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Pressure-induced structural changes in titanophosphate glasses studied by neutron and X-ray total scattering analyses

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ABSTRACT

In this paper, the densification mechanism of two titanophosphate glasses (binary $73TiO_2$-$27P_2O_5$ and ternary $68TiO_2$-$5Al_2O_3$-$27P_2O_5$) is investigated. The glasses are densified by isostatic N_2-mediated pressure treatment at elevated temperature and the pressure-induced structural changes are studied by neutron and X-ray total scattering analyses. The medium range structure change is revealed from the change in the first sharp diffraction peak (FSDP), where the density increase by pressurization is correlated with the decreased medium range repeating spacing calculated from the position of FSDP. The hot compression treatment also increases the medium range order, as shown by the increased correlation length calculated from the width of FSDP. The short range structure changes are examined by separating P—O and Ti—O pair distribution functions (PDF) using differential neutron and X-ray PDFs. Pressurization is also found to increase the coordination number of Ti, as previously observed for other network formers in densified glasses.

1. Introduction

Titanophosphate glasses are interesting as optical materials with high-refractive index [1], and for photonic devices because of the large nonlinear refractive index related to Ti polyhedron distortion [2]. The polyhedral arrangements in pseudo binary glasses $x TiO_2$-$(100 - x)P_2O_5$ ($0.55 \leq x \leq 0.70$) (containing 5 mol% Al_2O_3 from crucible contamination) have previously been characterized by Raman, ^{31}P nuclear magnetic resonance (NMR) and X-ray absorption spectroscopies [3,4]. The glass structure consists of distorted Ti octahedra linked to orthophosphate units through Ti—O—P bonds, which has been confirmed by additional neutron and X-ray scattering analyses of the same glass series with $x = 0.60$ and 0.65. Ti—O coordination numbers of 5.9 and 5.7, respectively, were calculated from the Ti—O peak of correlation functions [5].

Although total scattering analysis has long been applied to explore the short and medium range structure of glassy materials (see the pioneering work of Warren [6] in 1934), it has not yet reached the same level of success as for its application to crystalline materials. The reason is simple: unlike crystalline materials, oxide glasses do not have long range periodicity above 10 Å. In the reciprocal space total scattering structure function, the lack of long range periodicity in a glass leads to only a few broad peaks compared to the many sharp peaks in the diffraction pattern of a crystalline material. Therefore, unlike the crystalline materials, for glassy materials no structural information can be derived directly from the reciprocal structure function. This reciprocal structure function needs to be Fourier transformed into the real space pair distribution function (PDF) to obtain the atomic pair distribution. As expected, there will be no peaks above 10 Å in PDF due to the lack of long range periodicity, and also severely overlapped atomic pairs in the medium range (3–10 Å). Even in the short range, the first nearest neighbor bonds (such as Si—O and Al—O in aluminosilicate glass) overlap due to intrinsic atomic thermal vibrations. As such, it is almost impossible to make direct and unambiguous interpretation of the amorphous structure from PDF with such low resolution signal at short range *r*. The only way to solve this problem is to amplify the signal, which is typically achieved from three common experimental practices. First, utilize the complementary information obtained from different analytical techniques, such as NMR and Raman spectroscopy. Second, analyze large quantities of glass materials with systematically varied compositions, and/or same composition but different structures induced by either thermal annealing or pressurization. For example, high temperature, moderate pressure (1 GPa) densification has been found to be an effective way to prepare bulk glasses with permanent structure

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changes [7]. This is the reason why both as prepared and pressurized binary and ternary glasses are studied in this work. The third option is to double the signal by measuring the samples using both neutron and X-ray scattering and further significantly amplify the signal by differential pair distribution function (DPDF), which will be explained in detail in Section 4. Following the second and third strategies to understand the structure of titanophosphate glass, we here study eight structure patterns instead of one data measurement (one composition with one structure by one radiation source). That is, four glass samples (as-prepared and pressurized) from two compositions, with two patterns (neutron and X-ray) for each sample. We note that all the samples have also been analyzed by NMR and Raman spectroscopy, but as the interpretation is non-trivial and neither supports nor contradicts the scattering analyses, these results are not reported here.

In addition to obtaining an improved understanding of the densification mechanism in titanophosphate glasses, the aim of this paper is to report the practical guidance of using neutron and X-ray total scattering analyses to extract all the available structure information, both in short and medium range. All the analyses are based on the correctly scaled total scattering structure function ($S(Q)$), for which the normalization procedure is described in Section 2. The medium range structure change is illustrated in Section 3, followed by the short range structure change using differential neutron and X-ray scattering in Section 4. Conclusions are given in Section 5.

2. Experimental procedure

2.1. Sample preparation

In the TiO_2-P_2O_5 binary system, glasses can be formed in the range of 30–45 mol% P_2O_5 [8,9]. In this study, the glass was batched with 27 mol% P_2O_5, the lowest limit as reported in Ref. [3]. The glass was melted in a Pt crucible to obtain the pure binary titanophosphate glass, not the pseudo binary titanophosphate glasses with Al_2O_3 crucible contamination [3,5]. For comparison, a ternary glass was also prepared by intentionally adding 5 mol% Al_2O_3. High purity powders of TiO_2, H_3PO_4 and Al_2O_3 (for ternary glass) were first mixed according to the target compositions and the mixtures were melted in Pt crucibles at 1450 °C for 2 h. The melts were roller quenched into 1 mm thick glass sheets on a steel plate.

