Preparation and Properties of Phosphate Glasses and Glass-Ceramics Containing Large Amounts of Titanium (IV)

Akira KISHIOKA, Yuki MIYAZAWA, Kiyoshi ITATANI, F. Scott HOWELL and Makio KINOSHITA

Department of Chemistry, Faculty of Science and Technology, Sophia University, 7-1, Kioi-cho, Chiyoda-ku, Tokyo 102

多量のチタン(IV)を含有するリン酸塩ガラス及びガラスセラミックスの製造と性質

岸岡 昭・宮沢結樹・板谷清司・F. Scott Howell・木下眞喜雄

上智大学理工学部化学科, 102 東京都千代田区紀尾井町 7-1

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Phosphate glasses containing very large amounts of TiO_2 have been prepared in the compositions of $(3\text{Na}_2\text{O} \cdot 67\text{TiO}_2 \cdot 30\text{P}_2\text{O}_5) + 5\text{SiO}_2$ (mol%) (Glass-1) and $(3\text{Na}_2\text{O} \cdot 72\text{TiO}_2 \cdot 25\text{P}_2\text{O}_5) + 5\text{SiO}_2$ (mol%) (Glass-2). The thermal expansion coefficient (α) from 30 to 600°C were $7.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $6.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, respectively. The glass-ceramics prepared by heating Glass-1 at temperatures in 50°C intervals from 800 to 1000°C for 30h had $\alpha = 0.7\text{--}2.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and glass-ceramics prepared by heating Glass-2 at various temperatures from 900 to 1100°C for 30h had $\alpha = 1.6\text{--}8.4 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ in the same temperature range. The bending strengths of the glass-ceramics from Glass-1 were larger than those from Glass-2. The low thermal expansions of these glass-ceramics were attributed to $\text{NaTi}_2(\text{PO}_4)_3$ -like phase, TiO_2 and $(\text{TiO})_2\text{P}_2\text{O}_7$ produced by crystallization, and the bending strengths were greatly influenced by the crystalline phases. The $\text{NaTi}_2(\text{PO}_4)_3$ -like phase seems to be a solid solution of $\text{NaTi}_2(\text{PO}_4)_3$ and Si^{4+} , $\text{Na}_{1+x}\text{Ti}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$, as judged from the differences between the lattice parameters of this phase and those of $\text{NaTi}_2(\text{PO}_4)_3$.

Key-words: Glass, Phosphate glass, Titanate glass, Glass-ceramics, Crystallized glass, Low thermal expansion, Thermal expansion coefficient

1. Introduction

The addition of TiO_2 to phosphate glass contributes to the stabilization of the glass structure, as similar additions to Al_2O_3 and B_2O_3 do. One of the authors has reported that glasses containing large amounts of TiO_2 can be prepared in compositions with lower than 50 mol% of P_2O_5 in $\text{M}^{\text{I}}\text{O}-\text{TiO}_2-\text{P}_2\text{O}_5$ ($\text{M}^{\text{I}}=\text{Li}$, Na and K) and $\text{M}^{\text{II}}\text{O}-\text{TiO}_2-\text{P}_2\text{O}_5$ ($\text{M}^{\text{II}}=\text{Mg}$, Ca and Ba) systems.^{1,2)} These glasses are excellent in chemical durability.¹⁾ The double phosphates such as $\text{LiTi}_2(\text{PO}_4)_3$, $\text{NaTi}_2(\text{PO}_4)_3$ and $\text{CaTi}_4(\text{PO}_4)_6$ etc. are formed as main crystalline phases by crystallization.³⁻⁶⁾ Such compounds show a low thermal expansion coefficient and/or an ionic conductivity.⁷⁻¹³⁾ But without additions the powders of these double phosphates do not yield sintered materials with sufficient strength. Hanada et al. have reported that the amorphous film in the system TiO_2-

SiO_2 exhibits a decrease in thermal expansion coefficient up to about 15 mol% of TiO_2 .¹⁴⁾ Therefore, the phosphate glasses and glass-ceramics containing large amounts of TiO_2 are also interesting as low thermal expansion materials.

