The Structural Role of the Aluminum Ion in Alkali Aluminophosphate Glass Containing Less Than 50 mol% of P_2O_5

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(Received December 10, 1976)

Several series of alkali (Na and K) aluminophosphate glasses with a constant P_2O_5 content of less than 50 mol % were prepared. From the infrared absorption spectra of these glasses, and also from the paper chromatograms of aqueous solutions of these glasses, we obtained the following results: The PO_4^{3-} ion increased with an increase in the amount of Al_2O_3 when the P_2O_5 content was kept constant. The PO_4^{3-}/P_2O_5 ratio in the glass increased with an increase in the Al_2O_3 content, whereas it decreased with an increase in the P_2O_5 content. In the composition of 32.5 mol % of P_2O_5, the glass containing exclusively PO_4^{3-}-type ions as a phosphate species was found. The PO_4^{3-}/Al^{3+} ratio was smaller than unity in the case of a lower Al_2O_3 content and larger than unity in the case of a higher Al_2O_3 content. From these results, the structural role of the Al^{3+} ion can be revealed as follows: In the glass with a lower Al_2O_3 content, two kinds of Al^{3+} ions exist—(1) the Al^{3+} ion, which forms the P–O–Al linkage by the substitution of the P^{5+} ion in the P–O–P linkage, and (2) the Al^{3+} ion, which does not form such a linkage, whereas in the glass with a higher Al_2O_3 content all the Al^{3+} ions substitute the P^{5+} ion to form the P–O–Al linkage.

It is well known that Al_2O_3 stabilizes the structure of phosphate glass and increases the chemical durability. It has been considered that this effect of the Al_2O_3 in the phosphate glass is due to the formation of an ($AlPO_4$) group in the glass structure.[1] The detailed structural role of Al^{3+} ion in aluminophosphate glass, however, has not yet been clarified. The coordination number of the Al^{3+} ion in phosphate glass is particularly interesting in connection with the role of this ion in the glass structure. Sakka[2] has reported that most of the Al^{3+} ions in the glass with a higher P_2O_5 content were 6-fold coordinated, while those with a lower P_2O_5 content were 4-fold coordinated; the present authors[3] have also reported a similar change in the glass-forming regions in the Na_2O–Al_2O_3–P_2O_5 and K_2O–Al_2O_3–P_2O_5 systems.

In this investigation, several series of sodium and potassium aluminophosphate glasses with the same P_2O_5 content of less than 50 mol % (polyphosphate composition) were prepared, and the infrared absorption spectra of these glasses were examined and the aqueous solutions of these glasses were subjected to paper chromatography in order to separate the orthophosphate from the other polyphosphate ion species. The contents of the Al_2O_3, P_2O_5, and PO_4^{3-} ion were gravimetrically determined. The structural role of the Al^{3+} ion was discussed in terms of the Al_2O_3 and P_2O_5 contents as well as the PO_4^{3-}/P_2O_5 and PO_4^{3-}/Al^{3+} ratios obtained by these analyses.

Experimental

Preparation of Glass. Twenty-two kinds of glasses with the compositions represented in Tables 1 and 2 were prepared. Most of these compositions are selected inside the glass-forming regions of less 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.[3]

The materials used were sodium dihydrogenphosphate, anhydrous sodium carbonate, potassium dihydrogenphosphate, anhydrous potassium carbonate, aluminum oxide, and orthophosphoric acid (85%). They were all of a reagent grade. About a 40-g portion of a mixture obtained by mixing the necessary amounts of the above compounds was used for each batch. The samples were placed in platinum dishes and heated in a electric furnace. After the samples had been dehydrated by gradually heating them up to 500 °C over about a 5-h period, they were kept at this temperature for 2 h. Then, the temperature was raised further to 1350 °C over a 2-h period and kept at this temperature for 1 h. The melt of each batch was poured out and quenched by pressing it with copper plates cooled with water. All the quenched melts were obtained as transparent colorless glasses except for the sample with the initial composition of $30K_2O \cdot 30Al_2O_3 \cdot 40P_2O_5$ which was obtained as a mixture of glass and crystal, the glassy part being used for the experiment.

