

Structural Study of Binary Phosphate Glasses by X-ray and Neutron Diffraction

著者	Waseda Y., Matsubara E., Sugiyama K., Suh I.K., Kawazoe T., Kasu O., Ashizuka M., Ishida E.
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	35
number	1
page range	19-33
year	1990-03-23
URL	http://hdl.handle.net/10097/28324

Structural Study of Binary Phosphate Glasses
by X-ray and Neutron Diffraction*

Y.Waseda, E.Matsubara, K.Sugiyama, I.K.Suh, T.Kawazoe, O.Kasu,
M.Ashizuka** and E. Ishida**

Research Institute of Mineral Dressing and Metallurgy (SENKEN)

(Received January 8, 1990)

Synopsis

X-ray and neutron diffraction study on the structure of five binary metaphosphate glasses has been made by applying the pair function method coupled with the interference function refining technique. The distances and coordination numbers for the pairs of P-O, O-O and M-O (M=Li, Na, Zn, Mg, and Ca) were determined and a fundamental local ordering unit structure in these binary phosphate glasses has been confirmed to be a PO₄ tetrahedron and the particular features have also been recognized with respect to the numbers of oxygens around magnesium and zinc cations.

I. Introduction

Recently, there is an increasing need for the understanding of various properties of phosphate glasses, because their low transformation temperature and relatively large thermal expansion coefficient indicate a good applicability of glass to metal seals involving aluminum alloys and stainless steels [1,2]. The interest in phosphate glasses has also been intensified in parallel with recent progress in biological materials. For example, one of the main

* The 1721 th report of the Research Institute of Mineral Dressing and Metallurgy (SENKEN)

** Department of Materials Science, Faculty of Engineering, Kyusyu Institute of Technology, Kitakyushu 804, Japan.

components of bone and teeth is calcium phosphate and then glasses including calcium phosphate are quite promising for application to artificial bond and tooth materials [3-6].

In response to these requirements, the measurements of several properties such as density, elastic modulus, thermal expansion coefficient and refractive index were carried out for various phosphate glasses [7-9]. The determination of the atomic scale structure such as the fundamental local ordering unit and the coordination number around a metallic element in these phosphate glasses is essentially required for quantitative discussion of their physical and chemical properties. Some structural informations of phosphate glasses are available [10-13], but these previous studies have rarely been carried out systematically and experimental and theoretical difficulties were found frequently. Thus, some reservations are known to be stressed on the resultant information about the atomic scale structure.

The main purpose of this paper is to present a new systematic structural investigation of binary phosphate glasses of $M_2O-P_2O_5$ and $MO-P_2O_5$ by x-ray and neutron diffraction, where $M = Li, Na, Zn, Mg,$ and Ca .

II. Experimental

Five metaphosphate samples were prepared from high grade chemical reagents of lithium-phosphate, sodium-phosphate, zinc-phosphate, magnesium primary phosphate, calcium primary phosphate and orthophosphoric acid(85%). Calculated amounts of the reagents were weighed, thoroughly mixed and then charged into a platinum crucible, followed by melting for 10.8 ks (3h) at 1273-1623 K with intermediate stirring to ensure homogeneity [7]. The glass was then cast into rectangular graphite molds. The glass samples were then immediately annealed for 1.8 ks (30 min) in air at 653-723 K, depending upon its composition and slowly cooled to room temperature. After annealing, the glass samples were cut and polished to yield rectangular plates, approximately 20 mm high, 30 mm wide and 8 mm thick. The surface was polished smoothly with 6 and 1 μm diamond paste. Considering the results of chemical analyses of the several samples [7], evaporation of phosphorus during the sample preparation is considered not to be so severe for samples presently investigated. The densities of these glass samples were measured by

Archimedes' method with toluene and are tabulated in Table 1.

The sample was stored in a desiccator all the time until measurements by x-ray and neutron diffraction, and kept in He gas atmosphere during the measurements. X-ray diffraction profiles were measured using a singly-bent pyrolytic graphite monochromator in a diffracted beam and a pulse-height analyzer. The diffraction profile up to $Q=153 \text{ nm}^{-1}$ was determined with MoK_α radiation, where $Q=4\pi\sin\theta/\lambda$. θ is half of an angle between incident and diffracted beams and λ is a wavelength of incident beam. The diffraction profiles were taken in a fixed-count mode in order to obtain the same statistical error at every point. The fixed counts for each point were kept in 40,000. After correction for absorption, polarization, and Compton scattering [14,15], the measured patterns were converted into electron units, using the generalized Krogh-Moe-Norman method [16] and an interference function $i(Q)$ was obtained.

Neutron diffraction experiments were carried out using the two axis diffractometer of Institute of Solid State Physics, The University of Tokyo, PANSI, located at the high flux reactor of JRR-2. Reflection from the (200) planes of a pyrolytic graphite monochromator was used to select a beam with wavelength of 0.100 nm from the reactor neutron spectrum. The diffraction profiles were obtained up to 90 nm^{-1} and the accumulated intensity counts are over 20,000 for each point. The essential experimental arrangements and correction procedures of the measured intensity profiles to obtain the interference function were almost identical to those employed in the previous works for disordered systems by neutron diffraction [17], although the small angle data were corrected by the measurements with vanadium metal, along the way similar to the work of Wright and Sinclair[18].

