Properties and Structure of Alkali Aluminophosphate Glass

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Several series of alkali (sodium and potassium) aluminophosphate glasses were prepared with compositions of 32—63 mol % of P_2O_5 and the properties of these glasses were determined. In the glasses with a higher P_2O_5 content ($P_2O_5 \gtrsim 42.5$ mol % in the Na_2O–Al_2O_3–P_2O_5 glass and $P_2O_5 \gtrsim 45$ mol % in the K_2O–Al_2O_3–P_2O_5 glass), the density, refractive index, and chemical resistivity increased with increasing amounts of Al_2O_3. In the glasses with a lower P_2O_5 content ($P_2O_5 \lesssim 37.5$ mol % in the Na_2O glass and $P_2O_5 \approx 40$ mol % in the K_2O glass), however, almost no increase of the density was found by an increase of Al_2O_3; the increases in the refractive index and chemical resistivity were also smaller than those in the glasses with a higher P_2O_5 content. The infrared absorption spectra of the glasses varied also with the P_2O_5 content. These changes in the properties are due to a marked structural difference between the glasses with a higher P_2O_5 content and those with a lower P_2O_5 content, and are also associated closely with the structural role of Al^{3+} ions in the glass.

The structure and the role of Al^{3+} ions in aluminophosphate glasses are attracting the attention of many investigators because Al_2O_3 can be incorporated in fairly large quantities into phosphate glass and stabilizes the glass structure. Kreidl and Weyl[1] considered that the ($AlPO_4$) group was formed by AlO_4 and PO_4 tetrahedra in the glass structure. On the other hand, Sakka[2,3] has reported that there are two kinds of Al^{3+} ions with different coordination numbers in phosphate glass. The present authors[4] have investigated the formation of the glasses in the three-component diagram in alkali (sodium and potassium) aluminophosphate systems and found one Al_2O_3 peak in about 65 mol % of P_2O_5 and another peak in about 35 mol % of P_2O_5. We also reported the structural difference between the glasses with a higher P_2O_5 content and those with a lower P_2O_5 content. Reports concerning the fundamental properties such as density, refractive index, viscosity, *etc.* of aluminophosphate glass, however, are relatively few compared with those of aluminosilicate glass. Therefore, it may be interesting to investigate the changes of the properties of the glass with regard to the difference in glass structure.

In this investigation, the density, refractive index, and infrared absorption spectra and also the molar volume, volume per mole of oxygen, and molar refraction were determined for several series of the Na_2O–Al_2O_3–P_2O_5 and K_2O–Al_2O_3–P_2O_5 glasses with the same contents of P_2O_5, which ranged from 32 to 63 mol %. For Na_2O–Al_2O_3–P_2O_5 glass the chemical resistivity and solubility in water or hydrochloric acid were examined. From these results, the changes in the properties were discussed in connection with the glass structure.

Experimental

Preparation of Series of Glasses with the Same P_2O_5 Contents. The glass specimens containing 32.5—45 mol % of P_2O_5, as reported in the previous paper,[5] were used as the lower P_2O_5 alkali aluminophosphate glasses in this investigation. Furthermore, about fifty glass specimens containing more than 45 mol % of P_2O_5 were prepared in the glass-forming regions of the Na_2O–Al_2O_3–P_2O_5 and K_2O–Al_2O_3–P_2O_5 systems.[4] The materials used were reagent grade chemicals of sodium dihydrogenphosphate, potassium dihydrogenphosphate, aluminum oxide, and orthophosphoric acid (85 %). A batch (40-g) obtained by mixing appropriate amounts of the above chemicals was placed in Al_2O_3 crucible and heated in an electric furnace. After dehydration, the temperature of the batch was raised to 1350 °C and kept at this temperature for 1 h. The melt was poured out and quenched by pressing it with a copper plate cooled with water. All the quenched melts were obtained as transparent colorless glasses. The composition of these glasses were determined by chemical analyses and several series of glasses with the same P_2O_5 contents were selected and used in this experiment.

