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THE STRUCTURE OF LEAD-INDIUM PHOSPHATE GLASS

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ABSTRACT

Lead-indium phosphate glasses exhibit a number of useful properties such as a high index-of-refraction, low preparation temperature and melt viscosity, and good chemical durability. The structure of such a glass (composition in wt. %: 65 PbO, 29 P₂O₅, 6 In₂O₃) has been investigated by total neutron scattering using the GLAD diffractometer at Argonne's spallation neutron source IPNS. Peaks corresponding to the P-O, Pb-O/In-O, and O-O pairs were observed in the radial distribution function. The short-range structure in the glass, in terms of average coordination numbers and bond distances, is compared with those of a pure P₂O₅ glass and with the crystal structure of lead pyrophosphate, Pb₂P₂O₇. Unlike silicate glasses in which the SiO₄ tetrahedra form a 3-dimensional network, the PO₄ tetrahedra in phosphate glasses form a chain-like structure. The structural modification by the lead cations in phosphate glasses appears to occur mainly in the medium range-affecting the lengths and connectivity of the chain-like structure.

INTRODUCTION

Phosphate glasses are important for a variety of reasons encompassing both fundamental and technological relevance. Although the hygroscopic and volatile nature of pure vitreous P₂O₅ has hindered an extensive investigation of its glassy state, recently studies of the glass transition and viscosity,¹ and of the atomic dynamics² have been reported. The structure of vitreous P₂O₅ is thought to consist of a 3-dimensional network of corner-sharing PO₄ tetrahedra each of which is decorated with a non-bridging P=O bond. As M₂O (M = network-modifying elements such as alkali and transition metals) is added to form a binary glass of xM₂O+(1-x)P₂O₅, a structural transformation from a 3-D network of P₂O₅ (x=0) to a complex chain structure takes place through the generation of additional non-bridging oxygens. Unlike pure v-P₂O₅, the preparation of xM₂O+(1-x)P₂O₅ (x > 0.5) glasses is relatively easy, and various binary and ternary phosphate glasses have found important applications ranging from ionic conduction to biomedical applications. Therefore, understanding the correlation between the structural modification induced by various metal-oxide additives and the physical and chemical properties represents one of the most important aspects of materials research on phosphate glasses.

Among the two-component phosphate glasses, lead-phosphate glasses have been studied extensively. Although the low softening temperature and melt viscosity of lead phosphate glasses are attractive from the point of view of materials preparation, the relatively poor chemical durability when exposed to aqueous conditions was a major drawback to commercial utilization. However, Sales and Boatner³ have found that by adding a small amount (< 10 wt %) of iron oxide, the resulting dark-brown ternary Pb-Fe-P glasses show a dramatic improvement in the chemical durability without significantly raising the preparation temperature or the melt viscosity. In searching for an equally durable but optically clear glass, these workers have identified two useful candidates, Pb-In-P-O and Pb-Sc-P-O glasses.³ 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 to 1000° C), and the chemical durability and resistance to both weathering and γ-radiation are good. In a previous study³, the length distribution of the PO₄ tetrahedral chains in Pb-In-P-O and Pb-Sc-P-O glasses was determined by a novel liquid chromatographic technique. These PO₄ chains are held together by bonds connecting the non-bridging O of the tetrahedra and the metal cations. In this paper, we present the results of a neutron-diffraction study of the short-range atomic order in a Pb-In-O glass where we attempt to make an identification of the In-O and Pb-O spatial coordinations.

EXPERIMENTAL DETAILS

A lead-indium-phosphate glass composed of 65 PbO, 29 P₂O₅, and 6 In₂O₃ (wt. %) was prepared by a method described in detail elsewhere.³ The neutron time-of-flight diffraction experiment was carried out using the Glass, Liquid and Amorphous Diffractometer (GLAD) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. The use of cold-to-epithermal neutrons in conjunction with the large solid-angle coverage, position-sensitive detectors on GLAD permits simultaneous measurements of coherent scattering from the sample over a wide range of wavevectors Q .⁴ Overlapping data sets from different detectors are combined, normalized to the incident flux, corrected for absorption, multiple scattering and self-scattering, and are then merged to obtain the structure factor $S(Q)$. For transition-metal elements such as indium, severe neutron absorption occurs at certain neutron energies corresponding to nuclear resonance. Because Q at a fixed energy varies as $\sin \theta$, where 2θ is the scattering angle, such resonances appear at different Q values depending on the angle at which scattering is observed. Fig. 1 shows the neutron intensity spectra, $I(Q)$, observed at two typical scattering angles of 27.5° and 92.5°, where strong absorption due to resonances of the ¹¹⁵In nuclei at 1.46 and 3.86 eV were seen separately at 12.5 and 20 Å⁻¹, respectively. This makes it straightforward to identify the portions affected by the resonances and to avoid including them in the merged data set. As a result, the structure factor $S(Q)$ can be obtained over a Q range of 0.5 to 25 Å⁻¹, as shown in Fig. 2. This large Q range is essential to an accurate assessment of the near-neighbor atomic correlation in a glass.

