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Glass Formation and Crystallization in Ternary Phosphate Systems Containing Al_2O_3

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Glass formation and crystallization were investigated in two types of three-component systems, M_2O–Al_2O_3–P_2O_5 (M=Li, Na, and K) and MO–Al_2O_3–P_2O_5 (M=Mg, Ca, and Ba). In the Li_2O–Al_2O_3–P_2O_5 and MO–Al_2O_3–P_2O_5 systems, wide regions of glass formation were found in compositions containing more than 50 mol% of P_2O_5. In the Na_2O–Al_2O_3–P_2O_5 and K_2O–Al_2O_3–P_2O_5 systems, the two peaks in Al_2O_3 content were found in the regions of glass formation corresponding to about 35 and 65 mol% of P_2O_5. In the devitrified products of the glasses with 60 and 70 mol% of P_2O_5, $AlPO_4$, $Al(PO_3)_3$, and alkaline earth metaphosphate (in the MO–Al_2O_3–P_2O_5 system) were found by X-ray powder diffractometry. The crystalline phases in the samples obtained as mixtures of glass and crystal consisted of $AlPO_4$ in the composition containing 60 mol% of P_2O_5, while those with a P_2O_5 composition of 70 mol% consisted of $Al(PO_3)_3$. By heating those samples at 700—900 °C, the X-ray diffractions of $AlPO_4$ and $Al(PO_3)_3$ were intensified. On the other hand, in the samples with 37.5, 40, and 50 mol% of P_2O_5, all the crystalline phases consisted of $AlPO_4$, and the intensities of these X-ray diffractions decreased after the samples were heated at 600—700 °C. Thus, there is a marked structural difference between the two peak-regions in the Na_2O–Al_2O_3–P_2O_5 and K_2O–Al_2O_3–P_2O_5 systems.

The addition of Al_2O_3 to phosphate glass results in an improvement in the chemical durability, a decrease in the thermal expansion coefficient, and an increase in the deformation temperature of the glass, that is, the stabilization of the glass structure.[1] It has been suggested that these changes in properties are due to the formation of a ($AlPO_4$) group in the glass. There have been many investigations of the role of the Al^{3+} ion in silicate glass. On the Al^{3+} ion in phosphate glass, however, only a few investigations have been reported. Recently, Sakka investigated the coordination number of the Al^{3+} ion in silicate, phosphate, borate, and other glasses on the basis of measurements of the chemical shift of the Al $K\alpha$ line by X-ray emission spectroscopy,[2] while Watanabe *et al.* proposed the existence of –P–O–Al– linkage in the glass of the $NaPO_3$–Al_2O_3 system.[3]

In a previous paper, the authors reported the regions of glass formation in multicomponent phosphate systems containing TiO_2.[4] However, no investigations of those in aluminophosphate systems have been reported. The glass-forming region in a three-component diagram is important in the investigation of the glass structure, because it is determined by the role of cations in the glass. Therefore, it may be worthwhile to determine the glass-forming regions in ternary phosphate systems containing Al_2O_3.

In this paper, the regions of glass formation in three-component diagrams were determined for six kinds of phosphate systems containing Al_2O_3—the M_2O–Al_2O_3–P_2O_5 (M=Li, Na, and K) and MO–Al_2O_3–P_2O_5 (M=Mg, Ca, and Ba) systems. In addition, the devitrified products of the glasses and the crystalline phases in these systems were investigated by X-ray powder diffractometry. From the results obtained, the glass structure and the action of Al^{3+} ion in it were discussed in connection with the P_2O_5 content in the glass.