Determination of Al_2O_3. Glass powder containing about 0.1 g of Al_2O_3 was fused with 5—9 g of sodium carbonate and dissolved in 200 cm^3 of 1 mol/dm^3 hydrochloric acid. The Al^{3+} ion in the obtained solution was determined gravimetrically as $AlPO_4$.[6]

Determination of P_2O_5. Glass powder containing about 0.1 g of P_2O_5 was fused with about 3 g of sodium carbonate and dissolved in 100 cm^3 of 1 mol/dm^3 hydrochloric acid. The PO_4^{3-} ion in the solution was determined gravimetrically as $Mg_2P_2O_7$.[7]

Determination of H_2O. The H_2O content of the glass was determined gravimetrically by the method of Naruse *et al.*,[8] namely from the weight loss incurred by heating a mixture of the pulverized glass and preignited zinc oxide at 700 °C for 2 h.

Density and Volume of Glass. The density of the glass was determined pycnometrically using 1-butanol at 25 °C.

The molar volume and the volume per mole of oxygen of the glass were calculated by the following equations:[9]

$$V = \frac{W_f}{\rho} \quad (1)$$

and

$$V_0 = \frac{V}{N_0} \quad (2)$$

where V is the molar volume of the glass, V_0 is the volume per mole of oxygen, W_f is the gram formular weight of the glass based on the composition determined by chemical analyses, ρ is the density of the glass, and N_0 is the number of gram molecular weight of oxygen (32 g units) in the glass.

Refractive Index and Molar Refraction of Glass. The refractive index was estimated by the Becke oil immersion method.

The molar refraction of the glass was calculated by the following equation:[9]

$$R = \frac{n^2-1}{n^2+2}V \qquad (3)$$

where R is the molar refraction of the glass, n is the refractive index, and V is the molar volume.

Chemical Resistivity and Solubility of Glass. Glass grains (0.25—1 mm) of about 1 g were placed in a 100-cm^3 Erlenmeyer flask and 50 cm^3 of either water or hydrochloric acid were added into the flask. After shaking at a speed of 80 strokes per minute in the thermostat, the weight loss and the Al_2O_3/P_2O_5 (molar ratio) in the residual glass were determined. The experimental conditions: concentration of hydrochloric acid, temperature of the thermostat, and shaking time were selected so as to be suitable for the sample glass or the series of samples.

Infrared Spectra. The infrared absorption spectra ranging from 1500 to 600 cm^{-1} of the glasses were recorded by means of a Hitachi EPI-2G spectrophotometer, using the KBr pellet technique.

Results and Discussion

Composition of Glass. The analyses of the glasses with more than 45 mol % of P_2O_5 are given in Tables 1 and 2. The Na_2O or K_2O content was calculated by subtracting the Al_2O_3 and P_2O_5 contents from the weight of the sample. The H_2O content was in the range from 0.11 to 0.42 wt % in eight kinds of the glasses of two series of the Na_2O–Al_2O_3–P_2O_5 glass with 59—61 mol % of P_2O_5 and K_2O–Al_2O_3–P_2O_5 glass with 61—62 mol % of P_2O_5, and the H_2O content tended to decrease with an increase in the amount of Al_2O_3. Since

TABLE 1. COMPOSITION OF Na_2O–Al_2O_3–P_2O_5 GLASS

P_2O_5/mo l%[a]		Composition		
		Na_2O/mol %	Al_2O_3/mol %	P_2O_5/mol %
(1)	49	45.74	5.00	49.26
		39.99	9.81	49.20
(2)	55	39.68	5.03	55.29
		33.38	11.40	55.22
(3)	59—61	34.08	4.92	61.00
		29.24	10.78	59.98
		25.81	14.77	59.42
		20.86	18.70	60.43
(4)	63	20.53	16.59	62.88
		17.69	19.02	63.30
		13.38	23.31	63.32

a) P_2O_5 content in the glass.

TABLE 2. COMPOSITION OF K_2O–Al_2O_3–P_2O_5 GLASS

P_2O_5/mol %[a]		Composition		
		K_2O/mol %	Al_2O_3/mol %	P_2O_5/mol %
(1)	49	40.67	9.95	49.38
		36.19	14.61	49.20
(2)	55—56	38.89	4.98	56.13
		33.17	11.35	55.48
(3)	61—62	32.40	5.14	62.46
		27.68	10.20	62.12
		25.10	13.83	61.08
		21.41	17.34	61.25

a) P_2O_5 content in the glass.