III. Data Analysis

The method of analyzing measured x-ray or neutron diffraction data for disordered systems such as liquids and glasses is very common and has already been described in detail [14,15,19]. Consequently, only the essential features are given below using the case of x-ray diffraction.

The reduced interference function in electron units, $i(Q)$, which is related to the structurally sensitive part of the total scattering intensity, is directly obtained from experiments. This interference function is defined by;

$$i(Q) = [I_{eu}(Q) - \sum_{uc} f_j^2] / f_e^2 \quad (1)$$

where I_{eu}/N the intensity of unmodified scattering in electron units per unit of composition, f_j and f_e are the atomic scattering factor and the average scattering factor per electron, respectively. The electron RDF can be readily estimated from the interference function data by the following Fourier transformation;

$$RDF_{exp.} = 2\pi^2 r \rho_e \sum_{uc} Z_j + \int_0^{Q_{max}} Qi(Q) e^{-\alpha^2 Q^2} \sin Qr \, dQ \quad (2)$$

where ρ_e is the average number density of electrons and Z_j is the atomic number of j -element. The term $\exp[-\alpha^2 Q^2]$ is a convergence factor, introduced to minimize the truncation error and weigh down the uncertainties at the higher wave vector region. In this case, a zero value of α is assumed in the calculation of the experimental RDF.

On the other hand, the electron RDF can be calculated using the following equation for a particular distance r_{ij} and a coordination number N_{ij} of i - j pairs ;

$$RDF_{cal.} = \sum_{uc} \sum_i \frac{N_{ij}}{r_{ij}} \int_0^{Q_{max}} \frac{f_i f_j}{f_e f_e} e^{-\alpha^2 Q^2} \sin Qr_{ij} \sin Qr \, dQ \quad (3)$$

This theoretical RDF is usually estimated using a value of $\alpha = 0.06 \sim 0.07$, based on previous studies on various oxide glasses [20]. These two equations, using the concept of pair functions were originally employed by Mozzi and Warren [21] under the name of Pair Function Distribution (PFD). The interatomic distances are easily determined from the positions of the peaks in the experimental RDF data obtained from eq.(2). The number of neighbors can be estimated using a least-squares analysis, by finding the quantity of N_{ij} which will bring the calculated RDF using eq.(3) to the best fit with the experimental RDF. In this process, the variation of r_{ij} and N_{ij} in the theoretical RDF are ± 0.001 nm and ± 0.2 atom, respectively. The present approach by eq. (3) is easily seen to be effective only for a few near neighbor correlations such as P-O, O-O and M-O, in phosphate glasses.

Table 1. Structural parameters of local ordering and densities of metaphosphate glasses obtained in this work.

	Pair	Pair function method		Refining technique		Density (Mg/m ³)
		r _{ij} (nm)	N _{ij} (atom)	r _{ij} (nm)	N _{ij} (atom)	
Li ₂ OP ₂ O ₅	P - O	0.154	4.1	0.154	3.9	2.34
	Li - O	0.203	4.0	0.203	4.0	
	O - O	0.250	3.8	0.249	4.3	
Na ₂ OP ₂ O ₅	P - O	0.154	4.0	0.154	3.9	2.50
	Na - O	0.239	3.9	0.238	4.4	
	O - O	0.255	3.9	0.253	4.0	
ZnOP ₂ O ₅	P - O	0.153	4.0	0.152	4.1	2.90
	Zn - O	0.196	4.5	0.196	4.2	
	O - O	0.249	4.2	0.250	4.0	
MgOP ₂ O ₅	P - O	0.154	3.8	0.154	4.0	2.49
	Mg - O	0.203	4.5	0.203	4.3	
	O - O	0.250	4.0	0.249	4.4	
CaOP ₂ O ₅	P - O	0.154	4.0	0.154	4.1	2.66
	Ca - O	0.237	4.9	0.237	5.2	
	O - O	0.254	4.3	0.255	4.5	

In the case of neutron diffraction, the atomic scattering factor should be changed to the neutron scattering amplitude b_i which is constant, since the dimensions of the scattering nuclei are much smaller than the wavelength of neutrons. Compiled values of b_i [22] were used in this work.