Experimental

Preparation of Glass. The materials used were the following reagents. Aluminum oxide and orthophosphoric acid (85%) were used in all the systems, lithium hydroxide monohydrate was used in the Li_2O–Al_2O_3–P_2O_5 system, sodium dihydrogenphosphate dihydrate, sodium triphosphate, and anhydrous sodium carbonate in the Na_2O–Al_2O_3–P_2O_5 system, potassium dihydrogenphosphate and anhydrous potassium carbonate in the K_2O–Al_2O_3–P_2O_5 system, magnesium oxide in the MgO–Al_2O_3–P_2O_5 system, calcium hydrogenphosphate dihydrate in the CaO–Al_2O_3–P_2O_5 system, and barium hydroxide octahydrate in the BaO–Al_2O_3–P_2O_5 system. All the chemicals except sodium triphosphate were of a reagent grade. Commercial reagent-grade sodium triphosphate was purified by recrystallization and dehydrated.[5] A mixture obtained by mixing the necessary amounts of compounds selected from the compounds listed above was placed in platinum dishes or alumina crucibles. The former were used in the case of P_2O_5 contents up to 50 mol%, the latter, in the case of more than 50 mol%. In the case of a Na_2O/P_2O_5 or K_2O/P_2O_5 ratio of 1 as 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. The weight of each batch was about 20 g.

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. The temperature was slowly raised to 1350 °C over about a 7-h period and then kept at this temperature for 1 h. The melts of batches containing up to 55 mol% of P_2O_5 were poured out and quenched by pressing them with copper plate cooled with water. The other melts of a high viscosity were taken out from the furnace together with the alumina crucible and rapidly cooled by cold air flow generated by an electric fan. The homogeneity of the formed glass was immediately observed by the naked eye and also under a microscope or a polarizing microscope.

Because of the loss of P_2O_5 by vaporization during heating, the final copomistoin of the phosphate glass usually deviates to some extent from the initial composition, where the deviation depends on the condition of preparation. Therefore, all the diagrams for the glass formation were expressed in terms of the initial composition. In order to measure the volatiliza-

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tion loss of P_2O_5, the three components in the $MgO–Al_2O_3–P_2O_5$ glasses in the range from 50 to 80 mol% of P_2O_5 in the batch composition were determined gravimetrically—MgO and P_2O_5 as $Mg_2P_2O_7$ and Al_2O_3 as $AlPO_4$.

Devitrification of Glass. Glass grains (0.25—1 mm in diameter) of about 2 g placed in a small porcelain crucible were heated for 10 h at the temperatures given in Tables 1—7. The temperature at which the glass in each system was devitrified was in the range from 600 to 900 °C; this temperature increased with the increase in the P_2O_5 content.

X-Ray Powder Diffractometry. The obtained samples were finely pulverized with an alumina mortar and their diffraction patterns were taken by a Rigaku Denki Geigerflex diffractometer with nickel-filtered Cu $K\alpha$ radiation. The identification of the crystalline products was carried out by comparing the X-ray diffraction peaks of the sample with those of the ASTM data file.

Results and Discussion

The experimetal results for the glass formation in each system are given in Figs. 1—6. The ranges of the glass formation in the $M_2O–P_2O_5$ and $MO–P_2O_5$ two-component systems were in agreement with the data presented by Takahashi,[6] except for the $K_2O–P_2O_5$ system, in which the glass formation was found in the composition containing less than 50 mol % of P_2O_5. In the composition at which the transparent homogeneous glass was not formed, the following three types of products were obtained; (1) a mixture of glass and crystal (when the melt was partly devitrified and when the crystalline substance was separated out in the melt), (2) a crystalline product (when the melt was devitrified and when the sample was not melted), and (3) the fused mass consisting of a crystal and glassy substance. No liquid-liquid-phase separation in the melt was found in any system.

In the $MgO–Al_2O_3–P_2O_5$ glasses with 50 to 80 mol % of P_2O_5, the amount of the loss of P_2O_5 by the volatilization was in the range from 1.0 to 16.5 mol %; it increased with an increase in the P_2O_5 content in the batch composition. The results of the gravimetric determination of three components in the glass of this system showed that the contents of water in the glasses were in the range from 0.5 to 1.5 wt %. Similar results may also be affirmed in the other systems.

