Glass Formation in Multicomponent Phosphate Systems Containing TiO_2

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Glass formation was investigated in the Na_2O–TiO_2–P_2O_5, K_2O–TiO_2–P_2O_5, BaO–TiO_2–P_2O_5, Na_2O–BaO–P_2O_5, and Na_2O–BaO–TiO_2–P_2O_5 systems. In the Na_2O–TiO_2–P_2O_5 system, glass containing up to 45.5 mol% TiO_2 was found to be formed at the composition of $Na_2O/P_2O_5=1$, whereas in the K_2O–TiO_2–P_2O_5 system the glass formation was observed in a narrow region along the composition of $K_2O/P_2O_5=1$ in a three-component diagram. In the BaO–TiO_2–P_2O_5 system, only the glass containing about 10 mol% TiO_2 as a maximum was obtained. In the Na_2O–BaO–TiO_2–P_2O_5 system, the region of glass formation extended with an increase of Na_2O up to 30 mol%. These results suggested that a certain amount of Na_2O is necessary for the formation of glass containing a large amount of TiO_2 in the presence of BaO. The three-component diagrams of the Na_2O–TiO_2–P_2O_5 and Na_2O–BaO–P_2O_5 systems indicated that the most favorable amount of Na_2O for the glass formation in this four-component system is 27 to 28 mol%.

The region for glass formation in a three-component diagram is determined by the role of cations in the glass structure. The conditions and the region for glass formation in ternary systems of borate, silicate, germanate, and tellurite have been studied in detail by Imaoka *et al.*[1,2] However, there have been few investigations of glass formation in multicomponent phosphate systems of three or more components. From the studies of three-component diagram for glass formation in these multicomponent systems, one may be able to get some information on the role of cations, especially of such intermediate ions as Ti^{4+}, in the glass structure. It may also be worthwhile to determine the most favorable conditions for the glass formation in multicomponent phosphate systems.

In this work, the regions for glass formation in the three-component diagrams were determined for three kinds of phosphate systems containing TiO_2—the Na_2O–TiO_2–P_2O_5, K_2O–TiO_2–P_2O_5, and BaO–TiO_2–P_2O_5 systems. Based on the results of these ternary phosphate systems containing TiO_2 and that of the Na_2O–BaO–P_2O_5 system, the conditions for the formation of the glasses containing maximum amounts of TiO_2 and BaO were investigated for the four-component system of Na_2O–BaO–TiO_2–P_2O_5.

Experimental

Preparation of Glass. The raw materials used were sodium dihydrogenphosphate dihydrate, sodium triphosphate, anhydrous sodium carbonate, potassium dihydrogenphosphate, anhydrous potassium carbonate, barium carbonate, titanium dioxide, and orthophosphoric acid (85%). All the chemicals except sodium triphosphate were of a reagent grade. Commercial reagent-grade sodium triphosphate was purified before use by recrystallization and dehydration. Mixtures of from two to four kinds of the raw materials were placed in platinum evaporating dishes. For the batch of Na_2O/P_2O_5 or $K_2O/P_2O_5=1$ in the Na_2O–P_2O_5 or K_2O–P_2O_5 two-component system, $NaH_2PO_4 \cdot 2H_2O$ or KH_2PO_4 was used respectively. All the batches were about 15 g in weight.

Samples were heated in a Siliconit electric furnace BSH-1530 (Siliconit Konetsukogyo Co.) equipped with a platinum platinum-rhodium thermocouple with an automatic thermoelectric regulator. It took about 5 hr to heat them up to 1350 °C, and this temperature was kept for 1 hr. The melt was quenched by pressing with copper plate cooled with water. In the batches containing TiO_2 with more than 50 mol% P_2O_5, except for the composition in which the homogeneous glass was formed, the crystalline material was separated out in the melt. The homogeneity of the glass formed was immediately observed by the naked eye and under a microscope or a polarizing microscope. No phase separation of the melt itself was found in any of the systems.

The phosphate glass usually contains a small amount of water in its structure when prepared by dehydration and condensation.[3,4] In addition, the composition of the glass is varied by the loss of P_2O_5 during the heating, it depends on the conditions of preparation.[3] In the Na_2O–BaO–P_2O_5 system, the amount of the volatillization loss of P_2O_5 was in the range from 3.3 to 14.0 mol%. Taking these facts into account, all the diagrams for the glass formation were expressed in terms of the batch composition.

