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Structure–property relationships in barium borophosphate glasses modified with niobium oxide

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ABSTRACT

Phosphate glasses containing a high amount of niobium oxide exhibit non-linear optical properties which make them attractive for various optical devices. This contribution is devoted to the investigation of glasses of the series $(100 - x)[0.5BaO–0.1B_2O_3–0.4P_2O_5]–xNb_2O_5$ with $x = 0–45$ and $80[0.5BaO–yB_2O_3–(0.5 - y)P_2O_5]–20Nb_2O_5$ with $y = 0–0.25$. The basic characteristic parameters of the prepared glasses were determined. The index of refraction of these glasses increases substantially with increasing Nb_2O_5 content from 1.620 to 2.007 and the glass transition temperature increases within the range of 551–704 °C. The glass structure was investigated by ^{31}P, ^{11}B and ^{93}Nb NMR, and Raman spectroscopies. Raman spectra revealed that at low Nb_2O_5 content a strong vibrational band of isolated NbO_6 octahedra dominates the spectra. New bands appear in the Raman spectra in the glasses with 30 mol% of Nb_2O_5 that were assigned to vibrations of Nb–O–Nb bonds interconnecting NbO_6 octahedra. ^{11}B MAS NMR spectra reveal the dominant role of BO_4 units in the glass structure. ^{11}B MAS NMR spectra revealed that with increasing Nb_2O_5 content new resonances of BO_4 units appear in the spectra due to the replacement of B–O–P bonds by B–O–Nb and B–O–B bonds. With an increasing Nb_2O_5 content, part of the BO_4 units is also converted to BO_3 units. ^{93}Nb MAS NMR spectra primarily reflect changes in the length of Nb–O bonds in the NbO_6 octahedra manifested in a decreasing asymmetry of the octahedra with increasing Nb_2O_5 content and the formation of niobate clusters. Niobo-borophosphate glasses reveal very high chemical durability as well as high glass transition temperatures due to the replacement of weaker P–O bonds with stronger Nb–O bonds.

1. Introduction

Phosphate glasses containing a high amount of niobium oxide or titanium oxide exhibit non-linear optical properties which make them attractive for various optical devices [1]. During our previous study [2] we have found that for the preparation of phosphate or borophosphate glasses with a high content of Nb_2O_5 there is a need to use strongly basic oxides. We were not able to obtain such glasses with oxides such as ZnO or PbO having rather an amphoteric character.

Therefore, most papers devoted to phosphate glasses with a high content of niobium oxide contain sodium [1,3–9] or potassium [2, 10–12]. Martinelli et al. [10] investigated glasses in the system $BaO–K_2O–Nb_2O_5–P_2O_5$ containing 30 mol% of P_2O_5 and varied K_2O, BaO and Nb_2O_5 content. The maximum Nb_2O_5 content in these glasses was 40 mol%. Most samples were amorphous only when the melt was quenched. They also observed that a higher content of BaO and a lower content of K_2O increased the crystallization temperature of these quaternary glasses. In paper [11] the authors maintained the ratio of $BaO/K_2O/P_2O_5$ and the varied Nb_2O_5 content. They found that the glass transition temperature increased with increasing Nb_2O_5 content, which was ascribed to the formation of stronger Nb–O–P and Nb–O–Nb bonds replacing weaker P–O–P bonds [11]. Potassium–barium niobophosphate glasses doped with Nd, Ho, Er, or Yb were studied in [12] and the authors claimed that glasses containing 10 mol% Nb_2O_5 are the most promising materials to be used as rare-earth hosts.

The glass-formation region in the ternary system $BaO–Nb_2O_5–P_2O_5$ was determined by Shtcheglova and Avlas [13] who also studied the properties of these glasses. These authors were able to prepare glasses with Nb_2O_5 content up to 60 mol%. Glasses containing more than 25 mol% Nb_2O_5 were blue colored which the authors [13] ascribed to the reduction of Nb^{5+} to Nb^{4+} ions.

A NMR study of $xNb_2O_5–(1 - x)NaPO_3$ glasses with 0–40 mol% Nb_2O_5 was published by Flambard et al. [7]. These authors measured ^{31}P, ^{93}Nb and ^{17}O NMR spectra of glasses and came to the conclusion that Nb_2O_5 depolymerises the sodium metaphosphate network with the formation of Q^1 and Q^0 sites. ^{17}O MQ-MAS NMR spectroscopy confirmed the formation of Nb–O–P bridges. Their studies also revealed the formation of a niobate network for large Nb_2O_5 concentrations. A

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similar conclusion relating the incorporation of Nb_2O_5 was reached by Mazali et al. [14] from their studies of Li_2O–CaO–Nb_2O_5–P_2O_5 glasses by IR, Raman and NMR spectroscopies.

Information on alkaline-earth borophosphate glasses modified with niobium oxide are still lacking in the literature. Our present study is therefore devoted to the effect of Nb_2O_5 on the structure and properties of barium borophosphate glasses of the system BaO–B_2O_3–P_2O_5–Nb_2O_5. The aim of this work was to evaluate the glass-forming ability in this quaternary system and study the effect of Nb_2O_5 addition and the B_2O_3/P_2O_5 ratio on the properties and structure of these glasses.

2. Experimental

Glasses of the BaO–B_2O_3–P_2O_5–Nb_2O_5 system were prepared by melting analytical grade $BaCO_3$, H_3BO_3, H_3PO_4 and Nb_2O_5, using a total batch weight of 20 g. The homogenized starting mixtures were slowly calcined up to 600 °C to remove the water. The reaction mixtures were then melted at 1100–1450 °C (according to the Nb_2O_5 content) under ambient air in a platinum crucible. The melt was subsequently poured into a preheated graphite mold ($T < T_g$) 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 by X-ray diffraction analysis.