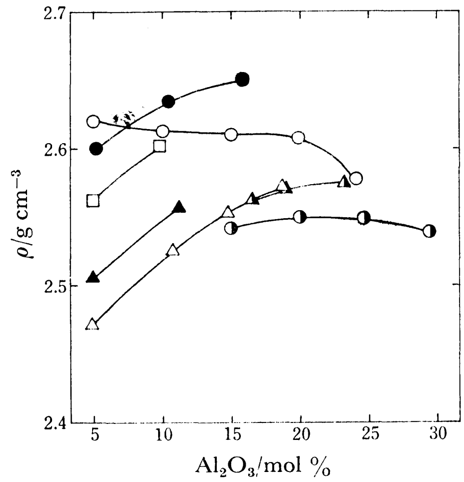

Fig. 1. Density (ρ) of Na_2O–Al_2O_3–P_2O_5 glass. ▲: 63 mol % P_2O_5, △: 59—61 mol % P_2O_5, ▲: 55 mol % P_2O_5, □: 49 mol % P_2O_5, ●: 42.5 mol % P_2O_5, ○: 37.5 mol % P_2O_5, ◑: 32.5 mol % P_2O_5.

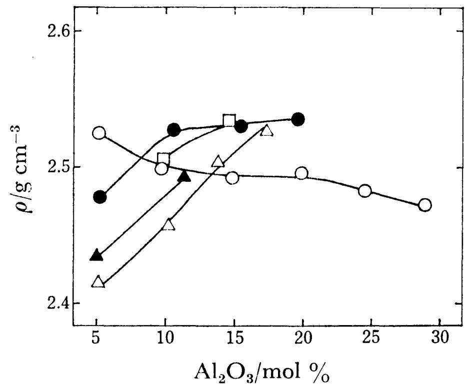

Fig. 2. Density (ρ) of K_2O–Al_2O_3–P_2O_5 glass. △: 61—62 mol % P_2O_5, ▲: 55—56 mol % P_2O_5, □: 49 mol % P_2O_5, ●: 45 mol % P_2O_5, ○: 40 mol % P_2O_5.

the H_2O content was less than 0.42 wt % in the above glasses, even though they were prepared by adding a large amount of orthophosphoric acid, it is considered that the properties of the glass are not seriously effected by water.

Density and Volume. The densities of these glasses are given in Figs. 1 and 2. In Fig. 1 the densities in the Na_2O–Al_2O_3–P_2O_5 glasses with the same P_2O_5 contents are plotted *vs.* the Al_2O_3 content; also in Fig. 2 those in the K_2O–Al_2O_3–P_2O_5 glasses are similarly plotted. The density of the Na_2O glass was larger than that of the K_2O glass in the same composition.

As shown in Figs. 1 and 2, a marked difference in the changes of the densities can be recognized between the glasses with a higher P_2O_5 content and those with a lower P_2O_5 content. The densities increased with an increase in the Al_2O_3 content in the glasses in the Na_2O–Al_2O_3–P_2O_5 system with 42.5 mol % of P_2O_5 or more and those in the K_2O–Al_2O_3–P_2O_5 system with 45 mol % of P_2O_5 or more. On the contrary, no increase of the densities was found in the glasses of 32.5, 37.5 (Na_2O system), and 40 mol % of P_2O_5 (K_2O system). Furthermore, the densities of the glasses with a lower Al_2O_3 content in both systems decreased with an increase in the P_2O_5 content. In the glasses with 32.5, 37.5, and 40 mol % of P_2O_5, the P–O–P chain is changed to the P–O–Al chain by an increase in the Al_2O_3 content.[5] The density should tend to decrease rather than to increase because the Na_2O or K_2O content decreases with increasing amounts of Al_2O_3 and also because the P–O–Al chain formed is not very long in such a glass. On the other hand, the increase in the densities in the glasses with a higher P_2O_5 content may be interpreted from the assumption that most of the Al^{3+} ions do not form the chain and network consisting of P–O–Al linkages. The Al^{3+} ions outside the P–O–P chain should easily strengthen the glass structure because the ionic field strength ($Z_i/(r_i+r_0)^2$; where Z_i: charge of cation, r_i: radius of cation, r_0: radius of oxygen ion)[10] of the Al^{3+} ion is much larger than that of the Na^+ or K^+ ion. In addition, the decrease in the densities with an increase in the P_2O_5 content in the glasses with a lower Al_2O_3 content may be interpreted from the following facts: an increase of PO_4 groups having one nonbridging O^{2-} ion in each and decrease of Na^+ or K^+ ions tend to open the structure compared with that of the glass with a lower P_2O_5 content.