Examination of Chemical Durability. Glass grains (0.25—1 mm) of about 0.5 g were weighed and each portion was placed in a 100-ml Erlenmeyer flask. Then 25 ml of water, 25 ml of 35% HCl, and 25 ml of 10% NaOH were added separately into each flask, and they were stoppered. After having been shaken at speed of 80 strokes per minute in the thermostat at 25 °C for 1 hr, the weight loss (%) of each sample was determined.

Results and Discussion

The experimental results for the glass-forming region in each system are given in Figs. 1, 3, and 5—11. Figures 7—11 show the glass-forming region in the Na_2O–BaO–TiO_2–P_2O_5 four-component system. In the systems containing TiO_2, the glasses were colored purple or brown due to the titanium ion reduced. The chemical durabilities of the Na_2O–TiO_2–P_2O_5 and K_2O–TiO_2–P_2O_5 glasses are shown in Figs. 2 and 4.

Na_2O–TiO_2–P_2O_5 System (Fig. 1). A slight amount of glass was obtained in the system with more than 50 mol% P_2O_5. However, glass with a large amount of TiO_2 was obtained by decreasing the amount of P_2O_5 to less than 50 mol%. It may be seen in Fig. 1 that the system containing Na_2O and P_2O_5 in the ratio of unity is most favorable for formation of the glass with a high TiO_2 content. This fact may possibly be interpreted by associating the increase in the glass-forming ability of the Ti^{4+} ion with the ring-opening polymerization of sodium trimetaphosphate ($Na_3P_3O_9$).[5] The composition of the glass containing a maximal

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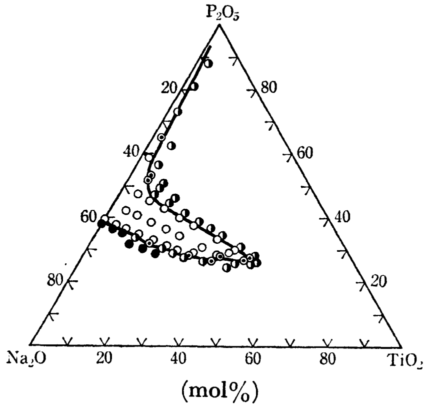

Fig. 1. Glass-forming region in Na_2O-TiO_2-P_2O_5 system
○: homogeneous glass, ⊙: trace amounts of crystal in glass, ◑: glass and crystal, ●: crystal.

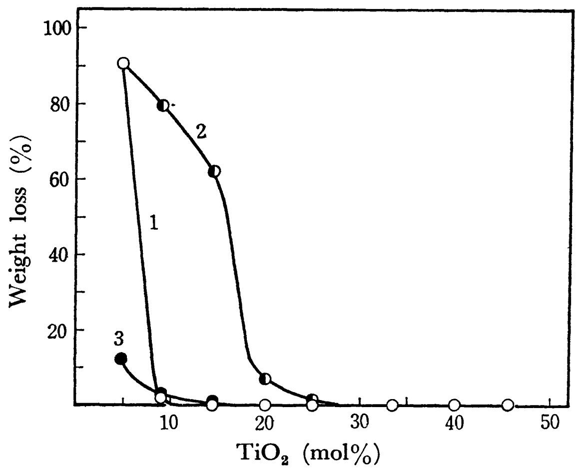

Fig. 2. Chemical durability of Na_2O-TiO_2-P_2O_5 glass ($Na_2O/P_2O_5=1$)
1 : water, 2: 35% HCl, 3 : 10% NaOH.

quantity of TiO_2 is Na_2O: 27.3, TiO_2: 45.5, and P_2O_5: 27.3 mol%.

Figure 2 shows that the chemical durability of the glass is very much increased by increasing the amount of TiO_2. The glass containing more than 20 mol% TiO_2 is insoluble or only slightly soluble in either water, 35% HCl, or 10% NaOH.