The glass density, ρ, was determined with bulk samples by the Archimedes method using toluene as the immersion liquid. The molar volume, V_M, was calculated using the expression $V_M = M/\rho$, where M is the average molar weight of the glass composition $aBaO$–bB_2O_3–cP_2O_5–dNb_2O_5 calculated for $a + b + c + d = 1$. The chemical durability of the glasses was evaluated from the measurement of the dissolution rate, DR, at 25 °C and 80 °C on glass cubes with a dimension of ~$5 \times 5 \times 5$ mm. The glass cubes were shaken in 100 cm^3 of distilled water (pH = 6) for 24 h. The dissolution rate was calculated from the expression $DR = \Delta\omega/St$, where $\Delta\omega$ is the weight loss(g), S is the area (cm^2) before the dissolution test, and t is the dissolution time (min).

The thermal behavior of the glasses was studied with a Netzsch DTA 404 PC operating in the DSC mode at a heating rate of 10 °C min^{-1} over the temperature interval 30–900 °C. The measurements were carried out with 60 mg powder samples (the average particle size was 10 μm) in a silica crucible under an inert atmosphere of N_2. The thermal expansion coefficient, α, the glass transition temperature, T_g, and the dilatometric softening temperature, T_d, were measured on bulk samples with dimensions of $20 \times 5 \times 5$ mm using a dilatometer DIL 402 PC (Netzsch) and a heating rate 5 °C min^{-1}. The evaluation of the dilatometric curves was carried out with Proteus software. 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 versus temperature and the dilatometric softening temperature, T_d, from the maximum of the expansion trace corresponding to the onset of viscous deformation. The thermal properties were also studied with hot stage microscopy (HSM, from HESSE Gmbh) which was carried out with powder samples (the average particle size was 10 μm) pressed into cylinders (3 mm in diameter and height) by a hand press. The specimen was placed on a corundum sample holder and the measurement was carried out with the heating rate of 5 °C min^{-1} under a static air atmosphere. The projected area and the height of the pressed powder sample were monitored by a CCD camera during the heating.

The linear refractive indices were measured by the prism coupling method, using a Metricon Model 2010/M at 453, 532 and 637 nm. Linear refractive index values n_D (587.6 nm) were obtained from the dispersion curve calculated with Metricon software.

The Raman spectra in the range 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 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.

^{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 relaxation (recycling) delay was 180 s. 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 10 s 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 the decomposition was carried out with a Gaussian-type function assuming that the line shape is dominated by a chemical shift distribution. Owing to the large width of ^{93}Nb NMR spectra, both static and MAS conditions were used for their recording.

The ^{93}Nb spectra were recorded at 18.8 T on a BRUKER Avance 800 spectrometer. For the static conditions, 4 mm rotors were used, and the solid echo pulse sequence (90-t-90) was used with t = 30 μs and a 90 pulse at 0.8 μs. The numbers of scans was 4096, and the relaxation delay was 0.2 s. For the MAS spectra, a high spinning rate of 60 kHz was reached thanks to 1.3 mm rotors. A single pulse sequence was used, with 0.5 μs pulse length (pi/10) and a recycling delay of 0.5 s. 1024 to 4096 scans were used, according to the Nb content of the samples. $LiNbO_3$ was used as a secondary chemical shift reference ($\delta = -1004$ ppm).

3. Results and discussion

3.1. Glass formation and physical properties

Fifteen homogeneous glass samples from the system BaO–B_2O_3–P_2O_5–Nb_2O_5 were prepared in this study in two compositional series $(100 - x)[0.5BaO$–$0.1B_2O_3$–$0.4P_2O_5]$–xNb_2O_5 with $x = 0$–45 and $80[0.5BaO$–yB_2O_3–$(0.5 - y)P_2O_5]$–$20Nb_2O_5$ with $y = 0$–0.25. The composition of all the studied glasses and their basic physical properties are provided in Table 1. Glasses with x ≥ 20 mol% Nb_2O_5 were blue colored and the color intensity increased with increasing Nb_2O_5 content. This blue color is caused by the presence of some amount of Nb^{4+} ions in the glass, which can be considered as negligible for the present structural study [13,16].

We measured the density and molar volume of the prepared glasses and their values are also shown in Table 1. The density and the molar volume of glasses in compositional series $(100 - x)[0.5BaO$–$0.1B_2O_3$–$0.4P_2O_5]$–xNb_2O_5 increases with increasing Nb_2O_5 content. In the compositional series $80[0.5BaO$–yB_2O_3–$(0.5 - y)P_2O_5]$–$20Nb_2O_5$ the density of glasses increases with increasing B_2O_3 content, while the molar volume decreases. The study of chemical durability shows that the dissolution rate for the glasses of both compositional series is very small. The weight changes of the samples after their interaction with distilled water for 24 h (both at 25 and 80 °C) are tenths of a mg, which are the values within the measurement error.

The thermal properties of glasses were studied by DTA, dilatometry and hot stage microscopy (HSM). DTA curves obtained from the compositional series $(100 - x)[0.5BaO$–$0.1B_2O_3$–$0.4P_2O_5]$–xNb_2O_5 are shown in Fig. 1. Pronounced exothermic crystallization peaks can be seen on all of these curves. It is evident that most glasses crystallize on heating within the temperature range of 750–850 °C. The values of the crystallization temperature, T_c, were determined as the onset of the peak and the obtained values of T_c are given in Table 1. The determination of