

Phase separation and crystallization in the system $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--B}_2\text{O}_3\text{--Na}_2\text{O}$ glasses

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Abstract

The phase separation and crystallization behavior in the system $(80 - X)\text{SiO}_2 \cdot X(\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5) \cdot 5\text{B}_2\text{O}_3 \cdot 15\text{Na}_2\text{O}$ (mol%) glasses was investigated. Glasses with $X = 20$ and 30 phase separated into two phases, one of which is rich in $\text{Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--SiO}_2$ and forms a continuous phase. Glasses containing a larger amount of $\text{Al}_2\text{O}_3\text{--P}_2\text{O}_5$ ($X = 40$ and 50) readily crystallize and precipitates tridymite type AlPO_4 crystals. It is estimated that the phase separation occurs forming continuous $\text{Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--SiO}_2$ phase at first, and then tridymite type AlPO_4 crystals precipitate and grow in this phase. Highly transparent glass–ceramics comparable to glass can be successfully obtained by controlling heat treatment precisely. The crystal size and percent crystallinity of these transparent glass–ceramics are 20–30 nm and about 50%, respectively.

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1. Introduction

Glass–ceramics can be defined as a two-phase system comprising crystals that have been controllably grown from a parent glass by precise heat treatment. Optical properties of glass–ceramics have been impaired by the scattering losses. However, the ability of some crystalline phases to partition rare-earth or transition metal ions into the crystal phase during crystallization has suggested that these materials could provide efficient lasing hosts [1–5]. Such systems would be capable of properties that are glass-like in most respects, except for the spectroscopy, which can be crystal-like.

In early 1960s, transparency which was sufficiently good, so that imaging through short pass length was possi-

ble, was observed in certain glass–ceramics materials [6] and this eventually led to a commercial cookware application. This work was instrumental in the subsequent discovery of many new transparent glass–ceramic systems [7–10].

From the structure of glass point of view, network mixed glasses in the system $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--B}_2\text{O}_3$ ($-\text{Na}_2\text{O}$) are also of special interest because all these may act as glass formers [11]. It is well known that AlPO_4 crystal readily precipitates from glasses containing relatively large amount of Al_2O_3 and P_2O_5 [12,13]. AlPO_4 crystal has all the three normal silica structures and has a bulk and surface acoustic wave function similar to α -quartz [14–17].

In order to obtain transparent glass–ceramics based on AlPO_4 crystal, the phase separation and crystallization behavior of glasses in the system $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--B}_2\text{O}_3\text{--Na}_2\text{O}$ was investigated, and highly transparent glass–ceramics could be successfully obtained. These results are reported.

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2. Experimental

2.1. Sample preparation

Five glasses were prepared, and their compositions were expressed by $(80 - X)\text{SiO}_2 \cdot X(\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5) \cdot 5\text{B}_2\text{O}_3 \cdot 15\text{Na}_2\text{O}$ (mol%, $X = 20, 30, 40, 45, 50$). High-purity silica sand, alumina and reagent grade chemicals of $(\text{NaPO}_3)_6$, $(\text{NH}_4)_2\text{HPO}_4$, H_3BO_3 and Na_2CO_3 (by Carlo Erba[®]) were used as raw materials. Batches corresponding to 200 g of glass were mixed thoroughly and pre-calcined at 400 °C for overnight to remove NH_3 . Then they were melted in 100 ml Pt/Rh10 crucible according to melting schedule, 1550 °C–3 h → 1500 °C–1 h, in an electric furnace in air, and poured onto iron plate and pressed by another iron plate. They were then annealed at 510 °C for 30 min and cooled to room temperature in the furnace.

The glasses were heat treated at just above the glass transition temperature for 5–10 h for nucleation and subsequently heat treated under various conditions for crystallization.

2.2. Thermal expansion and DTA

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

2.3. XRD and SEM

Crystalline phases, percent crystallinity and crystalline size were examined by X-ray diffraction analysis (XRD, Bruker AXS Model D5005) with $\text{Cu-K}\alpha$ radiation. The crystal size and percent crystallinity were determined by Scherrer's equation [18] and Ohlberg and Strickler's method [19], respectively. The fine structure of glasses and glass-ceramics was observed by scanning electron microscope (SEM, JEOL JSM 6400). The fractured surface of samples was etched by 0.5% HF solution for 1 min at room temperature for SEM observation.

2.4. Optical spectroscopy

The transmission spectra of glasses and glass-ceramics were measured using UV-Vis spectrometer (Varian, Carry 1E) in the range of 200–800 nm. The sample thickness was 3 mm.