IV. Results and Discussion

Figures 1 and 2 show the reduced interference function $Q i(Q)$ of five phosphate glasses determined by x-ray diffraction. The reason for the introduction of the factor Q is to complement the resolution for the small oscillating behavior in the high Q region. The experimental uncertainty in the present $Q i(Q)$ functions may be suggested as follows. A source of systematic error arising from the normalization procedure of measured intensity was estimated to be 2.3 %, by applying the Rahman method [23]. According to the detailed discussion by Greenfield et al. [24], the maximum error in the value of the atomic scattering factor and the Compton scattering intensity does not exceed 1.0 % in glasses presently investigated. Consequently, the total error including counting statistics [25] of the present $Q i(Q)$ functions is evaluated to be about 3.3 %. As a result, the uncertainty in the value of RDF using of eq. (2) is probably similar to that of the $Q i(Q)$ function, because the

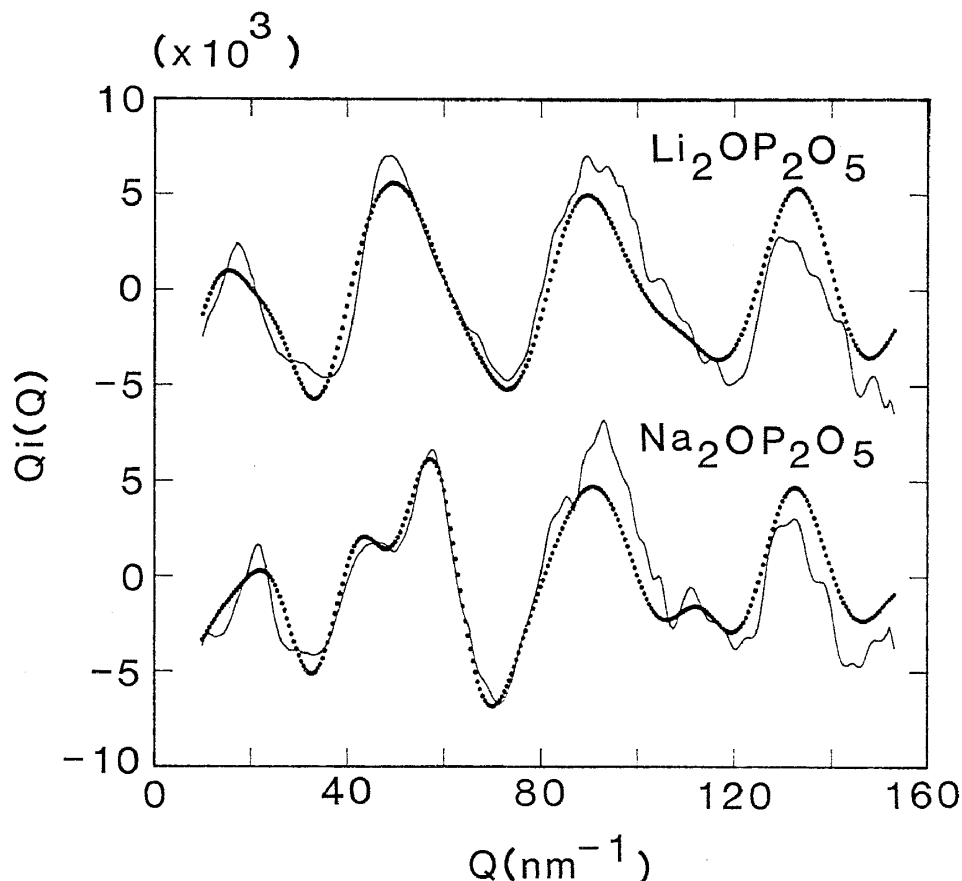


Fig.1 Reduced Interference function of $Q i(Q)$ of alkali metaphosphate glasses by x-ray diffraction. Solid line: experimental data, Dotted line: calculation by the interference function refining technique.

computation errors have been reduced to a minimum by the common numerical analysis[26].

The general feature of the reduced interference function $Q i(Q)$ for all glasses is similar, although there are some differences in detail. Namely, the profile of $Q i(Q)$ is composed of the first peak at about $Q=20 \text{ nm}^{-1}$ followed by a number of peaks, which contrasts to the cases of the metallic glasses where the damping behavior of the function $Q i(Q)$ is rapid and monotonous. If species having definite bond lengths and angles exist, persistence of the oscillation in $Q i(Q)$ would be clearly detected in the high Q region [15,27]. Therefore, the oscillations observed in these oxide glasses imply that a considerable fraction of the local ordering unit structure remains although its distribution appears to be random. The PO_4 tetrahedra are quite feasible with respect to the local ordering unit structure in these glasses which are given below.

