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Structure and properties of barium niobophosphate glasses

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ABSTRACT

Phosphate glasses of the ternary system BaO-Nb_2O_5-P_2O_5 were studied in two compositional series, namely 40BaO-xNb_2O_5-(60-x)P_2O_5 (series A), with x = 0–40 mol% Nb_2O_5, and yBaO-20Nb_2O_5-(80-y)P_2O_5 (series B), with y = 20–60 mol% BaO. Nine homogeneous glassy samples were prepared altogether in both series, and their basic physical properties (density, molar volume, glass transition temperature, dilatometric softening temperature and thermal expansion coefficient) were determined. The chemical durability of the Nb_2O_5-containing glasses is high and the dissolution rate at 80 °C is lower than 4–5 × 10^{-8} g cm^{-2} min^{-1}. The glass transition temperature of the glasses in series A increased significantly with increasing Nb_2O_5 content from 324 to 727 °C, whereas in the series B with increasing BaO content, T_g increased within the range 620–725 °C. The index of refraction increased more steeply in glass series A with increasing Nb_2O_5 content than in the glass series B. According to the Raman spectra in the glass series A, at low Nb_2O_5 content niobium forms isolated octahedra NbO_6 incorporated in the glass network, but when Nb_2O_5 content increases, these octahedra are linked into chains and further into three-dimensional clusters. In glass series B, NbO_6 octahedra form only —Nb—O—Nb—O— chains connecting NbO_6 octahedra. NbO_6 octahedra clustering is reflected also in the ^{31}P MAS NMR spectra of BaO-Nb_2O_5-P_2O_5 glasses showing on a non-monotonous transformation of phosphate units in the direction $Q^3 \rightarrow Q^2 \rightarrow Q^1 \rightarrow Q^0$, both with increasing Nb_2O_5 content in the first A series and BaO content in the second B series.

1. Introduction

Optical glasses containing Nb_2O_5 have been studied in several papers [1–3], due to their potential use as chemically stable nonlinear photonic materials. Phosphate glasses also exhibit high solubility for transition metal oxides such as Nb_2O_5, which not only improves the chemical durability of phosphate glasses, but also significantly increases their index of refraction [4]. Z.N. Shtcheglova and T.V. Avlas [5] studied the effect of Nb_2O_5 content on the index of refraction in BaO-Nb_2O_5-P_2O_5 glasses and observed a steep increase with increasing niobium oxide content. The authors also determined a large glass-forming region and found that glasses containing >25 mol% Nb_2O_5 turn blue, due to the reduction of Nb^{5+} to Nb^{4+} ions in the glasses.

Martinelli et al. [6–8] studied barium-potassium niobophosphate glasses. They looked for an optimum glass composition suitable for doping by rare-earth ions for the preparation of new laser materials [6]. They carried out glass preparation in corundum crucibles at 1300 °C, which could result in the dissolution of alumina in the prepared glasses [9]. They found the most perspective material for laser glass to be a $10K_2O \cdot 30BaO \cdot 30Nb_2O_5 \cdot 30P_2O_5$ composition due to its good transparency and the lack of absorption bands within the region of 400–2500 nm. The authors later studied barium-potassium niobophosphate glasses with various concentrations of all components [7] and then examined various properties of these glasses. Finally, they doped them with Er, Ho, Pr and Yb [8] and evaluated their luminescent properties.

In the present study we prepared and studied glasses from two compositional series with a constant BaO content and constant Nb_2O_5 content, which are of interest for the optical applications. Our aim is to bring some structural insight in the glass structure and properties relationship, which may enable to develop new compositions. Their structure was studied by Raman spectroscopy and ^{31}P MAS NMR spectroscopy. Physico-chemical properties of the glasses were also investigated.

2. Experimental

Glasses of the BaO-Nb_2O_5-P_2O_5 system were prepared by melting $BaCO_3$ (99%; Sigma-Aldrich), Nb_2O_5 (99.9; Sigma-Aldrich) and H_3PO_4 (85 wt%, p.a. Sigma-Aldrich) using a total batch weight of 30 g. The homogenized starting mixtures were slowly calcined up to 600 °C with the final calcination at the maximum temperature for 2 h in order to remove the water. The reaction mixtures were then melted at 1450 °C under

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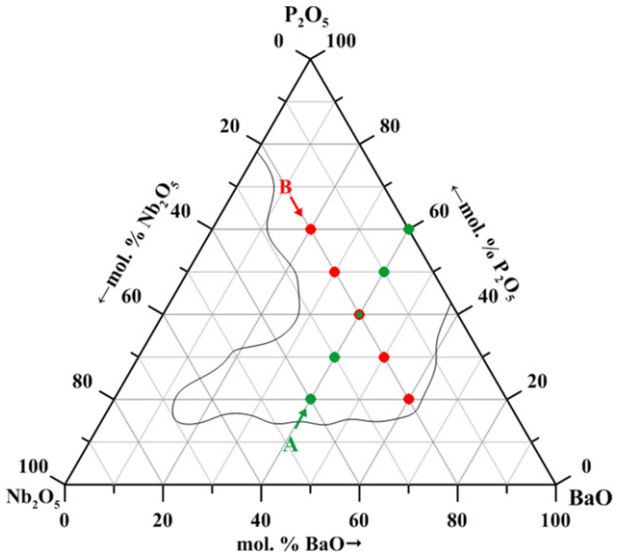

Fig. 1. Phase diagram of the BaO-Nb_2O_5-P_2O_5 system with the glass forming region [5] and the studied glass series A: 40BaO-xNb_2O_5-(60-x)P_2O_5, B: yBaO-20Nb_2O_5-(80-y)P_2O_5.

