Preparation and Properties of Glasses Containing Large Amounts of TiO_2
in $\text{TiO}_2\text{-P}_2\text{O}_5\text{-GeO}_2$ and $\text{Na}_2\text{O-TiO}_2\text{-P}_2\text{O}_5\text{-GeO}_2$ Systems

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Abstract Glasses containing TiO_2 in the range of 54 - 71 mol% were prepared in the systems of $\text{TiO}_2\text{-P}_2\text{O}_5\text{-GeO}_2$ and $\text{Na}_2\text{O-TiO}_2\text{-P}_2\text{O}_5\text{-GeO}_2$. Some physical properties of these glasses were determined. The thermal expansion coefficients (α) were $2.6 - 3.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ in the range from 30 - 550 $^\circ\text{C}$. These values are smaller than those for any other value among known glasses which contain P_2O_5 as the main component. The values are comparable to those of low thermal expansion double phosphate ceramics recently reported.

Introduction

Double phosphates containing Ti(IV) or Zr(IV) such as $\text{NaTi}_2(\text{PO}_4)_3$ and $\text{NaZr}_2(\text{PO}_4)_3$, have been extensively investigated as low thermal expansion materials¹⁾⁻¹⁴⁾. But without additions, the powders of these double phosphates do not yield sintered materials with sufficient strength. On the other hand, in $\text{Na}_2\text{O-TiO}_2\text{-P}_2\text{O}_5$ and $\text{MgO-TiO}_2\text{-P}_2\text{O}_5$ systems, it was found that the glasses with large amounts of TiO_2 can be prepared in lower P_2O_5 contents^{15),16)}. This fact indicates that low thermal expansion materials may be prepared from phosphate glasses containing TiO_2 . We prepared new titanate-phosphate glasses with a low

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thermal expansion coefficient in the systems of $\text{TiO}_2\text{-P}_2\text{O}_5\text{-GeO}_2$ and $\text{Na}_2\text{O-TiO}_2\text{-P}_2\text{O}_5\text{-GeO}_2$.

Experimental

Preparation of glasses

The materials used were reagent grade chemicals of NaH_2PO_4 , TiO_2 , GeO_2 and H_3PO_4 (85 %). Five or ten mol% of GeO_2 was added in each sample. 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 °C·h⁻¹ and heated further from 300 °C up to 500 °C at 20 °C·h⁻¹, it was kept at 500 °C for 3 h. Then the temperature was raised further to 1450 °C over a 2 h period and kept at this temperature for 1 h. The melt was poured out and quenched by pressing with a copper plate cooled with water to see if a homogeneous glass was obtained. In order to prepare the glasses for characterization, the batches which produced homogeneous glasses were melted in the same condition and the melt was poured out into a graphite mold (3 × 3 × 1.5 cm) and annealed.

Characterization of glasses

The thermal expansion coefficients (α) in the range from 30 to 550 °C and the glass transition temperatures (T_g) of the glasses were determined from the thermal expansion curves of glass specimens 5 × 5 × 4 mm in size. These expansion curves were obtained on a high-temperature-type thermomechanical analyzer (Rigaku Denki). The curves were calibrated using a standard fused silica sample. The density (ρ) was measured by the Archimedes method. The powdered glasses were subjected to differential thermal analysis (DTA, Rigaku Denki high-temperature-type TG-DTA) and the crystalline phases which formed during heating were investigated by X-ray powder diffractometry (XRD, Rigaku Denki RAD-IIA, $\text{CuK}\alpha$ radiation). The identifications of crystalline phases were

carried out by reference to the JCPDS cards and the previous paper^{17),18)}.

Results and discussion

Preparation and structure of glasses

The glass-forming regions are shown in Fig. 1. The homogeneous glasses were obtained in the batches with Na₂O smaller than 2 mol%. In the systems without Na₂O, we could incorporate TiO₂ in the range of 54 - 71 mol% into the glasses. The glasses were brownish black in color due to the titanium ions of lower

Fig. 1 Glass-forming regions in TiO₂-P₂O₅ and Na₂O-TiO₂-P₂O₅ systems. (a) with 5 mol% of GeO₂, (b) with 10 mol% of GeO₂. (1450 °C)

○: homogeneous glass, ◐: trace amounts of crystal in glass, ●: glass and crystal.

valency. The glass composition appear to be not appreciably different from those before melting, because the P₂O₅ contents are smaller and sufficient preheating was used in the same manner as in the previous work¹⁷⁾. In the NaPO₃-NaTiO₂ system, the glasses with more than 40 mol% of TiO₂ could be prepared^{15),16)}. According to the investigation by neutron scattering experiments for these glasses^{19),20)}, no more P-O-P bridges exist in the structure and the most probable configuration of the skeleton is TiO₆-PO₄-TiO₆ polyhedra sharing either corners or edges. Since the glasses in this work contain more than 54 mol% of TiO₂, our glasses consist of essentially the

Ti-O-Ti linkages of TiO_6 octahedra and PO_4 and GeO_4 tetrahedra.