Figure 1. The neutron-intensity spectra of Pb-In-P-O glass observed at scattering angles of 27.5° and 92.5°. In the 27.5° spectrum, resonances of the ¹¹⁵In nuclei in the glass result in a depletion of intensity at 12.5 and 20 Å⁻¹. These resonances occur at much higher Q (> 35 Å⁻¹) in the 92.5° spectrum.

Figure 2. The structure factor of Pb-In-P-O glass.

RESULTS AND DISCUSSION

Glasses do not possess 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 pair correlation function $G(r)$ is obtained from

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

where ρ_0 is the density. To minimize the Q -dependent effect of the resolution, it is conventional to express the results in terms of the total distribution function $T(r)$ and the radial distribution function $N(r)$ which are given by

$$T(r) = 4\pi r \rho_0 G(r), \quad (2)$$

and

$$N(r) = 4\pi r^2 \rho_0 G(r). \quad (3)$$

$N(r)dr$ 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 the atoms.

Fig. 3 displays $T(r)$ as obtained from the diffraction measurement of the Pb-In-P-O glass. It oscillates about a line with a slope equal to the density of the glass. The peaks in $T(r)$ represent the most probable (average) bond distances for various combinations of elements.

The peak centered at $\sim 1.55 \text{ \AA}$ corresponds to the mean nearest P-O distance, as observed in the diffraction data of many phosphate glasses. 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. Since there are many possible atomic pairs in the Pb-In-P-O glass, it is useful to compare the data with those of other related glasses obtained under identical conditions by the GLAD diffractometer. Recently we succeeded in preparing a pure P_2O_5 glass and measured its neutron static and dynamic structure factors at IPNS.⁵ We find that for $Q > 7 \text{ \AA}^{-1}$, the peak maxima in the $S(Q)$ of pure v- P_2O_5 and the present 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 v- P_2O_5 . This indicates that, besides a narrower distribution of bond lengths and bond angles in pure v- P_2O_5 , the short-range ($r < 3 \text{ \AA}$) P-O and O-O spatial correlation in these two glasses is similar. Therefore, the effects of structural modification by the metal cations occur mainly in the medium-range ordering. For comparison, the $T(r)$ curve of Pure v- P_2O_5 , which was scaled by a normalization factor of 0.6 to cover the same area under the first P-O peak (as in the Pb-In-P-O glass) is also shown in Fig. 3. It can be seen that within the region of 2-3 $\text{\AA}$ there is excess intensity in the Pb-In-P-O glass which may originate from the In-O and Pb-O coordination. (A comparison of the curves at longer distances is not valid because it requires using the low- Q data, which are markedly different between the two glasses.)

Figure 3. The total distribution functions of Pb-In-P-O and P-O glasses. The $T(r)$ of the P-O glass was scaled by a normalization factor of 0.6 so that both curves cover the same area under the first P-O peak.

In order to extract more information, albeit qualitative, about the short-range structure exhibited by the lead and indium ions, we fitted the P-O and O-O peaks in the $T(r)$ curves of pure v- P_2O_5 in Fig. 3 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. 4, reveals two broad peaks that may be attributed to In-O and Pb-O correlation at about 2.1 and 2.5 $\text{\AA}$, respectively, for the lead-indium-phosphate glass. From a fit of the $T(r)$ we also obtained, according to Eq. (3), the coordination numbers of 3.7 and 4.5 for P-O and O-O atomic pairs in the v- P_2O_5 .

Figure 4. The residual $T(r)$ obtained by subtracting the fitted $T(r)$ of P-O glass from the fitted $T(r)$ of Pb-In-P-O glass. Small oscillations at $r < 2$ Å due to truncation errors in the Fourier transformations were ignored.

The results from the above analysis are consistent with the expected structure estimated from the diffraction data of a $(\text{PbO})_{59}(\text{P}_2\text{O}_5)_{41}$ glass and the $\text{Pb}_2\text{P}_2\text{O}_7$ crystal.⁶ In the lead-phosphate glass, a "two-peak" structure, which was attributed to P-O and Pb-O + O-O spatial correlation at ~ 1.54 and 2.52 Å, respectively, was observed in the $T(r)$ curve. According to the crystal structure of $\text{Pb}_2\text{P}_2\text{O}_7$ the shortest bond distances for the P-O, Pb-O and O-O atomic pairs vary between 1.49 to 1.65, 2.43 to 3.35, and 2.46 to 2.60 Å, respectively.⁶ The qualitative agreement of the bond distances among these materials supports the notion that, within a short range comparable to nearest-neighbor distances, the spatial correlations between atoms in the glassy and crystalline phases of lead-phosphate are similar. The combined neutron-diffraction data of pure $\nu\text{-P}_2\text{O}_5$, $(\text{PbO})_{59}(\text{P}_2\text{O}_5)_{41}$, and Pb-In-P-O glasses, in conjunction with the liquid chromatographic results of lead phosphate glasses^{3,7} confirm that the major structural modification by introduction of metal cations in phosphate glasses occurs in the medium range involving the PO_4 chains.

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