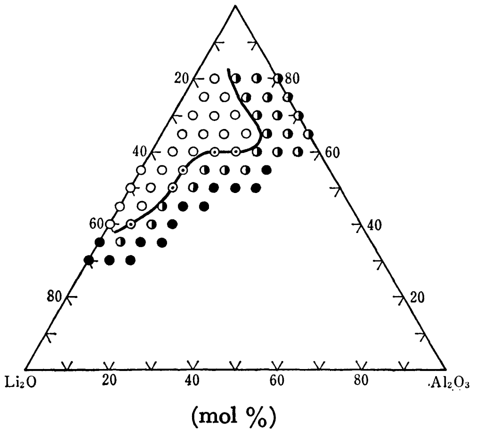

Fig. 1. Glass-forming region in $Li_2O–Al_2O_3–P_2O_5$ system.

○: Homogeneous glass, ⊙: trace amounts of crystal in glass, ◑: glass and crystal, ●: crystal.

The chemical formula of the crystalline products in the $M_2O–Al_2O_3–P_2O_5$ and $MO–Al_2O_3–P_2O_5$ systems, as identified by X-ray diffractometry, are listed in Tables 1—6, while those of the $Al_2O_3–P_2O_5$ two-component system are listed in Table 7.

Glass Formation in $M_2O–Al_2O_3–P_2O_5$ System. In the $Li_2O–Al_2O_3–P_2O_5$ system (Fig. 1), Al_2O_3 was incorporated into the glass composition when the P_2O_5 content exceeded about 35 mol %; the peak of the Al_2O_3 content appeared in the range from 60 to 70 mol % of P_2O_5. As can be seen from Figs. 1 and 4—6, the shape of the glass-forming region in this system is analogous to that in the $MO–Al_2O_3–P_2O_5$ system. As the properties of the Li^+ ion are similar to those of the alkaline earth ions, and as the electrostatic-bond strength of the Li^+ ion is larger than that of the Na^+ or K^+ ion, it may be considered that the Li^+ ion plays a role similar to that of the alkaline earth ion in the phosphate glass.

On the other hand, as is shown in Figs. 2 and 3, a large amount of Al_2O_3 was incorporated into the glass in composition of both about 35 as well as 65 mol %

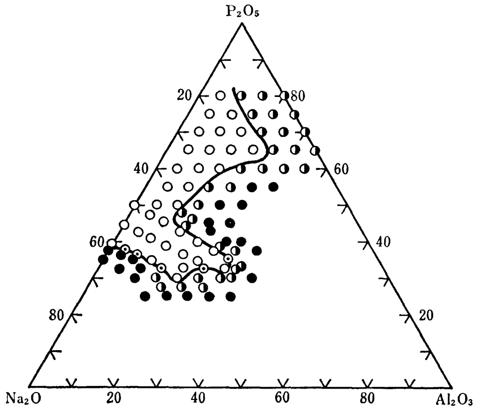

Fig. 2. Glass-forming region in $Na_2O–Al_2O_3–P_2O_5$ system.

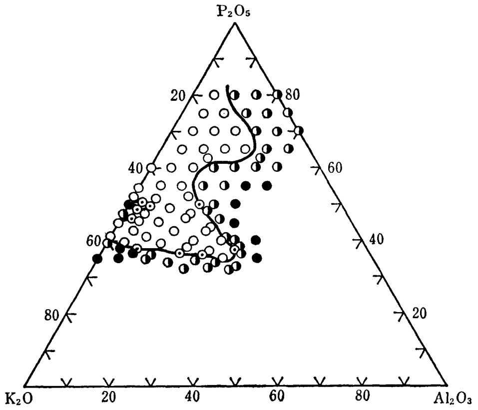

Fig. 3. Glass-forming region in $K_2O–Al_2O_3–P_2O_5$ system.

