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Glass Formation in the Li_2O-TiO_2-P_2O_5, MgO-TiO_2-P_2O_5, and CaO-TiO_2-P_2O_5 Systems

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The glass-forming regions in the Li_2O–TiO_2–P_2O_5, MgO–TiO_2–P_2O_5, and CaO–TiO_2–P_2O_5 systems have been determined. Homogeneous glasses were formed with compositions of less than 50 mol% P_2O_5 in all three systems. The largest quantities of TiO_2 could be introduced into glass for compositions of 30 mol% P_2O_5. In compositions with more than 50 mol% P_2O_5 only a mixture of the glass and crystal was formed. With an increase in the TiO_2 content, the density of the glass increased and the volume per mole of oxygen decreased. These results indicate that the TiO_2 had been easily incorporated into the glass with compositions of lower P_2O_5 contents, contributing to the stabilization of the glass structure.

The role of intermediate ions such as Ti^{4+} and Al^{3+} in glass formation in ternary phosphate systems is interesting, since it reflects the glass structure. Reports concerning the glass-forming regions in ternary phosphate systems, however, are relatively few compared with those in ternary systems containing other glass-forming oxides. Recently, glass formation in the BeO–TiO_2–P_2O_5, CaO–TiO_2–P_2O_5, and K_2O–TiO_2–P_2O_5 systems and the electrical resistivity have been reported by Hayashi *et al.*[1] The present authors have reported glass formation in the Na_2O–BaO–TiO_2–P_2O_5 four-component system,[2] the ternary phosphate systems containing Al_2O_3,[3] and the role of the Al^{3+} ion in alkali aluminophosphate glasses.[4]

In this paper, glass-forming regions for the Li_2O–TiO_2–P_2O_5, MgO–TiO_2–P_2O_5, and CaO–TiO_2–P_2O_5 systems have been determined. The density of the glass has been determined and the volume per mole of oxygen calculated. On the basis of these results, the role of the titanium ion in the glass has been discussed.

Experimental

Determination of Glass-Forming Region. The materials used were reagent grade chemicals of titanium dioxide, orthophosphoric acid (85%), lithium hydroxide monohydrate, magnesium oxide, calcium hydrogenphosphate dihydrate, and calcium carbonate. A batch (15-g) obtained by mixing appropriate amounts of the above chemicals was placed in platinum dishes and heated in an electric furnace. After dehydration, the batch was kept at 1350 °C for 1 h. The melt was poured out and quenched by pressing with a copper plate cooled with water. The homogeneity of the glass was checked with a polarizing microscope and the naked eye.

Density of Glass. The density of the glass was determined pycnometrically using 1-butanol at 25.0 °C. For samples containing a small amount of crystal, only the glassy part was used for measurement.

Volume of Glass. The volume of the glass per mole of oxygen was calculated by the following equation:[5]

$$V_0 = (G.F.W./D) \times 1/N_0,$$

where V_0 is the volume of the glass per mole of oxygen, *G.F.W.* is the gramme formula weight of the glass based on the batch composition, D is the density of the glass, and N_0 is the number of gramme molecular weights of oxygen (32 g units) in the glass.

Results and Discussion

Glass-Forming Tendency. The results are given in Figs. 1—3. The compositions whose batches melted completely at 1350 °C have been surrounded by dotted lines in the Figs. Homogeneous glasses were formed in compositions with less than 50 mol% P_2O_5. As shown by the arrows in Figs. 1—3, the content of TiO_2 in the glass was largest for compositions with 30 mol% P_2O_5 of each system; it was the largest for the MgO–TiO_2–P_2O_5 system. Considering that the phosphate species in the $47.5Na_2O \cdot 20Al_2O_3 \cdot 32.5P_2O_5$ glass were exclusively PO_4^{3-}-type ions,[4] those in the glasses with 30 mol% P_2O_5 containing more than 20 mol% TiO_2 are presumably also only PO_4^{3-} ions. Therefore, the above results indicate that the TiO_2 is incorporated easily into the glass with compositions of lower P_2O_5 content and the formation of the glass with higher TiO_2 contents is most favorable when there are no P–O–P chains.