Determination of Al_2O_3. Glass powder containing about 0.1 g of Al_2O_3 was dissolved in 150 ml of 1 M (1 mol dm^{-3}) HCl by boiling, after which the polyphosphate ion species in the sample were hydrolyzed to orthophosphate ions by prolonged boiling for 30 min. The Al^{3+} ion in this solution was gravimetrically determined as $AlPO_4$.[4]

Determination of Total Phosphate as P_2O_5. Glass powder containing about 0.1 g of P_2O_5 was dissolved in 80 ml of 1 M HCl. The experimental procedure after the hydrolysis of the polyphosphate ions to orthophosphate ions was the same as in the determination of the PO_4^{3-} ion.[5]

Determination of the Orthophosphate Ion. After 0.25—1.5 g of the pulverized glass had been dissolved in 40 ml of a 0.5 M (0.5 mol dm^{-3}) NaOH solution at room temperature, the PO_4^{3-} ion was gravimetrically determined as $Mg_2P_2O_7$ by the method described in a previous paper.[5]

Paper Chromatography. One-dimensional paper chromatography was used for the separation of orthophosphate from other polyphosphates.[6] The solvent was prepared by mixing 25 ml of a 20% trichloroacetic acid solution, 7 ml of water, and 68 ml of acetone. This solvent is a modification of the Solvent A reported by Bernhart and Chess.[7] Pulverized glass containing about 0.1 g of phosphorus was dissolved in 50 ml of a 0.5 M NaOH solution at room temperature. A spot of about 5 μl of this solution was developed on a strip of filter paper of No. 51A (2 cm×50 cm) for about 3 h at room temperature. After a perchloric acid-molybdate solution had been sprayed on the paper, the paper was exposed to day light until blue spots appeared. The phosphate species on the chromatogram was identified by comparing it with the spots of a reference solution containing known phosphates.

Infrared Spectra. The infrared absorption spectra of the glasses were obtained by means of a Hitachi EPI-2G

TABLE 1. COMPOSITION OF Na_2O–Al_2O_3–P_2O_5 GLASS

Batch composition	Na_2O (wt %)		Al_2O_3 (wt %)		P_2O_5 (wt %)	
	Calcd[a)]	Obsd	Calcd[a)]	Obsd	Calcd[a)]	Obsd
$52.5Na_2O\cdot5Al_2O_3\cdot42.5P_2O_5$	33.22	(33.41)	5.20	5.39	61.58	61.20
$47.5Na_2O\cdot10Al_2O_3\cdot42.5P_2O_5$	29.45	(29.42)	10.20	10.63	60.35	59.95
$42.5Na_2O\cdot15Al_2O_3\cdot42.5P_2O_5$	25.83	(25.70)	15.00	15.78	59.17	58.52
$57.5Na_2O\cdot5Al_2O_3\cdot37.5P_2O_5$	37.92	(38.65)	5.43	5.46	56.65	55.89
$52.5Na_2O\cdot10Al_2O_3\cdot37.5P_2O_5$	33.91	(34.63)	10.62	10.68	55.47	54.69
$47.5Na_2O\cdot15Al_2O_3\cdot37.5P_2O_5$	30.05	(30.59)	15.61	15.63	54.34	53.78
$42.5Na_2O\cdot20Al_2O_3\cdot37.5P_2O_5$	26.35	(26.86)	20.40	20.34	53.25	52.80
$37.5Na_2O\cdot25Al_2O_3\cdot37.5P_2O_5$	22.79	(23.74)	25.00	24.22	52.21	52.04
$52.5Na_2O\cdot15Al_2O_3\cdot32.5P_2O_5$	34.63	(35.03)	16.28	16.23	49.09	48.74
$47.5Na_2O\cdot20Al_2O_3\cdot32.5P_2O_5$	30.68	(31.10)	21.25	21.35	48.07	47.55
$42.5Na_2O\cdot25Al_2O_3\cdot32.5P_2O_5$	26.89	(27.77)	26.02	25.83	47.09	46.40
$37.5Na_2O\cdot30Al_2O_3\cdot32.5P_2O_5$	23.25	(23.79)	30.60	30.16	46.15	46.05

a) Calculated from the batch composition.