K_2O–TiO_2–P_2O_5 System (Fig. 3). With respect to more than 50 mol% P_2O_5, the region of glass formation of this system is similar to that of the Na_2O–TiO_2–P_2O_5 system. As is shown with arrow marks in Fig. 3, the region of glass formation in the composition along the line of $K_2O/P_2O_5=1$ is narrow. This is a marked difference from the Na_2O–TiO_2–P_2O_5 system, it may be interpreted in terms of the formation of straight-chain molecules of potassium metaphosphate.[6]

Rao[7,8] reported a formation of glass in the K_2O–TiO_2 system. Under the experimental conditions in the present work, however, no homogeneous glass was obtained in the same system.

In the A and B regions in Fig. 3, the maximum concentrations of TiO_2 were about 38 mol% and 35 mol% respectively. The coloration in the glass was observed in only the A region. As is shown in Fig. 4,

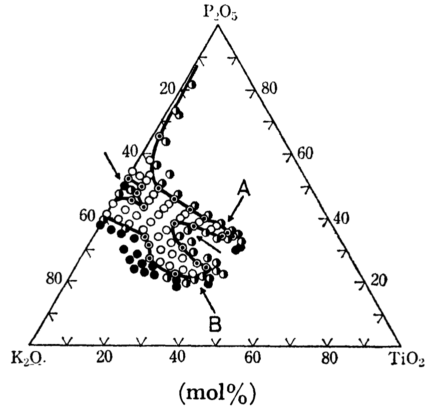

Fig. 3. Glass-forming region in K_2O-TiO_2-P_2O_5 system.
A; Region obtained the glass containing TiO_2 in the largest quantity in $K_2O/P_2O_5<1$
B: Region obtained the glass containing TiO_2 in the largest quantity in $K_2O/P_2O_5>1$

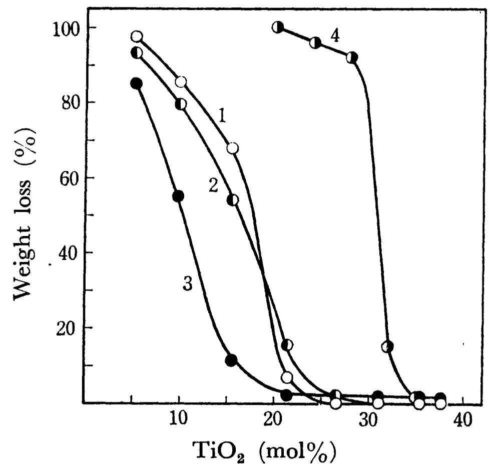

Fig. 4. Chemical durability of K_2O-TiO_2-P_2O_5 glass. 1: $K_2O/P_2O_5=0.83$, water, 2: $K_2O/P_2O_5=0.83$ 35% HCl, 3: $K_2O/P_2O_5=0.83$, 10% NaOH, 4: $K_2O/P_2O_5=1.67$, water.

the increase in the chemical durability of the glass formed in the system of K_2O–TiO_2–P_2O_5 was also observed with an increase in the TiO_2 content, as in the case of the NaO_2–TiO_2–P_2O_5 system

According to RaO,[7] the Ti^{4+} ion is able to act as a network former in silicate glass. The –P–O–Ti– linkage is probably formed in the phosphate glass. It seems that the increase in the chemical durability of the glass containing a large amount of TiO_2 results from the formation of such a linkage.

BaO–TiO_2–P_2O_5 System (Fig. 5). The homogeneous glass was obtained in the BaO–P_2O_5 system containing BaO up to approximately 58 mol%, but only about 10 mol% TiO_2 could be introduced in this glass at a maximum. This is very different from the glass formation in the NaO–TiO_2–P_2O_5 and K_2O–TiO_2–P_2O_5 systems (Figs. 1 and 3).