The molar volumes and the volumes per mole of oxygen in the Na_2O–Al_2O_3–P_2O_5 glass are given in Figs. 3(a) and 3(b) and those in the K_2O–Al_2O_3–P_2O_5 glass are given in Figs. 4(a) and 4(b). The molar volumes increased with an increase in the P_2O_5 content, while the volumes per mole of oxygen decreased. This indicates that the O^{2-} ions are packed more closely together as the Al_2O_3 and P_2O_5 contents increased. In the glasses with a lower P_2O_5 content in both systems the molar volumes exhibited the tendency to increase slightly with an increase in the Al_2O_3 content.

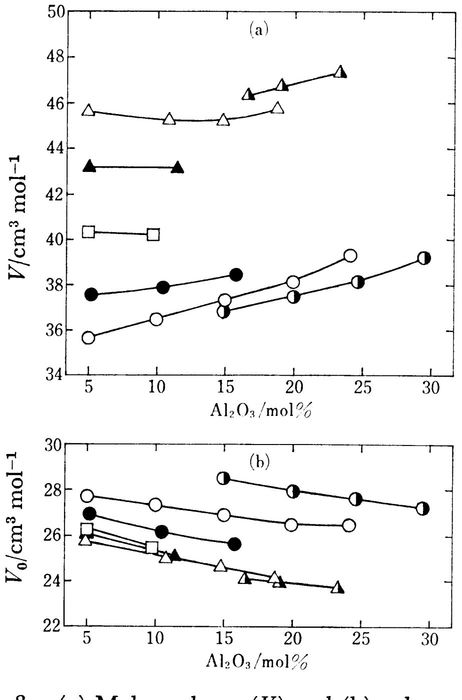

Fig. 3. (a) Molar volume (V) and (b) volume per mole of oxygen (V_0) of Na_2O–Al_2O_3–P_2O_5 glass.
◭: 63 mol % P_2O_5, △: 59—61 mol % P_2O_5, ▲: 55 mol % P_2O_5, □: 49 mol % P_2O_5, ●: 42.5 mol % P_2O_5, ○: 37.5 mol % P_2O_5, ◑: 32.5 mol % P_2O_5.

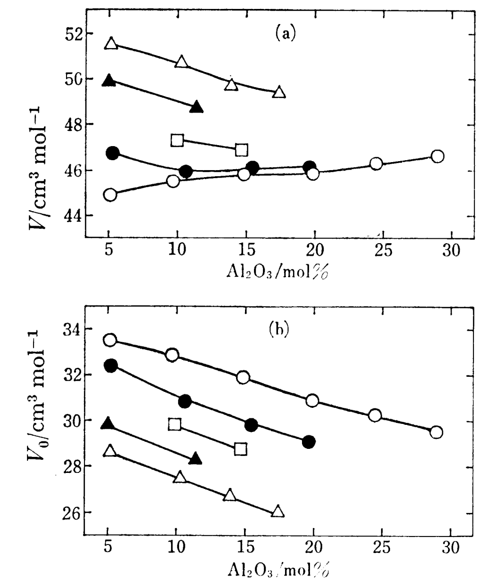

Fig. 4. (a) Molar volume (V) and (b) volume per mole of oxygen (V_0) of K_2O–Al_2O_3–P_2O_5 glass.
△: 61—62 mol % P_2O_5, ▲: 55—56 mol % P_2O_5, □: 49 mol % P_2O_5, ●: 45 mol % P_2O_5, ○: 40 mol % P_2O_5.