of P_2O_5 in the Na_2O–Al_2O_3–P_2O_5 and K_2O–Al_2O_3–P_2O_5 systems. This is a marked difference from the Na_2O–TiO_2–P_2O_5 and K_2O–TiO_2–P_2O_5 systems,4) where only a small amount of TiO_2 is introduced into the glass even when the content of P_2O_5 exceeds 50 mol %. This fact indicates a difference between Al^{3+} and Ti^{4+} ions in their behavior in the phosphate glass. Since the Al^{3+} ion has been regarded as an intermediate ion, it is able to act as a network modifier as well as a network former in the glass structure. According to Sakka,2) most of the Al^{3+} ions in the glass with a higher P_2O_5 content ($P/O \approx 0.33$) are 6-fold coordinated, while those with a lower P_2O_5 content ($P/O \lesssim 0.25$) are 4-fold coordinated. The existence of two peaks of Al_2O_3 content of the glass region in both the Na_2O–Al_2O_3–P_2O_5 and K_2O–Al_2O_3–P_2O_5 systems suggests the above-noted change in the coordination number of the Al^{3+} ion with the P_2O_5 content in the phosphate glass.

In the K_2O–P_2O_5 two-component system, the glass was not formed at $K_2O/P_2O_5=1$ (50 mol % of P_2O_5 in Fig. 3), but at $K_2O/P_2O_5>1$. Presumably a break in the long –P–O–P– straight-chain of potassium metaphosphate ($K_2O/P_2O_5=1$) by the excess K^+ ion favored the glass formation. The glass formation in the composition along the line of $K_2O/P_2O_5=1$ in the K_2O–Al_2O_3–P_2O_5 system was more extensive than that in the same composition in the K_2O–TiO_2–P_2O_5 system.4) This fact also suggests that the network-forming and glass-forming abilities of the Al^{3+} ion differ in some degree from those of the Ti^{4+} ion in the phosphate glass.

Glass Formation in MO–Al_2O_3–P_2O_5 System. In the systems of MgO–Al_2O_3–P_2O_5, CaO–Al_2O_3–P_2O_5, and BaO–Al_2O_3–P_2O_5 (Figs. 4, 5, and 6), the content of Al_2O_3 incorporated into the glass increased with an increase in the P_2O_5 content, and the peak of Al_2O_3 content was found in the range from 60 to 70 mol % of P_2O_5. As has been described above, the glass-forming regions in these systems were similar to that in the Li_2O–Al_2O_3–P_2O_5 system. The difference between Al_2O_3 and TiO_2 in the glass formation was observed also in the BaO–Al_2O_3–P_2O_5 and BaO–TiO_2–P_2O_5 systems, because in the latter system the amount of TiO_2 within the composition limits of glass formation decreased with an increase in the P_2O_5 content.4)

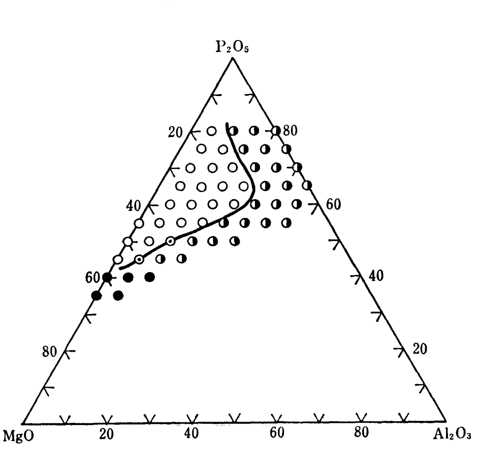

Fig. 4. Glass-forming region in MgO–Al_2O_3–P_2O_5 system.

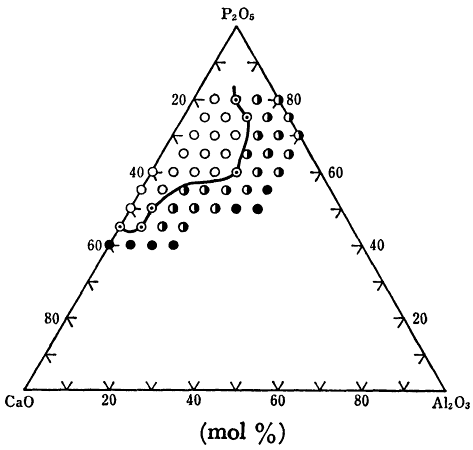

Fig. 5. Glass-forming region in CaO–Al_2O_3–P_2O_5 system.