According to Kordes *et al.*,[9] the BaO–P_2O_5 glass is classified as a "normal glass" among the binary glasses of alkaline earth oxides and P_2O_5, and the Ba^{2+} ion has been regarded as a network modifier. However, the

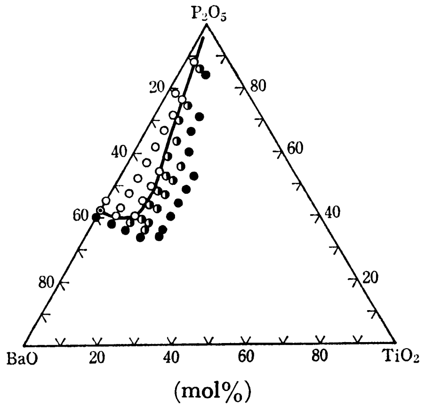

Fig. 5. Glass-forming region in $BaO-TiO_2-P_2O_5$ system.

electrostatic bond strength of the divalent Ba^{2+} ion, *i.e.*, the ratio of the charge number of the ion to its coordination number, is larger than that of the univalent Na^+ or K^+ ion. Thus it seems that BaO stabilizes the glass structure much more than Na_2O or K_2O in the phosphate glasses. The maximum content of TiO_2 in the $Na_2O-TiO_2-P_2O_5$ glass was found to be 45.5 mol% at $Na_2O/P_2O_5=1$, but that in the $BaO-TiO_2-P_2O_5$ glass only about 10 mol% at $BaO/P_2O_5=1$ (Figs. 1 and 5). The Ba^{2+} ion probably interferes with the introduction of the tetravalent Ti^{4+} ion into the glass structure.

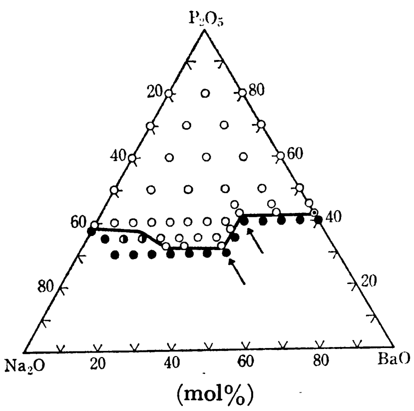

Fig. 6. Glass-forming region in $Na_2O-BaO-P_2O_5$ system.

$Na_2O-BaO-P_2O_5$ System (Fig. 6). This system consists of two kinds of network modifiers (Na_2O and BaO) and a network former (P_2O_5).

As is shown in Fig. 6, the glass is obtained over a considerably wide region. The lower limit of the P_2O_5 content in the glass formation is approximately 32 mol%. From the boundary curve in Fig. 6, it is known that the P_2O_5 content is constant in the regions of the Na_2O contents up to 20 mol%, 30—40 mol%, and 50—60 mol%, whereas the BaO content is constant in the region of 20 to 30 mol% Na_2O.

This shape of the boundary curve may possibly be interpreted as follows: the boundary of glass formation may be determined by the difference in the action between Na^+ and Ba^{2+} ions in the glass structure at the glass-forming limit. Thus, the increase in the Na_2O contents from 20 up to 30 mol% along the boundary (arrow marks in Fig. 6) seems to be the result of a break in the –P–O–P– linkage rather than of the substitution of the Ba^{2+} ion by the Na^+ ion. In the glass-forming boundary, the Ti^{4+} ion may be introduced quite easily into this glass when the Na_2O content is 20—30 mol%.

$Na_2O-BaO-TiO_2-P_2O_5$ System (Figs. 7—11). In order to observe the effect of Na_2O on the glass forma-

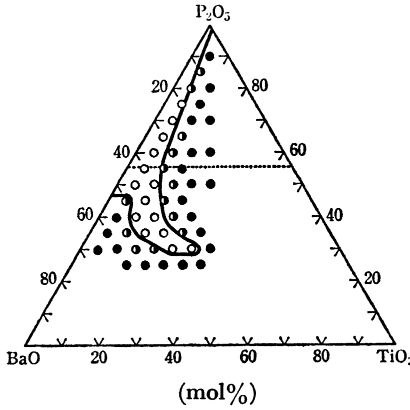

Fig. 7. Glass-forming region in $Na_2O-BaO-TiO_2-P_2O_5$ system containing 10 mol% Na_2O (dotted line represents P_2O_5 content is 50 mol%).