Refractive Index and Molar Refraction. The refractive indices of the Na_2O–Al_2O_3–P_2O_5 glass were in the range of 1.482—1.513 and those of the K_2O–Al_2O_3–P_2O_5 glass were 1.474—1.501. The values increased with increasing amounts of Al_2O_3 and P_2O_5, as shown in Figs. 5 and 6. The extent of the increase in the refractive indices with increasing amounts of Al_2O_3 in the glasses with a higher P_2O_5 content was much larger than that in the glasses with a lower P_2O_5

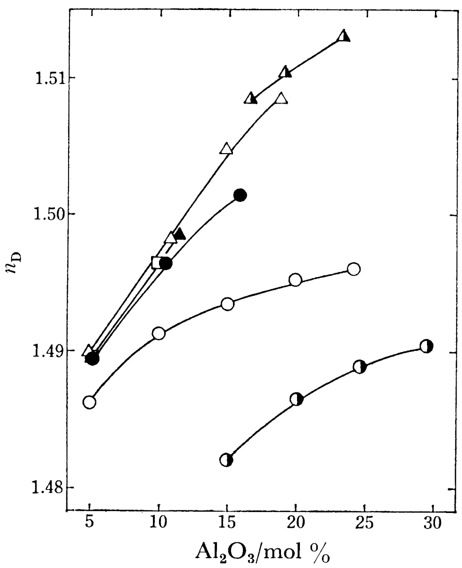

Fig. 5. Refractive index (n_D) of Na_2O–Al_2O_3–P_2O_5 glass.
◭: 63 mol % P_2O_5, △: 59—61 mol % P_2O_5, ▲: 55 mol % P_2O_5, □: 49 mol % P_2O_5, ●: 42.5 mol % P_2O_5, ○: 37.5 mol % P_2O_5, ◑: 32.5 mol % P_2O_5.

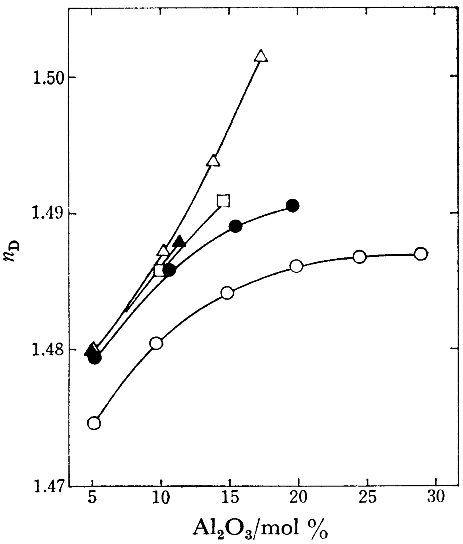

Fig. 6. Refractive index (n_D) of K_2O–Al_2O_3–P_2O_5 glass. △: 61—62 mol % P_2O_5, ▲: 55—56 mol % P_2O_5, □: 49 mol % P_2O_5, ●: 45 mol % P_2O_5, ○: 40 mol % P_2O_5.

content. In the glasses with a lower Al_2O_3 content in both systems, however, the increase in the refractive indices with an increase in the P_2O_5 content was extremely small in the compositions with more than 42.5 mol % of P_2O_5 (Fig. 5) and 45 mol % of P_2O_5 (Fig. 6).

On the other hand, as shown in Figs. 7 and 8, the changes in the molar refractions *vs.* the Al_2O_3 content were almost the same as those in the molar volumes of the glasses in both systems (Figs. 3(a) and 4(a)).

From the measurements of the chemical shift of the Al *Kα* line by X-ray emission spectroscopy, Sakka has reported that most of the Al^{3+} ions in the glasses with a higher P_2O_5 content (P/O≈0.33) are 6-fold coordinated, while those with a lower P_2O_5 content (P/O≲0.25) are 4-fold coordinated.[2,3] In the present investigation, the P/O ratios of the glasses with more than 42 mol % of P_2O_5 are in the range of 0.28—0.35 and those of the glasses with less than 42 mol % of P_2O_5 are 0.22—0.30. Therefore, the above results concerning the densities as well as the refractive indices can also be related with the difference in the coordination number of the Al^{3+} ion. From the changes in the densities and refractive indices with increasing amounts of Al_2O_3 shown in Figs. 1, 2, 5, and 6, it may be considered that the marked structural changes in the glasses with P_2O_5 content take place between 37.5 and 42.5 mol % of P_2O_5 in the Na_2O–Al_2O_3–P_2O_5 system and also between 40 and 45 mol % of P_2O_5 in the K_2O–Al_2O_3–P_2O_5 system. Therefore, in both systems the P_2O_5 content of 41—42 mol % may be taken as the boundary composition where the structural change occurs. This is associated closely with the above-mentioned change in the coordination number of Al^{3+} ion between the glasses with a higher P_2O_5 content and those with a lower P_2O_5 content.

