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# Study of colloidal phosphorus in barium phosphate glasses by gas chromatography and SAXS

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#### Abstract

Barium phosphate glasses were obtained by melting different precursors in oxidizing or reducing atmospheres. These glasses become orange-red after a heat treatment at 520 °C for 2 h. Glass samples were analyzed by X-ray diffraction, optical absorption spectroscopy, and SAXS. Hydrogen released by the decomposition of  $NH_4H_2PO_4$  reduces the valence state of phosphorus ions to neutral, and colloidal dispersions formed during a post heat treatment are responsible for the glass coloration. The particle size-distribution function was determined by SAXS. The coloration effect is caused by the change of the particle size distribution. The maximum colloidal particle size is displaced from 75 to 250 Å after the heat treatment. © 2003 Elsevier B.V. All rights reserved.

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## 1. Introduction

Phosphate glasses with improved chemical durability were developed for nuclear wasteforms [1]. By selecting suitable compositions glasses with optical transparency could be obtained and used for optical applications [2]. However, not only the composition affects the optical properties but also processing steps, and the choice of the precursor compounds.

Several previous works on glasses showed that atoms in the neutral valence state can form aggregates during glass annealing, and colloidal dispersion can cause light scattering and rending a color to the glass [3–6]. The glass color depends on the type of element, and some known examples are red ruby glasses due to gold, yellow due to Ag, and blue due to Cu in the glass matrix. The same effect was also noticed in phosphate glasses prepared in a reducing atmosphere or when an reducing element is added to the basic glass composition [7,8]. Generally precursor compounds used to produce phosphate glasses release reducing gases that would reduce the valence state of phosphorus ions to the neutral state.

When these elements form aggregates an orange–red color is observed [7,8]. An indication of the existence of colloidal aggregates in the size range of  $0.3-0.6 \mu m$  was observed by scanning electron microscopy in aluminoborophosphate glasses [7]. In that case X-ray diffraction was not suitable to detect those phases. In the present work, barium phosphate glasses containing colloidal dispersions were prepared after suitable heat treatments rendering a typical color to the glasses. These glasses were analyzed by X-ray diffraction, and small angle X-ray spectrometry (SAXS) to estimate the colloidal aggregate size distribution. It is also shown that the reduction of the valance state of phosphorus ions to neutral state is caused by the reduction action of H<sub>2</sub> released during the decomposition of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>.

## 2. Experimental procedure

Phosphate glasses with composition 40 BaO  $\cdot$  60 P<sub>2</sub>O<sub>5</sub> (mol%) were produced by mixing different precursor compounds. Glasses produced by mixing P<sub>2</sub>O<sub>5</sub> and BaCO<sub>3</sub> are named PB1, and the ones produced by mixing NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and BaCO<sub>3</sub> are named PB2. The processing stages were identical for both types of glasses. The precursors were mixed during 30 min and melted at 1300 °C in an alumina crucible in air. The melt

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was stirred for homogenization, and cast in a pre-heated aluminum mold, annealed at 440 °C for 2 h, and finally cooled down to room temperature following the furnace thermal inertia.

The PB1 type glasses, initially colorless, were heat treated at 520 °C ( $T_g = 490$  °C) for 2 h. No changes in color and optical transparence were observed. To check the reducing action of hydrogen, a sample of the PB1 type glass was re-melted at 920 °C for 30 min in an electric furnace under a flow of a gas mixture of 10% H<sub>2</sub> and 90% N<sub>2</sub>. The glass sample was then withdrawn from the furnace and quenched to room temperature. The glass sample was colorless and named PB3. This sample was then heat treated at 520 °C for 2 h in air, and became yellowish due to the presence of colloidal dispersion. This glass was analyzed by optical absorption spectroscopy.