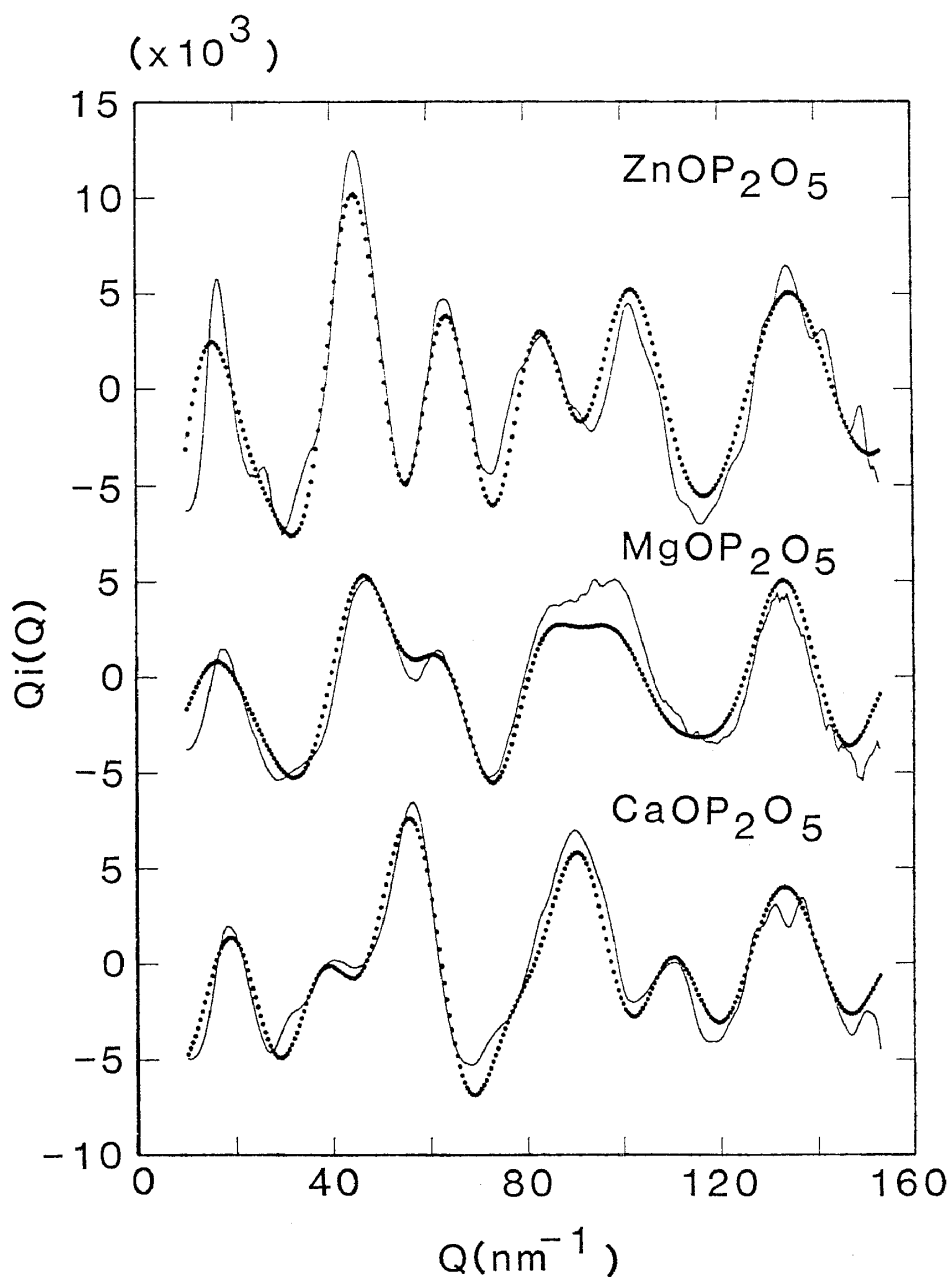


Fig.2 Reduced Interference function of $Q_i(Q)$ of alkaline-earth metaphosphate glasses by x-ray diffraction. Solid line: experimental data, Dotted line: calculation by the interference function refining technique.

Figures 3 and 4 provide the RDFs of five phosphate glasses containing alkali metal or alkaline earth metal oxides, respectively. The first peak in the RDFs of all glasses appears almost completely resolved and the subsequent oscillations are reduced so as to converge to the average number density value in the larger distance

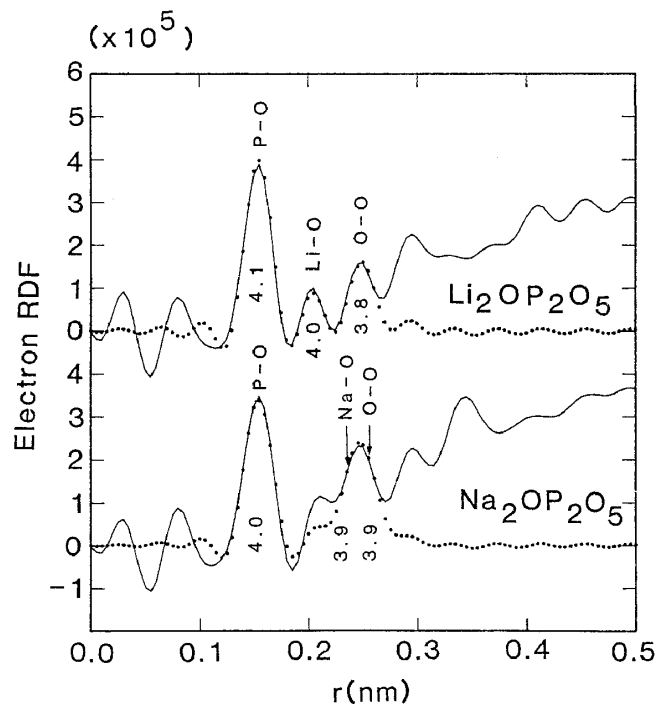


Fig.3 Electron radial distribution functions (RDFs) for $\text{Li}_2\text{OP}_2\text{O}_5$, and $\text{Na}_2\text{OP}_2\text{O}_5$ glasses. The solid line is the experimental data and the dotted line is the sum of the first three pair functions.

of r . This behavior is consistent with the contrast between the narrow distribution of local ordering unit structure and a complete loss of positional correlation in a few near neighbor distances away from any starting point [15,19]. The information of such local ordering unit structure could be obtained by an analysis of the area under the peaks in the RDFs.

