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# The structure of lead–indium phosphate and lead–scandium phosphate glasses

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## Abstract

Lead–indium phosphate and lead–scandium phosphate glasses exhibit a number of useful properties such as the efficient transmission of visible light, a high index of refraction, a low preparation temperature and low melt viscosity, and good chemical durability. The short-range and intermediate-range order structures of a  $(\text{PbO})_{56.3}(\text{In}_3\text{O}_2)_{4.2}(\text{P}_2\text{O}_5)_{39.5}$  and a  $(\text{PbO})_{54.2}(\text{Sc}_3\text{O}_2)_{3.6}(\text{P}_2\text{O}_5)_{42.2}$  glass were studied by time-of-flight neutron diffraction. From analyses of the measured structure factors of these glasses and those of a pure  $\text{P}_2\text{O}_5$  glass and a  $(\text{PbO})_{58.8}(\text{P}_2\text{O}_5)_{41.2}$  glass, both the breakdown of the  $\text{P}_2\text{O}_5$  network structure to short  $\text{PO}_4$ -chain-like units by the addition of metal oxides and the local environment of the dopant In and Sc ions were characterized. The In–O and Sc–O distance (2.1 Å) is shorter than that of Pb–O (2.52 Å) and the coordination number for Sc–O (6.1) and In–O (5.5) is slightly higher than that of Pb–O (5.3). © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The generally poor chemical durability of phosphate glasses has previously hampered large-scale investigations of their potential for industrial applications. However, the addition of appropriate modifying cations into the parent  $\text{P}_2\text{O}_5$  network former is known to produce phosphate glasses with drastically different physical and chemical properties [1–6]. An understanding of the atomic and electronic structural changes brought about by these network modifiers is essential to the

continuing development of phosphate-based novel materials and devices for technological applications.

The structure of vitreous  $\text{P}_2\text{O}_5$  consists of a 3D network of corner-sharing  $\text{PO}_4$  tetrahedra, each of which has a P=O (non-bridging O) double bond. The structural instability arises from the energetic imbalance between the  $d\pi$ – $\pi$  bonding character in the terminal P=O and the bridging P–O–P configurations which tends to break up the cross-linking network. [7] Accordingly, introducing metal oxides (MO) into  $\text{P}_2\text{O}_5$  will generate additional non-bridging O–M–O linkages across different  $\text{PO}_4$ -chains thereby forming a more stable structure [2]. In the case of oxides of divalent metals such as MgO or PbO, in principle, all the

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P=O bonds are replaced by P–O–M configurations at 33 mol% of metal ions. The 3D network transforms into a complex PO<sub>4</sub>-chain-like structure in which the average number of PO<sub>4</sub> units per chain varies from ∞ (metaphosphate) at 50 mol% to 2 (pyrophosphate) at a 66.7 mol% metal oxide concentration [2].

In reality, the chain-like structure and consequently the origins of the physical behavior, of phosphate glasses are poorly understood. The lead–phosphate glass system is one of the more extensively studied cases. Although binary PbO–P<sub>2</sub>O<sub>5</sub> glasses near the metaphosphate composition are somewhat susceptible to aqueous corrosion and crystallization at low temperatures [8], their chemical durability can be enhanced dramatically by adding a third metal-oxide component. Moreover, the resulting ternary glasses may exhibit unique properties that are desirable for novel applications. Sales and Boatner [9,10] have evaluated the durability and other properties of lead–iron phosphate glasses and indicated their potential application as a storage medium for high-level nuclear wastes. The same authors also searched for durable and optically clear lead–phosphate-based glasses and identified two candidates, namely Pb–In–P–O and Pb–Sc–P–O glass compositions [11]. These glasses have an index of refraction of 1.75–1.83 in the visible region, an ultraviolet absorption edge at a wavelength near 300 nm and strong infrared absorption beyond 2800 nm. The preparation temperatures are relatively low (900–1000°C) and the chemical durability and resistance to both weathering and  $\gamma$ -radiation are good. These glasses contain less than 5 mol% of In<sub>2</sub>O<sub>3</sub> or Sc<sub>2</sub>O<sub>3</sub>, hence their mechanical properties are similar to the corresponding binary lead–phosphate glasses. However, since the optical properties depend critically on the inter- and intra-ionic transitions of electrons as influenced by the dopant ions, information regarding the local environment of the In and Sc ions is valuable to theoretical modeling of the optical characteristics. Using the method of neutron diffraction, we have studied the structure of (PbO)<sub>56.3</sub>(In<sub>3</sub>O<sub>2</sub>)<sub>4.2</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>39.5</sub> and (PbO)<sub>54.2</sub>(Sc<sub>3</sub>O<sub>2</sub>)<sub>3.6</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>42.2</sub> glasses that were optimized for their optical properties. In this paper, we report the intermediate-to-short range atomic order pertinent

