

# Formation of colloidal phosphorus particles in barium phosphate glasses

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*Barium phosphate glasses 40BaO.60 P<sub>2</sub>O<sub>5</sub> mol% were prepared by melting mixtures of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and BaCO<sub>3</sub>. Coloured glasses were obtained after heat treatment at 520°C. The colour is caused by colloidal dispersions formed by phosphorus atoms that were reduced by hydrogen released from the decomposition of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. Samples were stored at room temperature for one year and x-ray diffraction and differential thermal analyses were performed to determine structural change. Colloidal particles formed during the glass preparation process are brought into contact with air when the glass monoliths are milled and participate in chemical reactions, finally forming the crystal phase Ba(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>. After heating at 238°C, water molecules are released and Ba(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> is transformed to β-Ba(PO<sub>3</sub>)<sub>2</sub>. The latter compound is stoichiometrically consistent with the original glass composition.*

Several types of phosphate glasses with improved chemical durability have been developed recently which can even be compared to the better known, commercial silicate glasses.<sup>(1)</sup> These glasses were suitable for nuclear wasteforms, and when optical transparent in the ultraviolet region, they could potentially be used as optical fibres and as laser components.<sup>(2)</sup>

For a long time it has been known that colloidal dispersions of silver, copper, gold and phosphorus are responsible for the colour in glasses.<sup>(3,4)</sup> Phosphate glasses prepared in reducing conditions have colloidal dispersions in their structure.<sup>(5)</sup> When chemical compounds containing ammonium are used as glass precursors, hydrogen is released upon heating. Phosphate glasses prepared under these conditions are usually colourless. However, after suitable heat treatment they become yellowish or orange, because of the presence of colloidal dispersions formed by phosphorus atoms reduced by hydrogen.<sup>(6)</sup> In the present work, barium phosphate glasses were prepared by using NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> as a precursor, and were stored at room temperature for one year. X-ray diffraction (XRD) and differential thermal analysis (DTA) were used to determine struc-

tural changes due to the presence of colloidal dispersions. It was observed that crystallisation was induced by colloidal particles formed by red phosphorus, one of the stable allotropic forms of phosphorus. Thermogravimetric measurements and infrared reflectance spectroscopy were used to determine mass loss and the water molecule content of the glasses, respectively.

## Experimental procedure

Phosphate glasses with composition 40BaO.60P<sub>2</sub>O<sub>5</sub> mol% were prepared by mixing NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and BaCO<sub>3</sub> for 30 min, and melting in an alumina crucible at 1300°C in air inside an electric furnace. The glass precursors were heated at 10°C/min up to 1300°C. Just after reaching this temperature, the liquid was cast into an aluminium mould previously heated at 520°C. A glass was obtained; it was heat treated at 520°C for 1 h and named PB1t. This glass is strongly yellowish in colour probably due to a relatively high amount of colloidal P<sup>0</sup> dispersions. By using the same preparation procedure, except that no heat treatment was performed after forming, the glass named PB1 was obtained. This glass is colourless and clear.

To verify if this effect depends on the starting compounds containing NH<sub>4</sub>, glasses were also obtained using P<sub>2</sub>O<sub>5</sub> as a glass precursor instead of compounds containing NH<sub>4</sub>, and the same experimental procedure was followed. These glasses do not show any coloration after heating at 520°C for 1 h. However, if NH<sub>4</sub>CO<sub>3</sub> is added to that mixture (a compound containing NH<sub>3</sub> and H<sub>2</sub>), the glasses so produced become coloured after heat treatment. The decomposition of NH<sub>4</sub>CO<sub>3</sub> releases the H<sub>2</sub> which causes the reducing action. Therefore we concluded that compounds containing NH<sub>4</sub> promote the glass coloration.