As shown in Figs. 3 and 4, the oscillations in the small r region of the first peak are relatively distinct, compared with the metallic glasses case [15]. However, according to the methods proposed by Finbak [28] and Morimoto [29], the corresponding oscillations seem not to be attributed to the spurious ripples arising from the finite truncation of Q_{max} in the Fourier transformation by eq. (2). Additional serial tests using the numerical analysis by computer and the similar structural investigation in another samples produced by the different preparation process were carried out, which confirm the significance of the principal features of the RDF of the phosphate glass given in Figs. 3 and 4. It may also be worth mentioning that these oscillations before the first peak do not critically affect the evaluation of interionic distances and their coordination numbers for

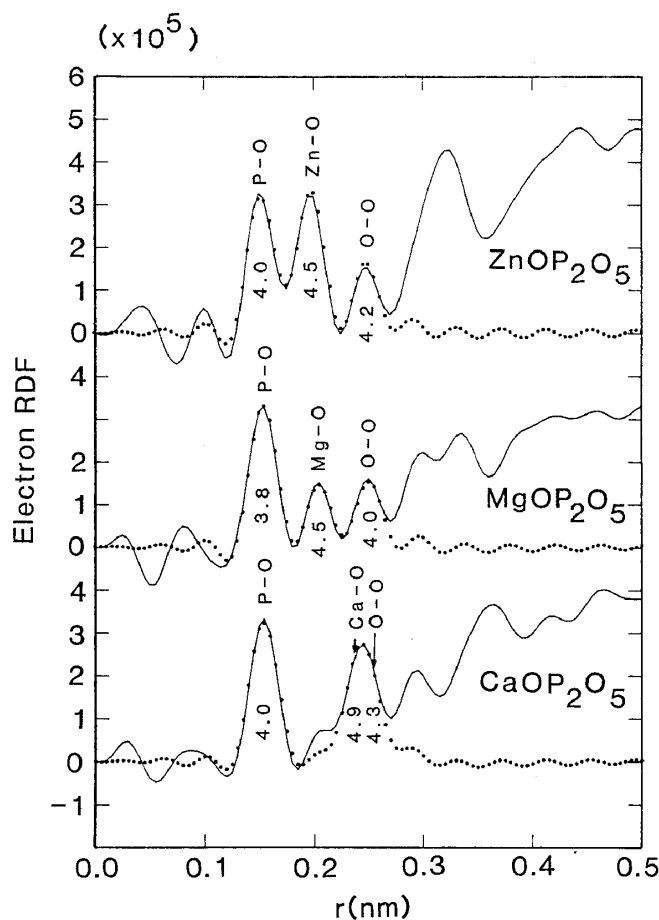


Fig.4 Electron radial distribution functions (RDFs) for ZnOP_2O_5 , MgOP_2O_5 and CaOP_2O_5 glasses. The solid line is the experimental data and the dotted line is the sum of the first three pair functions.

the resolved first peak[30], but the origin of these oscillations cannot be certainly identified at the present time.

The arrows in Figs. 3 and 4 denote the average distance of some pairs expected in these glasses and the numerical numbers are the coordination numbers of respective pairs, estimated by using the pair function method, although such numerical values themselves include an error of ± 0.2 due to the experimental uncertainty and the limitation of an analysis by the use of the pair functions [21]. The most striking result is as follows. The number of oxygens around phosphorus in these five phosphate glasses is found to be four at a distance of 0.152-0.154 nm and then the PO_4 tetrahedra is quantitatively confirmed as a local ordering unit structure in these glasses. However, the distribution of these tetrahedral units with the breaking of the so-called network structure of pure P_2O_5 due to

the addition of M_2O or MO oxides could not be drawn from the present RDF data alone. The structural parameters obtained by the pair function method are listed in Table 1 together with the measured density data.

