figure 1 shows XRD patterns of two glass ceramics heat treated under various conditions. The main crystalline phase of Li glass is the lithium disilicate crystal (Li₂O·2SiO₂, hereafter L·2S) with a small amount of lithium metasilicate crystal (Li₂O·SiO₂, hereafter L·S); α -quartz starts to precipitate at 800°C. On the other hand, in K3 glasses, only the L·S crystal precipitates at first despite the SiO₂/Li₂O ratio being large, and L·2S and α -quartz precipitate at above 800°C. Finally, the L·S crystal disappears in both glasses. According

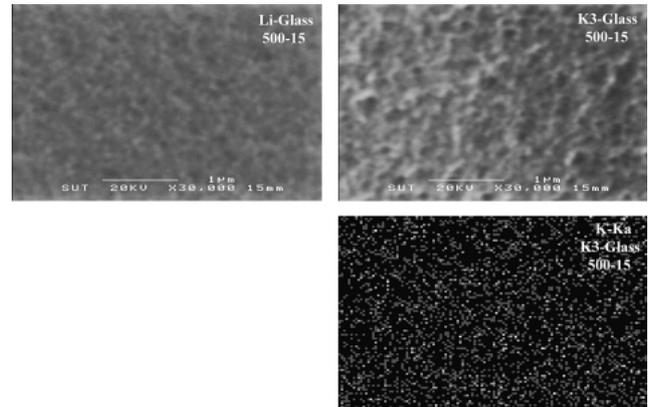


Fig. 3. SEM images of Li and K3 glasses and K distribution of K3 glass.

to the phase diagram, the stable crystalline phases are L·2S and SiO₂ crystals, therefore, this result agrees with the phase diagram above 800°C. Thus it is clear that K₂O suppresses the crystallization of L·2S, but promotes the precipitation of the L·S crystal.

In order to clarify this behavior, the early stage of phase separation or crystallization was investigated. Figure 2 shows XRD patterns of Li and K3 glasses heat treated at 500–550°C for 15–30 h. No crystals precipitate in either glass heat treated at 500°C for 15 h. Crystals start to precipitate in both glasses heat treated at 500°C-30 h. The crystalline phases are L·S and L·2S for Li glass and L·S for K3 glass. On further heat treatment, only the L·2S crystal grows in Li glass.

Figure 3 shows the SEM images of glasses heat treated at 500°C-15 h and the K distribution of K3 glass. No crystals precipitate by this heat treatment in both glasses. It is clearly

seen that phase separation occurs. The phase etched by HF solution seems to be an isolated droplet phase in Li glass. However, the continuous phase was etched in K3 glass.⁹⁾ This indicates that the Li-rich phase is an isolated droplet phase for Li glass and a continuous phase for K3 glass. It is observed that K is enriched in the continuous phase, which indicates that K₂O also exists in the Li₂O-rich phase after phase separation in K3 glass.

3.2 Crystal growth rate

Figure 4 shows the crystal growth rate against the heat treatment time at various temperatures. The crystal size increases proportionally to cube root of time ($t^{1/3}$). This indicates that the crystal grows according to the mechanism in which the small crystals fuse together, resulting in the growth of a large crystal after the volume fraction comes constant.

Figure 5 shows the Arrhenius plots for crystal growth in both glasses. The activation energy of crystal growth was estimated from the Arrhenius equation, $U = A \cdot \exp(-\Delta E/RT)$,

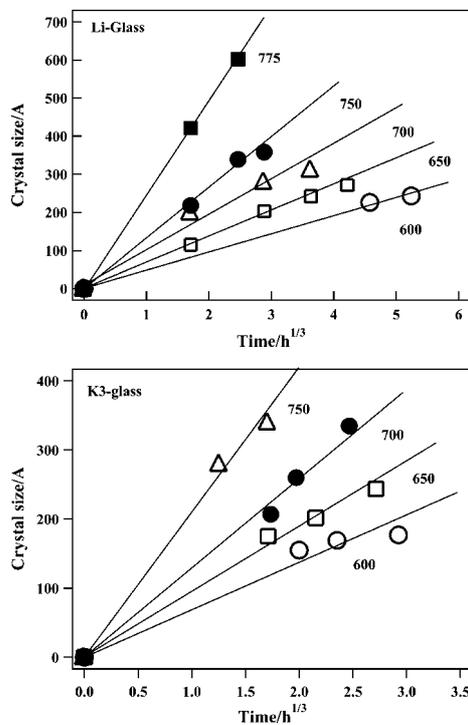


Fig. 4. Crystal growth rate against heat treatment time at various temperatures. Numbers indicate heat treatment temperatures, °C. Initial heat treatment: 500°C-15 h.