All glasses were colored by the titanium ion of lower valency and the MgO–TiO_2–P_2O_5 glasses with higher TiO_2 content were brownish black. The Li_2O–TiO_2–

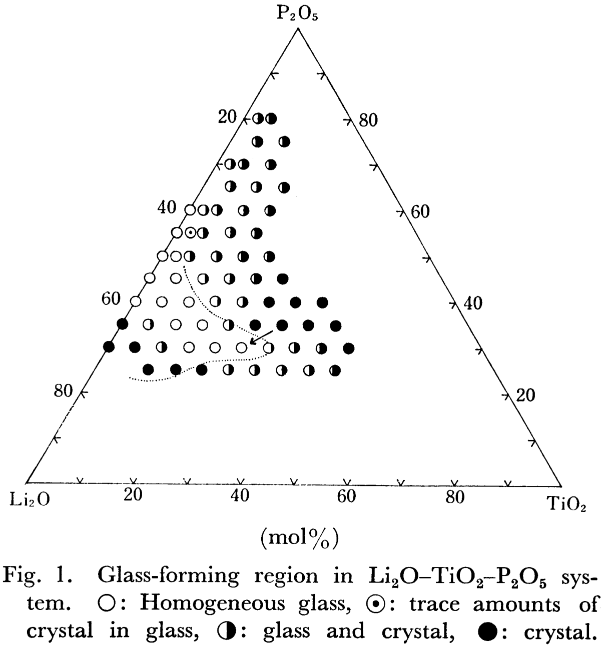

Fig. 1. Glass-forming region in Li_2O–TiO_2–P_2O_5 system. ○: Homogeneous glass, ⊙: trace amounts of crystal in glass, ◑: glass and crystal, ●: crystal.

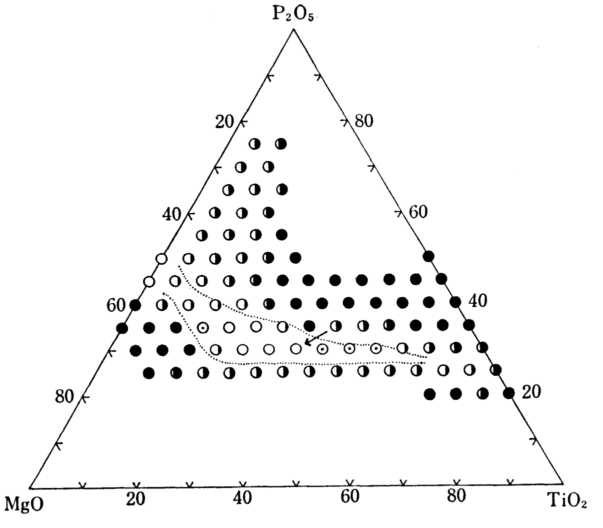

Fig. 2. Glass-forming region in $MgO-TiO_2-P_2O_5$ system.

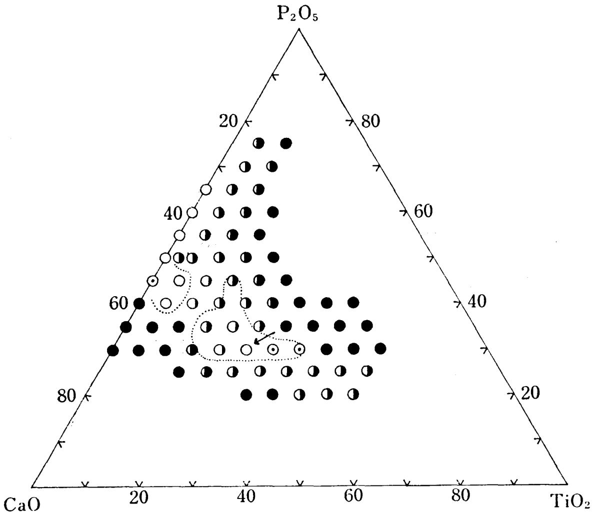

Fig. 3. Glass-forming region in $CaO-TiO_2-P_2O_5$ system.