TABLE 2. COMPOSITION OF K_2O–Al_2O_3–P_2O_5 GLASS

Batch composition	K_2O (wt %)		Al_2O_3 (wt %)		P_2O_5 (wt %)	
	Calcd[a)]	Obsd	Calcd[a)]	Obsd	Calcd[a)]	Obsd
$50K_2O\cdot5Al_2O_3\cdot45P_2O_5$	40.58	(40.83)	4.39	4.62	55.03	54.55
$45K_2O\cdot10Al_2O_3\cdot45P_2O_5$	36.40	(36.61)	8.75	9.33	54.85	54.06
$40K_2O\cdot15Al_2O_3\cdot45P_2O_5$	32.25	(32.24)	13.09	13.45	54.66	54.31
$35K_2O\cdot20Al_2O_3\cdot45P_2O_5$	28.13	(28.95)	17.39	17.09	54.48	53.96
$55K_2O\cdot5Al_2O_3\cdot40P_2O_5$	45.58	(46.07)	4.48	4.59	49.94	49.34
$50K_2O\cdot10Al_2O_3\cdot40P_2O_5$	41.29	(42.13)	8.94	8.66	49.77	49.21
$45K_2O\cdot15Al_2O_3\cdot40P_2O_5$	37.04	(37.78)	13.36	13.25	49.60	48.97
$40K_2O\cdot20Al_2O_3\cdot40P_2O_5$	32.80	(33.65)	17.76	17.70	49.44	48.65
$35K_2O\cdot25Al_2O_3\cdot40P_2O_5$	28.61	(29.42)	22.12	21.69	49.27	48.89
$30K_2O\cdot30Al_2O_3\cdot40P_2O_5$	24.45	(25.81)	26.45	25.61	49.10	48.58

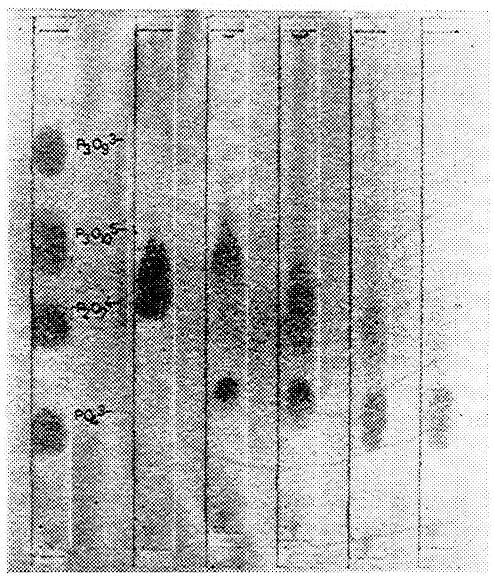
a) Calculated from the batch composition.

spectrophotometer, using the KBr pellet technique.

Results and Discussion

Composition of Glass. The composition of the glasses determined from the analyses is shown in Tables 1 and 2. The Na_2O or K_2O content given in parentheses is the value obtained by subtracting the Al_2O_3 and P_2O_5 contents from the weight of the sample. Since the phosphate glass usually contains a small amount of water in its structure,[8,9] the Na_2O or K_2O content shown in parentheses is actually the (Na_2O+H_2O) or (K_2O+H_2O) content in the glass. As is shown in Tables 1 and 2, in each series of the glasses with a constant P_2O_5 content, the heating loss of P_2O_5 was less than 0.8 wt %. Therefore, it can be said that the contents of P_2O_5 in these glasses are practically constant.

Papaer Chromatography. The paper chromatography was carried out for each sample of 37.5 mol % of P_2O_5 in the Na_2O–Al_2O_3–P_2O_5 system and of 40 mol % of P_2O_5 in the K_2O–Al_2O_3–P_2O_5 system. As is shown in the chromatograms in Figs. 1 and 2, the amount of the PO_4^{3-} ion increased with an increase in the Al_2O_3 content. When a two-component sample of 62.5 $Na_2O\cdot$37.5 P_2O_5 was heated for 1 h at 1350 °C, converted to an aqueous solution, and examined by paper chromatography, the P O $^{4-}$ and $P_3O_{10}^{5-}$ ions were found, while



(1) (2) (3) (4) (5) (6)

Fig. 1. Paper chromatograms of $(62.5-x)Na_2O\cdot xAl_2O_3\cdot 37.5P_2O_5$ glass.
(1) Reference sample, (2)x=5, (3)x=10, (4)x=15, (5) x=20, (6)x=25.