3. Results and discussion

3.1. Properties of glass

Transparent and bubble free glasses were obtained for Nos. 1–4 composition ($X = 20, 30, 40$ and 45), while No. 5 composition ($X = 50$) crystallized during casting.

Fig. 1 shows the thermal expansion curves of glasses. T_g increases slightly with increase in X and reaches to a constant, while Y_p decreases markedly with increase in X . The temperature interval between T_g and Y_p of No. 1, No. 2 and No. 3 glasses is very wide, 184, 116 and 83 °C, respectively. This abnormal expansion phenomenon is often observed in phase separated $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glasses. This suggests that the phase separation may occur in these glasses. In No. 4 glasses, on the other hand, two peaks of Y_p can be observed, lower one shows the true Y_p and higher one indicates the beginning of crystallization.

DTA runs of No. 1 and No. 2 glasses show no exothermic or endothermic peak, whilst in No. 3 and No. 4 glasses the exothermic peaks due to the crystallization appear. Thermal properties of glasses, T_g , Y_p , α , onset temperature (T_{onset}) at which crystallization starts and peak temperature for crystallization (T_{peak}), are summarized in Table 1. The crystallization temperature of No. 4 glass decreases enormously compared with No. 3 glass. This suggests that No. 4 glass crystallizes much easier than No. 3 glass.

3.2. Phase separation and crystallization

The occurring of phase separation was suggested in No. 1 and No. 2 glasses by thermal expansion and DTA measurement. Fig. 2 shows SEM photographs of these glasses after the heat treatment. The phase separation can be observed clearly in both glasses, and the size of which is about 100 nm. The matrix phase (continuous phase) might be rich in $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2$ [11,12].

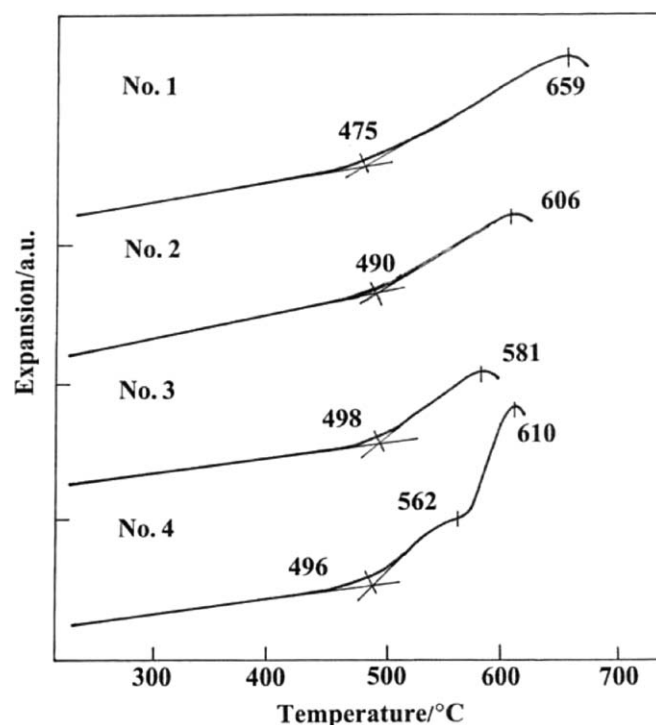


Fig. 1. Thermal expansion curves of glasses. Heating rate: 5 K/min.

Table 1
Thermal properties of glasses studied

Glass		Thermal expansion			DTA		
No.	<i>X</i>	T_g (°C) ±3 °C	T_p (°C) ±3 °C	α (10 ⁻⁷ /K) ^a ±5	T_g (°C) ±5 °C	T_{onset} (°C) ±3 °C	T_{peak} (°C) ±3 °C
1	20	475	659	77.8	460	Not detected	
2	30	490	606	77.8	501	Not detected	
3	40	498	581	74.1	503	653	716
4	45	496	562	70.4	498	600	619
5	50	Crystallized during casting					

^a Mean expansion coefficient: 30–300 °C.

On the other hand, No. 3 and No. 4 glasses readily crystallize resulting in transparent to opaque glass–ceramics depending on the heat treatment condition. Fig. 3 shows XRD patterns of these glass–ceramics, and only tridymite type $AlPO_4$ crystal [JCPDS 051-1674] was detected. The transparent glass–ceramics can be obtained by the heat treatment at relatively low temperature. Fig. 4 shows the percent crystallinity (%C) and crystallite size (D nm) of No. 3 and No. 4 glass–ceramics with heat treatment temperature. The crystallite size increases gradually with increase in temperature for No. 3. However, it increases rapidly with increase in temperature and exceeds 100 nm by the heat treatment at above 650 °C for No. 4. The glass–ceramics containing above 100 nm of $AlPO_4$ crystal appears to be opaque in appearance.