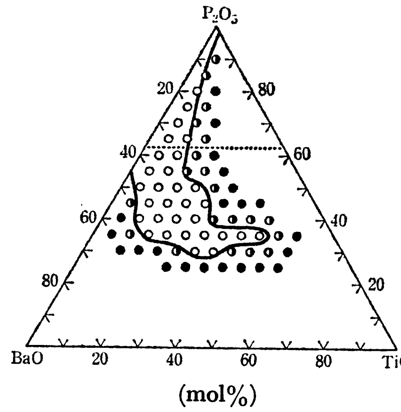

Fig. 8. Glass-forming region in $Na_2O-BaO-TiO_2-P_2O_5$ system containing 20 mol% Na_2O (dotted line represents P_2O_5 content is 50 mol%).

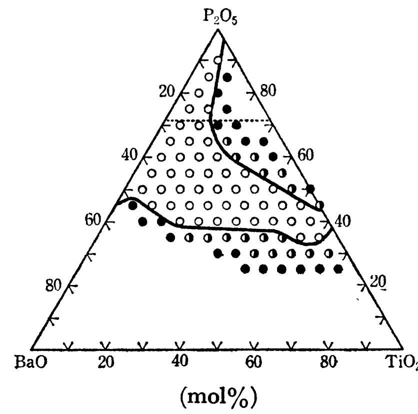

Fig. 9. Glass-forming region in $Na_2O-BaO-TiO_2-P_2O_5$ system containing 30 mol% Na_2O (dotted line represents P_2O_5 content is 50 mol%).

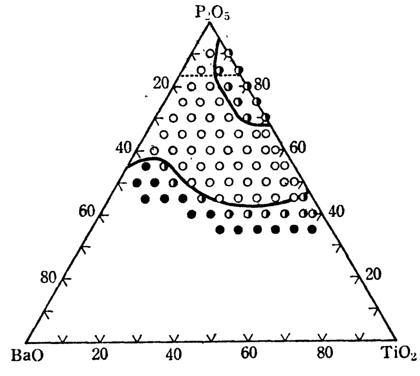

Fig. 10. Glass-forming region in Na_2O-BaO-TiO_2-P_2O_5 system containing 40 mol% Na_2O (dotted line represents P_2O_5 content is 50 mol%).

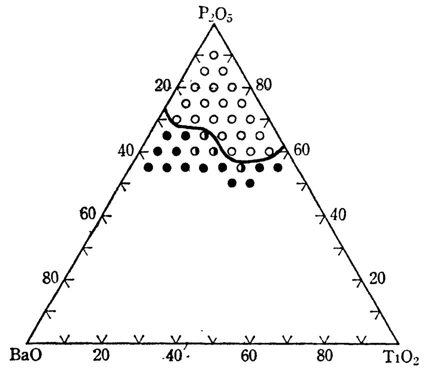

Fig. 11. Glass-forming region in Na_2O-BaO-TiO_2-P_2O_5 system containing 50 mol% Na_2O.

tion in the Na_2O–BaO–TiO_2–P_2O_5 system, the glass-forming region was studied for batches with different Na_2O contents (10, 20, 30, 40 and 50 mol%).

The results are shown in Figs. 7—11. The region in which the glass containing TiO_2 is formed extends up to 30 mol% of Na_2O. The decrease in the P_2O_5 content causes an increase in the TiO_2 content and a decrease in the BaO content in the glass. In addition, the tendency of the glass-forming region to be extended was observed in the system of up to 30 mol% Na_2O along with the compositions of the P_2O_5 contents of 27—28 mol%. The Ti^{4+} ion seems to be introduced easily into the glass structure at this amount of P_2O_5. The P_2O_5 content corresponds to the lower limit of the P_2O_5 contents in the Na_2O–TiO_2–P_2O_5 system (about 27 mol%). The glass-forming region in the Na_2O–BaO–TiO_2–P_2O_5 system (Figs. 7—11) extends to the boundary line in the Na_2O–TiO_2–P_2O_5 system (Fig. 1) when the Na_2O content is 27—28 mol%.

These results suggest that a certain amount of Na_2O is necessary for the formation of the glass containing a large amount of TiO_2 in the presence of BaO. This amount is probably in the range from 27 to 28 mol% Na_2O. Thus, it may be concluded that the Ti^{4+} ion is easily introduced into the glass when both Na_2O and P_2O_5 are 27—28 mol%; $Na_2O/P_2O_5 \approx 1$. These results also support the interpretation of the boundary of glass formation in the Na_2O–BaO–P_2O_5 system (Fig. 6).

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