Properties of glasses

Figure 2 shows the DTA curves of the obtained glasses. No endothermic effects owing to the melting of crystalline phases were observed up to 1000 $^{\circ}\text{C}$. The devitrified products obtained from these glasses may be expected to be excellent in resistance to heating. As shown in XRD patterns of Fig. 3, the crystalline phases in devitrified products obtained from $65\text{TiO}_2 \cdot 30\text{P}_2\text{O}_5 \cdot 5\text{GeO}_2$ glass by heating at 753 $^{\circ}\text{C}$ were $(\text{TiO})_2\text{P}_2\text{O}_7$ and $\text{Ti}_2\text{P}_2\text{O}_7$, and those from $2\text{Na}_2\text{O} \cdot 65\text{TiO}_2 \cdot 28\text{P}_2\text{O}_5 \cdot 5\text{GeO}_2$ glass at 551 $^{\circ}\text{C}$ were a solid solution of $\text{NaTi}_2(\text{PO}_4)_3$

Fig. 2 DTA curves of glasses.
(a) $65\text{TiO}_2 \cdot 30\text{P}_2\text{O}_5 \cdot 5\text{GeO}_2$,
(b) $2\text{Na}_2\text{O} \cdot 65\text{TiO}_2 \cdot 28\text{P}_2\text{O}_5 \cdot 5\text{GeO}_2$.

Fig. 3 XRD patterns of crystalline phases of devitrified glasses.
(a) $65\text{TiO}_2 \cdot 30\text{P}_2\text{O}_5 \cdot 5\text{GeO}_2$,
(b) $2\text{Na}_2\text{O} \cdot 65\text{TiO}_2 \cdot 28\text{P}_2\text{O}_5 \cdot 5\text{GeO}_2$.
□: $(\text{TiO})_2\text{P}_2\text{O}_7$, ■: $\text{Ti}_2\text{P}_2\text{O}_7$,
○: $\text{NaTi}_{2-x}\text{Ge}_x(\text{PO}_4)_3$ (NTGP),
■: TiO_2 (anatase).

(NTP) with Ge^{4+} ($\text{NaTi}_{2-x}\text{Ge}_x(\text{PO}_4)_3$) (NTGP)^{17),18)}, TiO_2 (anatase). Table 1 shows the physical properties of the glasses. Because of lower Na_2O contents, the glass transition temperatures are higher than those of the glasses reported in the previous paper.¹⁷⁾ The thermal expansion coefficients of these glasses were $2.6 - 3.5 \times 10^{-6} \text{ } ^{\circ}\text{C}^{-1}$ in the range from 30 to 550 $^{\circ}\text{C}$. These values were comparable to those of low thermal expansion double phosphate ceramics recently

reported. The thermal expansion coefficient (α) of $2.6 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ is the smallest value for glasses which contain P_2O_5 as the main component. As reported in the previous paper^{1,7)}, the structural condition that produces the solid solutions (NTGP) and $(\text{TiO})_2\text{P}_2\text{O}_7$ during heating seems to be responsible for the lowering of thermal expansion in the glasses.

Table 1 Properties of Glasses

Composition / mol%	T _g / $^{\circ}\text{C}$	ρ / $\text{g}\cdot\text{cm}^{-3}$	$\alpha^* / \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$
$65\text{TiO}_2 \cdot 30\text{P}_2\text{O}_5 \cdot 5\text{GeO}_2$	638	2.99	2.6
$71\text{TiO}_2 \cdot 24\text{P}_2\text{O}_5 \cdot 5\text{GeO}_2$	611	3.10	2.8
$\text{Na}_2\text{O} \cdot 59\text{TiO}_2 \cdot 35\text{P}_2\text{O}_5 \cdot 5\text{GeO}_2$	619	2.97	3.1
$\text{Na}_2\text{O} \cdot 65\text{TiO}_2 \cdot 29\text{P}_2\text{O}_5 \cdot 5\text{GeO}_2$	614	3.04	2.9
$2\text{Na}_2\text{O} \cdot 65\text{TiO}_2 \cdot 28\text{P}_2\text{O}_5 \cdot 5\text{GeO}_2$	611	3.10	2.8
$63\text{TiO}_2 \cdot 27\text{P}_2\text{O}_5 \cdot 10\text{GeO}_2$	629	3.05	2.7
$69\text{TiO}_2 \cdot 21\text{P}_2\text{O}_5 \cdot 10\text{GeO}_2$	624	3.14	2.6
$\text{Na}_2\text{O} \cdot 57\text{TiO}_2 \cdot 32\text{P}_2\text{O}_5 \cdot 10\text{GeO}_2$	635	2.99	3.5
$\text{Na}_2\text{O} \cdot 63\text{TiO}_2 \cdot 26\text{P}_2\text{O}_5 \cdot 10\text{GeO}_2$	623	3.08	2.9
$2\text{Na}_2\text{O} \cdot 63\text{TiO}_2 \cdot 25\text{P}_2\text{O}_5 \cdot 10\text{GeO}_2$	624	3.06	2.7

* 30 - 550 $^{\circ}\text{C}$

Conclusion

The glasses containing TiO_2 in the range of 54 - 71 mol% could be prepared in the systems of $\text{TiO}_2\text{-P}_2\text{O}_5\text{-GeO}_2$ and $\text{Na}_2\text{O-TiO}_2\text{-P}_2\text{O}_5\text{-GeO}_2$. These glasses showed thermal expansion coefficients (α) of $2.6 - 3.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ in the range from 30 - 550 $^{\circ}\text{C}$. These values were comparable to those of low thermal expansion double phosphate ceramics.

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