P_2O_5 glasses were less colored than those containing MgO or CaO of the same molar composition.

In addition to the homogeneous glass, the following two types of products were formed; (a) a mixture of glass and crystal (produced by partial devitrification of the melt during quenching or separation of crystalline substance in the melt) and (b) a crystalline product formed as a result of devitrification during quenching or non-melting of the batch.

The glass-forming region in each system in the present work was smaller than those reported by Hayashi *et al.*[1] However, the observed tendency of glass formation in compositions with less than 50 mol% P_2O_5 agrees well with the results reported.[1]

In compositions with more than 50 mol% P_2O_5, only the mixture of the glass and the crystal was formed as the result of the separation of the crystalline substance in the melt. This makes a marked difference from the alkali (or alkaline earth) aluminophosphate system[3] where the homogeneous glasses were formed in the region with more than 50 mol% P_2O_5 in a three-component diagram. It can be considered that the action of the titanium ion in the glass formation is fairly different from that of the Al^{3+} ion in the same P_2O_5 content.

Density and Volume of Glass. The density and the volume per mole of oxygen of the glasses are given in Figs. 4—7. In Figs. 4 (a) and (b), the density and the volume in the $Li_2O-TiO_2-P_2O_5$ glasses with the same Li_2O contents are plotted *vs.* the TiO_2 content respectively. The plots of the density and the volume *vs.* the TiO_2 content in the glasses with the same P_2O_5 contents are given in Figs. 5—7. Except for Fig. 4 (b), these plots showed linear relationships. The density of the glass increased and the volume of the glass per mole of oxygen decreased with an increase in the TiO_2 content in all the systems. This indicates the

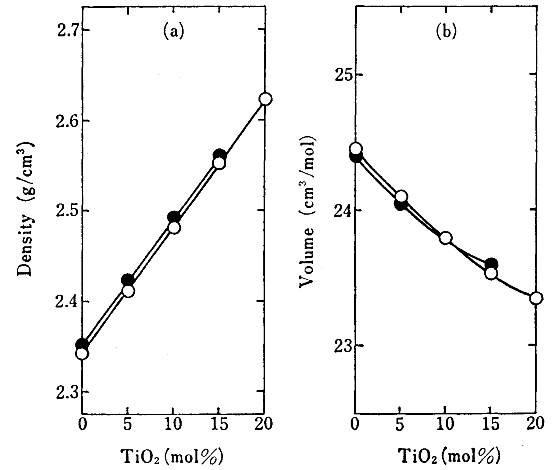

Fig. 4. Plots of (a) density *vs.* TiO_2 content, and (b) volume per mole of oxygen *vs.* TiO_2 content in the $Li_2O-TiO_2-P_2O_5$ glass with the same Li_2O contents. ○: 50 mol% Li_2O, ●: 55 mol% Li_2O.

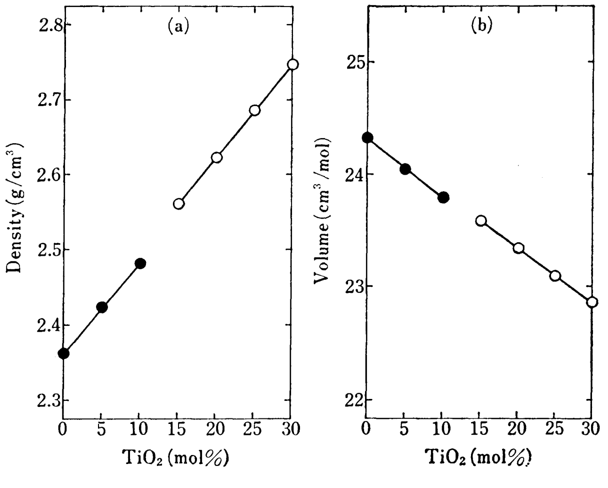

Fig. 5. Plots of (a) density *vs.* TiO_2 content, and (b) volume per mole of oxygen *vs.* TiO_2 content in the $Li_2O-TiO_2-P_2O_5$ glass with the same P_2O_5 contents. ○: 30 mol% P_2O_5, ●: 40 mol% P_2O_5.