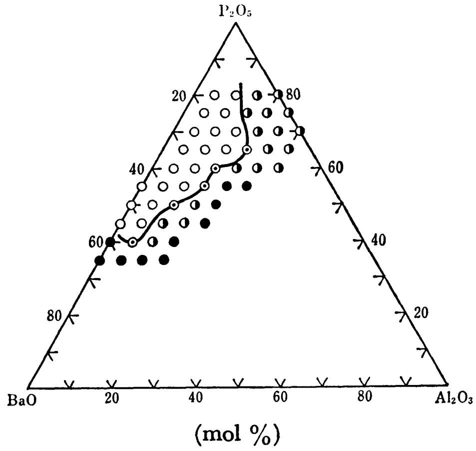

Fig. 6. Glass-forming region in BaO–Al_2O_3–P_2O_5 system.

X-Ray Powder Diffractometry. The devitrified products of the glasses obtained in the glass-forming region of the M_2O–Al_2O_3–P_2O_5 system were mainly aluminum metaphosphate in the composition containing 70 mol % of P_2O_5, aluminum metaphosphate and aluminum orthophosphate in 60 mol % of P_2O_5, and alkali metaphosphate (sodium trimetaphosphate in the Na_2O–Al_2O_3–P_2O_5 system) and aluminum orthophosphate in 50 mol % of P_2O_5 (Tables 1, 2, and 3). In each of the MO–Al_2O_3–P_2O_5 systems, alkaline earth metaphosphate as well as aluminum orthophosphate or aluminum metaphosphate was found in the compositions containing 50, 60, and 70 mol % of P_2O_5 (Tables 4, 5, and 6).

The crystalline phases in the samples outside the boundary for the glass formation in the M_2O–Al_2O_3–P_2O_5 and MO–Al_2O_3–P_2O_5 systems consisted mainly of aluminum metaphosphate in the composition containing 70 mol % of P_2O_5, aluminum orthophosphate and aluminum metaphosphate in 60 mol % of P_2O_5, and aluminum orthophosphate in 50 mol % of P_2O_5 (Tables 1—6). In the Na_2O–Al_2O_3–P_2O_5 system containing 37.5 mol % of P_2O_5 and the K_2O–Al_2O_3–P_2O_5 system containing 40 mol % of P_2O_5, the crystalline phases consisted mainly of aluminum orthophosphate (Tables 2 and 3).

As is marked with (+) sign in Tables 1—7, in all the samples outside the glass-forming range of 70 mol % of P_2O_5, the X-ray diffraction patterns of aluminum metaphosphate increased in intensity upon heating at 800—900 °C, while in the composition containing 60 mol % of P_2O_5 the crystallization of aluminum orthophosphate was promoted by heating at 700—900 °C. The same phenomena were also observed in the Al_2O_3–P_2O_5 two-component system (Table 7). The devitrified product of $25Al_2O_3\cdot75P_2O_5$ glass consisted predominantly of aluminum metaphosphate. These facts suggest that the network consisting of aluminum, oxygen, and phosphorous ions in the M_2O–Al_2O_3–P_2O_5 and MO–Al_2O_3–P_2O_5 glasses containing 60 mol % or more P_2O_5 is analogous to that in the Al_2O_3–P_2O_5 two-component glass. According to Pauling and Sherman,[7] the alumi-

