JOURNAL OF MATERIALS SCIENCE 23 (1988) 547–550

Oxygen coordination of magnesium and calcium in binary magnesia and calcia metaphosphate glasses

E. MATSUBARA, T. KAWAZOE, Y. WASEDA
Research Institute of Mineral Dressing and Metallurgy (SENKEN), Tohoku University, Sendai 980, Japan

M. ASHIZUKA, E. ISHIDA
Department of Metallurgy and Metal Processing Engineering, Kyushu Institute of Technology, Kitakyushu 804, Japan

An X-ray diffraction study has been carried out on binary phosphate and silicate glasses with MgO or CaO in equimolar composition. The structure of a 60 mol % CaO–40 mol % Al_2O_3 glass was also investigated for comparison. The electron radial distribution function was calculated by the usual Fourier transformation and interpretation of it was made in terms of pair functions. The number of oxygens around magnesium is evaluated to be four in both phosphate and silicate glasses. On the other hand, the number of oxygens which surround calcium appears to depend upon the component of network formers: namely, the oxygen coordination numbers around calcium are five in phosphate, six in silicate and four in aluminate glasses, respectively.

1. Introduction

Recently much attention has been devoted to phosphate glasses, because their low transformation temperature and relatively large thermal expansion coefficient indicate a good applicability to glass to metal seals involving aluminium alloys and stainless steels [1, 2]. The interest in phosphate glasses has also been intensified in parallel with recent progress in biological materials, e.g. calcium phosphate-based glasses and ceramics are quite promising for application to artificial bond and tooth materials [3–6], because calcium phosphates are some of the main components of bone and teeth. Such growing technological importance has, therefore, led to an increasing need for an understanding of various properties of phosphate glasses and ceramics, particularly for magnesium and calcium phosphate glasses.

In response to these requirements, measurements of several properties such as density, elastic modulus, thermal expansion coefficient and refractive index have been carried out for various phosphate glasses [7–9] and the results were discussed in terms of the concepts of the normal and abnormal types as proposed by Kordes and his colleagues [10–12]. According to their discussion, magnesium phosphate glass is classified as being typical of the abnormal type attributed to four oxygens around Mg^{2+}. On the other hand, it is recognized that calcium phosphate glass, whose coordination number of oxygens around Ca^{2+} is six, is typed as being typical normal.

Direct information concerning the coordination number of oxygens around a specific element in glass can be obtained from X-ray and neutron diffraction studies. Some structural information on phosphate glasses is available [13–16], but previous studies have rarely been carried out systematically and severe experimental and theoretical difficulties were frequently found. Thus, some reservations are known to be held in the resultant coordination numbers around a specific element.

The main purpose of this paper is to present a new systematic structural investigation of metaphosphate glasses of $MgOP_2O_5$ and $CaOP_2O_5$ by X-ray diffraction. In addition, structural studies for metasilicate glasses of $MgOSiO_2$ and $CaOSiO_2$ and a 60 mol % CaO–40 mol % Al_2O_3 glass were made by X-ray diffraction to present a contrast of such information.

2. Experiments and data processing

Metaphosphate samples were prepared from high-grade chemical reagents of monomagnesium orthophosphate and monocalcium orthophosphate. Calculated amounts of the reagents were weighed, thoroughly mixed and then charged into a platinum crucible, followed by melting for 10.8 ksec at 1623 to 1673 K with intermediate stirring to ensure homogeneity [7]. The glass was then cast into rectangular graphite moulds. The glass samples were then immediately annealed for 1.8 ksec in air at 673 to 773 K, depending upon its composition and slowly cooled to room temperature. After annealing, the glass samples were ground and polished to yield rectangular plates, approximately 20 × 30 × 8 mm^3. Metasilicate and 60 mol % CaO–40 mol % Al_2O_3 samples were prepared from high-grade chemical reagents of magnesia, silica, alumina and calcium carbonate, in a similar

0022–2461/88 $03.00 + .12

manner to the phosphate samples using an electric furnace in order to operate at temperatures up to 1973 K. The densities ($Mg\,m^{-3}$) of these glasses are: $MgOSiO_2$ 2.585, $MgOP_2O_5$ 2.435, $CaOSiO_2$ 2.673, $CaOP_2O_5$ 2.664 and 60 mol % CaO–40 mol % Al_2O_3 2.885.