In this study, the glasses with large amounts of TiO_2 were prepared by addition of small quantities of SiO_2 to $\text{Na}_2\text{O}-\text{TiO}_2-\text{P}_2\text{O}_5$ system with low Na_2O content. The crystalline phases in devitrified products of these glasses were investigated by X-ray powder diffractometry. In addition, the relation between the thermal expansion values of crystallized glasses and the crystalline phases has been considered. Such data allowed the authors to prepare new titanate-phosphate glass-ceramics with a very low thermal expansion coefficient.

2. Experimental

2.1 Preparation of glasses

Based on the results of fusing and quenching for the nine kinds of samples with different compositions, two kinds of glasses with the compositions of $(3\text{Na}_2\text{O} \cdot 67\text{TiO}_2 \cdot 30\text{P}_2\text{O}_5) + 5\text{SiO}_2$ (mol%) (Glass-1) and $(3\text{Na}_2\text{O} \cdot 72\text{TiO}_2 \cdot 25\text{P}_2\text{O}_5) + 5\text{SiO}_2$ (mol%) (Glass-2) were prepared. The materials used were reagent grade chemicals of NaH_2PO_4 , TiO_2 , SiO_2 and H_3PO_4 (85%). A batch (15 g) obtained by mixing the necessary amounts of these chemicals was placed in a platinum evaporating dish and heated in an electric furnace. After the sample had been preheated up to 300°C at a heating rate of $10^\circ\text{C} \cdot \text{h}^{-1}$ and further from 300°C up to 500°C at $20^\circ\text{C} \cdot \text{h}^{-1}$, it was kept at 500°C for 3h. Then, the temperature was raised further to 1450°C over a 2h period and kept at this temperature for 1h. The melt of each batch was poured out in a graphite mold (either 0.5 cm inside diameter $\times$ 1.2 cm or $3 \times 3 \times 1.5$ cm) and annealed.

2.2 Characterization and crystallization of glasses

The thermal expansion coefficients (α) in the range from 30 to 600°C and the glass transition temperatures (T_g) of the glasses were determined from the thermal expansion curves of glass specimens $5 \times 5 \times 3$ mm in size. The density (ρ) was measured

by the Archimedes method. The powdered glasses were subjected to differential thermal analysis (DTA). The crystallization of the bulk glasses was carried out by heating rectangular glass bars of $5 \times 5 \times 25$ mm in size at various temperatures in intervals of 50°C from 800 to 1100°C for 30h. The 800°C is close to the termination temperature of exothermic effects in the DTA for the glasses (Fig. 2). In order to prepare the stable glass-ceramics on heating, the glasses were subjected to heating at 800°C or higher for a long time. The pulverized glass-ceramics were examined by X-ray powder diffractometry (XRD). The identifications of crystalline phases were carried out by reference to the JCPDS cards; then the desired compounds were prepared separately. The solid solution of $\text{NaTi}_2(\text{PO}_4)_3$ and Si^{4+} formed by heating was confirmed by comparing the lattice parameters calculated for this compound with those of $\text{NaTi}_2(\text{PO}_4)_3$.¹⁵⁾ For the glass-ceramics obtained by heating at these temperatures, the thermal expansion coefficients in the range from 30 to 600°C were determined and the bending strengths were measured. The fracture surfaces of these glass-ceramics were also observed by scanning electron microscopy (SEM).

2.3 Analyzers and analysis conditions

The following analyzers were used, under the conditions given in the parentheses.

High-temperature type differential thermobalance, Rigaku Denki TG-DTA (quantity of the sample: approximately 70 mg of powdered glass under $74 \mu\text{m}$; the standard sample: $\alpha\text{-Al}_2\text{O}_3$; heating rate: $10^\circ\text{C} \cdot \text{min}^{-1}$; heated in air; DTA sensitivity: $\pm 100 \mu\text{V}$).

