Formation of metallic cation-oxygen network in binary phosphate glass with anomalous thermal expansion coefficients

Oxide glass prepared by melt-quenching is usually composed of network former (NWF) and network modifier (NWM) groups [1]. P_2O_5 is generally classified as NWF groups from the viewpoint of glass-forming ability. However, P_2O_5 differs from other NWF oxides since the P=O bond allows delocalized electrons in phosphate glasses. Phosphate glasses are often considered for practical applications because of their durability but also have significant potential for several other uses owing to their distinctive physical and structural properties. Understanding the network structure of a phosphate glass system is therefore one of the most important unresolved issues facing glass science.

In contrast to the conventional NWF group, several metal oxides, which are classified as intermediate groups, can act as either NWF or NWM groups [1], depending on the glass composition. Zinc oxide is classified as being part of the intermediate group. Zinc phosphate (ZP) glass is a promising material for use as lead-free sealing glass or as a good host for emitting centers. The structure of ZP glass has been extensively analyzed using various methods. Several groups have also performed structural analyses using neutron and X-ray diffraction with the aid of reverse Monte Carlo (RMC) modeling [2,3]. However, previous investigations have shown that metal oxides have a small oxygen coordination in glass since the rigid glass network enables the metastable species of metal oxides to be sustained in the glass matrix. Therefore, the modeling of a reliable atomic arrangement in glass based on metal-cation-specific experimental data and conventional diffraction data is essential. In this article [4], we report on the reliable atomic configuration of ZP glass from the viewpoint of 3D network linkage, i.e., the connectivity of each oxide. We use a combination of ^{31}P magic angle spinning (MAS) NMR, Zn *K*-edge extended X-ray absorption fine structure (EXAFS), and X-ray and neutron diffraction data [2] to determine the dependence of this connectivity on the chemical composition and on the zinc coordination. Moreover, we discuss the relationship between several properties and the glass structure and find that the thermal expansion coefficient is sensitive to the substitution of the phosphate chain network by a network consisting of Zn-O units in zinc-rich glass.

Figure 1(a) shows the thermal expansion curves for xZnO-(100-x)P_2O_5 (xZP) glasses ($x = 58$, 60, 65, and 70). Figure 1(b) shows the linear thermal expansion coefficients of these glasses as a function of the amount of ZnO. The thermal expansion coefficients increase with increasing ZnO fraction. If the glass network is similar, i.e., if the glass has the same NWF, the lower T_g glass generally exhibits a higher thermal expansion coefficient. However, the obtained results show that a higher T_g glass exhibits a higher thermal expansion coefficient. The anomaly of the thermal expansion coefficients suggests that the glass networks might change depending on ZnO fraction.

We performed RMC modeling using data of XRD measured at SPring-8 **BL04B2**, neutron diffraction [2], and EXAFS measured at **BL01B1** with several constraints on the coordination numbers to identify several chemical coordination states around phosphorus in order to reveal the behavior of the oxygen coordination around zinc. The modeling was based on the results of ^{31}P MAS NMR, which revealed a significant change in Q^2 species between the 60ZP and 70ZP glasses. Figure 2 shows the experimentally determined X-ray and neutron structure factors, $S(Q)$ and EXAFS $k^3\chi(k)$, respectively, of the 60ZP and 70ZP glasses along with those obtained by the RMC modeling. Since there is good agreement between the experimentally determined and RMC-modeled data, we have succeeded in modeling atomic configurations that reproduce the X-ray, neutron, EXAFS, and NMR data.

To understand the 3D atomic configuration in ZP glasses, the connectivity of PO_4 and Zn-O polyhedra was analyzed. Figures 3(a) and 3(b) show the 3D linkage of the phosphate network in terms of the chain length, as calculated from the total number of atoms in each phosphate. Figure 3(a) shows the fraction of Q^1 units and Q^2 chains of PO_4 polyhedra in the 60ZP glass and a typical RMC-modeled Q^2 chain. As can be seen in Fig. 3(b), the 70ZP glass consists of only isolated PO_4 tetrahedra (Q^0) and P_2O_7 dimers (Q^1). Thus, our RMC models reproduce the modification of the 3D phosphate network as observed

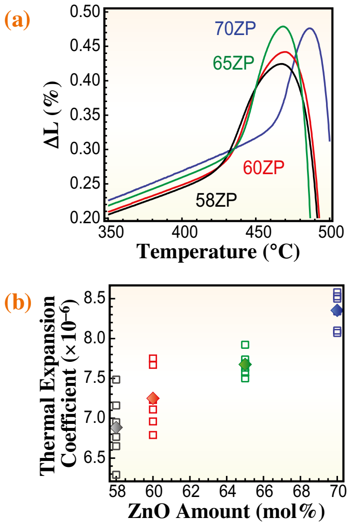

Fig. 1. Linear thermal expansion coefficients of ZP glasses. **(a)** Thermal expansion curves of 58ZP, 60ZP, 65ZP, and 70ZP glasses. **(b)** Thermal expansion coefficients below T_g as a function of ZnO. The 70ZP glass exhibits a higher T_g and a higher thermal expansion coefficient below and above T_g than those of 60ZP glass. Closed squares indicate mean values [4].