The method of analysing the measured X-ray scattering intensity for non-crystalline systems such as liquids and glasses is very common and has already been described in detail [17–19]. Consequently, only the essential features are given below, for convenience of discussion.

A reduced interference function in electron units, $i(Q)$, $Q = 4\pi \sin\theta/\lambda$ where θ is the half the scattering angle and λ is the wavelength, is related to the structurally sensitive part of the total scattering intensity directly determined by the experiments and is defined by

$$i(Q) = \left(I_{eu}/N - \sum_{uc} f_j^2 \right) / (f_e)^2, \qquad (1)$$

where I_{eu}/N is 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 so-called electron radial distribution function (RDF) can readily be evaluated from $i(Q)$ by Fourier transformation, and the use of pair functions [20] is known to be convenient for interpretation of such RDF data. When the pair functions are employed, the following useful relation is obtained with respect to the theoretical and experimental radial distribution functions [20].

$$\sum_{uc} \sum_{i} \frac{N_{ij}}{r_{ij}} \int_0^{Q_{max}} \frac{f_j f_i}{f_e^2}\, e^{-\alpha^2 Q^2} \sin(Q r_{ij}) \sin(Qr)\, dQ$$
$$= 2\pi^2 r\, \varrho_e \sum_{uc} Z_j + \int_0^{Q_{max}} Q i(Q)\, e^{-\alpha^2 Q^2} \sin(Qr)\, dQ \qquad (2)$$

where r_{ij} and N_{ij} are the distance and its coordination number of i–j pairs, respectively, Z_j is the atomic number and ϱ_e is the average number density of electrons. The left-hand side of Equation 2 provides the theoretical RDF, whereas the right-hand side of Equation 2 corresponds to the experimental RDF data. The term $\exp[-\alpha^2 Q^2]$ in Equation 2 is a convergence factor, introduced to minimize the truncation error and weight down the uncertainties at high wave vector Q region. The artificial parameter of α does not have to be critically selected, but the value of α is zero in the calculation of the experimental RDF from the right-hand side of Equation 2. On the other hand, the theoretical RDF on the left-hand side of Equation 2 is calculated using the value of $\alpha = 0.05$. The valuable information of r_{ij} and N_{ij} for near neighbours was evaluated by a least-square analysis, in order to fit the experimental RDF. In this process, the variations of r_{ij} and N_{ij} in the theoretical RDF are ±0.001 nm and ±0.2 atom, respectively. The present approach using Equation 2 is easily seen to be effective only for a few near neighbour correlations such as P–O, O–O and M–O, where M = Mg or Ca in the phosphate glasses. However, it is also realized that the main purpose of this work can be achieved with much higher reliability than those in the previous works on the structure of glasses [20]. That is, from the present approach it is possible to determine quantitatively accurate information about the fundamental local unit and the oxygen coordination number around Mg^{2+} or Ca^{2+} ions in glasses.

3. Results and discussion

Fig. 1 shows the reduced interference function $Q\,i(Q)$ of five glasses. The reason for the introduction of the factor Q is to complement the resolution for the small oscillating behaviour in the high Q region. The experimental uncertainty in the present $Q\,i(Q)$ functions may be suggested as follows. A fixing count mode, the accumulated counts = 40 000, was applied to hold the counting statistics approximately uniform. A source of systematic error arising from the normalization procedure of measured intensity was estimated to be 2.3%, by applying the Rahman method [21]. According to the detailed discussion by Greenfield *et al.* [22], the maximum error in the value of the atomic scattering factor and the Compton scattering intensity does not exceed 1% in the glasses investigated here. Consequently, the total error 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 the right-hand side of Equation 2 is probably similar to that of the $Q\,i(Q)$ function, because the computation errors have been reduced to a minimum by the common numerical analysis.