to the polymeric PO<sub>4</sub>-chain structure in these glasses as well as the In–O and Sc–O spatial coordination. The neutron diffraction results of (PbO)<sub>58.8</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>41.2</sub> and P<sub>2</sub>O<sub>5</sub> glasses are also presented in order to distinguish the effects of In<sub>2</sub>O<sub>3</sub>, Sc<sub>2</sub>O<sub>3</sub> and PbO on the structures of these glasses.

## 2. Experimental details

The preparation method and the basic chemical and optical properties of (PbO)<sub>56.3</sub>(In<sub>3</sub>O<sub>2</sub>)<sub>4.2</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>39.5</sub> and (PbO)<sub>54.2</sub>(Sc<sub>3</sub>O<sub>2</sub>)<sub>3.6</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>42.2</sub> glasses were described in detail previously [11]. The (PbO)<sub>58.5</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>41.2</sub> glass was prepared from calcining the proper mixture of reagent grade PbO and H<sub>3</sub>PO<sub>4</sub> (85%) liquid. The material was melted in a platinum crucible for 3 h in air at 1173 K, then quenched into a preheated stainless steel mould. The anhydrous P<sub>2</sub>O<sub>5</sub> glass was prepared according to a procedure described elsewhere [12,13]. The compositions of all the glasses are batched compositions. Possible deviations from the batched compositions due to weight loss, for example from volatilization of P<sub>2</sub>O<sub>5</sub>, are estimated to be much less than 1 mol%. Water retention is not a problem for the present lead–(indium or scandium) phosphate glasses with PbO concentration beyond the metaphosphate composition. In preparing the P<sub>2</sub>O<sub>5</sub> glass, all materials were handled in an Ar dry-box atmosphere (O<sub>2</sub> + H<sub>2</sub>O < 2 ppm) and the glass was melted and quenched in a vitreous carbon crucible which was sealed inside a silica ampoule. Neutrons are very sensitive to the presence of residual protons because of the large scattering cross-section of hydrogen. We found no measurable intensities from hydrogen in the form of inelasticity effects in the diffraction data or hydrogen local vibrations in spectroscopic data. The mass densities of the (PbO)<sub>56.3</sub>(In<sub>3</sub>O<sub>2</sub>)<sub>4.2</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>39.5</sub>, (PbO)<sub>54.2</sub>(Sc<sub>3</sub>O<sub>2</sub>)<sub>3.6</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>42.2</sub>, (PbO)<sub>58.5</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>41.2</sub> and P<sub>2</sub>O<sub>5</sub> glasses are 5.30, 5.20, 5.250 and 2.385 g/cm<sup>3</sup>, respectively.

Powdered glass samples about 10 g each were used for the neutron diffraction experiments conducted on the Glass, Liquid and Amorphous-Materials Diffractometer (GLAD) [14] at the Intense Pulsed Neutron Source of Argonne National

Laboratory. Bursts of polychromatic (cold-to-epithermal) neutrons were incident on the sample and the total scattering intensities were recorded by a bank of position-sensitive detectors covering a wide range of scattering angles ( $8 < 2\theta < 120^\circ$ ). The intensity profile as a function of neutron wavevector,  $I(Q)$ , was obtained by the time-of-flight technique. Overlapping data sets from different detectors were combined, normalized to the incident flux, corrected for absorption, multiple scattering and self-scattering using a standard procedure and were then merged to obtain the neutron-weighted average structure factor  $S(Q)$  over a  $Q$  range of 0.5 to  $\sim 40 \text{ \AA}^{-1}$ . This large  $Q$  range is essential to an accurate assessment of the near-neighbor atomic correlation in a glass.