The percent crystallinity increases gradually with increasing temperature, and reaches to about 50% for No. 3 and about 60% for No. 4. If all of Al_2O_3 and P_2O_5

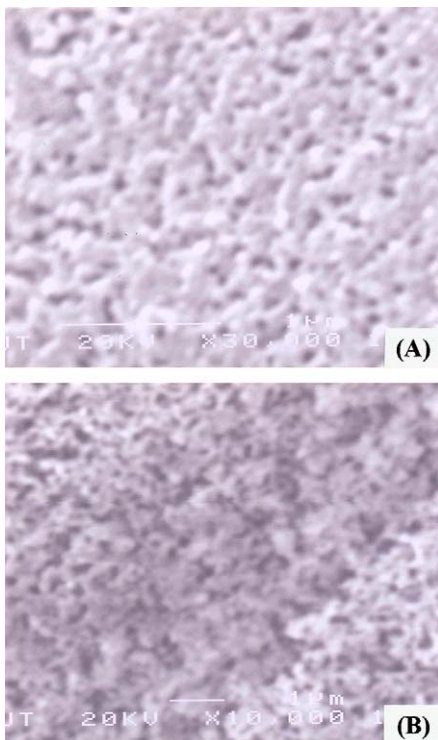


Fig. 2. SEM photos of No. 1 and No. 2 glasses. (A) No. 1: 550 °C–10 h, 800 °C–5 h, (B) No. 2: 550 °C–10 h, 750 °C–5 h.

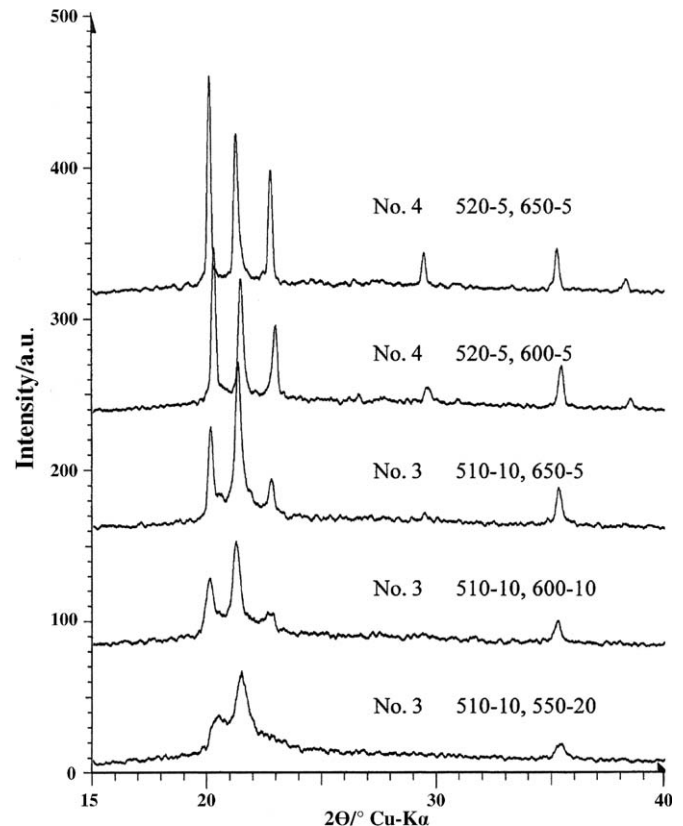


Fig. 3. XRD patterns of No. 3 and No. 4 glass–ceramics. Inset denotes heat treatment condition, °C–h.

would be spent for the formation of $AlPO_4$ crystal, the amount of $AlPO_4$ being precipitating may be 57% for No. 3 and 62% for No. 4, respectively. Thus, the experimental result is thought to be reasonable.

Fig. 5 shows the SEM photos of No. 3 transparent glass–ceramics. This glass was pre-heat treated at 510 °C for 10 h and subsequently heat treated at higher temperature. Although an individual crystal cannot be found clearly, a phase separation-like structural change occurs in sample A (510 °C–0 h, 550 °C–20 h). A very fine continuous and interconnected structure consisting of fine crystals can be observed in sample B (510 °C–10 h, 600 °C–10 h). In sample C (510 °C–10 h, 650 °C–5 h), an individual $AlPO_4$ crystal can be observed clearly. The percent crystallinity and crystal size of these transparent glass–ceramics