Glasses named PB2t and PB2 were also prepared by melting mixtures of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and BaCO<sub>3</sub>, keeping the liquid at 1300°C for 30 min and casting it in an aluminium mould. The glass type PB2t was heat treated at 520°C for 1 h, but no visual changes in colour were observed. The glass type PB2 was not heat treated. The absence of colour in these glasses is explained by assuming that the release of H<sub>2</sub> decreases as a function

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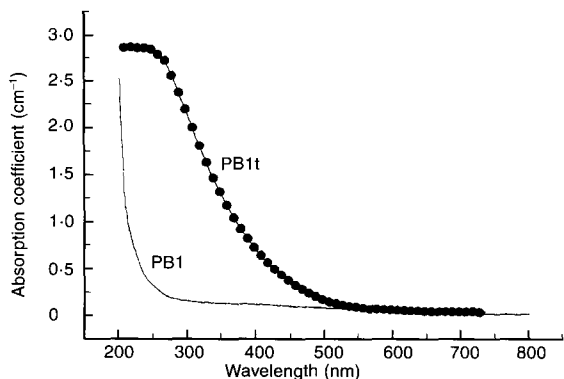


Figure 1. Optical absorption spectra for coloured and colourless glasses type PB1 and PB1t, respectively<sup>(6)</sup>

of time. Consequently the concentration of P atoms in the neutral valence state is relatively low because the liquid was kept at 1300°C for 30 min before casting.<sup>(6)</sup> Therefore, the concentration of colloidal dispersion in the glass types PB2t and PB2 is lower when compared to the glass types PB1t and PB1, and it is not enough to cause light scattering. PB1t glass samples were cut and polished in 10×10×1 mm<sup>3</sup> slices for optical measurements (CARY/OLIS model 17D). Powder samples were prepared for x-ray diffraction analyses (XRD) (Bruker-AXS model D8 Advance). As-prepared and one year-stored samples were also analysed by differential thermal analyses (DTA) (NETZSCH model 404S), and thermogravimetric analyses (SHIMADZU model TGA-50). In the case of infrared spectroscopy, the use of KBr was avoided to ensure that water molecules were from the glass samples and not from the KBr pellets. Therefore, the reflectance method (BOMEM model Series 100–Arid Zone) was used where glass powders were deposited on the surface of a ZnSe crystal.

Glasses were stored in air at room temperature in small dark closed plastic containers (35 cm<sup>3</sup>).

**Results and discussion**

The glass type PB1 is red-orange after heat treatment at 520°C/1 h. Assuming that the colour is caused by the presence of P<sup>0</sup>, as reported by Abe,<sup>(7,8)</sup> neutral phosphorus colloidal dispersions should be present in the glass structure after heating the samples close to the glass transition temperature, T<sub>g</sub>. These colloidal dispersions are responsible for the scattering and absorp-

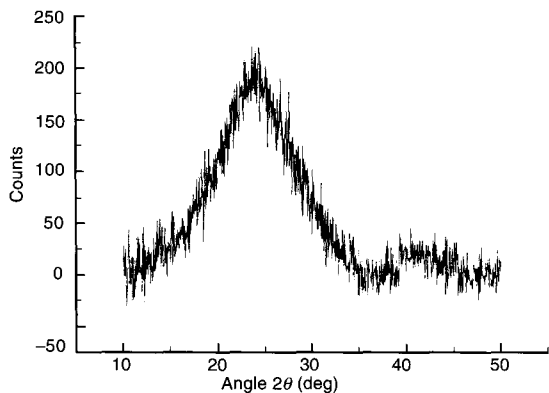


Figure 2. XRD pattern for the as prepared PB1 glass

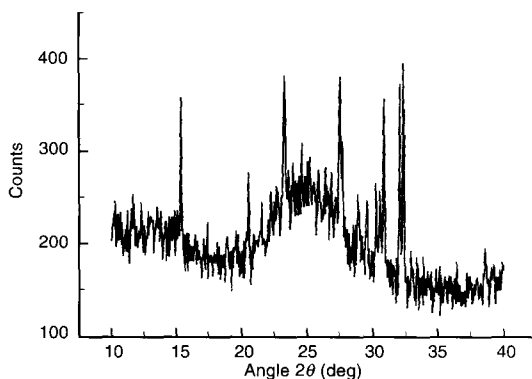


Figure 3. XRD patterns for the glass type PB1 after 1 year storage

tion of light.<sup>(9)</sup> Figure 1 shows the optical absorption spectra of colourless and coloured glass type PB1.

The maximum colloidal particle size is between 75 to 250 Å, as previously determined by SAXS.<sup>(6)</sup>

Figure 2 shows the XRD pattern for the as-prepared PB1 glass. There is no evidence of crystalline phases. Similar results were observed for PB1t, PB2 and PB2t glasses.

Glass powder samples were stored for 1 year to study the structural changes due to the colloidal dispersion in the glass structures. After 1 year these samples were analysed by XRD. Figures 3 and 4 show the XRD patterns for the glass types PB1 and PB1t.