Powder X-ray diffractometer, Rigaku Denki RAD-II A Model ($\text{Cu K}\alpha$, applied voltage: 35 kV ; tube current: 22.5 mA ; full-scale count: 4000 or 8000 cps).

High-temperature type thermomechanical analyzer, Rigaku Denki (the specimen was heated at $10^\circ\text{C} \cdot \text{min}^{-1}$ in air and calibrated using a standard fused silica sample).

Autostrain, Yasuda Seiki No. 216YZ-500-1-PC Model (load application rate: $0.5 \text{ mm} \cdot \text{min}^{-1}$, span: 10 mm or 20 mm).

Scanning electron microscope, Hitachi S-430 Model (acceleration voltage: 25 kV ; the fracture surface of the specimen was polished and coated with a thin film of gold).

3. Results and discussion

3.1 Thermal behaviour and physical properties of glasses

The glasses were brownish black in color due to the titanium ions of lower valency. The glass bar and the glass-ceramics obtained from Glass-1 are shown in Fig. 1. From the density of Li_2O (or MgO , CaO)- TiO_2 - P_2O_5 glasses with 30 mol% P_2O_5 ,²⁾ the compositions of the glasses appear to be not appreciably

different from those before melting, if sufficient pre-heating is used as in the present work.

Figure 2 shows the DTA curves of the obtained glasses. The exothermic reactions observed at 680 to 820°C are due to the crystallization of glasses. No endothermic effects owing to the melting of crystalline phases were observed up to 1000°C . The glass-ceramics obtained from these glasses may be expected to be excellent in resistance to heating.

The physical properties of both glasses are given in Table 1. The densities are higher than those of Li_2O (or MgO)- TiO_2 - P_2O_5 glasses²⁾ already reported and the thermal expansion coefficients are lower than those of various soda-lime glasses.¹⁶⁾ These

Fig. 1. Photograph of (a) Glass-1 and (b) glass-ceramics prepared from Glass-1.

Fig. 2. DTA curves of (1) Glass-1 and (2) Glass-2.
(1) Glass-1: $(3\text{Na}_2\text{O} \cdot 67\text{TiO}_2 \cdot 30\text{P}_2\text{O}_5) + 5\text{SiO}_2$ (mol%),
(2) Glass-2: $(3\text{Na}_2\text{O} \cdot 72\text{TiO}_2 \cdot 25\text{P}_2\text{O}_5) + 5\text{SiO}_2$ (mol%).

Table 1. Physical Properties of Glass-1 and Glass-2

Glass	T _g / °C	ρ / g · cm ⁻³	α / °C ⁻¹
Glass-1	645	2.97	7.7×10^{-6}
Glass-2	635	3.05	6.9×10^{-6}

results suggest that the structures of the glasses are extremely stable, although each contains P_2O_5 as the main component. In the case of the alkali aluminophosphate glasses containing less than 50 mol% of P_2O_5 , the phosphate ion species in the glasses with the highest Al_2O_3 content are composed of the PO_4^{3-} ion.¹⁷⁾ In addition, in the richest TiO_2 glasses of $NaPO_3$ - TiO_2 system, no more P-O-P bridges exist and the most probable configuration of the skeleton is TiO_6 - PO_4 - TiO_6 polyhedra sharing either corners or edges.¹⁸⁾ Since very large amounts of TiO_2 are incorporated into the glasses of this work and the Na_2O content is very small, the glasses consist of essentially the -Ti-O-Ti- linkages of TiO_6 octahedra and the PO_4^{3-} ions. These facts appear to be responsible for the higher densities and the low thermal expansions of these glasses.