Indium represents an infrequent case in which resonance occurs in the scattering of slow neutrons from the  $^{115}\text{In}$  nuclei (95.7% abundance), causing severe neutron absorption at energies near the nuclear resonance. Since  $Q$  varies as  $\sin\theta$  at a fixed energy, a resonance appears at different  $Q$  values depending on the angle at which the scattering is observed. Fig. 1 shows the neutron intensity spectra observed at two typical scattering angles. At  $2\theta = 27.5^\circ$ , strong absorption due to resonances of the  $^{115}\text{In}$  nuclei at 1.46 and 3.86 eV was seen at 12.5 and  $20 \text{ \AA}^{-1}$ , respectively, whereas at  $2\theta = 92.5^\circ$ , the intensity profile is not affected because the reso-

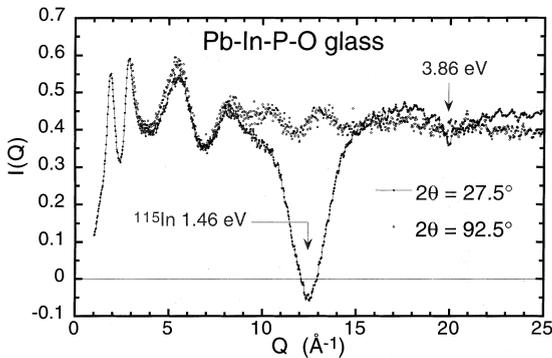


Fig. 1. The neutron-intensity spectra of the Pb–In–P–O glass observed at scattering angles of  $27.5^\circ$  and  $92.5^\circ$ . In the  $27.5^\circ$  spectrum, resonances of the  $^{115}\text{In}$  nuclei result in a depletion of the intensity at  $12.5$  and  $20 \text{ \AA}^{-1}$ . These resonances are not seen in the  $92.5^\circ$  spectrum because they occur at much higher  $Q$  ( $> 35 \text{ \AA}^{-1}$ ).

nances occur at  $Q$  values beyond  $35 \text{ \AA}^{-1}$ . This makes it straightforward to identify those portions contaminated by the resonances and to avoid including them in the merged data set.

### 3. Experimental results and analysis

Glasses do not exhibit long-range order, so it is conventional to express their structure in terms of distribution functions obtained from the Fourier transform of their structure factors. The neutron-weighted pair correlation function  $G(r)$  is obtained from

$$G(r) = 1 + \frac{1}{2\pi^2\rho_0} \int_0^\infty [S(Q) - 1] Q^2 \frac{\sin Qr}{Qr} dQ, \quad (1)$$

where  $\rho_0$  is the density. In practice, the integration is carried out up to a finite  $Q$  value ( $Q_{\max}$ ) dictated by the experiment and, consequently, Eq. (1) is modified so as to reduce the spurious ripples introduced by the finite cutoff, as follows:

$$G(r) = 1 + \frac{1}{2\pi^2\rho_0} \int_0^{Q_{\max}} M(Q) \times [S(Q) - 1] Q^2 \frac{\sin Qr}{Qr} dQ, \quad (2)$$

where  $M(Q)$  is a modification function due to Lorch [15]. To accurately determine the average bond lengths and coordination numbers, it is convenient to express the results in terms of the total distribution function  $T(r)$ :

$$T(r) = 4\pi r \rho_0 G(r). \quad (3)$$

The peak positions in  $T(r)$  represent the most probable (average) bond distances for various combinations of elements because  $T(r)$  is symmetrically broadened as a result of the finite upper limit  $Q_{\max}$ . The radial distribution function  $N(r)$  is given by

$$N(r) = 4\pi r^2 \rho_0 G(r). \quad (4)$$

$N(r) dr$  has a direct physical interpretation as the number of atoms lying within a range  $(r, r + dr)$  from any given atom. The area under a peak in  $N(r)$  is directly proportional to the coordination number of a pair of atoms. In order to determine

the areas of these peaks which may overlap with each other, we first fit the  $T(r)$  with multiple Gaussian functions convolved with the instrumental peak-shape function. The positions and areas of the peaks are then derived from the fitting parameters.

Using  $r_1 \cong 1.54 \text{ \AA}$  as the mean nearest P–O bond length for phosphate glasses [16], the approximate characteristic lengths,  $L = 2\pi/Q$ , for short-range order (SRO,  $r_1 Q > 4$ ), intermediate-range order (IRO,  $2 < r_1 Q < 4$ ) and extended-range order (ERO,  $r_1 Q < 2$ ) roughly correspond to  $L < 3$ ,  $3 < L < 5$  and  $L > 5 \text{ \AA}$ , respectively. The present GLAD diffractometer provided reliable data over the  $Q$ -range appropriate to the characterization of SRO and IRO [14]. For investigations of possible extended-range order structures, measurements extending to smaller  $Q$  values would be more suitable.