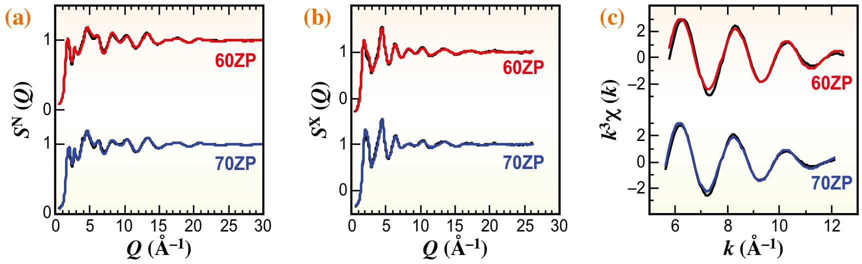

Fig. 2. Comparison between neutron/synchrotron X-ray data and RMC model for the ZP glasses. **(a)** Neutron total structure factor $S^N(Q)$, **(b)** X-ray total structure factor $S^X(Q)$, and **(c)** EXAFS $k^3\chi(k)$. The EXAFS $k^3\chi(k)$ data were obtained by back Fourier transformation of $|FT(R)|$ for the first correlation peak. Black curve, experimental data; colored curve, RMC model [4].

by ^{31}P MAS NMR. The probabilities of the formation of polyhedral connections between PO_4 tetrahedra and Zn-O polyhedra were calculated in order to elucidate the mechanism of glass formation in binary oxide glasses with low amounts of network former. The total number of atoms constituting the Zn_xO_y units was estimated to determine the origin of the glass network in the glass. As the figure shows, the Zn_xO_y units do not form a network in 60ZP glass, and the size of the fragments (consisting of up to 41 atoms, as shown in the inset of Fig. 3(c)) is <20 Å. In contrast, 10% of the Zn_xO_y units in the 70ZP glass form networks consisting of more than 40 atoms, as manifested by their atomic configurations consisting of up to 1,300 atoms, as shown in the inset of Fig. 3(d). The unusual network structure units formed by the Zn_xO_y polyhedra can be attributed to the smaller oxygen coordination of the zinc than that of the ZnO crystal; the high glass-forming ability of the 70ZP glass stems from this small oxygen coordination. On the other hand, it is suggested from our RMC model that the small Zn-O coordination is a signature of the network former, according to Zachariasen's rule [1], in our model for 70ZP glass.

In summary, by performing structural modeling based on a combination of an advanced quantum beam technique and spectroscopic measurement, we found that the thermal expansion coefficient reflected the substitution of the network of phosphate by a network consisting of Zn_xO_y units in zinc-rich glasses. The results obtained in this study via several structural analysis methods are significant since they clearly reveal the fundamental properties that determine the functionality of these types of glass. The results obtained in the current study should constitute a significant milestone in the design of phosphate glasses for practical applications.

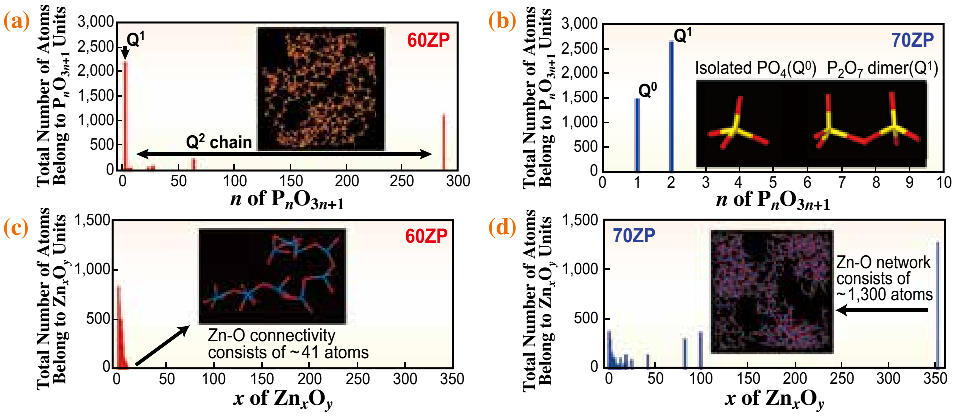

Fig. 3. Connectivity of PO_4 tetrahedra and Zn_xO_y polyhedra in the ZP glasses. Size distribution of PO_4 tetrahedral chains in **(a)** 60ZP glass and **(b)** 70ZP glass. Size distribution of Zn_xO_y polyhedral chains in **(c)** 60ZP glass and (d) 70ZP glass. P, Zn, and O atoms are shown in yellow, blue, and red, respectively [4].

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