3.2 Crystalline phases in glass-ceramics

The crystalline phases produced from Glass-1 during heating at 800 to 1050°C are shown in Fig. 3 and those from Glass-2 at 850 to 1100°C in Fig. 4. In Glass-1, a $NaTi_2(PO_4)_3$ -like phase, of which the diffraction lines were shifted slightly from those of $NaTi_2(PO_4)_3$, were produced at 800 to 1050°C, TiO_2 (anatase) at 800 to 950°C, TiP_2O_7 at 950°C, and $(TiO)_2P_2O_7$ was formed by reaction of TiO_2 and TiP_2O_7 at 1000 to 1050°C. In Glass-2, $NaTi_2(PO_4)_3$ -like phase and TiO_2 (anatase) were produced at 850 to 1100°C, TiP_2O_7 was produced at 950°C, and $(TiO)_2P_2O_7$ at 900 to 1100°C. In the glass-ceramics prepared from Glass-2, TiO_2 was formed over the

Fig. 3. XRD patterns of crystalline phases in the glass-ceramics prepared from Glass-1 at various temperatures.

Fig. 4. XRD patterns of crystalline phases in the glass-ceramics prepared from Glass-2 at various temperatures.

temperature range from 850 to 1100°C. The temperature at which $(TiO)_2P_2O_7$ was formed was higher in Glass-1 than in Glass-2. These facts suggest that the structural differences between the two glass-ceramics are due to a higher TiO_2 content in Glass-2 than in Glass-1.

The $NaTi_2(PO_4)_3$ -like phase seems to be the solid solution of $NaTi_2(PO_4)_3$ and Si^{4+} , namely $Na_{1+x}Ti_2P_{3-x}Si_xO_{12}$ (NTPS). The lattice parameters of NTPS decreased slightly in a -axis (0.0033Å in glass-ceramics from Glass-1, 0.0075Å in glass-ceramics from Glass-2) and increased greatly in c -axis (0.3351Å in glass-ceramics from Glass-1, 0.2909Å in glass-ceramics from Glass-2) compared to those (a -axis: 8.4876Å, c -axis: 21.8008Å) of $NaTi_2(PO_4)_3$.¹⁵⁾

3.3 Properties of glass-ceramics

The thermal expansion curves as a function of temperature for the five kinds of glass-ceramics prepared from Glass-1 and for the three kinds from Glass-2 are given in Fig. 5 and Fig. 6, respectively. Table 2 and Table 3 show the thermal expansion coefficients from 30 to 600°C of the same specimens. The thermal expansion coefficients of these glass-ceramics are comparable to or lower than those of Zr (IV) or Ti (IV)-containing double phosphate ceramics so far reported.⁷⁾⁻¹²⁾ In particular, the thermal expansion coefficient of the glass-ceramics obtained by heating Glass-1 at 1000°C for 30h ($\alpha = 0.7 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$) and those by heating Glass-2 at 900 or 1100°C for 30h ($\alpha = 1.6 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ and $2.2 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$,

Fig. 5. Thermal expansion curves of glass-ceramics prepared from Glass-1 at various temperatures.

(1) 800°C, (2) 850°C, (3) 900°C, (4) 950°C, (5) 1000°C.

Fig. 6. Thermal expansion curves of glass-ceramics prepared from Glass-2 at various temperatures.

(1) 900°C, (2) 1000°C, (3) 1100°C.

Table 2. Thermal Expansion Coefficients (α) of 30–600°C for Glass-Ceramics Prepared from Glass-1 at Various Temperatures
(1) 800°C, (2) 850°C, (3) 900°C, (4) 950°C, (5) 1000°C

Glass-ceramics	$\alpha / ^\circ\text{C}^{-1}$
(1)	2.2×10^{-6}
(2)	1.9×10^{-6}
(3)	1.4×10^{-6}
(4)	1.7×10^{-6}
(5)	0.7×10^{-6}

Table 3. Thermal Expansion Coefficients (α) of 30–600°C for Glass-Ceramics Prepared from Glass-2 at Various Temperatures
(1) 900°C, (2) 1000°C, (3) 1100°C

Glass-ceramics	$\alpha / ^\circ\text{C}^{-1}$
(1)	1.6×10^{-7}
(2)	8.4×10^{-7}
(3)	2.2×10^{-7}

respectively) are lower than those of the double phosphate ceramics. In the crystalline phases formed, TiP_2O_7 has a larger thermal expansion coefficient,

Fig. 7. Relations between bending strengths of glass-ceramics and temperatures for crystallizations of Glass-1 and Glass-2.