Up to now, the crystalline phase indicated by the XRD peaks noticed for the glass type PB1 could not be identified by using the JCPDS files. Since the glass was not annealed, it is assumed that the thermal stresses could lead to the nucleation of a distorted crystalline structure, making it difficult to be identified from the XRD pattern.

From the XRD pattern of Figure 4 (glass type PB1t), Ba(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> (corresponding to the ICDD-JCPDS no. 32-0069) was identified. No crystalline phases were detected by XRD for glass type PB2 after 1 year storage. The presence of the crystalline phase Ba(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> was also determined for the glass type PB2t after one year storage.

Based on the experimental procedures used in the present work to prepare phosphate glasses, the glass types PB2, PB2t, PB1 and PB1t contain increased amounts of phosphorus colloidal dispersions and pronounced crystallisation, respectively. Therefore, it is

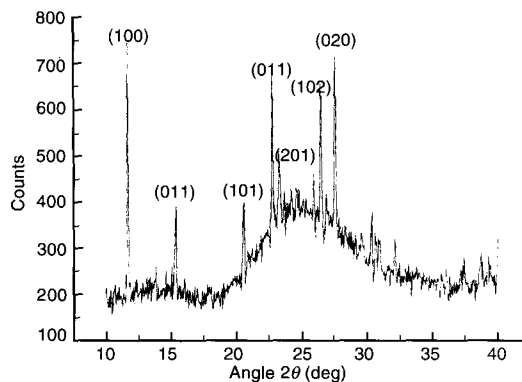
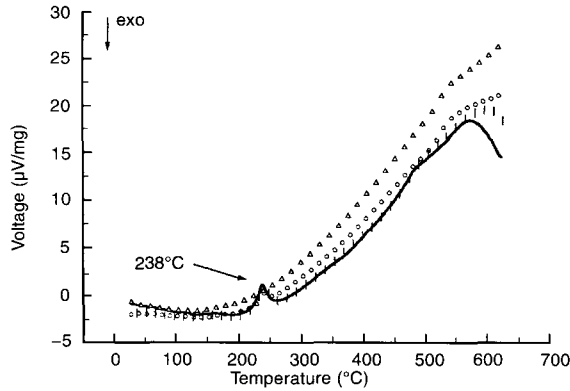


Figure 4. XRD patterns for the glass type PB1t after 1 year storage



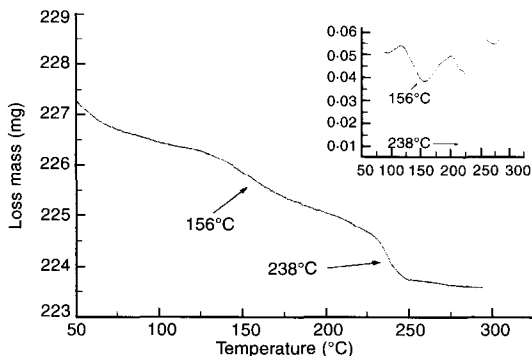
**Figure 5.** DTA curves for the glass types PB1, PB1t, PB2 and PB2t and  $T_g$  values after storing for one year  
 || PB1,  $T_g=488^\circ\text{C}$  - PB1t,  $T_g=480^\circ\text{C}$   
 $\Delta$  PB2,  $T_g=514^\circ\text{C}$   $\circ$  PB2t,  $T_g=511^\circ\text{C}$

assumed that phosphorus colloids contribute to the crystallisation process.

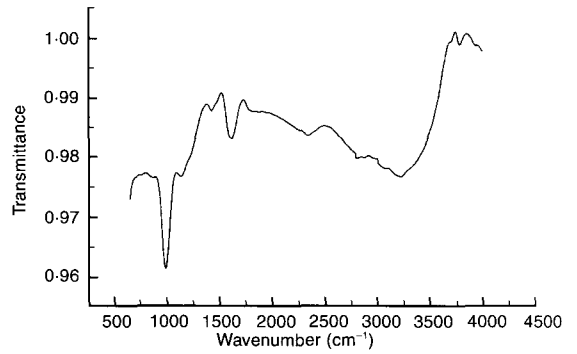
The XRD pattern from monolithic samples stored for 1 year do not show any evidence of crystalline phases. This result corroborates the fact that crystalline phases were not nucleated from the colloidal phosphorus (glass type PB1t) during this period of time, but some reaction was induced by milling the glass pieces.

