



Characterization and structural investigation of lead borophosphate glasses modified by tungsten oxide



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ABSTRACT

The effect of WO_3 on the properties and structure of $\text{PbO}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5-\text{WO}_3$ quaternary system was studied. Glasses containing up to 60 mol% WO_3 were prepared and the variation of several physical properties was determined with respect to chemical composition in a broad compositional range. Chemical durability of WO_3 -containing glasses is very high and their thermal stability as well. Glass transition temperature increases with increasing WO_3 content up to 566 °C. Glass structure was studied by Raman spectroscopy and ^{31}P and ^{11}B MAS NMR spectroscopy. NMR spectroscopy reveals the formation of B–O–W linkages and also the existence of tetrahedral BO_4 units and trigonal units BO_3 in the glass structure. With increasing WO_3 content in the glasses, the number of starting tetrahedral $\text{B}(\text{OP})_3\text{O}$ units decreases and B–O–P bridges are replaced gradually by B–O–W and B–O–B bridges, while the number of BO_3 units increases. Raman spectra of the studied glasses possess a doublet of strong vibrational bands in the range at 800–1000 cm^{-1} , assigned to vibrations of W–O[−] and W=O bonds in tungstate structural units. In glasses with a higher WO_3 content WO_6 octahedra form tungstate clusters interconnected by W–O–W bridges as reflected in the Raman spectra. The formation of strong P–O–W and B–O–W linkages in the studied glasses explains high chemical durability of the glasses and the observed increase in the glass transition temperature.

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1. Introduction

Our previous studies [1–3] indicated that tungsten oxide WO_3 is able to induce large glass-forming regions both in phosphate and borophosphate glasses with a relatively high WO_3 content. Tungsten oxide containing glasses have been studied because of their unusual photochromic properties [4] and specific thermal, mechanical and optical properties which are obtained with the incorporation of tungstate units in the glass network [5]. Structural studies of the incorporation of tungsten oxide WO_3 into metaphosphate glasses were carried out by Araujo et al. [6] within the compositional series $(1-x)\text{NaPO}_3-x\text{WO}_3$ and Santagnelli et al. [7] within the compositional series $(1-x)\text{AgPO}_3-x\text{WO}_3$.

Glasses combining lead phosphates and tungsten oxide were studied as early as 1949 by Rothermel et al. [8], who determined the

glass-formation region in the $\text{PbO}-\text{WO}_3-\text{P}_2\text{O}_5$ ternary system. They also studied their X-ray and gamma-ray absorption for several glass compositions. The authors [8] observed that in contrast to the lead-silicate system, lead phosphate glasses dissolve large amounts of WO_3 . They explained the high solubility of WO_3 by the “intermediate” role of this oxide against P_2O_5 as a glass-former providing together a strong glass network. They also observed the blue colouration of glasses containing more than 20 wt% WO_3 or less than 50 wt% PbO . Owing to their high index of refraction and relatively low dispersion, they proposed their application for optical purposes.

Structural studies of $\text{PbO}-\text{WO}_3-\text{P}_2\text{O}_5$ glasses have been published recently [2]. Lead tungstate-phosphate glasses possess relatively high chemical durability and higher T_g values than the lead metaphosphate glass. Glasses with a medium WO_3 content also possess extremely good thermal stability. From structural studies by ^{31}P MAS NMR spectroscopy and Raman spectroscopy, the authors [2] found that the tungsten atoms in these glasses form predominantly WO_6 octahedra, although the existence of WO_4

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units cannot be excluded in the glasses with a high PbO content and a low P₂O₅ content. An extremely large glass-forming region was also reported in Pb₂P₂O₇–WO₃ system by Manzani et al. [9], who obtained and studied glasses containing 0–80 mol% WO₃.

This paper is devoted to the PbO–B₂O₃–P₂O₅–WO₃ glasses studied in two compositional series with the ratio B₂O₃/P₂O₅ = 10/40 and 20/30. We have determined their basic physical properties and studied their structure with ³¹P and ¹¹B MAS NMR spectroscopy and Raman spectroscopy. The ¹¹B MAS NMR spectroscopy possesses an ability to discriminate between tetrahedral BO₄ boron coordination and trigonal BO₃ coordination [10] due to the different ranges of chemical shift values for BO₄ and BO₃ units. Moreover, it can also reveal the formation of B–O–W bridges as observed previously in zinc borophosphate glasses with additions of WO₃ [1]. The links between structural changes and changes in physical properties will be discussed as well.

2. Experimental

PbO–B₂O₃–P₂O₅–WO₃ glasses were prepared from an analytical grade PbO, WO₃, H₃BO₃ and H₃PO₄ using a total batch weight of 30 g. The homogenized starting mixtures were slowly heated in a platinum crucible from a room temperature up to 600 °C maintaining the maximum temperature for 2 h to remove water. The reaction mixtures were consequently heated up to 1150–1400 °C in the crucible covered with a lid. The melt was held at a maximum temperature for 20 min and then poured into a preheated graphite mould. The obtained glasses were then transferred to an annealing furnace for 2 h at a temperature 5 °C below their glass transition temperature, *T_g*, and then cooled to room temperature. The total volatilization losses checked by weighing were smaller than 0.3 wt %, hence the batch compositions were considered as reflecting actual compositions. The amorphous character of the glasses was checked by X-ray diffraction. A structureless spectrum (not shown) was obtained for all the glass compositions.