It may be suggested the structural parameters in the near neighbor region (for only a few near neighbor correlations), estimated by the pair function method can be quantified with a much higher reliability compared with those obtained in the previous investigation, because the present results are free from the ambiguity in the procedure for estimating the area under each peak in the experimental RDF data[15]. However, the simultaneous use of other methods for estimating the coordination numbers is one way to confirm the structural parameters in disordered systems. For this purpose, the interference function refining technique[26,31] is employed in this work. This technique is based on the characteristic structural features of silicate melts and glasses; namely the contrast between the narrow distribution of local ordering and a complete loss of positional correlation in the longer distance region. In other words, the average number of j elements around i -elements, N_{ij} , is separated by an average distance, r_{ij} . The distribution can be approximated by a discrete Gaussian like distribution with a mean-square variation $2\sigma_{ij}$. The distribution for higher neighbor correlations is approximately expressed by a continuous distribution with an average number density of a system. These features can provide the following expression with respect to the reduced interference function, $Q i(Q)$;

$$[f_e]^2 i(Q) = \sum_{i=1}^m \sum_k N_{ik} \exp(-\sigma_{ik} Q^2) f_i f_k \frac{\sin Q r_{ik}}{Q r_{ik}} + \sum_{\alpha=k}^m \sum_{\beta=1}^m [\exp(-\sigma'_{\alpha\beta} Q^2) f_{\alpha} f_{\beta} 4\pi\rho_0 (Q r'_{\alpha\beta} \cos Q r'_{\alpha\beta} - \sin Q r'_{\alpha\beta})] / Q^3 \quad (4)$$

The quantities $r'_{\alpha\beta}$ and $\sigma'_{\alpha\beta}$ are the parameters of the boundary region which need not be sharp[26,31]. The structural parameters for near neighbor correlations are determined by a least-squares analysis so as to fit the experimental interference function by iteration with the initial structural parameters determined by the pair function method. In this analysis, the variation of the coordination number is in the order of about ± 0.5 atom. This interference function refining technique has frequently been used for structural investigation of inorganic liquid and glasses. However, it should be kept in mind that this method is not a unique mathematical procedure, but a semiempiri-

cal one for the resolution of the peaks in the RDF of disordered systems.

The dotted lines in Figs. 1 and 2 are the resultant interference function calculated from eq.(4) with the structural parameters determined by the interference function refining technique, which are summarized in Table 1. The consistency between the experimental and calculated interference functions appears to be satisfactory. Comparing the structural parameters estimated by two different methods, the parameters obtained in the present study can be considered quite realistic.

The scattering power of x-rays for light element such as oxygen is small relative to that of metallic elements, because x-rays are scattered by the outer electrons of atoms and then the scattering power is known to increase in magnitude with increasing the atomic number. On the other hand, scattering of neutrons arises from the magnetic scattering process as well as that of nucleus and thus neutron diffraction experiments provide useful information, since the scattering power of oxygen is larger than that of other elements, Na, Mg, Ca etc. For this reason, neutron diffraction experiments were carried out for four phosphate glasses and the results are given in Figure 5 using the expression of the interference function $Q_i(Q)$. The profiles of neutron diffraction considerably differ from those of x-ray diffraction of Figs. 1 and 2. This follows from the fact, for example, that x-rays are scattered more by phosphorus than by oxygen, but the reverse is the case for the scattering of neutrons.

The conventional neutron diffraction measurements are known to restrict the upper value of Q , in the present case up to 90 nm^{-1} . In this regards, it is no doubt that the high Q measurements using time-of-flight (TOF) pulsed neutron diffraction by making available the diffraction profile up to about 300 nm^{-1} is strongly required for determining the accurate structural parameters in the near neighbor region. In other words, the RDF analysis of the present neutron diffraction data up to 90 nm^{-1} is affected, more or less, by the truncation effect. Therefore, the present authors maintain the view that the neutron diffraction data of Fig.5 should only be used to check the validity of structural parameters determined from the the x-ray diffraction data by applying the interference function refining technique.

The dotted lines in Fig.5 are the neutron interference function calculated from eq.(4) with the same structural parameters determined by applying the interference function refining technique to the present x-ray data. The agreement is not complete, but appears to be