### 3.1. Lead–indium phosphate glass

Fig. 2 shows the measured  $S(Q)$  of the  $(\text{PbO})_{56.3}(\text{In}_2\text{O}_3)_{4.2}(\text{P}_2\text{O}_5)_{39.5}$  glass and of a pure, anhydrous  $\text{P}_2\text{O}_5$  glass. In  $\text{a-P}_2\text{O}_5$  the first two peaks at  $1.30$  and  $2.12 \text{ \AA}^{-1}$  are characteristic of its IRO of the 3D network of  $\text{PO}_4$  tetrahedra. A drastic change of the IRO in the  $(\text{PbO})_{56.3}(\text{In}_2\text{O}_3)_{4.2}(\text{P}_2\text{O}_5)_{39.5}$  glass can be seen from the replacement of the two peaks of  $\text{a-P}_2\text{O}_5$  by a single peak for  $\text{a-Pb-In-P-O}$  at  $1.90 \text{ \AA}^{-1}$ , which corresponds to a correlation length of  $3.3 \text{ \AA}$ . This indicates that the IRO structure in  $\text{a-P}_2\text{O}_5$ , characterized by the corner-sharing  $\text{PO}_4$  tetrahedra

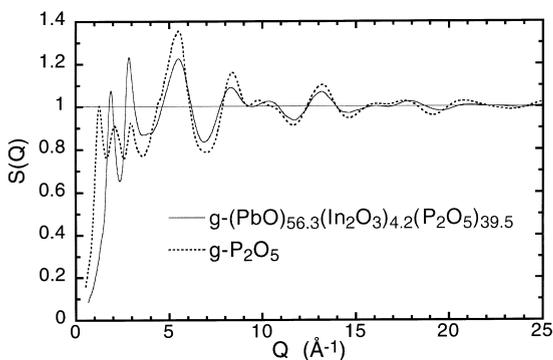


Fig. 2. The structure factors of the Pb–In–P–O and pure  $\text{P}_2\text{O}_5$  glasses.

each of which is occupied by three bridging and one terminated oxygen vertices, is broken down into smaller units by the modifier cations. On the other hand, for  $Q > 2.5 \text{ \AA}^{-1}$ , the peak maxima in the  $S(Q)$  of pure  $\text{a-P}_2\text{O}_5$  and the Pb–In–P–O glass coincide. The main difference in the high- $Q$  data between two glasses is that the widths of the oscillations in  $S(Q)$  are somewhat sharper in pure  $\text{a-P}_2\text{O}_5$ . This indicates that the SRO related to the P–O and O–O spatial correlation in these two glasses is similar: the larger widths and stronger damping of the oscillations for the Pb–In–P–O glass may reflect the smaller weight (scattering cross-section) of the P–O correlation and/or a narrower distribution of bond lengths and bond angles between  $\text{PO}_4$  units in pure  $\text{a-P}_2\text{O}_5$ . Therefore, the effects of structural modification by the metal cations occur mainly in the IRO, while the SRO of the basic  $\text{PO}_4$  tetrahedral units is retained.

The  $T(r)$  of the Pb–In–P–O glass, obtained according to Eqs. (1) and (2) where a Lorch function was used in the Fourier transform with  $Q_{\text{max}} = 25 \text{ \AA}^{-1}$ , is shown in Fig. 3(a). It oscillates about a line with a slope given by the density of the glass. The peak centered at  $\sim 1.54 \text{ \AA}$  corresponds to the mean nearest P–O distance, as observed in the diffraction data of many phosphate glasses [1,17–22]. The peak at  $\sim 2.5 \text{ \AA}$  includes a major contribution of the nearest O–O correlation as well as the Pb–O correlation. For comparison, the  $T(r)$  of pure  $\text{a-P}_2\text{O}_5$ , scaled by a normalization factor of 0.6 so as to produce the same area under the first P–O peak, is also shown in Fig. 3(a). It can be seen that within the region of  $2\text{--}3 \text{ \AA}$  there is excess intensity in the Pb–In–P–O glass data which arises from the In–O and Pb–O coordination. (A comparison of the curves at longer distances is not valid because the structure of the  $\text{PO}_4$  network is significantly affected by the introduction of  $\text{PbO}$  and  $\text{In}_2\text{O}_3$ .)

