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Structural studies of boron and tellurium coordination in zinc borophosphate glasses by ^{11}B MAS NMR and Raman spectroscopy

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ABSTRACT

Zinc borophosphate glasses doped with TeO_2 with different B_2O_3/P_2O_5 ratio were prepared, their basic properties were determined and their structure was studied by ^{11}B MAS NMR and Raman spectroscopies. Structural studies were devoted to the investigation of changes in boron coordination in the dependence on changes in TeO_2 content and in B_2O_3/P_2O_5 ratio in the borophosphate glasses. A special attention was devoted to the formation of mixed structural units $B(OP)_{4-n}(OTe)_n$ in the studied borophosphate glasses, where by the deconvolution of ^{11}B MAS NMR spectra quantitative data on the number of BO_3 and $B(OP)_{4-n}(OTe)_n$ mixed structural units were obtained. Raman spectra showed shortening of phosphate chains both with increasing TeO_2 and B_2O_3 content. Raman spectra also showed that with the replacement of P_2O_5 by B_2O_3 in the studied glasses TeO_4 units are replaced by TeO_3 units as the number of oxygen atoms in the glass decreases when the B_2O_3/P_2O_5 ratio increases.

1. Introduction

Borophosphate glasses reveal better thermal stability and chemical durability than phosphate glasses. The reason for such improvements in the properties of borophosphate glasses is ascribed to the transformation of linear-chain structure of metaphosphate glasses into three-dimensional structure of borophosphate glasses due to the addition of B_2O_3. When the boron oxide content is low, tetrahedral BO_4 units are formed inside the structural network [1–3]. At higher B_2O_3 content BO_3 groups are formed as well. Tetrahedral BO_4 units reticulate phosphate network and thus increases glass transition temperature and chemical durability of phosphate glasses.

These changes in the network structure of borophosphate glasses can be sensitively detected from the changes in Raman spectra of borophosphate glasses. Due to the much stronger efficiency of Raman scattering by phosphate structural units than by borate units Raman spectra of the borophosphate glasses reveal only characteristic vibrational bands of phosphate structural units [4]. The most active in the Raman spectra of metaphosphate glasses are symmetric stretching vibrations of P=O and P–O bonds in PO_4 units and symmetric stretching vibrations of bridging oxygen atoms in P–O–P bridges [5]. In phosphate glasses, the coordination of phosphorus can be also studied by ^{31}P MAS NMR spectroscopy [2,6]. Nevertheless in borophosphate glasses ^{31}P MAS NMR spectra are usually broad and not well resolved especially in glasses with a higher B_2O_3 content [7,8], this is why present study focuses on Raman data.

On the other side in borophosphate glasses the information on coordination of boron can be obtained by ^{11}B MAS NMR spectroscopy since it enables to discriminate between tetrahedral BO_4 boron coordination and trigonal BO_3 coordination [9]. Its application on borophosphate glasses was reported in several papers [1,2,4,10]. ^{11}B MQMAS NMR spectra were able to supply information on medium range order in lead borophosphate glasses [3] and to differentiate between two types of BO_4 units—$B(OP)_4$ and $B(OP)_3(OB)$. In the latter units boron atoms are linked to three PO_4 groups and one BO_3 group [3].

Doping of borophosphate glasses with heavy metal oxides like Nb_2O_5, MoO_3, WO_3 or TeO_2 can bring new glassy materials with promising electronic applications [11]. TeO_2-containing glasses possess interesting physical properties as low melting temperatures, high dielectric constant and good infrared transmissions [12,13]. Structural investigations of tellurite glasses and corresponding stoichiometric crystalline phases led to the conclusion that the coordination state of tellurium can be classified into TeO_4 trigonal bipyramids (tpb), TeO_3 trigonal pyramids (tp) and their intermediate states, such as TeO_{3+1} polyhedron [14,15]. The identification of these structural units is usually carried out from the Raman spectra within the spectral region of 400–800 cm^{-1}.

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In a recent study [16] of the structure of zinc borophosphate glasses, Raman spectra were deconvoluted in the middle-frequency region into four bands lying at ~620–630 cm^{-1} (band A), ~660–670 cm^{-1} (B), ~720–750 cm^{-1} (C) and ~760–800 cm^{-1} (D), which can be assigned to stretching vibrations of TeO_3 tp (C, D) and TeO_4 tbp (A, B) structural units [16]. Vibrational bands of Te–O stretching vibrations can be observed also within the spectral range of 600–800 cm^{-1} in the infrared spectra of TeO_2-containing ZnO–TeO_2 glasses [17] and multicomponent glasses [18].

This paper is devoted to the ZnO–B_2O_3–P_2O_5–TeO_2 glasses with the composition $(1-y)[50ZnO-(50-x)P_2O_5-xB_2O_3]-yTeO_2$ with $y=0.2$, 0.4, 0.6 and $x=5$, 10, 15. The aim of this work is to study changes in boron and tellurium coordination by ^{11}B MAS NMR and Raman spectroscopies, respectively. ^{11}B MAS NMR spectra were recorded at a high static magnetic field of 18.8 T, which enabled to obtain a high resolution, sufficient to investigate changes in boron coordination. The relations between structural changes and changes in physical properties will be discussed as well.