□ glass-ceramics prepared from Glass-1,
○ glass-ceramics prepared from Glass-2.

namely, $1.2 \times 10^{-5} ^\circ\text{C}^{-1}$ (50–100°C).¹⁹⁾ For the NTPS a lower thermal expansion may be expected, because it is a solid solution of low thermal expansion materials, $\text{NaTi}_2(\text{PO}_4)_3$ and Si^{4+} . In addition, since the TiO_2 and the $(\text{TiO})_2\text{P}_2\text{O}_7$ were produced over a wide range of temperature during heating of glasses, these compounds also appear to contribute to a lowering in the thermal expansion of glass-ceramics. This fact is particularly obvious in the glass ceramics prepared from Glass-2.

Figure 7 shows the relations between the bending strengths of glass-ceramics and the temperatures for crystallizations of Glass-1 and Glass-2. The bending strengths of the glass-ceramics prepared from Glass-1 were larger than those from Glass-2. Those of glass-ceramics prepared from Glass-1 at 800 and 1100°C were larger than 100 MPa and that at 1000°C was 91 MPa. In the case of the glass-ceramics prepared from Glass-1 at 950°C, however, the bending strength had the lowest value: 25 MPa. According to the SEM photographs for the fracture surfaces of glass-ceramics shown in Figs. 8(a)–8(d), the glass-ceramics prepared from Glass-1 at 800°C (a) were characterized by the uniform and dense structure consisting of fine particles, whereas the glass-ceramics prepared at 950°C (b) consisted of larger particles and in the structure many cracks existed. Such a microstructure was observed in the glass-ceramics prepared from Glass-2 at 1000°C (d). The decrease of bending strength in the glass-ceramics prepared from Glass-1 at 1000°C is due to the development of particles (c). The great decrease of the strength in the glass-ceramics prepared from Glass-1 at 950°C appears to be due to the occurrence of cracks caused by the formation of TiP_2O_7 at this temperature, be-

Fig. 8. SEM images for fracture surfaces of glass-ceramics.
 (a) prepared from Glass-1 at 800°C,
 (b) prepared from Glass-1 at 950°C,
 (c) prepared from Glass-1 at 1000°C,
 (d) prepared from Glass-2 at 1000°C.

cause the same phenomenon is observed in the crystallization of Glass-2 (Fig. 4) and the bending strength of the glass-ceramics prepared from Glass-2 at 950°C (Fig. 7).

4. Conclusion

Phosphate glasses with large amounts of TiO_2 have been prepared in the compositions of $(3\text{Na}_2\text{O} \cdot 67\text{TiO}_2 \cdot 30\text{P}_2\text{O}_5) + 5\text{SiO}_2$ (mol%) (Glass-1) and $(3\text{Na}_2\text{O} \cdot 72\text{TiO}_2 \cdot 25\text{P}_2\text{O}_5) + 5\text{SiO}_2$ (mol%) (Glass-2). The thermal expansion coefficients (α) of the glass-ceramics prepared from these glasses were comparable to or lower than those of Zr (IV) or Ti (IV)-containing double phosphate ceramics so far reported. In particular, the glass-ceramics obtained by heating

Glass-1 at 1000°C for 30h showed $\alpha = 0.7 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ and the bending strength of this glass-ceramics was 91 MPa. The low thermal expansions of these glass-ceramics were due to the formation of $\text{Na}_{1+x}\text{Ti}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$, TiO_2 and $(\text{TiO})_2\text{P}_2\text{O}_7$.

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