TABLE 1. CRYSTALLINE PHASES IN Li_2O–Al_2O_3–P_2O_5 SYSTEM

Sample (batch composition)	Crystalline phase after quenching	Heat treatment (°C)	Crystalline phase after heat treatment
$15Li_2O\cdot15Al_2O_3\cdot70P_2O_5$ (glass)		800	$Al(PO_3)_3$
$5Li_2O\cdot25Al_2O_3\cdot70P_2O_5$ (glass & crystal)	$Al(PO_3)_3$, $AlPO_4$	800	$Al(PO_3)_3$(+),[a] $AlPO_4$(+)
$30Li_2O\cdot10Al_2O_3\cdot60P_2O_5$ (glass)		700	$Al(PO_3)_3$, $AlPO_4$
$20Li_2O\cdot20Al_2O_3\cdot60P_2O_5$ (glass)		700	$Al(PO_3)_3$, $AlPO_4$
$15Li_2O\cdot25Al_2O_3\cdot60P_2O_5$ (glass & crystal)	$AlPO_4$	700	$AlPO_4$(+), $Al(PO_3)_3$
$40Li_2O\cdot10Al_2O_3\cdot50P_2O_5$ (glass)		600	$LiPO_3$, $AlPO_4$
$35Li_2O\cdot15Al_2O_3\cdot50P_2O_5$ (crystal & glass)	$AlPO_4$	600	$AlPO_4$(−),[b] $LiPO_3$

a) Intensity of X-ray diffraction increased. b) Intensity of X-ray diffraction decreased.

TABLE 2. CRYSTALLINE PHASES IN Na_2O–Al_2O_3–P_2O_5 SYSTEM

Sample (batch composition)	Crystalline phase after quenching	Heat treatment (°C)	Crystalline phase after heat treatment
$15Na_2O\cdot15Al_2O_3\cdot70P_2O_5$ (glass)		800	$Al(PO_3)_3$, $AlPO_4$
$5Na_2O\cdot25Al_2O_3\cdot70P_2O_5$ (glass & crystal)	$Al(PO_3)_3$	800	$Al(PO_3)_3$(+), $AlPO_4$
$30Na_2O\cdot10Al_2O_3\cdot60P_2O_5$ (glass)		700	$Al(PO_3)_3$, $AlPO_4$
$20Na_2O\cdot20Al_2O_3\cdot60P_2O_5$ (glass & crystal)		700	$Al(PO_3)_3$, $AlPO_4$
$15Na_2O\cdot25Al_2O_3\cdot60P_2O_5$ (glass & crystal)	$AlPO_4$	700	$AlPO_4$(+), $Al(PO_3)_3$
$40Na_2O\cdot10Al_2O_3\cdot50P_2O_5$ (glass)		600	$(NaPO_3)_3$, $AlPO_4$
$35Na_2O\cdot15Al_2O_3\cdot50P_2O_5$ (glass & crystal)	$AlPO_4$	600	$(NaPO_3)_3$, $AlPO_4$(−)
$42.5Na_2O\cdot20Al_2O_3\cdot37.5P_2O_5$ (glass)		600	Unknown
$32.5Na_2O\cdot30Al_2O_3\cdot37.5P_2O_5$ (crystal& glass)	$AlPO_4$	600	Unknown
$27.5Na_2O\cdot35Al_2O_3\cdot37.5P_2O_5$ (crystal)	$AlPO_4$	600	$AlPO_4$(−), Unknown