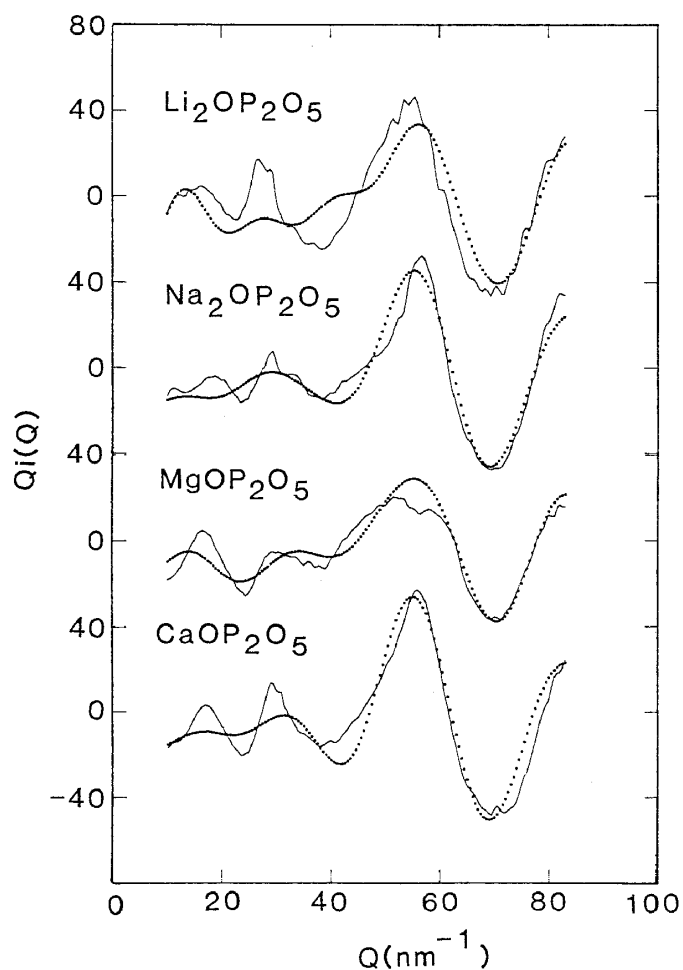


Fig.5 Reduced Interference function of $Q_i(Q)$ of binary metaphosphate glasses by neutron diffraction. Solid line: experimental data, Dotted line: calculation by the interference function refining technique.

acceptable in the higher Q region. This implies that the structural parameters employed as the initial information can be accepted at least in a sense of the necessary condition, although they might be not sufficient condition. More detailed structural parameters, particularly in the higher ordering should be included, in order to obtain the agreement between calculation and experiment in the whole Q region, although such modification is out of the scope of this work.

It will be of interest to recall the description about the oxygen coordination numbers around M element in phosphate glasses systematically obtained in this work. Figure 6 shows the mean molar volumes estimated from measured density data as a function of the cube of cation radius for divalent cations or as a function of three

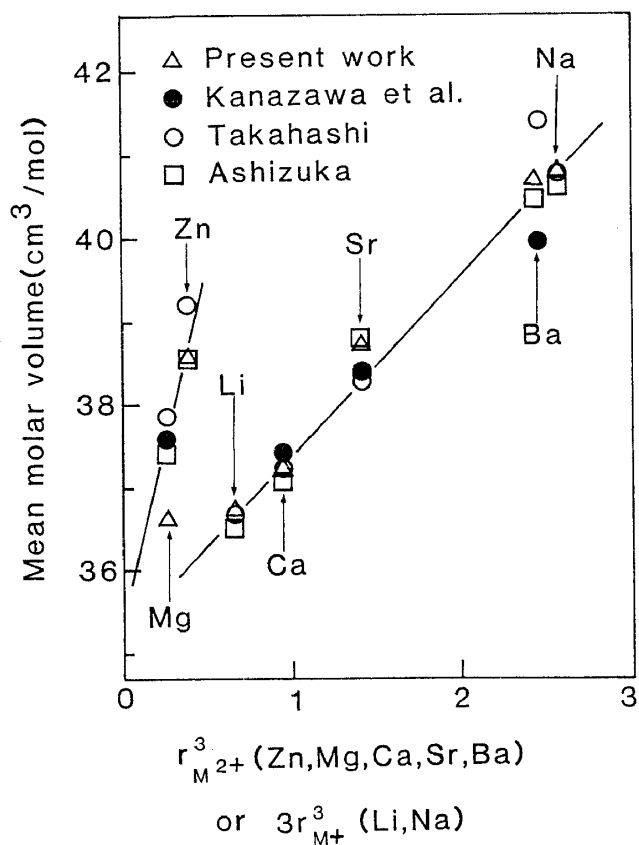


Fig.6 Mean molar volumes estimated from measured density data as a function of the cube of cation radius for divalent cations or as a function of three times the cube of cation radius for monovalent cations.

times the cube of cation radius for monovalent cations. Here, Pauling's ionic radius [32] was used. The factor of three is taken from the reason that one mole alkaline earth metal phosphate produce one gram-ion cations, whereas one mole alkali metal phosphates produce two gram-ion cations. In the latter case, two alkali metal cations most likely occupy more than two times their own volume in phosphate glasses and it is known to be approximated by about three times the cube of cation radius, as first suggested by Tomlinson et al [33].

The linear relationship is readily found in Fig.6, which implies that the accommodation of the cations is approximately constant and the volumes of the anions are comparable in these phosphate glasses. However, the linear relationship is classified into two groups, for Li, Na, Ca, Sr and Ba and for Mg and Zn. This is consistent with the previous discussion for phosphate glasses in terms of the concepts of the normal and abnormal types as proposed by Kordes and his

colleagues [34,35]. It is generally recognized that the oxygen coordination number around cation in oxides is proportional to the cation radius and phosphate glasses containing Li, Na, Ca, Sr and Ba are included in this category as being the normal type. On the other hand, magnesium phosphate and zinc phosphate glasses are classified as being the abnormal type attributed to four oxygens around Mg^{+2} and Zn^{+2} cations. The present structural information supports the discussion of Kordes et al.[35,36] about the role of Zn or Mg cation and rather contrasts to the suggestion of Isozaki et al.[36] who proposed the six coordinated magnesium in phosphate glass, based on the measurements of x-ray emission spectra. However, the definite comment on the origin of the abnormal behavior for phosphate glasses is not certainly identified from the present structural information alone, although it is plausible that the differences in the oxygen coordination number around cations play an important role in the normal or abnormal classification of phosphate glasses exemplified by the results of Fig.6. For this purpose, some further structural studies such as the concentration dependence of the oxygen coordination number around cations are required in a wider composition range.

