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The structural role of tellurium dioxide in lead borophosphate glasses

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ABSTRACT

Lead borophosphate glasses formulated with TeO_2 were prepared and studied in the compositional series $(1 - x)[50PbO\text{-}10B_2O_3\text{-}40P_2O_5]\text{-}xTeO_2$ with $x = 0$–0.7 and glasses with 20 and 60 mol% TeO_2 with also the B_2O_3/P_2O_5 ratio of 5/45 and 15/35. Structural studies by ^{31}P and ^{11}B MAS NMR and Raman spectroscopies revealed the formation of P–O–Te bonds. The addition of TeO_2 resulted in the depolymerisation of phosphate chains as revealed from the ^{31}P MAS NMR spectra. The addition of TeO_2 to the parent lead borophosphate glass resulted in the formation of B–O–Te bonds and $B(OP)_{4-n}(OTe)_n$ mixed structural units, the number of which increases with increasing TeO_2 content and also with the increasing B_2O_3/P_2O_5 ratio in the glasses. Only a small number of BO_3 units (less than 4%) are formed in glasses with a higher TeO_2 content and at a high B_2O_3/P_2O_5 ratio. The Raman spectra also indicated that at low TeO_2 concentrations, tellurium atoms form preferentially TeO_3 structural units, whereas at higher TeO_2 content, TeO_4 units are predominant in the glass network. With the replacement of P_2O_5 by B_2O_3 in the studied glasses, TeO_4 units are converted into 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

Glasses containing tellurium dioxide reveal several unique properties such as a low melting temperature, a high refractive index and dielectric constant or a good transparency in the infrared region [1–3]. These glasses can also serve as host glasses for rare earth ions and can thus be applied as laser materials [4]. Tellurium atoms in crystalline TeO_2 are coordinated by four oxygen atoms and, due to the presence of a lone pair of electrons on the central tellurium atom, form trigonal bipyramids (tbp) with the hybridisation sp^3d. The lone pair of electrons is situated in the equatorial plane, while four Te–O bonds occupy the remaining positions in the trigonal bipyramidal structure resulting in the distorted TeO_4 tbp [5]. The addition of alkali oxides to TeO_2 results in the formation of binary tellurite glasses. An investigation of their structure with Raman spectroscopy [6] revealed that the addition of M_2O (M–Li, Na, K, Rb and Cs) into pure TeO_2 glass changes the Te coordination polyhedron from TeO_4 to TeO_3 trigonal pyramid (tp) in which the tellurium atom forms sp^3 hybrid orbitals with three Te–O bonds and one lone pair of electrons. Similar structural changes were also reported in tellurite glasses with divalent cations [7] and tri- and tetravalent cations [8].

Tellurium dioxide also forms glasses with phosphorus pentoxide P_2O_5 [9] and various ternary glasses with univalent oxides $M_2O\text{-}P_2O_5\text{-}TeO_2$ and divalent oxides $MO\text{-}P_2O_5\text{-}TeO_2$ [10]. Lead metaphosphate glasses doped with TeO_2 were studied by Sudarsan et al. [11] in two compositional series, where tellurium dioxide TeO_2 replaces either P_2O_5 or PbO (0–20 mol% TeO_2). From the study of ^{31}P MAS NMR spectra, the authors [11] found that in the series $50PbO\text{-}(50 - x)P_2O_5\text{-}xTeO_2$, the depolymerisation of phosphate chains took place, and the Q^2 units were transformed into Q^1 units by the incorporation of tellurite structural units into the glass network. This indicates the network modifier function of PbO in this glass series. In the $(50 - y)PbO\text{-}50P_2O_5\text{-}yTeO_2$ glass series, no discernible change was observed in the ^{31}P MAS NMR spectra. This result was ascribed to the formation of P–OH bonds in the glasses due to the interaction of P_2O_5-rich glasses with water.

Mošner et al. [12] have studied the structure of lead tellurite-phosphate glasses with Raman spectroscopy in two compositional series $(100 - x)Pb(PO_3)_2\text{-}xTeO_2$ and $50PbO\text{-}(50 - y)P_2O_5\text{-}yTeO_2$. In the first series, glasses with 0–80 mol% TeO_2 were prepared, in which the Raman spectra revealed that tellurium forms both TeO_4 and TeO_3 units, but in glasses with a high TeO_2 content, TeO_4 units predominate in the structure. In the latter series, glasses are formed within the range of 0–25 mol% TeO_2 while TeO_3 units predominate in their structure. Zinc borophosphate glasses doped with TeO_2 were studied in the compositional series $(100 - x)[0.5ZnO\text{-}0.1B_2O_3\text{-}0.4P_2O_5\text{-}xB_2O_3]\text{-}xTeO_2$ [13] and in the series $(1 - y)[50ZnO\text{-}(50 - x)P_2O_5\text{-}xB_2O_3]\text{-}yTeO_2$ containing 0–70 mol% TeO_2 and with the ratio of $B_2O_3/P_2O_5 = 5/45$, 10/40 and 15/35 [14]. The structural studies [14] were devoted to the investigation of changes in boron coordination, based on changes in TeO_2 content and the B_2O_3/P_2O_5 ratio in borophosphate glasses. ^{11}B MAS NMR spectra revealed the formation of mixed structural units $B(OP)_{4-x}(OTe)_x$ in the glasses and a small tendency towards the transformation of tetrahedral BO_4 units into BO_3 units.

