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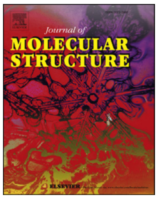

Structural investigation of $BaO-B_2O_3-P_2O_5$ glasses by NMR and Raman spectroscopy

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ABSTRACT

Glasses of the ternary system $BaO-B_2O_3-P_2O_5$ were prepared and studied in broad concentration limits covering the whole vitrification domain: 20–50 mol% BaO, 0–40 mol% B_2O_3 and 20–60 mol% P_2O_5. Their structure was studied with combinations of Raman spectroscopy, ^{31}P MAS NMR spectroscopy and ^{11}B MAS NMR spectroscopy. The obtained results are discussed in several compositional lines A: $(100\text{-}x)Ba(PO_3)_2-xB_2O_3$, B: $40BaO-yB_2O_3-(60\text{-}y)P_2O_5$, C: $(50\text{-}z)BaO-zB_2O_3-50P_2O_5$, D: $(60\text{-}w)BaO-wB_2O_3-40P_2O_5$ and E: $uBaO-40B_2O_3-(60\text{-}u)P_2O_5$. Boron oxide incorporates into the phosphate network in the form of BO_4 and BO_3 groups and increases their glass transition temperature. Nevertheless, the increase in T_g is only steep within the region of 0–20 mol% B_2O_3 reaching a maximum at the glasses with ~30 mol% B_2O_3. In the lines A, B and E a decrease in the P_2O_5 and an increase of B_2O_3 content results in the shortening of phosphate chains with decreasing P_2O_5 content; these changes are most pronounced in line B with a constant BaO content. In lines C and D with a constant P_2O_5 content a decrease in the BaO content results, in contrast, in the reverse transformation of phosphate structural units in the direction $Q^1 \rightarrow Q^2 \rightarrow Q^3$ as detected from Raman spectra and ^{31}P MAS NMR spectra. ^{11}B MAS NMR spectra revealed that only BO_4 units are present in the glasses with 0–20 mol% B_2O_3. In the glasses of the E series the fraction of BO_3 units increases with a decreasing P_2O_5 content. By the decomposition of the ^{11}B MAS NMR spectra it is possible to estimate the fractions of basic structural units formed by boron - $B(OP)_3O$, $B(OP)_2O_2$ and BO_3 in all the glasses of the glass forming region.

1. Introduction

Boron oxide was used to modify the properties of phosphate glasses by cross-linking phosphate chains to improve the properties of phosphate glasses, mainly their chemical durability [1,2]. For structural studies of borophosphate glasses, Raman and NMR spectroscopies were applied [2–6]. ^{31}P MAS NMR spectra of borophosphate glasses are generally broadened and with an increasing B_2O_3 content their maximum shifts downfield [7–9]. ^{31}B MAS NMR spectra make it possible to differentiate between tetragonal BO_4 units and trigonal BO_3 units and the application of high magnetic field for the measurement of boron spectra enables the quantification of these two structural units formed by boron in borophosphate glasses. The application of NMR spectroscopy in structural studies makes it possible not only to study the short range order in these glasses, but the methods of two-dimensional NMR spectroscopy allowed to study the middle-range order as well [8–10].

Structural studies of borophosphate glasses were frequently devoted to alkali borophosphates [2,8,10,11], but the borophosphate glasses of alkaline earth metals were not studied as often. The glass-forming region in the ternary system BaO–⊖ $B_2O_3-P_2O_5$ was published by Sedmale et al. [12], who specifically investigated the optical properties of the glasses and Raman spectra in the compositional series $(BaO\cdot B_2O_3)-P_2O_5$. There are two separated glass-forming regions in this ternary system. The first one is smaller and close to the $BaO-B_2O_3$ line; the maximum amount of P_2O_5 does not exceed 10 mol%. The second region is larger and associated with $BaO-P_2O_5$ line, where glasses with a maximum content of 56 mol% of BaO were prepared and studied [13]. The glass-forming region in this part of the ternary diagram

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reached up to 40 mol% B_2O_3. Harada et al. [14] investigated barium phosphate glasses with additions of 0–10 mol% B_2O_3 in order to improve the thermal stability of the barium phosphate glasses.

The aim of the present study was to prepare $BaO-B_2O_3-P_2O_5$ glasses within the large glass-forming region [12] with the B_2O_3 content 0–40 mol% and BaO content 20–60 mol%. We have studied their structure with ^{11}B and ^{31}P MAS NMR spectroscopy and with Raman spectroscopy. We discuss their compositional dependences in several series A: (100-x)$Ba(PO_3)_2$–xB_2O_3, B: 40BaO–yB_2O_3–(60-y)P_2O_5, C: (50-z)BaO–zB_2O_3–50P_2O_5, D: (60-w)BaO–w-B_2O_3–40P_2O_5 and E: uBaO–40B_2O_3–(60-u)P_2O_5 in order to obtain structural information from the evolution of the spectra with changing concentrations of various components. Structural changes are also discussed with regard to changes in the glass properties.

2. Experimental

Glasses of the $BaO-B_2O_3-P_2O_5$ system were prepared by melting analytical grade $BaCO_3$, H_3BO_3 and H_3PO_4, using a total batch weight of 30 g. The homogenized starting mixtures were slowly calcined up to 600 °C with the final calcination at a maximum temperature for 2 h in order to remove the water. The reaction mixtures were then melted at 1000–1300 °C (according to the composition) under ambient air, in a platinum crucible. The melt was subsequently poured into a preheated graphite mould ($T < T_g$) and the obtained glasses were then cooled to room temperature. The weight loss measurements indicated that the volatilization losses were not significant, even at the highest temperature, and hence the batch compositions can be considered as reflecting actual compositions. The amorphous character of the prepared glasses was checked with X-ray diffraction analysis.