Chemical Resistivity and Solubility of Glass. The chemical resistivities in hydrochloric acid in two series of the Na_2O–Al_2O_3–P_2O_5 glasses with 37.5 mol % and 59—61 mol % of P_2O_5 are given in Fig. 9. Although

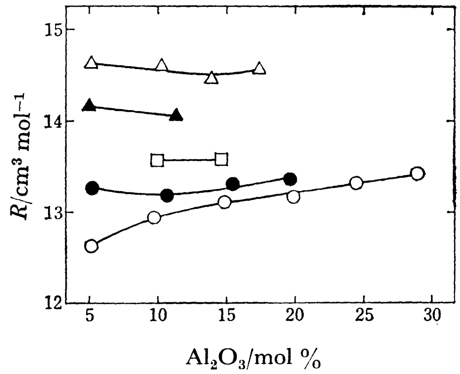

Fig. 8. Molar refraction (R) of K_2O–Al_2O_3–P_2O_5 glass. △: 61—62 mol % P_2O_5, ▲: 55—56 mol % P_2O_5, □: 49 mol % P_2O_5, ●: 45 mol % P_2O_5, ○: 40 mol % P_2O_5.

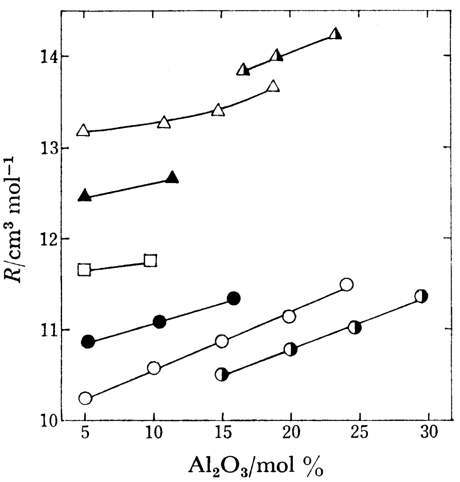

Fig. 7. Molar refraction (R) of Na_2O–Al_2O_3–P_2O_5 glass. ◭: 63 mol % P_2O_5, △: 59—61 mol % P_2O_5, ▲: 55 mol % P_2O_5, □: 49 mol % P_2O_5, ●: 42.5 mol % P_2O_5, ○: 37.5 mol % P_2O_5, ◑: 32.5 mol % P_2O_5.

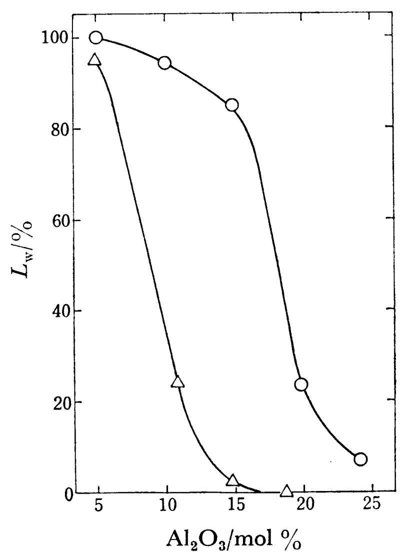

Fig. 9. Chemical resistivity of Na_2O–Al_2O_3–P_2O_5 glass in hydrochloric acid (L_w: weight loss).
○: 37.5 mol % P_2O_5, 1 mol/dm^3 HCl, 25 °C, 1 h, △: 59—61 mol % P_2O_5, concd HCl, 50 °C, 1 h.

the glasses of both series are strengthened chemically with an increase in the Al_2O_3 content, the resistivity of the glass with 59—61 mol % of P_2O_5 is very much larger than that of the glass with 37.5 mol % of P_2O_5. This indicates that the strengthening of the structure by the incorporation of Al_2O_3 is very effective in the glasses with a higher P_2O_5 content. This seems to be due to the tightening of the structure by the Al^{3+} ions outside the P–O–P network or chain in these glasses.