In order to extract more information about the SRO exhibited by the lead and indium ions, we fitted the P–O and O–O peaks in the scaled  $T(r)$  curves of pure  $\text{a-P}_2\text{O}_5$  in Fig. 3(a) by Gaussian functions and then removed the fitted Gaussians from the  $T(r)$  of the Pb–In–P–O glass. The residual  $T(r)$ , as shown in Fig. 3(b), reveals two broad peaks that can be attributed to In–O and Pb–O correlation at about  $2.1$  and  $2.5 \text{ \AA}$ , respectively, for

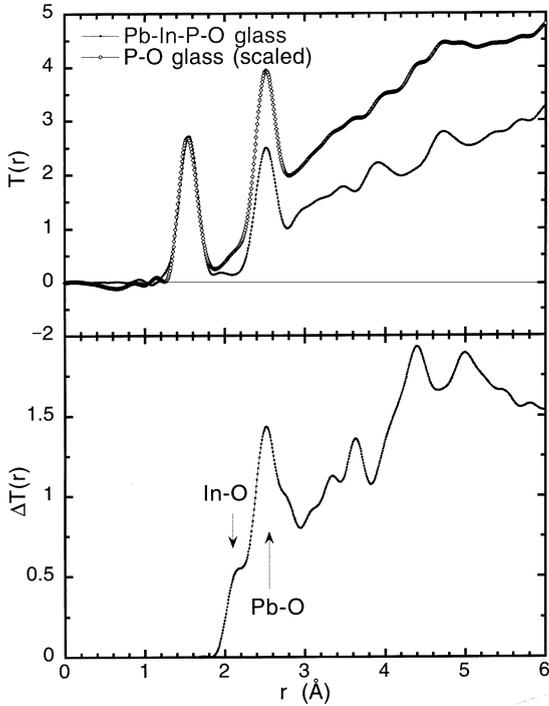


Fig. 3. (a) The total distribution functions of the Pb–In–P–O and pure  $P_2O_5$  glasses. The  $T(r)$  of the  $P_2O_5$  glass was scaled by a normalization factor of 0.6 so that both curves cover the same area under the first P–O peak. (b) The residual  $T(r)$  obtained by subtracting the fitted Gaussian functions for  $T(r)$  of the P–O glass from the  $T(r)$  of the Pb–In–P–O glass. Small oscillations at  $r < 2$  Å due to truncation errors in the Fourier transformations were ignored.

the Pb–In–P–O glass. Based on this information we performed a peak-fitting analysis of the P–O, In–O and Pb–O+O–O contributions, which is described in Section 3.2. The average distance ( $2.10 \pm 0.04$  Å) and coordination number ( $5.5 \pm 0.5$ ) for the In–O pair were found to be close to the octahedral arrangement of oxygens around a central indium atom (In–O bond length of 2.18 Å) in the  $In_2O_3$  crystal structure [23].

### 3.2. Lead–scandium phosphate glass

Unlike indium, scandium has a large coherent scattering cross-section and exhibits no resonance within the neutron energy range of interest here, hence the  $(PbO)_{54.2}(Sc_2O_3)_{3.6}(P_2O_5)_{42.2}$  glass is more suitable for neutron studies. In order to achieve a

quantitative analysis of the local environment of the  $Sc^{3+}$  ions, we prepared a  $(PbO)_{58.8}(P_2O_5)_{41.2}$  glass for diffraction measurements under identical experimental conditions. As can be seen in Fig. 4, a significant difference only appears at the low- $Q$  region. In other words, the presence of the Sc atoms mainly affects the IRO structure.