TABLE 3. CRYSTALLINE PHASES IN K_2O–Al_2O_3–P_2O_5 SYSTEM

Sample (batch composition)	Crystalline phase after quenching	Heat treatment (°C)	Crystalline phase after heat treatment
$15K_2O\cdot15Al_2O_3\cdot70P_2O_5$ (glass)		900	$Al(PO_3)_3$
$5K_2O\cdot25Al_2O_3\cdot70P_2O_5$ (glass & crystal)	$Al(PO_3)_3$	900	$Al(PO_3)_3$(+), $AlPO_4$
$30K_2O\cdot10Al_2O_3\cdot60P_2O_5$ (glass)		800	$Al(PO_3)_3$, $AlPO_4$
$20K_2O\cdot20Al_2O_3\cdot60P_2O_5$ (glass & crystal)		800	$Al(PO_3)_3$, $AlPO_4$
$15K_2O\cdot25Al_2O_3\cdot60P_2O_5$ (glass & crystal)	$AlPO_4$	800	$AlPO_4$, $Al(PO_3)_3$
$40K_2O\cdot10Al_2O_3\cdot50P_2O_5$ (glass)		600	KPO_3, $AlPO_4$, Unknown
$35K_2O\cdot15Al_2O_3\cdot50P_2O_5$ (glass)		600	KPO_3, $AlPO_4$, Unknown
$30K_2O\cdot20Al_2O_3\cdot50P_2O_5$ (glass & crystal)	$AlPO_4$	600	$AlPO_4$(−), KPO_3, Unknown
$40K_2O\cdot20Al_2O_3\cdot40P_2O_5$ (glass)		600	Unknown
$30K_2O\cdot30Al_2O_3\cdot40P_2O_5$ (glass &crystal)	Unknown	600	Unknown
$25K_2O\cdot35Al_2O_3\cdot40P_2O_5$ (crystal)	$AlPO_4$	600	$AlPO_4$

TABLE 4. CRYSTALLINE PHASES IN MgO–Al_2O_3–P_2O_5 SYSTEM

Sample (batch composition)	Crystalline phase after quenching	Heat treatment (°C)	Crystalline phase after heat treatment
$15MgO\cdot15Al_2O_3\cdot70P_2O_5$ (glass)		900	$Al(PO_3)_3$, $Mg(PO_3)_2$
$10MgO\cdot20Al_2O_3\cdot70P_2O_5$ (glass & crystal)	$Al(PO_3)_3$	900	$Al(PO_3)_3$(+), $AlPO_4$, $Mg(PO_3)_2$
$20MgO\cdot20Al_2O_3\cdot60P_2O_5$ (glass)		900	$Al(PO_3)_3$, $AlPO_4$, $Mg(PO_3)_2$
$15MgO\cdot25Al_2O_3\cdot60P_2O_5$ (glass & crystal)	$AlPO_4$	900	$AlPO_4$(+), $Al(PO_3)_3$, $Mg(PO_3)_2$
$40MgO\cdot10Al_2O_3\cdot50P_2O_5$ (glass)		750	$Mg(PO_3)_2$, $AlPO_4$
$35MgO\cdot15Al_2O_3\cdot50P_2O_5$ (glass & crystal)	$AlPO_4$		

Table 5. Crystalline phases in $CaO–Al_2O_3–P_2O_5$ system

Sample (batch composition)	Crystalline phase after quenching	Heat treatment (°C)	Crystalline phase after heat treatment
$15CaO \cdot 15Al_2O_3 \cdot 70P_2O_5$ (glass)		900	$Al(PO_3)_3$, $Ca(PO_3)_2$
$10CaO \cdot 20Al_2O_3 \cdot 70P_2O_5$ (glass & crystal)	$Al(PO_3)_3$, $AlPO_4$	900	$Al(PO_3)_3(+)$, $AlPO_4$, $Ca(PO_3)_2$
$20CaO \cdot 20Al_2O_3 \cdot 60P_2O_5$ (glass)		900	$Al(PO_3)_3$, $AlPO_4$, $Ca(PO_3)_2$
$15CaO \cdot 25Al_2O_3 \cdot 60P_2O_5$ (glass & crystal)	$AlPO_4$	900	$AlPO_4(+)$, $Al(PO_3)_3$, $Ca(PO_3)_2$
$35CaO \cdot 15Al_2O_3 \cdot 50P_2O_5$ (glass & crystal)	$AlPO_4$		