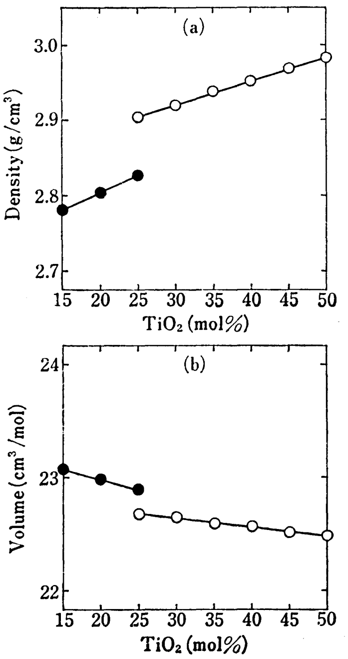

Fig. 6. Plots of (a) density *vs.* TiO_2 content, and (b) volume per mole of oxygen *vs.* TiO_2 content in the MgO-TiO_2-P_2O_5 glass with the same P_2O_5 contents. ○: 30 mol% P_2O_5, ●: 35 mol% P_2O_5.

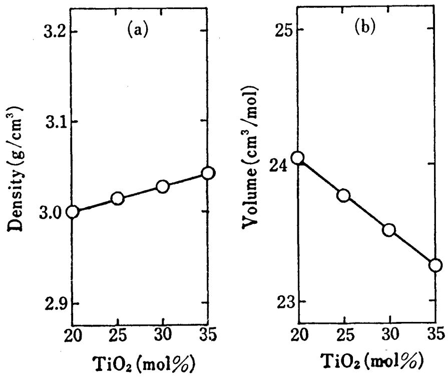

Fig. 7. Plot of (a) density *vs.* TiO_2 content, and (b) volume per mole of oxygen *vs.* TiO_2 content in the CaO-TiO_2-P_2O_5 glass with 30 mol% P_2O_5.

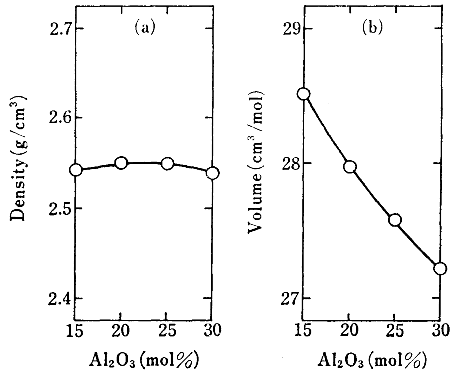

Fig. 8. Plot of (a) density *vs.* Al_2O_3 content, and (b) volume per mole of oxygen *vs.* Al_2O_3 content in the Na_2O-Al_2O_3-P_2O_5 glass with 32.5 mol% P_2O_5.

strength of the titanium ion contribution to the strengthening of the glass structure.

The contractions in the volume of the MgO-TiO_2-P_2O_5 glasses with an increase in the TiO_2 content (Fig. 6 (b)) are less than those of the glasses in the Li_2O- and CaO-systems (Figs. 5 (b) and 7 (b)). It can be said that the role of the titanium ion in the glass structure is similar to that of the Mg^{2+} ion and also that the titanium ion replaces the Mg^{2+} ion.

As shown in Fig. 8 (a), no increase was found in the density on an increase in the Al_2O_3 content for the Na_2O-Al_2O_3-P_2O_5 glass with 32.5 mol% P_2O_5. This suggests that the role of the titanium ion in the glass structure is different from that of the Al^{3+} ion in compositions with less than 50 mol% P_2O_5.

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