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 of the glass sample together with the remaining melt in the crucible was usually >98.5 wt% and thus the weight loss was usually <1.5 wt%. Therefore we considered the batch compositions as reflecting actual compositions. The amorphous character of the prepared glasses was checked by X-ray diffraction analysis (not shown).

The glass density, ρ, was determined with bulk samples with the Archimedes method using toluene as the immersion liquid. The molar volume, V_m, was calculated using the expression $V_m = \overline{M}/\rho$ where $\overline{M}$ is the average molar weight of the glass composition $a\cdot M(BaO) + b\cdot M(Nb_2O_5) + c\cdot M(P_2O_5)$ calculated for $a + b + c = 1$.

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 dimensions of ~5 × 5 × 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 sample area (cm^2) before the dissolution test and t is the dissolution time (min).

The thermal behaviour of the glasses was studied with the DTA 404 PC (Netzsch) operating in the DSC mode at a heating rate of 10 °C min^{-1} over the temperature interval 30–1000 °C. The measurements were carried out with 100 mg powder samples, obtained by milling of bulk glasses in the laboratory vibrational mill. The thermal expansion coefficient, α, the glass transition temperature, T_g, and the dilatometric softening temperature, T_d, were measured using a dilatometer DIL 402 PC (Netzsch). Bulk samples used for the measurements, with dimensions of 20 × 5 × 5 mm, were cut out from larger piece with a diamond saw.

The linear refractive indices were measured by the prism coupling method, using a MetriconModel 2010/Mat 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 and powder 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 chemical shifts of ^{31}P nuclei are given relative to H_3PO_4 at 0 ppm.

3. Results and discussion

3.1. Physico-chemical properties

We prepared nine BaO-Nb_2O_5-P_2O_5 ternary system glass samples by slow-cooling the corresponding melt in air at room temperature. Their composition is provided in the ternary diagram in Fig. 1. For the evaluation of their structure and properties, we studied glasses from two compositional series, namely 40BaO-xNb_2O_5-(60-x)P_2O_5 (series A), with x = 0–40 mol% Nb_2O_5, and yBaO-20Nb_2O_5-(80-y)P_2O_5 (series B), with y = 20–60 mol% BaO. Two glasses from the second series, with contents of 50 and 60 mol% P_2O_5, were deep-blue in colour, thus suggesting the presence of some Nb^{4+} ions, whereas the other glasses were clear or slightly yellow. Glass properties are summarised in Table 1. As can be seen from Table 1, glass density increases in series A with an increasing Nb_2O_5 content and in the series B with an increasing BaO content. Molar volume in the first series 40BaO-xNb_2O_5-(60-x)P_2O_5 decreases slightly with increasing Nb_2O_5 content despite the covalent radius of a niobium atom (1.34 Å) being larger than that of a phosphorus atom (1.06 Å). We assume that the observed decrease is due mainly to structural and bonding changes, as discussed later. Molar volume decreases more rapidly in the second glass series, yBaO-20Nb_2O_5-(80-y)P_2O_5, whereby seven atoms in the P_2O_5 molecule are replaced by only two atoms in BaO.

The thermal behaviour of the studied glasses was studied first by DTA, the obtained curves are shown in Figs. 2 and 3. As can be seen from these curves, most glasses reveal a strong exothermic crystallisation peak within the temperature range 750–900 °C. In some glasses, crystallisation proceeds in two consecutive steps. We also determined from these curves the glass transition temperature, T_g, nevertheless in Table 1 we gave its values as determined by

Table 1
Composition, density, ρ, molar volume, V_M, glass transition temperature T_g, dilatometric softening temperature T_d, thermal expansion coefficient, α, index of refraction, n_d, of BaO-Nb_2O_5-P_2O_5 glasses.

Series	BaO mol%	Nb_2O_5	P_2O_5	ρ ± 0.02 [g cm^{-3}]	V_m ± 0.5 [cm^3 mol^{-1}]	T_g ± 2 [°C]	T_d ± 2 [°C]	α ± 0.3 (100–200 °C) [ppm $°C^{-1}$]	n_d ± 0.005 –
A	40	–	60	3.28	44.7	324	359	14.5	1.558
	40	10	50	3.60	44.1	546	580	10.7	1.651
	40	20	40	3.97	43.5	676	710	8.6	1.745
	40	30	30	4.26	43.0	729	758	8.0	1.863
	40	40	20	4.61	42.5	727	750	8.7	1.993
B	20	20	60	3.26	51.8	620	671	7.3	1.670
	30	20	50	3.52	48.4	650	680	8.1	1.694
	40	20	40	3.96	43.5	676	710	9.3	1.745
	50	20	30	4.37	38.9	718	743	11.6	1.801
	60	20	20	4.73	36.7	725	750	13.1	1.835