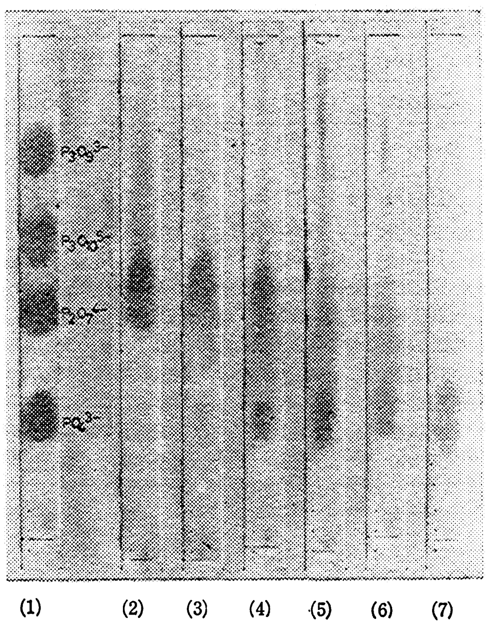


Fig. 2. Paper chromatograms of $(60-x)K_2O \cdot xAl_2O_3 \cdot 40P_2O_5$ glass.
(1) Reference sample, (2)$x=5$, (3)$x=10$, (4)$x=15$, (5) $x=20$, (6)$x=25$, (7)$x=30$.

the PO_4^{3-} ion was not found. Thus, it seems that the above PO_4^{3-} ion was given by the substitution of the P^{5+} ion in P–O–P linkage by the Al^{3+} ion, and the increase in the amount of this PO_4^{3-} ion may be due to the increase in the P–O–Al linkage in the glass. The phosphate species in the glasses with the highest Al_2O_3 content ($x=25$ in Fig. 1 and $x=30$ in Fig. 2) were substantially composed of the PO_4^{3-} ion. It is natural to consider that a large number of the chains in these

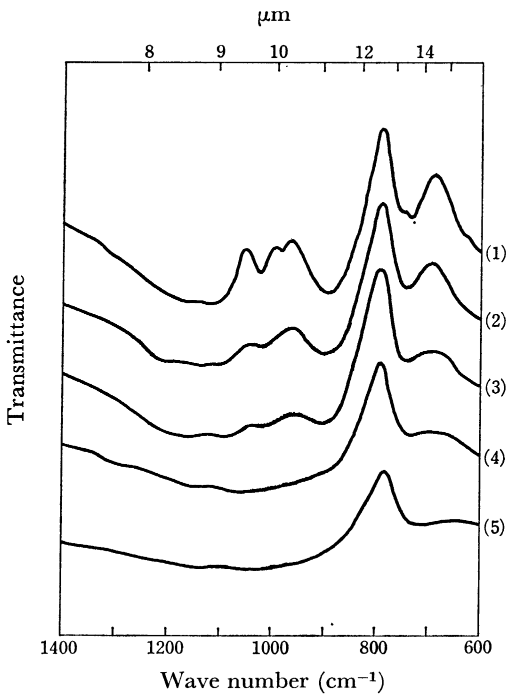


Fig. 3. Infrared spectra of $(62.5-x)Na_2O \cdot xAl_2O_3 \cdot 37.5P_2O_5$ glass.
(1)$x=5$, (2)$x=10$, (3)$x=15$, (4)$x=20$, (5)$x=25$.

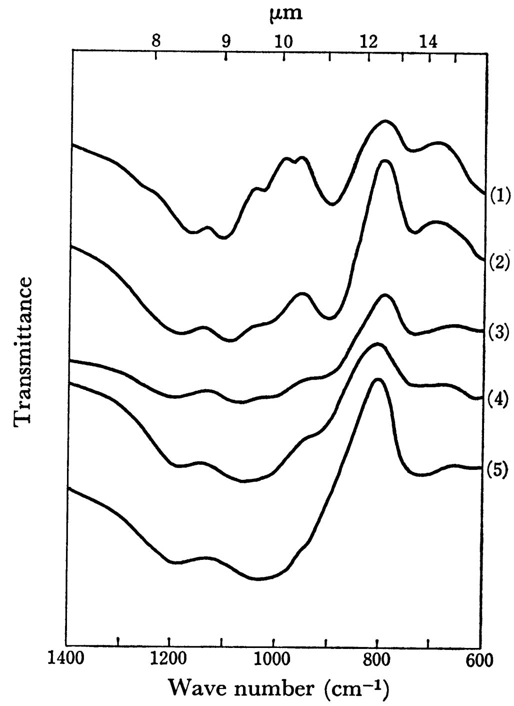


Fig. 4. Infrared spectra of $(60-x)K_2O \cdot xAl_2O_3 \cdot 40P_2O_5$ glass.
(1)$x=10$, (2)$x=15$, (3)$x=20$, (4)$x=25$, (5)$x=30$.

glasses are in the form of an alternate arrangement of the PO_4 tetrahedron and the AlO_4 tetrahedron.