The chemical compositions were measured by inductively coupled plasma optical emission spectroscopy, with results given in Table 1 with a relative uncertainty lower than ± 1%. The samples are named according to the composition. The glass transition temperatures (T_g) measured by DTA measurements (Seiko TG/DTA 220, with EXSTAR6000 software from Seiko Instruments Inc.) in N_2 atmosphere with 10 K/min heating rate are also listed in Table 1. The glass sheets were annealed at their respective T_g for 1 h and named as as-prepared glasses.

The as-prepared glasses were isostatically compressed at 1 GPa at their respective ambient pressure T_g in a gas pressure reactor with N_2 as the compression medium [7,10]. The permanent compression of the glass samples was achieved by maintaining the high pressure and high temperature conditions for 1 h before cooling to room temperature at 60 K/min, followed by decompression at room temperature at 30 MPa/min.

Table 1
Composition, glass transition temperature (T_g) and density (ρ) of as-prepared (AP) and pressurized (1 GPa) glasses.

Glass ID	Composition (mol%)			T_g	ρ (g/cm^{-3})		Rel. ρ change (%)
	TiO_2	P_2O_5	Al_2O_3	°C	AP	1 GPa	
73TP	72.7	27.3	0	646	3.04	3.14	3.3
5A68TP	67.3	27.7	5.0	634	2.93	3.07	4.9

The density of the as-prepared and 1 GPa compressed glasses was measured using Archimedes' principle with ethanol as the immersion medium. As shown in Table 1, pressurization increased the densities of both glasses from 3 to 5% relative.

2.2. Total scattering measurements

Time-of-flight (TOF) neutron scattering measurements were performed on the nanoscale-ordered materials diffractometer (NOMAD) at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory. Powdered samples (~ 200 mg) were loaded into a fused quartz capillary (3 mm diameter), and a data acquisition time of ~ 30 min was used, achieving a total proton charge of 1.8×10^{12}. Both neutron total scattering structure function and pair distribution function (NPDF) data were processed using the IDL software developed for the NOMAD instrument [11]. The background scattering intensity (empty capillary) was first subtracted from the raw scattering intensity. Then the resulting intensity was normalized by dividing the background corrected scattering intensity of a vanadium rod measured with the same configuration. The total scattering structure function $S(Q)$ was derived from Eq. (1) with least-square polynomial fitting of Eq. (2) to reach $S(Q) \rightarrow 1$ as $Q \rightarrow \infty$, where Q is the scattering vector.

$$S^N(Q) - 1 = \frac{I_{coh-I_{poly}}}{I_{poly}} \tag{1}$$

Here I_{coh} is the background corrected and vanadium-normalized scattering intensity, while I_{poly} is a polynomial equation.

$$\boldsymbol{I_{poly} = a_0 + a_1 q + a_2 q^2 + \ldots a_n q^n} \tag{2}$$

High-energy X-ray scattering data were collected on the 11-ID-B beamline of the Advanced Photon Source (APS) at Argonne National Laboratory using incident beam energy of 86.7 KeV (λ = 0.143 Å) and a Perkin Elmer amorphous silicon detector. The powdered samples were loaded into 1 mm diameter Kapton capillaries and measured for 12 min. The sample to-detector distance and tilt of the detector relative to the beam were refined with Fit-2D based on an image obtained for a CeO_2 standard. The raw images were reduced using Fit-2D to obtain one-dimensional scattering data (Q vs intensity) [12]. The X-ray data were analyzed using PDFgetX2 [13]. First, the contributions from the sample environment and background were subtracted from the raw intensities. Then the oblique incidence correction was applied. The resulting intensity was scaled to match the sum of self-scattering, $\Sigma_\alpha c_\alpha w_\alpha(Q) w^*_\alpha(Q)$, Compton scattering empirically corrected by X-ray energy, and the structure function. In practice, the structure function $S(Q)$ can be obtained by Eq. (3),

$$\boldsymbol{S^X(Q) - 1 = \frac{I_{scaled} - I_{Compton-} \sum_\alpha c_\alpha w_\alpha(Q) w^*_\alpha(Q)}{|\langle f(Q)\rangle|^2}}, \tag{3}$$

where $|\langle f(Q)\rangle|^2 = \sum_\alpha \sum_\beta c_\alpha c_\beta w_\alpha(Q) w^*_\beta(Q)$, c_α is the atomic fraction of chemical species α, w_α and $w_{*\alpha}$ are the X-ray form factor and its complex conjugate for species α, respectively, and they are Q-dependent. Empirically corrected Compton scattering is the adjusting parameter to fulfill $S(Q) \rightarrow 1$ as $Q \rightarrow \infty$.

2.3. Renormalization of total scattering structure function

As described above, both neutron and X-ray data reduction procedures utilize empirical correction terms to fulfill the $S(Q)$ criterion ($S(Q) \rightarrow 1$ as $Q \rightarrow \infty$). Such corrections are inadequate and will lead to the difference between true $S(Q)$ and measured/processed $S(Q)$, as shown by Eq. (4),

$$S_{true}(Q) = \alpha(Q) S_{measured}(Q) + \beta(Q), \tag{4}$$

where $\alpha(Q)$ is a multiplicative correction factor and can be simply treated as a Q-independent α. It comes from the fact that scattering data