The DTA curves for the glass types PB1, PB1t, PB2, and PB2t after one year storage are shown in Figure 5.

The curves are very similar to the ones obtained before storing, except for the presence of an endothermic peak located at  $238^\circ\text{C}$  (not noticed before storing) for the glass types PB1, PB1t and PB2t. This peak is attributed to the release of water molecules previously adsorbed by the samples during the prolonged storage time. It is noticed that for the glass types PB1 and PB1t (produced just after the liquid reached  $1300^\circ\text{C}$ ) the glass transition temperatures are very close (480 and  $488^\circ\text{C}$ , respectively). The same feature is noticed for the glass types PB2 and PB2t, that were produced from liquids kept at  $1300^\circ\text{C}$  for 30 min. However, in this case the  $T_g$  are 511 and  $514^\circ\text{C}$ , respectively. The difference of  $T_g$  between PB1, PB1t and PB2, PB2t can be caused by several effects such as the volatilisation of phosphorus when the liquid is thermally soaked at  $1300^\circ\text{C}$ , with consequent increase of barium oxide concentration in the final glass composition, the presence of different amounts and size of colloidal parti-



**Figure 6.** Thermogravimetric curve for glass type PB1t



**Figure 7.** Infrared reflectance spectrum for glass type PB1t after storing for 1 year at room temperature

cles in the glass matrix, different amounts of dissolute alumina in the melt deriving from the corrosion of the crucible walls or less  $\text{OH}^-$  contamination.

The thermogravimetric curve in Figure 6 shows a noticeable mass loss at  $238^\circ\text{C}$ . Therefore, the endothermic reaction detected by the DTA at  $238^\circ\text{C}$  might be related to this mass loss.

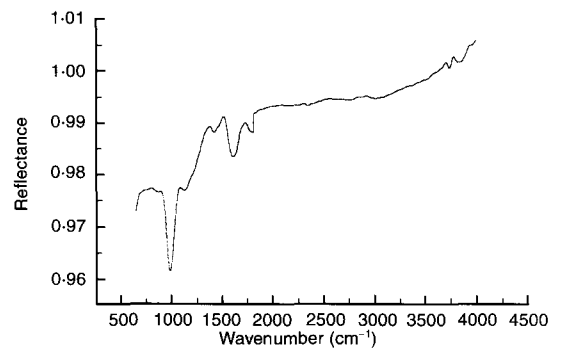
The mass loss at  $156^\circ\text{C}$  is not as pronounced as at  $238^\circ\text{C}$ . Samples were then heat treated at  $238^\circ\text{C}$ .

By comparing the infrared spectra of Figures 7 and 8 for samples with and without heat treatment at  $238^\circ\text{C}$  for 40 h, a change in the absorption intensity in the range  $2800\text{--}3400\text{ cm}^{-1}$ , assumed to be due to 'free' or 'bond'  $\text{OH}$  groups, is noticed. Therefore, the endothermic peak at  $238^\circ\text{C}$  in the DTA curves can be attributed to the water release. As the water molecules leave the samples, a mass loss is detected by the thermogravimetric analysis, Figure 7.

Assuming that the phosphorus colloidal dispersion is in the bulk of the glass monolithic, and therefore, not in contact with the atmosphere, when the glass is milled the phosphorus colloidal dispersion is brought into contact with air, and reacts with oxygen to form phosphorus pentoxide, according to the following reaction<sup>(10)</sup>



$\text{P}_2\text{O}_5$  is very hygroscopic and when in contact with the atmosphere, reacts with the water vapour producing  $\text{H}_3\text{PO}_4$ , according to the following reaction<sup>(10)</sup>



**Figure 8.** Infrared reflectance spectrum for glass type PB1t after storing for 1 year at room temperature, after heat treatment at  $238^\circ\text{C}$

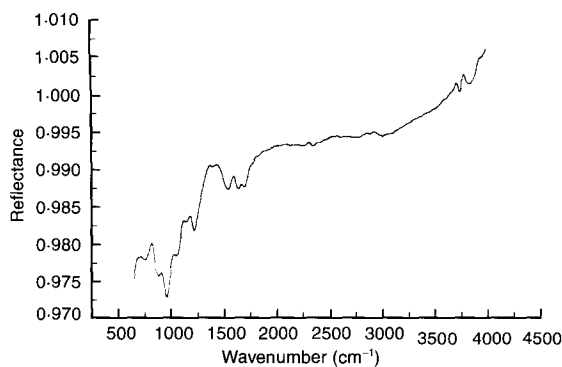
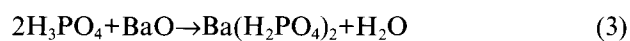