Infrared Spectra. The infrared absorption spectra of the same series of glasses as those examined by paper chromatography are shown in Figs. 3 and 4. Between the glasses with a lower Al_2O_3 content ($x=5$ and 10) and those with a higher Al_2O_3 content ($x=20$, 25, and 30), marked differences are found in the absorption spectra in the range from 1100 to 900 cm^{-1}. With the increase in the Al_2O_3 content, the absorptions in the above-noted range increased and the absorption bands became broad. According to Corbridge and Lowe,[10,11] the absorption band in the range from 1100—900 cm^{-1} is to be assigned to ionic P–O stretching, $-P\!\left<\begin{smallmatrix}O\\O^{(2-)}\\O\end{smallmatrix}\right.$ group, P–O–P stretching, and P–O–H bending vibrations; especially, the absorption of the $-P\!\left<\begin{smallmatrix}O\\O^{(2-)}\\O\end{smallmatrix}\right.$ group appears at about 1030—960 cm^{-1}. Therefore, the change in the infrared spectra with the increase in the Al_2O_3 content can be considered to be concordant with the results of the paper chromatography. It can also be mentioned that the broad absorption in the glasses with a higher Al_2O_3 content is due to the increase in the disorder derived from the formation of P–O–Al linkage in the glass structure.

Orthophosphate Ion in the Glass. The contents of the PO_4^{3-} ion in all the glasses were determined gravimetrically. In Figs. 5 and 6 these results are given by plotting the change in the PO_4^{3-}/P_2O_5 ratio (the ratio of the amount of PO_4^{3-} ion, expressed as P_2O_5 against the total P_2O_5 content) with the Al_2O_3 content in the glass. In all the series of glasses with a constant P_2O_5

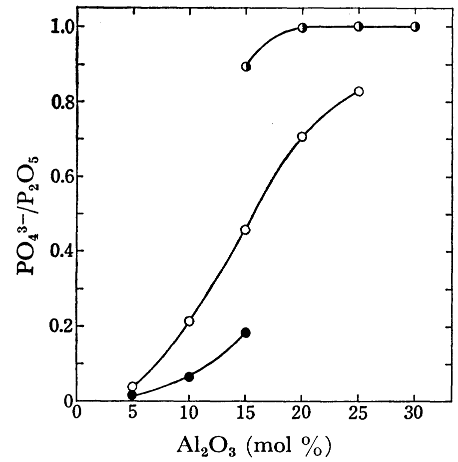


Fig. 5. Relation between PO_4^{3-}/P_2O_5 ratio and Al_2O_3 content in Na_2O–Al_2O_3–P_2O_5 glass.
◐: 32.5 mol % P_2O_5, ○: 37.5 mol % P_2O_5, ●: 42.5 mol % P_2O_5.

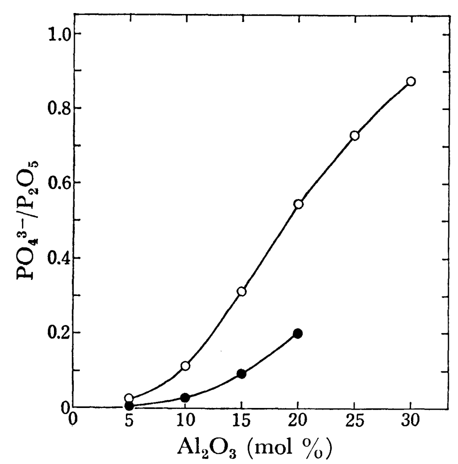


Fig. 6. Relation between PO_4^{3-}/P_2O_5 ratio and Al_2O_3 content in K_2O–Al_2O_3–P_2O_5 glass.
○: 40 mol % P_2O_5, ●: 45 mol % P_2O_5.

content in both the Na_2O–Al_2O_3–P_2O_5 and K_2O–Al_2O_3–P_2O_5 systems, the PO_4^{3-}/P_2O_5 ratio increases with an increase in the Al_2O_3 content, while this ratio decreases with an increase in the P_2O_5 content. In the glass with 32.5 mol % of P_2O_5, the PO_4^{3-}/P_2O_5 ratio rises to unity when the Al_2O_3 content approaches 25 mol % or more, as is shown in Fig. 5.