Table 3. Solubility of $52.5Na_2O \cdot 10Al_2O_3 \cdot 37.5P_2O_5$ glass in H_2O (25 °C)

t_s [b)]/h	L_w [c)]/%	Al_2O_3/P_2O_5 [d)]
0	—	0.27
1	14.51	0.28
3	38.99	0.29
5	59.30	0.29

b) t_s is the shaking time. c) L_w is the weight loss. d) Molar ratio in the glass.

Table 4. Solubility of $42.5Na_2O \cdot 20Al_2O_3 \cdot 37.5P_2O_5$ glass in 0.5 mol/dm³ HCl (25 °C)

t_s [b)]/h	L_w [c)]/%	Al_2O_3/P_2O_5 [d)]
0	—	0.54
1	8.64	0.53
3	21.75	0.52
5	37.82	0.52
7	48.12	0.53

b) t_s is the shaking time. c) L_w is the weight loss. d) Molar ratio in the glass.

Table 3 shows the solubility of the $52.5Na_2O \cdot 10Al_2O_3 \cdot 37.5P_2O_5$ glass in water and Table 4 shows that of the $42.5Na_2O \cdot 20Al_2O_3 \cdot 37.5P_2O_5$ glass in 0.5 mol/dm³ hydrochloric acid. The increase in the weight loss of each glass is approximately proportional to the shaking time. The molar ratio Al_2O_3/P_2O_5 in the residual glass is substantially the same value as that in the original glass. These facts indicate that a network consisting of PO_4 tetrahedra does not exist but short P–O–P or short P–O–Al chains exist in the glasses with a lower P_2O_5 content, and thus the structure of such a glass may be taken as "aggregates of molecules." This is an important result for the structure of the glasses with a lower P_2O_5 content.

Infrared Spectra. The infrared absorption spectra of the $Na_2O-Al_2O_3-P_2O_5$ and $K_2O-Al_2O_3-P_2O_5$ glasses are given in Figs. 10 and 11, respectively. Between the glasses with a higher P_2O_5 content ((1), (2), and (3) in Figs. 10 and 11) and those with a lower P_2O_5 content ((4), (5), and (6) in Fig. 10; (4) and (5) in Fig. 11), the following marked differences are found in the absorption bands: the absorptions in 1300 cm^{-1} (P=O stretching[8,11,12,13]) move to lower frequencies with decreasing P_2O_5 content and those in 900 cm^{-1} (P–O–P stretching[8,11,12,13]) to higher frequencies with increasing Al_2O_3 content, and also the absorptions in 1000 cm^{-1} (PO_4^{2-} group[8,11,12,13]) increase in intensity with increasing Al_2O_3 content in the glasses with a lower P_2O_5 content. These results show the structural changes of the glasses corresponding to the variation of P_2O_5 and Al_2O_3 contents. Especially in the glasses with a lower P_2O_5 content the infrared spectra indicate the change of the short P–O–P chain to the short P–O–Al chain with increasing amounts of Al_2O_3.

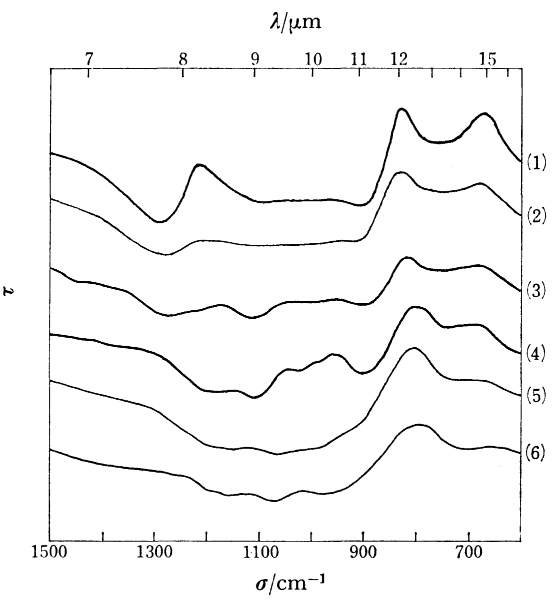

Fig. 10. Infrared spectra of $Na_2O-Al_2O_3-P_2O_5$ glass (τ: transmittance, σ: wave number).
(1) $29.24Na_2O \cdot 10.78Al_2O_3 \cdot 59.98P_2O_5$,
(2) $20.86Na_2O \cdot 18.70Al_2O_3 \cdot 60.43P_2O_5$,
(3) $39.99Na_2O \cdot 9.81Al_2O_3 \cdot 49.20P_2O_5$,
(4) $52.5Na_2O \cdot 10Al_2O_3 \cdot 37.5P_2O_5$,
(5) $42.5Na_2O \cdot 20Al_2O_3 \cdot 37.5P_2O_5$,
(6) $47.5Na_2O \cdot 20Al_2O_3 \cdot 32.5P_2O_5$.