The glass density, ρ , was determined on bulk samples with the Archimedes' method using toluene as the immersion liquid. The molar volume, V_M , was calculated as $V_M = M/\rho$, where M is the average molar weight of the glass composition $a\text{PbO}-b\text{B}_2\text{O}_3-c\text{P}_2\text{O}_5-d\text{WO}_3$ calculated for $a+b+c+d=1$. Thermal behaviour of the glasses was studied by the differential thermal analysis (DTA) with the Netzsch DTA 404 PC equipment operating in the DSC (differential scanning calorimetry) mode at a heating rate of 10 °C min⁻¹. The measurements were carried out with 100 mg powder samples under an inert atmosphere of N₂. The thermal expansion coefficient, α , and the glass transition temperature, *T_g*, were measured on bulk samples with dimensions of 25 × 5 × 5 mm using a dilatometer DIL 402 PC (Netzsch). From the obtained dilatation curves, the coefficient of thermal expansion, α , was determined as a mean value in the temperature range of 150–250 °C, the glass transition temperature, *T_g*, was determined from the change in the slope of the elongation vs. temperature plot. The dilatometric measurements were carried out in the air at a heating rate of 5 °C min⁻¹. The chemical durability of glasses was evaluated from the measurement of the dissolution rate, DR, at 25 °C on $\approx 5 \times 5 \times 5$ mm glass cubes. The glass cubes were immersed in 100 cm³ of agitated distilled water (pH = 6) for 48 h. The dissolution rate, DR, was calculated using $DR = \Delta w/St$, where Δw is the weight loss [g], S is the surface area [cm²] before the dissolution test and t is the dissolution time [min]. The measurements were made on three cubes for each composition. We did not observe changes in the sample volume during dissolution test, hence the surface area was considered to remain constant in the calculation of DR. No reaction layer was observed on the sample surface after 48 h and the pH of the leaching water was negligibly changed.

The Raman spectra were measured on bulk samples at room temperature using a Horiba-Jobin Yvon LabRam HR spectrometer. The spectra were recorded in back-scattering geometry under excitation with Nd-YAG laser radiation (532 nm) at a power of 12 mW on the sample. The spectral slit width was 1.5 cm⁻¹ and the total integration time was 50 s.

³¹P magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were acquired at 9.4 T (Larmor frequency 161.9 MHz) on a BRUKER Avance spectrometer equipped with a 4 mm probe and at a MAS frequency of 10 kHz. A 1 μ s pulse was used ($\pi/9$), with 180 s recycling time. 16 or 32 transients were recorded before processing. The chemical shifts of ³¹P nuclei are given relative to an 85% H₃PO₄ solution at 0 ppm, used as an external chemical shift reference.

¹¹B MAS NMR spectra were measured at 18.8T on a BRUKER Avance 800 spectrometer with a 2.5 mm probe and a spinning frequency of 20 kHz. The spectra were acquired with a single short (0.5 μ sec) radiofrequency pulse ($\pi/12$), in order to compensate for the different nutation behaviour of the two boron sites, which enabled the BO₃/BO₄ quantification. 16 transients were recorded before they were processed. The recycling delay was 10s. The chemical shifts of ¹¹B nuclei are given relative to BPO₄ at –3.6 ppm. The NMR spectra decomposition was performed with the Dmfit NMR software [11], using quadrupolar lineshape model for the BO₃ sites. BO₄ resonances are known to be subjected to a negligible second-order quadrupolar effect; hence the decomposition was carried out with a Gaussian-type function assuming that the line shape is dominated by a chemical shift distribution.

3. Results and discussion

3.1. Glass formation and physical properties

23 homogeneous glass samples from the system PbO–B₂O₃–P₂O₅–WO₃ were prepared in this study. Eight samples were obtained in the compositional series (100–x)[0.5PbO–0.1B₂O₃–0.4P₂O₅]-xWO₃ with x = 0–60 mol% WO₃ and nine samples in the series (100–y)[0.5PbO–0.2B₂O₃–0.3P₂O₅]-yWO₃ with y = 0–40 mol% WO₃. Another six samples were prepared with the ratio of B₂O₃/P₂O₅ equal to 5/45 (45PbO–4.5B₂O₃–40.5P₂O₅–10WO₃, 35PbO–3.5B₂O₃–31.5P₂O₅–30WO₃, 25PbO–2.5B₂O₃–22.5P₂O₅–50WO₃) and 15/35 (45PbO–13.5B₂O₃–31.5P₂O₅–10WO₃, 35PbO–10.5B₂O₃–24.5P₂O₅–30WO₃, 25PbO–7.5B₂O₃–17.5P₂O₅–50WO₃) for glasses with 10, 30 and 50 mol% WO₃. The composition of all the studied glasses and their basic physical properties are provided in Table 1. Glasses with the highest WO₃ content of 50–60 mol% in the first series and 35–40 mol% in the second series were prepared by quenching between two copper blocks. Glasses containing WO₃ were of blue colour due to the presence of W⁵⁺ ions [12]. The ESR signal of W⁵⁺ ions was very weak and we suppose that their relative amount W⁵⁺/W^{total} is under 1%.

We have determined the density and molar volume of the prepared glasses and their values are also shown in Table 1. The density of glasses in both compositional series increases with increasing WO₃ content, while the molar volume changes are small. The chemical durability of the glasses is extremely high, very small weight changes were obtained at the samples after their interaction with water for 48 h at room temperature corresponding to values of DR = 3.7–5.5 × 10⁻⁸ g cm⁻² min⁻¹ at the room temperature.

3.2. Thermal properties

The thermal properties were studied by DTA and dilatometry. DTA curves obtained from the first glass series (100–x)[0.5PbO–0.1B₂O₃–0.4P₂O₅]-xWO₃ are shown in Fig. 1. From these curves glass

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