In Figs. 7 and 8, the PO_4^{3-}/Al^{3+} ratios are plotted *vs.* the Al_2O_3 content. The ratio increases with an increase in the Al_2O_3 content except for the Na_2O–Al_2O_3–P_2O_5 glass with 32.5 mol % of P_2O_5 (Fig. 7), whereas the ratio decreases with an increase in the P_2O_5 content in all the glasses. The PO_4^{3-}/Al^{3+} ratio can be regarded as showing the degree of the substitution of the P^{5+} ion in P–O–P linkage by the Al^{3+} ion. Therefore, the above-mentioned change in this value can be explained as follows. When the PO_4^{3-}/Al^{3+} ratio is smaller than unity, there exist two sorts of Al^{3+} ions, the Al^{3+} ion forming the P–O–Al linkage and the Al^{3+} ion not forming such a linkage. When this ratio is equal to or larger than unity, however, all the Al^{3+} ions are in the form

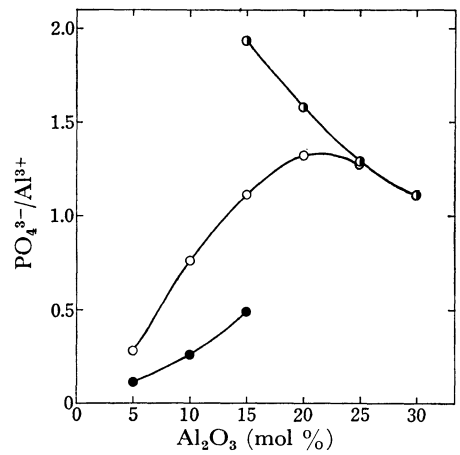


Fig. 7. Relation between PO_4^{3-}/Al^{3+} ratio and Al_2O_3 content in Na_2O–Al_2O_3–P_2O_5 glass.
◐: 32.5 mol % P_2O_5, ○: 37.5 mol % P_2O_5, ●: 42.5 mol % P_2O_5.

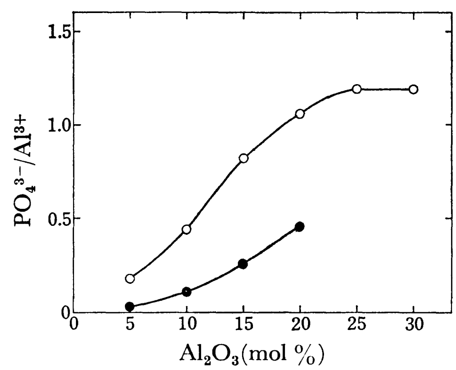


Fig. 8. Relation between PO_4^{3-}/Al^{3+} ratio and Al_2O_3 content in K_2O–Al_2O_3–P_2O_5 glass.
○: 40 mol % P_2O_5, ●: 45 mol % P_2O_5.

of P–O–Al linkage. Since the PO_4^{3-}/Al^{3+} ratios of the glasses with a lower Al_2O_3 content are smaller than 0.5, it can be considered that more than half of the Al^{3+} ions do not form the P–O–Al linkage. In the glass with 32.5 mol % of P_2O_5, when the value of PO_4^{3-}/Al^{3+} is larger than 1.5, it is possible that the "cluster" may be formed by the linkage between more than two PO_4 tetrahedra and one AlO_4 tetrahedron.

From the results of the determination of the PO_4^{3-} ion in the glasses, it can also be presumed that, in metaphosphate (50 mol % of P_2O_5) and ultraphosphate (more than 50 mol % of P_2O_5) compositions, no substitution of the P^{5+} ion by the Al^{3+} ion occurs; hence, the P–O–Al linkage described above is not formed in these compositions of glasses.

The author wishes to thank Associate Professor Makio Kinoshita of Sophia University for his interest and encouragement, and also Mr. Samon Isogai for his assistance in the experimental work.

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