A sample of colorless PB2 type glass was cut in two  $10 \times 10 \text{ mm}^2$  pieces, grounded and polished to 150 µm thickness; one piece was re-heated to 520 °C for 1 h and became red. These samples were analyzed by SAXS to determine the size-distribution function of the colloidal particles. SAXS was performed in a Syncrotron by using an X-ray radiation with  $\lambda = 1.488$  A, and the scattered radiation was record as a function of the module of the scattering vector q by position sensitive detector. The distance between the sample and the detector was set to cover values of q in the range of 0.01–0.4 Å<sup>-1</sup>. The radiation beam path was under vacuum to reduce the parasite scattering due to air. Among 5-10 frames of 600 s were registered to follow possible radiation damages in the samples caused by X-ray, as well to monitor possible variations in the incident beam position. Since barium makes part of the glass composition, the glass absorption was relatively high.

#### 3. Results

Fig. 1 shows the optical absorption spectra for the PB1 and PB3 type glasses after a heat treatment at 520 °C for 2 h.

Fig. 2 shows the optical absorption spectra for the PB2 type glasses before and after a heat treatment at 520  $^{\circ}$ C for 2 h.

Fig. 3 shows the chromatography spectra of gas samples collected during the PB2 type glass preparation. Two spectra are shown: one when the melt just reached 1300 °C (these glasses are prone to be colored after heat treating at 520 °C), and one after 30 min in this temperature (these glasses are colorless even after heat treating at 520 °C). In both cases nitrogen and hydrogen were detected. The concentration of H<sub>2</sub> varied from 2% when the temperature just reached 1300 °C, to 0.4% after 30 min. An ultra pure H<sub>2</sub> standard sample was used for comparison.

Fig. 1. Optical absorption spectra for PB1 and PB3 type glasses after 520  $^{\circ}\text{C}/2$  h.

500

600

Wavelength (nm)

700

300

200

400

PB1

PB3



Fig. 2. Optical absorption spectra for PB2 type glasses before and after 520  $^{\circ}\text{C/2}$  h.



Fig. 3. Gas chromatography spectra for PB2 type glass.

Fig. 4 shows the X-ray diffraction patterns for the PB2 type glasses before and after a heat treatment at 520 °C for 2 h.

Fig. 5 shows the SAXS spectra for PB2 type glass.

2.5

2.0

1.5

1.0

0.5

0.0

Absobance (a.u.)

900

800



Fig. 4. X-ray diffraction patterns for PB2 type glass before and after 520  $^{\circ}\text{C/2}$  h.



Fig. 5. SAXS spectra for PB2 type glass before and after 520 °C/2 h.

# 4. Discussion

In Fig. 1 it is shown that the optical absorption for glasses re-melted in reducing atmosphere (PB3 type glass), and heat treated at 520 °C, are higher than for the PB1 type glasses (produced from  $P_2O_5$ ) in the range of 200–485 nm. Fig. 2 shows that the optical absorption for the PB2 type glasses, produced from NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, is higher in the range of 200–565 nm when these glasses are heat treated at 520 °C/2 h. That is an indication that phosphate glasses containing colloidal dispersions show an strong optical absorption close to 500 nm and that this effect can be reproduced when glasses are re-melted under a reducing gas flow. These results are in agreement with the previously published results for copper ruby glasses and phosphates that also present an absorption band at 560 nm [7,9].

Generally  $NH_4H_2PO_4$  is used as a precursor to prepare phosphate glasses because  $P_2O_5$  is hygroscopic and the volatilization rate is higher. Ammonium dihydrogen phosphate decomposes to  $P_2O_5$ , ammonia, and water (Eq. (1)). By increasing the temperature, ammonia decomposes to nitrogen and hydrogen (Eqs. (2)–(4)), that causes the reduction of the valence state of phosphorus ions to neutral [10]. The gas chromatographic spectra of Fig. 3 show that  $H_2$  is released during the decomposition of  $NH_4H_2PO_4$  to produce phosphate glasses.