Fig. 5(a) shows the  $T(r)$  functions of lead–phosphate glasses with and without Sc. The good data quality allowed the use of a  $Q_{max}$  ( $\sim 34 \text{ \AA}^{-1}$ ) higher than that in the case of a-Pb–In–P–O. The peak centered at 1.54 Å corresponds to the mean nearest P–O distance. The peak at 2.52 Å includes a major contribution of the nearest O–O correlation as well as the Pb–O correlation. The residual  $T(r)$  obtained by subtracting the Pb, P and O contributions of the a-Pb–P–O data from the data of the a-Pb–Sc–P–O reveals the correlation of Sc and O around 2.0–2.1 Å. We fitted the  $T(r)$  profiles representing the appropriate P–O, Pb–O+O–O and Sc–O for both glasses. The result of the fit for the a-Pb–Sc–P–O is shown in Fig. 5(b). The average bond distance and coordination number of P–O ( $1.54 \pm 0.01$  Å,  $4.0 \pm 0.1$ ), Pb–O (2.52 Å, 5.3) and O–O (2.52 Å, 3.67) are the same for the two glasses. In the calculations of Pb–O coordination number, we assumed an identical Pb–O and O–O bond distance which was determined by the position of the single peak at 2.52 Å. The  $N_{O-O}$  coordination number was first determined from the composition of the Pb–P–O or Pb–Sc–P–O glass using the expression [24]

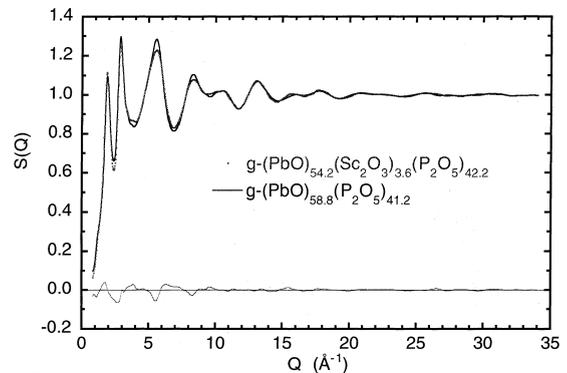


Fig. 4. The structure factors of the Pb–Sc–P–O and Pb–P–O glasses. The difference- $S(Q)$  is shown at the bottom of the graph.

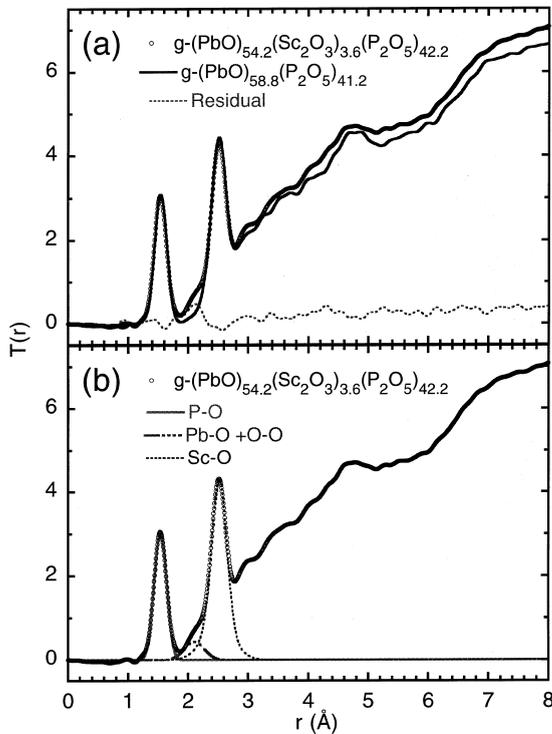


Fig. 5. (a) The total distribution functions of Pb–Sc–P–O and Pb–P–O glasses and the residual  $T(r)$  (bottom curve). (b) A fit of the  $T(r)$  of the Pb–Sc–P–O glass with convolved Gaussian functions representing the correlations of nearest atomic pairs.

$$N_{\text{O-O}} = \frac{24}{5 + y}, \quad (5)$$

where  $y$  is the molar ratio of PbO to  $\text{P}_2\text{O}_5$  and the corresponding contribution in  $T(r)$  was evaluated. An  $N_{\text{Pb-O}}$  of 5.2 was then obtained from the residual peak area. We did not assign any uncertainties to these values. Finally, the average bond distance and coordination number of Sc–O in the Pb–Sc–P–O glass ( $2.11 \pm 0.02$  Å,  $6.2 \pm 0.3$ ) were obtained (see Table 1). The coordination numbers for Pb–O<sup>1</sup> and Sc–O agree well with those found

<sup>1</sup> The definition of  $N_{\text{Pb-O}}$  is not consistent among different authors. Here we define  $N_{\text{Pb-O}}$  as the number of O atoms surrounding a Pb atom at a mean distance of  $\sim 2.52$  Å. The Pb–O numbers obtained by different authors are in good agreement.

in a lead–metaphosphate glass by Hoppe et al. [19] and Musinu et al. [25] and in a  $\text{Sc}_2\text{O}_3$  crystal by Knop and Hartley [26].