Raman spectra in a range of 1400–200 cm^{-1} were measured on bulk samples at room temperature using a Horiba-Jobin Yvon LaBRam HR spectrometer. The spectra were recorded in backscattering 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.

^{31}P MAS NMR spectra were measured at 9.4 T on a BRUKER Avance 400 spectrometer with a 4 mm probe. The spinning speed was 12.5 kHz and the relaxation (recycling) delay was 120s. The pulse length was 2 μs (pi/4). The chemical shifts of ^{31}P nuclei are given relative to H_3PO_4 at 0 ppm.

^{11}B MAS NMR spectra were measured at 18.8 T on a BRUKER Avance 800 spectrometer with a 2.5 mm probe. The spectra were acquired with a single short (1 μs) radiofrequency pulse (pi/10), in order to compensate for the different nutation behavior of the two boron sites, which enabled the BO_3/BO_4 quantification. The recycling delay was 5s and the spinning rate was 20 kHz. The chemical shifts of ^{11}B nuclei are given relative to BPO_4 at −3.6 ppm. The NMR spectra decomposition was performed with the Dmfit NMR software [15] using the quadrupolar lineshape model for the BO_3 sites. BO_4 resonances are known to be subjected to a negligible second-order quadrupolar effect; hence their 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

We prepared 14 glass samples of the $BaO-B_2O_3-P_2O_5$ ternary system by slow cooling of the corresponding melt in air at a room temperature. Their composition is provided in the ternary diagram in Fig. 1. All the prepared glasses were clear and homogeneous. Glass properties are described in the paper [16] and the dependence of the glass transition temperature on the B_2O_3 content is shown in Fig. 2. The results of the structural studies by Raman spectroscopy and by ^{31}P and ^{11}B MAS NMR spectroscopies will be discussed further in each compositional series A: (100-x) $Ba(PO_3)_2$–xB_2O_3, B: 40BaO–yB_2O_3–(60-y)P_2O_5, C: (50-z)BaO–z-B_2O_3–50P_2O_5, D: (60-w)BaO–wB_2O_3–40P_2O_5 and E: uBaO–40-B_2O_3–(60-u)P_2O_5.

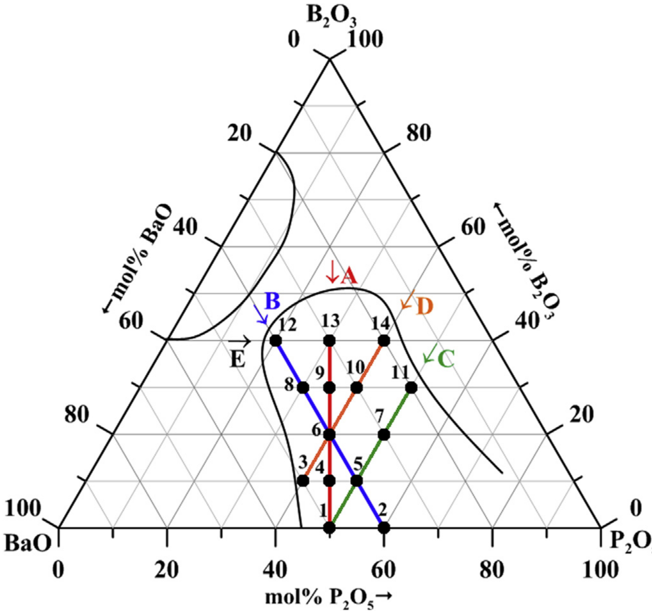

Fig. 1. Phase diagram of the $BaO-B_2O_3-P_2O_5$ system with the glass forming regions and the studied glass series A: (100-x)Ba(PO3)2–xB2O3, B: 40BaO–yB2O3–(60-y) P2O5, C: (50-z)BaO–zB_2O_3–50P_2O_5 and D: (60-w)BaO–wB_2O_3–40P_2O_5.

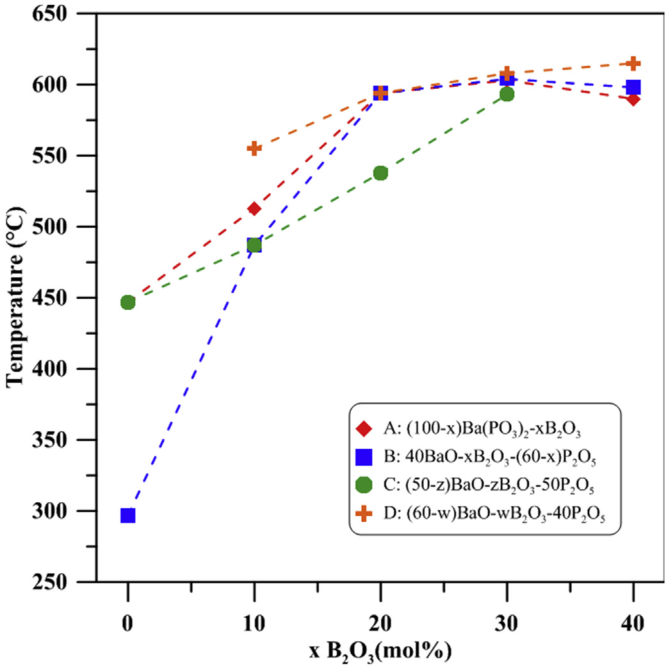

Fig. 2. Compositional dependence of the glass transition temperature on B_2O_3 content in the glass-forming region of the ternary system $BaO-B_2O_3-P_2O_5$. The lines are only a guide for the eye.