$$4[NH_4H_2PO_4] \xrightarrow{400-600 \, {}^{\circ}C} 4NH_3 + 6H_2O + 2P_2O_5.$$
(1)

$$2\mathbf{NH}_3 + \mathbf{O} \to 2\mathbf{NH}_2 + \mathbf{H}_2\mathbf{O}.$$
 (2)

$$2NH_2 + O \rightarrow 2NH + H_2O. \tag{3}$$

$$2NH \rightarrow N_2 + H_2. \tag{4}$$

Therefore  $H_2$  reacts with  $P_2O_5$ , and phosphorus ions are reduced to  $P^0$  according to Eq. (5).

$$2P_2O_5 + 10H_2 \rightarrow 4P + 10H_2O.$$
 (5)

Neutral P atoms are spread out in the glass structure, and when these glasses are heat treated at temperatures close to  $T_g$ , aggregates of P atoms are formed, because of the faster relaxation. Therefore a colloidal dispersion is formed as shown schematically in Fig. 6.

As expected, and previously observed [6], no evidences of the presence of colloidal particles could be inferred from the X-ray diffraction patterns shown in Fig. 4. However, a small difference in the intensity of the diffraction halos is observed between glasses before and after heat treatment. This difference could be an indication that the degree of local ordering changed, but not enough to produce diffraction peaks. SAXS would be a more appropriate technique to detect such effect.

From the SAXS spectra shown in Fig. 5 it was possible to calculate the probability to have colloidal particles as a function of the particle size, assuming a spherical particle shape. The probabilities for the PB2 type glasses before and after heat treatment at 520 °C were calculated by using a software and are presented in Fig. 7.

It is noticed that for glasses without heat treatment the largest particles are approximately 250 Å. Mean-



Fig. 6. Schematic model for the colloidal dispersion in an glass structure.



Fig. 7. The probability to have colloidal particles as a function of the particle size (r is the equivalent spherical particle radius) for the PB2 type glasses with and without heat treatment at 520 °C.

while after heat treatment the largest particles are in the range of 370-380 A. That is also evidence that phosphorus atoms form colloidal particles in the heat treated glass matrix. This result is in agreement with previously results obtained for ruby copper and phosphorus glasses [7], where the presence of immiscible drops is not enough to produce colored glasses, but as the size of these drops increases an orange-red color is observed. From Figs. 7 and 2 it is noticed that the colloidal particle size increases, and colored glasses are observed, respectively. In the heat treatment temperature (520 °C), the P atoms relaxation is faster than at the annealing temperature (440 °C); therefore the colloidal particle size in the PB2 type glass is larger. Assuming again a spherical shape model and a dispersion of colloidal particles in the glass matrix, the size-distribution function (D) is calculated from the SAXS spectra, as shown in Fig. 8 for the PB2 type glass.

It is noticed that for the PB2 type glasses before heat treatment, the size-distribution function is bimodal with maxima located at 35 and 114 Å, respectively. After heat treating the sample, the size-distribution function is



Fig. 8. Size-distribution function (D) as a function of the equivalent spherical particle radius (r) for the PB2 type glass.

trimodal with maxima located at 35, 114, and 208 Å, respectively. It is also noticed that the size-distribution function peak at 35 Å is higher after the heat treatment; that means that new colloidal particles were formed. That is also evidence that the coloration of the glass is related to the change of the colloidal particle size.

## 5. Conclusion

Phosphate glasses produced from the decomposition of  $NH_4H_2PO_4$  show a typical coloration related to the presence of colloidal dispersion formed by neutral phosphorus atoms. This effect depends on the specific heat treatments. Phosphorus ions are reduced to the neutral valence state by the hydrogen released during the decomposition of the precursor compounds. A later heat treatment causes the increase of the colloidal particle size. Initially the particle size-distribution function is bimodal with maxima located at 35 and 114 Å, respectively. After the heat treatment, the size-distribution function is trimodal with maxima located at 35, 114, and 208 Å, respectively. The coloration of the glass depends on the colloidal particle size distribution.

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