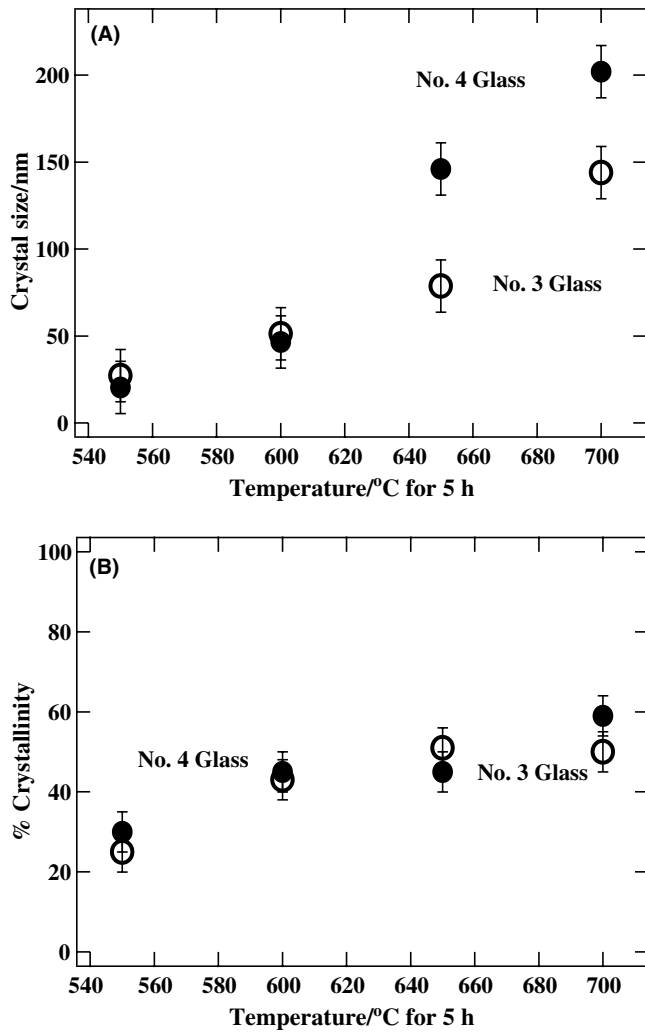


Fig. 4. Relationship between percent crystallinity and crystal diameter and heat treatment temperature of No. 3 and No. 4 glasses. (A) Crystal size vs second heat treatment temperature. (B) Percent crystallinity vs second heat treatment temperature. 1st heat treatment: 520 °C–5 h.

are 34% and 21 nm for sample A, 48% and 34 nm for sample B and 50% and 60 nm for sample C, respectively. From SEM observation, the mechanism of crystallization might be thought as follows: (1) phase separated into two phases, one of which is rich in $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2$ and forms a continuous phase [11,12], (2) AlPO_4 crystal starts to precipitate in this continuous phase [20], (3) AlPO_4 crystal grows in this phase resulting in individual crystallites.

Table 2 summarizes the properties of glass–ceramics. The thermal expansion coefficient of glass–ceramics increases with increase in the amount of AlPO_4 crystal.

3.3. Transparency

The transparency of glass and glass–ceramics in UV–Vis region is compared. Fig. 6 shows the transmission spectra of glass and glass–ceramics. Glass–ceramics (510 °C–10 h, 600 °C–20 h) has a very high transparency comparable to

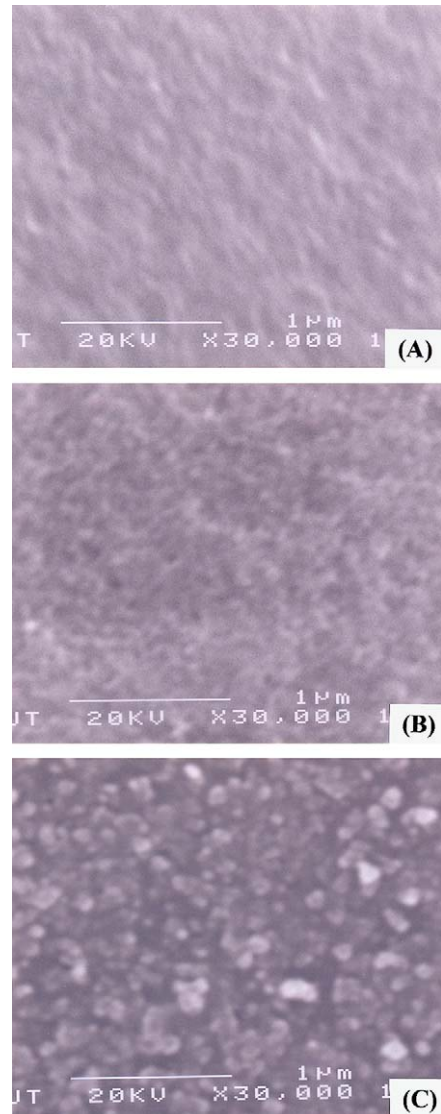


Fig. 5. SEM photos of No. 3 glass–ceramics. (A) 510 °C–10 h, 550 °C–20 h, (B) 510 °C–10 h, 600 °C–10 h, (C) 510 °C–10 h, 650 °C–5 h.

glass. However, glass–ceramics (510 °C–10 h, 650 °C–5 h) appears to be a low transmittance due to the scattering in the range of 250–800 nm.