The general feature of the 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 $Q = 20\,nm^{-1}$ followed by a number of peaks, which contrasts to the metallic glass cases where the damping behaviour of the function

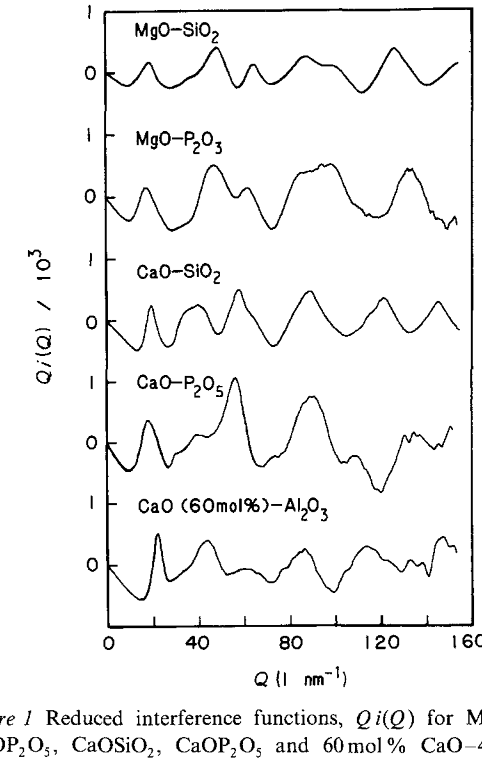

Figure 1 Reduced interference functions, $Q\,i(Q)$ for $MgOSiO_2$, $MgOP_2O_5$, $CaOSiO_2$, $CaOP_2O_5$ and 60 mol % CaO–40 mol % Al_2O_3 glasses.

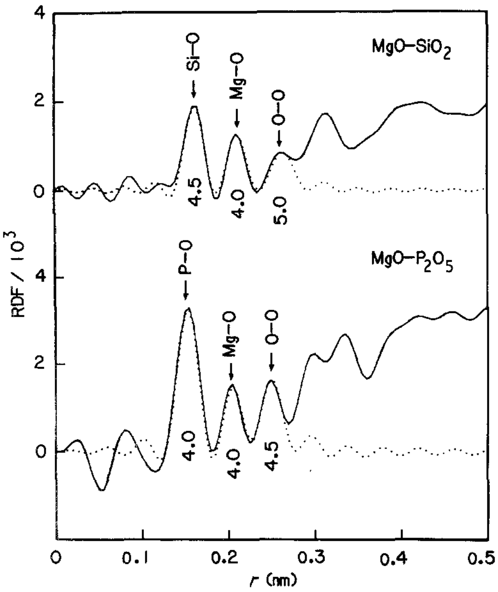

Figure 2 Electron radial distribution functions (RDFs) for $MgOSiO_2$ and $MgOP_2O_5$ glasses. The solid line is the measured curve and the dotted line is the sum of the first three pair functions.

$Q\,i(Q)$ is rapid and monotonic. 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 [19, 23]. 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 or SiO_4 tetrahedra are quite feasible with respect to the local ordering unit structure in these glasses which are given below.

Fig. 2 shows the RDFs of phosphate and silicate glasses containing MgO, calculated from $Q\,i(Q)$ using Equation 2 with the measured density data. The first peak in the RDFs of both glasses appears almost completely resolved and the subsequent oscillations are reduced in order to converge on the average number density value in the larger distance of r. This behaviour 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 neighbour distances away from any starting point [17–19]. The information of such local ordering unit structure could be obtained by an analysis of the area under the peaks in the RDFs.

The arrows in Fig. 2 denote the average distance of some pairs expected in these glasses and the numbers are the coordination numbers of respective pairs, evaluated by the use of pair functions. The most striking result in Fig. 2 is that each silicon is surrounded by four oxygens at a distance of 0.161 nm in silicate and the number of oxygens around phosphorus in phosphate is also four at a distance of 0.153 nm. Thus, the SiO_4 or 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 or SiO_2 due to the addition of magnesia could not be drawn from the present RDF data alone. In addition, the oxygen coordination number around Mg^{2+} at a distance of about 0.210 nm is found to be four in both glasses, although this value itself has an error of ± 0.2 due to the experimental uncertainty and the limitation of an analysis made by the use of the pair functions [17].