Acknowledgements

The authors wish to express their thanks to Drs. W.R.Busing and A.H.Narten, Oak Ridge National Laboratory for providing a GENERAL FORTRAN LEAST-SQUARES PROGRAM in magnetic tape form. The authors are also grateful to The Institute of Solid State Physics, The University of Tokyo, for providing us facilities to use the neutron diffractometer PANSI at JRR-2. This work was carried out as a part of the research project on Structure and Properties of Slags. Financial Support from Association of Cement Materials is acknowledged.

References

1. T.Minami and J.D.Mackenzie, *J. Amer. Ceram. Soc.*, **60**,232(1977).
2. J.A.Wilder Jr., *J. Non-Cryst. Solids*, **38/39**,879(1980).
3. F.Pernot, J.Zarzycki, F.Bonnel, P.Rabischong and P.Baldet, *J. Mater. Sci.*, **14**,1694(1979).
4. M.Akao, H.Aoki and K.Kato, *J. Mater. Sci.*, **16**,809(1981).
5. G.De With, H.J.A.Van Dijk, N.Hattu and K.Prijs, *J. Mater. Sci.*, **16**,1592(1981).
6. S.Sakka and T.Kokubo, *Ceramics Japan*, **17**,342(1982).

7. M.Ashizuka, T.Sakai and A.Iwata, *Yogyo-Kyokai-shi*, **91**,87(1983).
8. M.Ashizuka and T.Sakai, *Yogyo-Kyokai-shi*, **91**,176(1983).
9. M.Ashizuka and R.C.Bradt, *J. Amer. Ceram. Soc.*, **65**,C-70(1982).
10. J.Biscoe, A.G.Pincus, C.S.Smith Jr. and B.E.Warren, *J. Amer. Ceram. Soc.*, **24**,116(1941).
11. G.W.Brady, *J. Chem. Phys.*, **28**,48(1958).
12. R.A.Harper and A.S.Posner, *Mater. Res. Bull.*, **5**,129(1970).
13. F.Betts and A.S.Posner, *Mater. Res. Bull.*, **9**,353(1974).
14. C.N.J.Wagner, *J. Non-Cryst. Solids*, **31**,1(1978).
15. Y.Waseda, *The Structure of Non-Crystalline Materials*, McGraw-Hill, New York, (1980).
16. C.N.J.Wagner, H.Ocken and M.L.Joshi, *Zeit. Naturforsch.*, **20a**,325(1965).
17. S.Takeda, S.Tamaki and Y.Waseda, *J. Phys. Soc. Japan*, **53**,3830(1984).
18. A.C.Wright and R.N.Sinclair, *J. Non-Cryst. Solids*, **76**,351(1985).
19. B.E.Warren, *X-ray Diffraction*, Addison-Wesley, Reading, Massachusetts (1969).
20. A.C.Wright and A.J.Leadbetter, *Phys. Chem. Glasses*, **17**,122(1976).
21. R.L.Mozzi and B.E.Warren, *J. Appl. Cryst.*, **2**,164(1969).
22. G.E.Bacon, *Acta Cryst.*, **A28**,357(1972).
23. A.Rahman, *J. Chem. Phys.*, **42**,3540(1965).
24. A.J.Greenfield, J.Wellendorf and N.Wiser, *Phys. Rev.*, **A4**,1697(1971).
25. B.D.Cullity: *Elements of X-ray Diffraction*, Addison-Wesley, Reading, Massachusetts,(1978).
26. A.H.Narten: *J. Chem. Phys.*, **56**,1905(1972).
27. K.Suzuki and P.A.Egelstaff, *Can. J. Phys.*, **52**,241(1974).
28. C.Finbak: *Acta Chem. Scand.*, **3**(1949),1279 and 1293.
29. H.Morimoto: *J. Phys. Soc. Japan*, **13**(1958),1015.
30. K.Furukawa: *Rep. Progr. Phys.*, **25**(1962),395.
31. W.R.Busing and H.A.Levy: *Oak Ridge National Laboratory Report*, ORNL-TM-271, (1962).
32. L. Pauling, *The Nature of Chemical Bond*, Cornell Univ. Press, Ithaca, New York, (1945).
33. J.W.Tomlinson, M.S.R.Heynes and J.O'.M. Bockris, *Trans. Faraday Soc.*, **54**,1822(1958).
34. E.Kordes, W.Vogel and R.Feterowsky, *Zeit. Elektrochem.*, **57**,282(1953).
35. E.Kordes and J.Navarrete, *Glastechn. Ber.*, **46**,113(1973).
36. K.Isozaki, H.Hosono, H.Kokumai, H.Kawazoe, T.Kanazawa, and Y.Goshi, *J. Mater. Sci.*, **16**,2318(1981).