Table 6. Crystalline phases in $BaO–Al_2O_3–P_2O_5$ system

Sample (batch composition)	Crystalline phase after quenching	Heat treatment (°C)	Crystalline phase after heat treatment
$15BaO \cdot 15Al_2O_3 \cdot 70P_2O_5$ (glass)		800	$Al(PO_3)_3$, $AlPO_4$, $Ba(PO_3)_2$
$10BaO \cdot 20Al_2O_3 \cdot 70P_2O_5$ (glass & crystal)	$Al(PO_3)_3$	800	$Al(PO_3)_3(+)$, $AlPO_4$, $Ba(PO_3)_2$
$30BaO \cdot 10Al_2O_3 \cdot 60P_2O_5$ (glass)		750	$Ba(PO_3)_2$, $Al(PO_3)_3$, $AlPO_4$
$20BaO \cdot 20Al_2O_3 \cdot 60P_2O_5$ (glass & crystal)		800	$Ba(PO_3)_2$, $Al(PO_3)_3$, $AlPO_4$
$15BaO \cdot 25Al_2O_3 \cdot 60P_2O_5$ (glass & crystal)	$AlPO_4$	800	$AlPO_4(+)$, $Al(PO_3)_3$, $Ba(PO_3)_2$
$40BaO \cdot 10Al_2O_3 \cdot 50P_2O_5$ (glass)		700	$Ba(PO_3)_2$, $AlPO_4$
$35BaO \cdot 15Al_2O_3 \cdot 50P_2O_5$ (glass & crystal)	$AlPO_4$	700	$Ba(PO_3)_2$, $AlPO_4(-)$

Table 7. Crystalline phases in $Al_2O_3–P_2O_5$ system

Sample (batch composition)	Crystalline phase after quenching	Heat treatment (°C)	Crystalline phase after heat treatment
$20Al_2O_3 \cdot 80P_2O_5$ (crystal & glass)	$Al(PO_3)_3$	900	$Al(PO_3)_3(+)$, $AlPO_4$
$25Al_2O_3 \cdot 75P_2O_5$ (glass)[a]		900	$Al(PO_3)_3$, $AlPO_4$
$30Al_2O_3 \cdot 70P_2O_5$ (crystal & glass)	$Al(PO_3)_3$, $AlPO_4$	900	$Al(PO_3)_3(+)$, $AlPO_4(+)$
$40Al_2O_3 \cdot 60P_2O_5$ (crystal & glass)	$AlPO_4$, $Al(PO_3)_3$	900	$AlPO_4(+)$, $Al(PO_3)_3(+)$

a) This glass was prepared by heating the mixture of aluminum orthophosphate and orthophosphoric acid (85%) at 1500 °C.

num metaphosphate consists of AlO_6 octahedra and rings of four PO_4 tetrahedra. Gill and Riaz reported that the ultraphosphate glasses with M/P=0.7—1.0 consisted of trimetaphosphate rings, polyphosphate chains, and branched chains.[8] Consequently, the AlO_6 octahedra seem to stabilize these glass structures by linking them to the rings of PO_4 tetrahedra and the branching points of phosphate chains.

On the other hand, the X-ray diffraction gave rather complex patterns for the devitrified samples of the $Na_2O–Al_2O_3–P_2O_5$ glasses with 37.5 mol % of P_2O_5 and $K_2O–Al_2O_3–P_2O_5$ glasses with 40 mol % of P_2O_5. In the diffraction patterns for the samples outside the glass-forming range in the systems of 37.5, 40, and 50 mol % of P_2O_5, the diffraction patterns of aluminum orthophosphate weakened upon heating at 600—700 °C. These facts suggest that the structure of the glass in the range from 37.5 to 50 mol % of P_2O_5 differs markedly from that in the composition containing more than 50 mol % of P_2O_5 (ultraphosphate). Therefore, the above results also suggest that the action of the Al^{3+} ion the glass structure varies with the P_2O_5 content in the glasses of the $Na_2O–Al_2O_3–P_2O_5$ and $K_2O–Al_2O_3–P_2O_5$ systems.

In the composition containing less than 50 mol % of P_2O_5 (polyphosphate), the structures of the $Na_2O–Al_2O_3–P_2O_5$ and $K_2O–Al_2O_3–P_2O_5$ glasses may be regarded as random aggregates of the –P–O–P– and –P–O–Al– chains (clusters) consisting of PO_4 and AlO_4 tetrahedra and the Na^+ or K^+ ions.

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