where U is the growth rate and ΔE is the activation energy. The measured activation energies were 48.5 kJ/mol in Li glass and 39.6 kJ/mol in K3 glass. ΔE for L·S crystal growth is about 20% smaller than that for the L·2S crystal, and these values are much smaller than those measured for $X\text{Na}_2\text{O} \cdot (1-X)\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass.^{10,11)}

3.3 Ion exchange

Ion exchange was carried out to clarify the SEM result. The results are shown in Table 3. For Li glass, the amount of weight gain due to ion exchange decreases markedly with the progress of heat treatment. On the other hand, the amount of weight gain increases initially and then decreases slightly for K3 glass. This suggests that the weight change due to ion exchange depends strongly on the mechanism of phase separation. If the isolated droplet phase is rich in Li₂O, which is surrounded by a SiO₂-rich phase, Li⁺-K⁺ ion exchange does not take place easily and the amount of weight gain may decrease with the progress of phase separation and crystallization. On the contrary, if the continuous phase is rich in Li₂O, ion exchange occurs much more easily, the amount of weight gain may increase. It is confirmed that the Li-rich phase is an isolated droplet phase for Li glass and a continuous phase for K3 glass.¹²⁾

Thus, K3 glass separates into two phases, one of which is a continuous phase rich in Li₂O and containing a considerable amount of K₂O. L·S crystals precipitate and grow in this phase upon further heat treatment. Mishima et al.^{10,11)} discussed the crystallization behavior of $X\text{Na}_2\text{O} \cdot (1-X)\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass and reported that the crystalline phase precipitated varied from the L·2S to L·S crystal with an increase in the amount of Na₂O(X). The author also confirmed that the crystallization temperature of the L·S crystal decreases on replacing Li₂O with Na₂O.¹³⁾ Consequently K₂O suppresses the

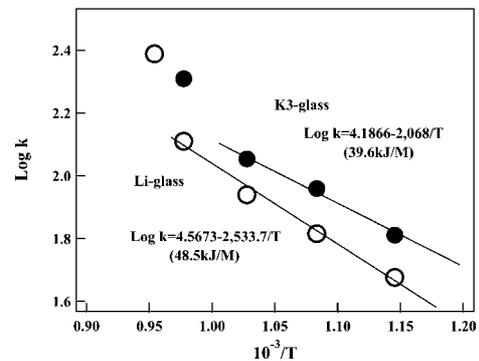


Fig. 5. Arrhenius plots for crystal growth.

Table 3. Ion Exchange Test Results

Glass No.	Heat treatment (°C-h)	Surface area(cm ²)	Weight before(g)	Weight after(g)	Weight gain(g)	Weight gain(mg/cm ²)
Li	As poured	10.0922	1.6039	1.6107	0.0068	0.674
	500-15	14.0215	2.8722	2.8752	0.003	0.214
	500-30	8.1627	1.1812	1.1818	0.0006	0.074
K3	As poured	12.9568	2.4962	2.5020	0.0058	0.448
	500-15	13.5301	2.6867	2.6946	0.0079	0.584
	500-30	15.5562	3.1601	3.1666	0.0065	0.418

Ion exchange: KNO₃ salt bath, KNO₃/Glass=10.0, 400° C-70h.

precipitation of L·2S crystals and promotes the precipitation of L·S crystals.

4. Conclusion

The effect of a small amount of K₂O on the crystallization behavior of the system of Li₂O–SiO₂ was investigated.

Lithium disilicate (Li₂O·2SiO₂, L·2S) and lithium metasilicate (Li₂O·SiO₂, L·S) crystals precipitate simultaneously, but only L·2S crystals grow upon further heat treatment in the glass without K₂O (Li glass). However, only L·S crystals precipitated and grew in the glass containing K₂O (K3 glass). The stable crystalline phases were L·2S and SiO₂ crystals in both glasses.

Phase separation was observed before crystallization; a Li₂O-rich phase formed an isolated droplet phase in Li glass and the continuous phase in K3 glass, respectively. The Li⁺–K⁺ ion exchange test confirmed these structures. The amount of weight gain due to ion exchange decreased markedly with the progress of heat treatment for Li glass. On the other hand, the amount of weight gain due to ion exchange increased initially and decreased slightly in K3 glass. SEM–EDX analysis confirmed that K₂O existed in the Li₂O-rich phase after phase separation in K3 glass.

Thus, K3 glass separates into two phases, one of which was a continuous phase rich in Li₂O and containing a considerable amount of K₂O. L·S crystals precipitated and grew in this phase upon further heat treatment. Consequently, K₂O suppressed the crystallization of L·2S, and promoted the precipitation of L·S crystals.

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