2. Experimental

ZnO–B_2O_3–P_2O_5–TeO_2 glasses were prepared by conventional melt-quenching method from analytical grade ZnO, TeO_2, H_3BO_3 and H_3PO_4 using a total batch weight of 20 g. The homogenized starting mixtures were slowly heated up to 600 °C for 2 h to remove water. After that, the reaction mixtures were heated up to 950–1250 °C in a platinum crucible with a lid. The melt was held at maximum temperature for 30 min and then cooled slowly in a graphite mold. Obtained glasses were annealed for 30 min at a temperature 5 °C below their glass transition temperature, T_g. The volatilization losses checked by weighting were not significant, hence the batch compositions can be considered as reflecting actual compositions. The amorphous character of the glasses was checked by X-ray diffraction. A structure less spectrum was obtained for all glass compositions. The obtained homogeneous glasses were characterized by the measurement of density, molar volume, chemical durability and thermal properties. Their structure was studied by Raman and ^{11}B MAS NMR spectroscopy.

The glass density, ρ, was determined on bulk samples by the Archimedes' method using CCl_4 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 aZnO–$b$$B_2O_3$–$c$$P_2O_5$–$d$$TeO_2$ calculated for $a+b+c+d=1$. The chemical durability of glasses was evaluated from the measurement of the dissolution rate, DR, at 25 °C on glass cubes with dimension of ca. $5\times5\times5$ mm^3. Glass cubes were shaken in 100 cm^3 of distilled water (pH=6) for 5 h. The dissolution rate, DR, 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]. Thermal behavior of glasses was studied with a DTA 404 PC operating in the DSC mode at a heating rate of 10 °C min^{-1}. Measurements were carried out with 50 mg powder samples with a mean diameter 8–10 μm in platinum crucibles under inert atmosphere of N_2.

The Raman spectra were measured on bulk samples at room temperature using a Renishaw RM 1000 Raman microscope. The spectra were recorded in back-scattering geometry under excitation with Ar-laser radiation (514.5 nm) at a power of 5 mW. The spectral slit width was 1.5 cm^{-1} and the total integration time was 100 s.

^{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 single short (0.5 μsec) radiofrequency pulse (pi/12), in order to compensate for the different nutation behavior of the two boron sites. 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 deconvolution was done using the Dmfit NMR software [19]. BO_4 lines are known to be subjected to negligible second-order quadrupolar effect; hence the decomposition was done by Gaussian-type function assuming that the line shape is dominated by chemical shift distribution.

3. Results and discussion

We have prepared and studied 9 glasses of $(1-y)[50ZnO-(50-x)P_2O_5-xB_2O_3]-yTeO_2$. For the TeO_2 content of 20, 40 and 60 mol% we have prepared 3 samples with different B_2O_3/P_2O_5 ratio equal to 5/45, 10/40 and 15/35. Their composition and basic physical properties are given in Table 1. As can be seen in this table, the density of the glasses increases both with increasing TeO_2 content and the B_2O_3/P_2O_5 ratio. On the other hand molar volume slightly decreases both with increasing TeO_2 and B_2O_3 contents. Glass transition temperature decreases with increasing TeO_2 content and the differences in T_g between the glasses with different B_2O_3/P_2O_5 ratio decrease as the borophosphate content decreases and TeO_2 content increases. Chemical durability of glasses with 20 and 40 mol% TeO_2 is lower for glasses with a low B_2O_3 content, because the reticulation effect of B_2O_3 is smaller than in glasses with a higher B_2O_3 concentration.

Structural studies were aimed especially on the boron coordination as the ^{11}B MAS NMR spectra measured with the NMR spectrometer at 18.8 T enables to obtain a higher resolution than previous studies conducted at a lower magnetic field [20], since the quadrupolar effect of ^{11}B (nuclear spin=3/2) is scaled down at high field. The obtained NMR spectra are given in Figs. 1–3. Previous ^{11}B MAS NMR studied of boro-phosphate glasses [1,4] showed that BO_3 units in borophosphate glasses have chemical shift values ranging from +5 ppm to +15 ppm, whereas BO_4

Table 1
Density, ρ, molar volume, V_M, dissolution rate, DR, glass transition temperature, T_g^* (onset on DSC curve), T_g (measured by dilatometry), dilatation softening temperature, T_d, and thermal expansion coefficient, α, of $(1-y)[50ZnO-(50-x)P_2O_5-xB_2O_3]-yTeO_2$ glasses.

xB_2O_3 (mol%)	$yTeO_2$ (mol%)	$\rho\pm0.02$ (g cm^{-3})	$V_M\pm0.2$ (cm^3 mol^{-1})	$(DR\times10^6)\pm0.5$ (g cm^{-2} min^{-1})	$T_g^*\pm2$ (°C)	$T_g\pm2$ (°C)	$T_d\pm2$ (°C)	$\alpha\pm0.5$ (ppm $°C^{-1}$)
5	0.2	3.50	33.8	32.0	410	408	429	13.1
10	0.2	3.59	32.2	2.8	435	442	461	11.2
15	0.2	3.67	30.7	0.7	449	450	471	12.9
5	0.4	4.01	32.1	24.1	400	398	411	12.0
10	0.4	4.08	31.0	0.6	410	412	432	12.6
15	0.4	4.15	30.0	0.8	409	409	429	12.1
5	0.6	4.54	30.6	4.4	380	380	391	17.1
10	0.6	4.57	30.1	0.6	382	381	395	18.4
15	0.6	4.67	29.4	1.2	382	382	397	15.6