#### 4. Discussion

From the neutron diffraction results for the four phosphate glasses studied, certain definite observations can be made. First, the linkage of corner-sharing  $\text{PO}_4$  tetrahedra in vitreous  $\text{P}_2\text{O}_5$  is broken down by the incorporation of PbO. The origin of a prepeak at  $1.30 \text{ \AA}^{-1}$  followed by the otherwise first peak at  $2.12 \text{ \AA}^{-1}$  in the structure factor of  $\alpha\text{-P}_2\text{O}_5$  (see Fig. 2) was investigated by several authors [13,16,27–29]. Elliott [28] described the appearance of the prepeak by a model based on structural ordering of interstitial voids. Hoppe et al. [16,29] studied this feature by reverse Monte Carlo simulations and a careful comparison of it with the crystalline phases of  $\text{P}_2\text{O}_5$ . We attempted a qualitative description in terms of a Random Packing of Structural Unit (RPSU) model [30] based on oriented  $\text{P}_4\text{O}_{10}$  molecular-like units with pairwise orientations derived from the pseudo-body-center unit cell of the crystalline form of  $\text{P}_2\text{O}_5$  (space group  $R\bar{3}c$ ) [13,31,32]. Although the exact nature of the IRO is not completely understood, the present results support a transformation from a network structure in  $\alpha\text{-P}_2\text{O}_5$  to one of short  $\text{PO}_4$ -chains terminated by metal–oxygen bonds in the Pb–(In, Sc)–P–O glasses. Second, the SRO structure, i.e., P–O correlations in the  $\text{PO}_4$  distorted tetrahedra, does not change dramatically over the ultra- to meta- to pyro-phosphate composition range. Third, doping a small amount of  $\text{In}^{3+}$  and  $\text{Sc}^{3+}$  ions to the lead–phosphate glasses further changes the IRO. We analyzed the local structure of the In and Sc atoms by the methods described in Sections 3.1 and 3.2 and obtained consistent results for both cases. The correlation distances and coordination numbers of various atomic pairs in these four glasses are given in Table 1. The In–O and Sc–O distances (2.1 Å) were found to be shorter than that of Pb–O (2.52 Å) and the coordination number for In–O (5.5) and Sc–O (6.1) were found to be higher than that for Pb–O (5.3). The structural environment of In or Sc is smaller

Table 1  
The atomic correlations in phosphate glasses

Atomic pair		Glass sample	
		$\text{P}_2\text{O}_5$ ( $Q_{\text{max}} = 30$ ) ( $\text{Å}^{-1}$ )	$(\text{PbO})_{58.8}(\text{P}_2\text{O}_5)_{41.2}$ ( $Q_{\text{max}} = 30 \text{ Å}^{-1}$ )
		$(\text{PbO})_{56.3}(\text{In}_2\text{O}_3)_{4.2}$ $(\text{P}_2\text{O}_5)_{39.5}$ ( $Q_{\text{max}} = 25 \text{ Å}^{-1}$ )	$(\text{PbO})_{54.2}$ $(\text{Sc}_2\text{O}_3)_{3.6}(\text{P}_2\text{O}_5)_{42.2}$ ( $Q_{\text{max}} = 30 \text{ Å}^{-1}$ )
Correlation distance (Å)	Coordination number	Correlation distance (Å)	Coordination number
P–O	$1.54 \pm 0.01^a$	$1.54 \pm 0.01$	$1.54 \pm 0.01$
Sc–O/In–O	–	$2.10 \pm 0.04$	$2.11 \pm 0.02$
Pb–O	–	$2.52^b$	$2.52^b$
O–O	$2.52 \pm 0.02$	$2.52^b$	$2.52^b$
		Coordination number	Coordination number
		$3.9 \pm 0.2$	$4.0 \pm 0.2$
		–	$5.5 \pm 0.5$
		–	$5.27^c$
		$5.1 \pm 0.4$	$3.67^d$

<sup>a</sup> Average bond length of bridging P–O and terminal P=O obtained by fitting a single peak that contains two unresolved P–O distances.

<sup>b</sup> Position of single peak for Pb–O and O–O.

<sup>c</sup> Parameter was calculated from the total area of the single peak (Pb–O and O–O) and fixed value (O–O).