According to the scattering theory, the coefficient of scattering (σ) is governed by the size of crystals (R) dispersed in glassy phase, [$\sigma \propto R^3$], and the refractive index difference between crystal (n) and glass matrix (n_0), [$\sigma \propto \{(n^2 - n_0^2)/(n^2 + n_0^2)\}^2$]. Therefore, much smaller crystals and smaller refractive index difference provide the lower scattering. The transparency of the most transparent glass–ceramics is achieved by the smaller crystal size [8]. Though tridymite type AlPO_4 crystal has a birefringence, its mean refractive index is about 1.46 [21]. The refractive index of residual glassy phase is estimated to be about 1.51, the difference in refractive index may be 0.05. This value is sufficiently too low, and the crystallite size is also much smaller by 20–30 nm, thus the lower scattering can be achieved.

Table 2
Properties of glass–ceramics

Glass No.	Heat treatment (°C–h)	Appearance	Crystalline phase	α^a ($10^{-7}/\text{K}$) ± 5	Percent crystallinity ± 5	Crystal size (nm) ± 5
3	–	Transparent	Glassy	74.1	–	–
	510–10	”	”	–	–	–
	510–10, 550–20	”	AlPO ₄	–	34	21
	510–10, 600–10	”	”	–	48	34
	510–10, 650–5	Slightly translucent	”	–	50	60
	520–5, 600–10	”	”	110 ^b	44	42
	520–5, 650–5	Translucent	”	140 ^b	50	70
4	–	Transparent	Glassy	70.4	–	–
	520–5, 550–5	”	AlPO ₄	–	30	18
	520–5, 600–10	Translucent	”	125 ^b	50	106

^a 30–300 °C.

^b 100–300 °C.

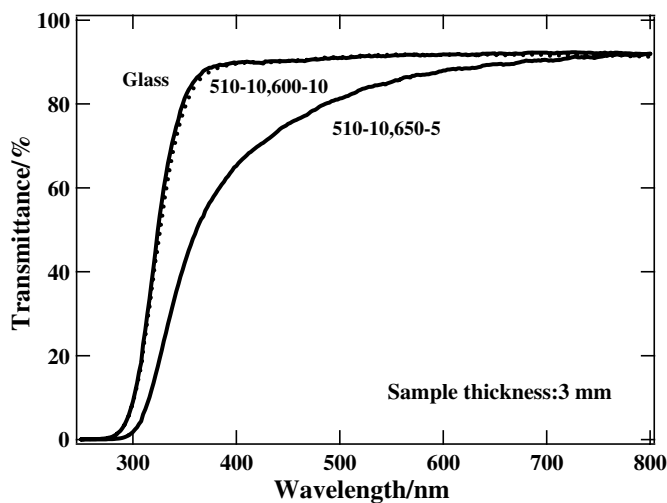


Fig. 6. Optical transmittance of No. 3 transparent glass–ceramics in UV–Vis region. Sample thickness: 3 mm.

4. Conclusion

The phase separation and crystallization in $(80 - X)\text{SiO}_2 \cdot X(\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5) \cdot 5\text{B}_2\text{O}_3 \cdot 15\text{Na}_2\text{O}$ (mol%, $X = 20\text{--}50$) glasses was investigated. The phase separation was observed in all glasses, especially $X = 20$ and 30 composition, and the interconnected continuous phase seems to be rich in $\text{Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--SiO}_2$. The crystallization tendency increases with increase in X , the precipitation of tridymite type AlPO_4 crystal was observed in $X = 40, 45$ and 50 glasses. The amount of AlPO_4 crystal precipitated is about 50–60%. It is found that the phase separation occurs at first, forming continuous phase rich in $\text{Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--SiO}_2$ and then tridymite type AlPO_4 crystal precipitates and grows in this phase.

A highly transparent glass–ceramics comparable to glass can be successfully obtained by controlling the heat treatment precisely. The crystallite size and percent crystallinity of these transparent glass–ceramics are 20–30 nm and about 50%, respectively.

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