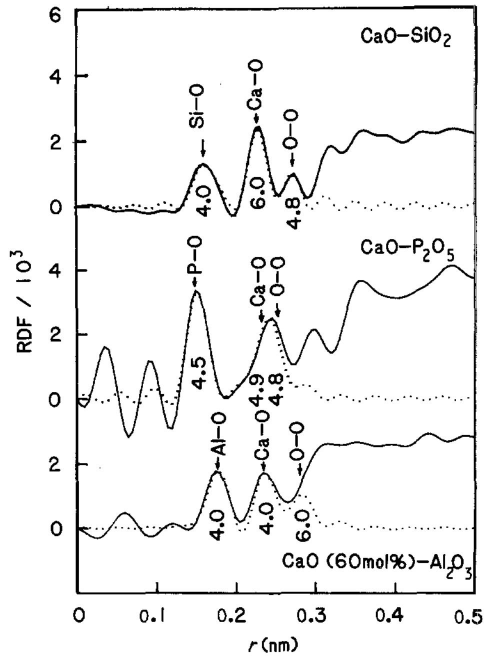

Figure 3 Electron radial distribution functions (RDFs) for $CaOSiO_2$, $CaOP_2O_5$ and 60 mol % CaO–40 mol % Al_2O_3 glasses. The solid line is the measured curve and the dotted line is the sum of the first three pair functions.

A similar analysis has been made for three kinds of glasses containing CaO and the resultant RDFs are given in Fig. 3. The near neighbour distances and their coordination numbers for a few pairs of current interest obtained in this work are summarized in Table I, together with magnesia phosphate and silicate glasses. Because in the case of $CaOP_2O_5$, the resolution of the peaks for Ca–O and O–O pairs is not good enough to evaluate correctly their coordination numbers by the pair functions, the information of the geometry of the PO_4 tetrahedron and the ionic radii of Ca^{2+} and O^{2-} were employed. It should also be noted

TABLE I Parameters of the near neighbour correlations determined by the use of the pair functions

Sample	*i–j* pair	r_{ij} (nm)	N_{ij} (atoms)
MgO SiO_2	Si–O	0.161	4.5
	Mg–O	0.210	4.0
	O–O	0.265	5.0
MgO P_2O_5	P–O	0.153	4.0
	Mg–O	0.206	4.0
	O–O	0.250	4.5
CaO SiO_2	Si–O	0.161	4.0
	Ca–O	0.228	6.0
	O–O	0.267	4.8
CaO P_2O_5	P–O	0.152	4.5
	Ca–O	0.233	4.9
	O–O	0.252	4.8
60 mol % CaO 40 mol % Al_2O_3	Al–O	0.175	4.0
	Ca–O	0.238	4.0
	O–O	0.280	6.0

r_{ij} = average distance, N_{ij} = average coordination number.

that the oscillations in the shorter distance side of the first peak are relatively distinct in the phosphate glass. According to the methods proposed by Finbak [24, 25] and Morimoto [26], the corresponding oscillations do not seem to be attributable to the spurious ripples arising from the finite truncation of $Q_{\max}$ in the Fourier transformation by Equation 2. Serial tests using numerical analysis by computer and the similar structural investigation in another sample of a $CaOP_2O_5$ glass 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 Fig. 3. Although these oscillations before the first peak do not critically affect the evaluation of an interionic distance and its coordination number for the resolved first peak, the origin of these oscillations cannot be identified with certainty at the present time.

The results of Fig. 3 clearly indicate the formation of SiO_4 in silicate, PO_4 in phosphate and AlO_4 in aluminate, respectively. They are well-recognized as the local ordering unit structure in these glasses. On the other hand, the oxygen coordination numbers around Ca^{2+} are six in silicate, five in phosphate and four in aluminate, respectively. The present results on silicate and aluminate glasses are in good agreement with the literature values [27]. Thus, the number of oxygens which surround calcium is concluded to depend upon the component of network formers of SiO_2, P_2O_5 and Al_2O_3. It contrasts with the oxygen coordination number around magnesium confirmed by the results of Fig. 2.

From the present systematic X-ray diffraction study of phosphate glasses including silicate and aluminate glasses for comparison, it is possible to draw the following conclusions about the structure of magnesia and calcia metaphosphate glasses. All the phosphate ions are tetrahedrally bonded to four oxygens with an average P–O distance of 0.152 to 0.153 nm in both magnesia and calcia phosphate glasses. The oxygen coordination number around magnesium is four, whereas the value of five is quantitatively suggested for the corresponding value around calcium. The schematic diagram of the difference in the oxygen coordination numbers between magnesium and calcium in phosphate glasses is illustrated in Fig. 4, to interpret the present experimental results by X-ray diffraction. Further higher order correlations are, of course, required to construct a detailed structural model, but it is out of the scope of this work. It is our intention that the present experimental facts should support the previous discussion [7–9] on phosphate glasses in terms of the concepts of the normal and abnormal types first suggested by Kordes and his colleagues [10], rather than the discussion of Isozaki *et al.* [28] who proposed the six coordinated magnesium in phosphate glass, based on measurements of X-ray emission spectra.