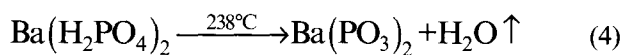
Figure 9. Infrared reflectance spectrum for the PB2 glass after storing for 1 year

The  $H_3PO_4$  then reacts with barium oxide (part of the glass composition) producing barium dihydrogen orthophosphate ( $Ba(H_2PO_4)_2$ ),<sup>(11,12)</sup> as follows



The XRD patterns show that  $Ba(H_2PO_4)_2$  is formed from the PB1, PB1t and PB2t powder glasses, after storing them for 1 year. For the PB2 glass, no infrared absorption bands corresponding to the  $OH^-$  groups are noticed in the reflectance spectra, Figure 9. Therefore, in this case, the  $Ba(H_2PO_4)_2$  crystalline phase is not also noticed.

According to previously reported results<sup>(11,12)</sup> by heating  $Ba(H_2PO_4)_2$  at  $238^\circ C$ , barium metaphosphate is produced according to



The PB2t glass was heated at  $238^\circ C$  for 40 h and the  $Ba(PO_3)_2$  phase was formed. Figure 10 shows the XRD patterns for the glass type PB2t after storing for 1 year and after heat treating at  $238^\circ C$  for 40 h. A variation of the XRD peaks is observed and the  $\beta$   $Ba(PO_3)_2$  crystalline phase (corresponding to the ICDD-JCPDS no. 43-0518) was identified after the heat treatment.

The powdered glasses remained coloured even after being stored for 1 year. This fact can be explained considering that the colloidal phosphorus inside the colourless phosphate glasses (glasses that were not annealed) are white phosphorus ( $P_4$ ) while red-orange glasses (glasses that were annealed) contain mainly red phosphorus.<sup>(8)</sup> White phosphorus is very unstable in contact with oxygen and can be oxidised, Equation (1); on the other hand, red phosphorus is relatively stable. Therefore PB1t glass powders did not change their coloration after 1 year storage, because only colloidal  $P_4$  s are oxidised to  $P_2O_5$ .

### Conclusions

Crystalline phases are nucleated in barium phosphate glasses containing colloidal dispersions when stored at room temperature for 1 year. Colloidal particles are formed during the glass preparation process, due to the reduction of phosphorus atoms by hydrogen re-

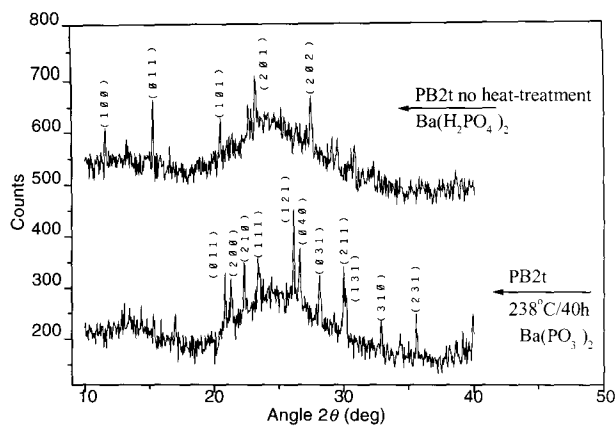


Figure 10. Comparison of the XRD patterns for the glass type PB2 after storing and heat treated at  $238^\circ C/40$  h, the  $\beta$ - $Ba(PO_3)_2$  crystalline phase was identified

leased during the decomposition of  $NH_4H_2PO_4$ . After glass milling, the colloidal dispersions are brought into contact with air and participate in chemical reactions during storage, finally forming the crystalline phase  $Ba(H_2PO_4)_2$ , identified by XRD. After heating at  $238^\circ C$ , water molecules are released, and  $Ba(H_2PO_4)_2$  is transformed into  $\beta$ - $Ba(PO_3)_2$ . The latter compound is stoichiometrically consistent with the original glass composition. The crystallisation peak for the  $BaO.60P_2O_5$  glass is usually at  $710^\circ C$ . Glasses produced according to the experimental procedure followed in the present work show a kind of crystallisation that unusually happens at lower temperatures.

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