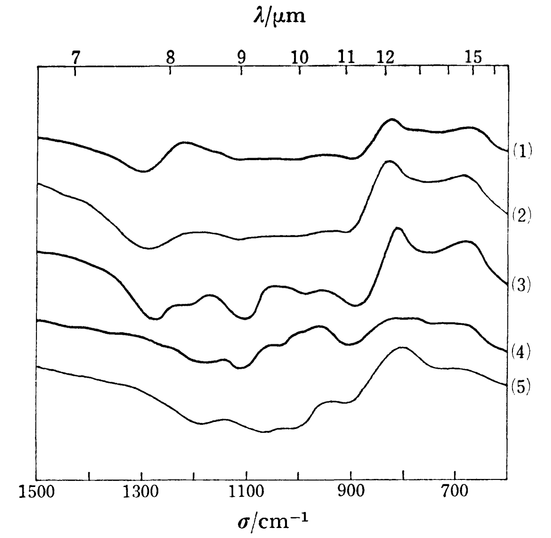

Fig. 11. Infrared spectra of $K_2O-Al_2O_3-P_2O_5$ glass (τ: transmittance, σ: wave number).
(2) $27.68K_2O \cdot 10.20Al_2O_3 \cdot 62.12P_2O_5$,
(2) $21.41K_2O \cdot 17.34Al_2O_3 \cdot 61.25P_2O_5$,
(3) $40.67K_2O \cdot 9.95Al_2O_3 \cdot 49.38P_2O_5$,
(4) $50K_2O \cdot 10Al_2O_3 \cdot 40P_2O_5$,
(5) $40K_2O \cdot 20Al_2O_3 \cdot 40P_2O_5$.

From the changes in the properties described above and the coordination number of the Al^{3+} ion in phosphate glass,[2,3] the structure of alkali aluminophosphate glass may be considered to be as follows: the glasses with a higher P_2O_5 content consist of a network or long chain of PO_4 tetrahedra, Al^{3+}, and alkali metal ions, while those with a lower P_2O_5 content are formed from random aggregates of short P–O–P chains, Al^{3+}, and alkali metal ions (low Al_2O_3 glass) or random aggregates of short P–O–Al chains of PO_4 and AlO_4 tetrahedra and alkali metal ions (high Al_2O_3 glass).

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References

1) N. J. Kreidl and W. A. Weyl, *J. Am. Ceram. Soc.*, **24**, 372 (1941).
2) S. Sakka, *Bull. Inst. Chem. Res., Kyoto Univ.*, **49**, 349 (1971).
3) S. Sakka, *Yogyo Kyokai Shi*, **85**, 299 (1977).
4) A. Kishioka, M. Hayashi, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **49**, 3032 (1976).
5) A. Kishioka, *Bull. Chem. Soc. Jpn.*, **50**, 2088 (1977).
6) E. P. Treadwell and W. T. Hall, "Analytical Chemistry," 9th English ed, (1951), Vol. 2, pp. 150—151.
7) A. Kishioka and M. Kinoshita, *Nippon Kagaku Kaishi*, **1976**, 608.
8) A. Naruse, Y. Abe, and H. Inoue, *Yogyo Kyokai Shi*, **76**, 36 (1968).
9) Bh. V. J. Rao, *Phys. Chem. Glasses*, **4**, 22 (1963).
10) T. Kokubo and M. Tashiro, *Bull. Inst. Chem. Res., Kyoto Univ.*, **52**, 633 (1974).
11) D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, **1954**, 493.
12) D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, **1954**, 4555.
13) "Topics in Phosphorus Chemistry," ed by M. Grayson and E. J. Griffith, Interscience Publishers, New York (1969), Vol. 6, pp. 307, 320—321.