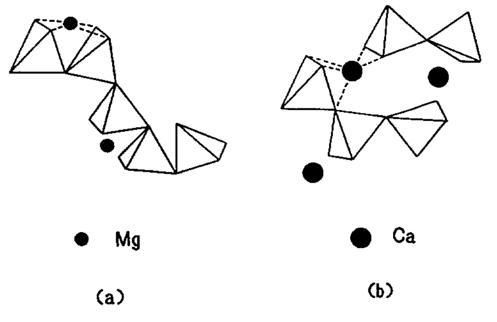

Figure 4 Schematic diagrams of the atomic structural models for (a) $MgOP_2O_5$ and (b) $CaOP_2O_5$ glasses.

Acknowledgements

This work was carried out as a part of the research project on Structure and Properties of Slags. Financial support from Nippon Steel Corporation is gratefully acknowledged.

References

1. T. MINAMI and J. D. MACKENZIE, *J. Amer. Ceram. Soc.* **60** (1977) 232.
2. J. A. WILDER Jr, *J. Non-Cryst. Solids* **38/39** (1980) 879.
3. F. PERNOT, J. ZARZYCKI, F. BONNEL, P. RABIS-CHONG and P. BALDET, *J. Mater. Sci.* **14** (1979) 1694.
4. M. AKAO, H. AOKI and K. KATO, *ibid.* **16** (1981) 809.
5. G. DE WITH, H. J. A. VAN DIJK, N. HATTU and K. PRJS, *ibid.* **16** (1981) 1592.
6. S. SAKKA and T. KOKUBO, *Ceram. Jpn* **17** (1982) 342.
7. M. ASHIZUKA, T. SAKAI and A. IWATA, *Yogyo-Kyokai-Shi* **91** (1983) 86.
8. M. ASHIZUKA and T. SAKAI, *ibid.* **91** (1983) 176.
9. M. ASHIZUKA and R. C. BRADT, *J. Amer. Ceram. Soc.* **65** (1982) C-70.
10. E. KORDES, W. VOGEL and R. FETEROWSKY, *Z. Elektrochem.* **57** (1953) 282.
11. E. KORDES and R. NIEDER, *Glastech. Ber.* **41** (1968) 41.
12. E. KORDES and J. NAVARRETE, *ibid.* **46** (1973) 113.
13. J. BISCOE, A. G. PINCUS, C. S. SMITH Jr and B. E. WARREN, *J. Amer. Ceram. Soc.* **24** (1941) 116.
14. G. W. BRADY, *J. Chem. Phys.* **28** (1958) 48.
15. R. A. HARPER and A. S. POSNER, *Mater. Res. Bull.* **5** (1970) 129.
16. F. BETTS and A. S. POSNER, *ibid.* **9** (1974) 353.
17. B. E. WARREN, in "X-ray Diffraction" (Addison-Wesley, Reading, 1969).
18. C. N. J. WAGNER, *J. Non-Cryst. Solids* **31** (1978) 1.
19. Y. WASEDA, "The Structure of Non-Crystalline Materials" (McGraw-Hill, New York, 1980).
20. R. L. MOZZI and B. E. WARREN, *J. Appl. Crystallogr.* **2** (1969) 164.
21. A. RAHMAN, *J. Chem. Phys.* **42** (1965) 3540.
22. A. J. GREENFIELD, J. WELLENDORF and N. WISER, *Phys. Rev.* **A4** (1971) 1697.
23. K. SUZUKI and P. A. EGELSTAFF, *Can. J. Phys.* **52** (1974) 241.
24. C. FINBAK, *Acta Chem. Scand.* **3** (1949) 127.
25. *Idem, ibid.* **3** (1949) 1293.
26. H. MORIMOTO, *J. Phys. Soc. Jpn* **13** (1958) 1015.
27. A. C. WRIGHT and A. J. LEADBETTER, *Phys. Chem. Glasses* **17** (1976) 82.
28. K. ISOZAKI, H. HOSONA, H. KOKUMAI, H. KAWAZOE, T. KANAZAWA and Y. GOSHI, *J. Mater. Sci.* **16** (1981) 2318.

*Received 9 March
and accepted 15 May 1987*