<sup>d</sup> Parameter was fixed.

and more compact than that of Pb, which suggests that the addition of  $\text{In}_2\text{O}_3$  or  $\text{Sc}_2\text{O}_3$  cannot be regarded as a simple replacement of corresponding Pb and O atoms.

## 5. Conclusions

The present study of the Pb–In–P–O and Pb–Sc–P–O glasses is motivated by their favorable optical characteristics combined with the unique physical properties of phosphate glasses such as their relatively low preparation temperature, low melt viscosity and large thermal expansion [11,33]. The optical behavior depends on, among other factors, the nature of the oxygen–metal electronic structure as well as the intra- and inter-ionic transitions associated with the bonding and anti-bonding states. Such electronic structure and the associated optical properties of amorphous semi-conducting materials are too complex to assess rigorously by theory [34]. Accurate structural information is often lacking. In the case of MO– $\text{P}_2\text{O}_5$  glasses, the increasing covalency and polarizability in going from Zn to Cd to Pb and the consequences to the ligand–field interactions between dopant ions and neighboring ions are noted by Klonkowski [35]. The optical basicity was estimated without the knowledge of the local environment of the dopant ions. For transition-metal ions with  $d^n$ -configurations, the optical properties are usually explained by excitations of  $d$ -electrons among the ligand–field-split states [36,37]. However, for Sc and In ions, the delocalized outer orbitals and their hybridization with the neighboring oxygen states are more important [38]. The present neutron data suggest that an octahedral surrounding ( $N_{\text{M–O}} = 6$ ) is appropriate for the modeling of the electronic environment for the In and Sc ions in lead–phosphate glasses.

A key factor in the potential applications of Pb–In–P–O and Pb–Sc–P–O glasses is the significantly enhanced chemical durability compared to the parent Pb–P–O glasses. Sales and Boatner [11] demonstrated the excellent staining, acid and climate resistance of these glasses and discussed the corrosion mechanisms in terms of the hydration process and acid/base reactions in the kinetic

regime and long-term durability in the solubility-limit regime. This phenomenon is usually discussed in terms of the IRO structure introduced by the modifier cations, i.e., the induced structural organization of the building blocks of the  $\text{PO}_4$  tetrahedra and the  $\text{MO}_n$  polyhedra [39–42]. The present neutron-diffraction data clearly show the breakdown of the 3D corner-sharing network of  $\text{PO}_4$  tetrahedra in the lead phosphate glasses. This result is consistent with most diffraction and spectroscopic studies of many binary and ternary phosphate glasses [1,13,19–21,43–46]. Specifically, the Pb–O distance (2.52 Å) and coordination number (5.2) agree well with diffraction data obtained by Hoppe et al. [19] and Musinu et al. [47] and with the EXAFS results of Greaves et al. [25,45]. Furthermore, additional modifiers such as M=Fe, Al, or Cu added to lead- or alkali-phosphate glasses play a key role in the strengthening of the glass structure by cross-linking different  $\text{PO}_4$  chains. The local structure of these cross-linking junctions is thought to consist of  $\text{MO}_n$  polyhedra. Configurations of  $\text{FeO}_6$ ,  $\text{AlO}_4$ ,  $\text{AlO}_5$ ,  $\text{AlO}_6$ ,  $\text{MoO}_6$  and  $\text{CuO}_6$  have been proposed in various phosphate glasses [21,37,41,44,45,47,48]. The present study suggests that octahedrally coordinated  $\text{InO}_6$  and  $\text{ScO}_6$  structures are relevant to the increased chemical durability of Pb–In–P–O and Pb–Sc–P–O glasses.

The structure of the shortened  $\text{PO}_4$  chains in terms of their length and orientation distribution in phosphate glasses is another important structural factor. It was found empirically that a short average  $\text{PO}_4$  chain length in the glass structure is essential to high corrosion resistance. High-performance liquid chromatography measurements showed an average chain length of 2.2 and 3 for the Pb–In–P–O and Pb–Sc–P–O glasses, respectively and the chemical durability is somewhat higher for the Pb–In–P–O glass [11]. However, the spatial organization and length distribution of the chains cannot be assessed by the present neutron-diffraction experiment because the data did not extend to sufficiently low- $Q$  values. The nature of the  $\text{PO}_4$  chain-like structure should be manifested through the ERO in the diffraction profile. Investigations of the chain structure *in the solid state* by means of small-angle neutron scattering are currently under way.

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