This paper is devoted to structural studies of $PbO–B_2O_3–P_2O_5–TeO_2$ glasses. For these studies, ^{31}P and ^{11}B MAS NMR and Raman spectroscopies were used. ^{11}B MAS NMR spectra were recorded at a high static

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magnetic field of 18.8 T, which made it possible to obtain a high resolution, sufficient to investigate changes in boron coordination. The studies were completed with Raman spectroscopy, which made an evaluation of tellurium coordination in the glasses possible.

2. Experimental

PbO-B_2O_3-P_2O_5-TeO_2 glasses were prepared from an analytical grade PbO, TeO_2, H_3BO_3 and H_3PO_4 using a total batch weight of 20 g. The homogenised starting mixtures were slowly heated up to 600 °C for 2 h in order to remove water. The reaction mixtures were consequently heated up to 900–1050 °C in a platinum crucible with a lid. The melt was held at a maximum temperature for 30 min and then poured into a graphite mold. The obtained glasses were annealed for 5 h at a temperature 5 °C below their glass transition temperature, T_g. The volatilisation 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 structureless spectrum was obtained for all glass compositions.

The glass density, ρ, was determined by the Archimedes' method using toluene as the immersion liquid. The molar volume, V_M, was calculated as $V_M = \overline{M}/r$, where $\overline{M}$ is the average molar weight of the glass composition. The glass transition temperature, T_g, was measured on bulk samples with dimensions of $20 \times 5 \times 5$ mm using a dilatometer DIL 402 PC (Netzsch). Its value was determined as the intersection at the change in the slope of the elongation vs. temperature plot between the solid and undercooled liquid lines. The dilatometric measurements were carried out in air at a heating rate of 5 °C min^{-1}.

^{31}P MAS NMR spectra were measured at 9.4 T using a BRUKER Avance 400 spectrometer with a 4-mm probe. The spinning speed was 14 kHz. The pulse length was 2.5 μs (pi/4), and the recycle delay was 300 s, which was sufficient to enable relaxation at this field strength. ^{11}B MAS NMR spectra were measured at 18.8 T on a BRUKER Avance 800 spectrometer with a 2.5-mm probe. The spinning speed was 20 kHz. A rotor synchronised echo was used with selective pulse lengths of 5 μs, with an echo delay of 50 μs and a 10-s recycling delay. The chemical shifts of ^{11}B nuclei are given relative to BPO_4 at −3.6 ppm. The ^{11}B spectra have been processed to remove the background signal coming from the probe, by subtracting the signal recorded on an empty rotor. The NMR spectra decomposition was carried out using the Dmfit NMR software [15]. BO_4 lines are known to be subjected to a negligible second-order quadrupolar effect; hence, the decomposition was performed with a Gaussian-type function assuming that the line shape is dominated by a chemical shift distribution.

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 10 mW taking 10 scans with an exposition time of 2 s.

3. Results and discussion

We have prepared 12 samples of lead borophosphate glasses doped with TeO_2. In the glass series $(1-x)[50PbO\text{-}10B_2O_3\text{-}40P_2O_5]\text{-}xTeO_2$, we prepared 8 glasses containing 0–70 mol% TeO_2. The B_2O_3/P_2O_5 ratio is 10/40 in this series. For the evaluation of the boron coordination in these glasses, we also prepared glasses $(1-x)][50PbO\text{-}yB_2O_3(50-y)P_2O_5]\text{-}yTeO_2$ with 20 and 60 mol% TeO_2 and with a B_2O_3/P_2O_5 ratio of 5/45 and 15/35. The composition of the studied glasses and their density, molar volume and glass transition temperature are provided in Table 1. The glass density increases with the increasing TeO_2 content, whereas the molar volume decreases. The glass transition temperature decreases with the increasing TeO_2 content in the $(1-x)[50PbO\text{-}10B_2O_3\text{-}40P_2O_5]\text{-}xTeO_2$ glass series and has a maximum for the B_2O_3/P_2O_5 ratio 10/40.

Table 1
Composition, density, ρ, molar volume, V_M, and glass transition temperature, T_g, of PbO-B_2O_3-P_2O_5-TeO_2 glasses.

Sample	PbO (mol%)	B_2O_3	P_2O_5	TeO_2	$\rho \pm 0.02$ [$g\cdot cm^{-3}$]	$V_M \pm 0.5$ [$cm^3\cdot mol^{-1}$]	$T_g \pm 2$ °C [°C]
LBPT0	50	10	40	0	4.97	35.2	398
LBPT1	45	9	36	10	5.14	33.8	396
LBPT2	40	8	32	20	5.16	33.4	395
LBPT3	35	7	28	30	5.19	32.9	391
LBPT4	30	6	24	40	5.31	31.8	378
LBPT5	25	5	20	50	5.37	31.2	370
LBPT6	20	4	16	60	5.38	30.8	363
LBPT7	15	3	12	70	5.42	30.3	354
LBPT2A	40	4	36	20	5.09	34.4	374
LBPT2B	40	12	28	20	5.21	32.4	367
LBPT6A	20	2	18	60	5.33	31.4	356
LBPT6B	20	6	14	60	5.49	29.9	351

^{31}P MAS NMR spectra were only measured for the glass series $(1-x)[50PbO\text{–}10B_2O_3\text{–}40P_2O_5]\text{–}xTeO_2$ with their evolution with the TeO_2 content presented in Fig. 1. Tellurium atoms enter the glass network by the formation of P–O–Te bonds, as can be deduced from the ^{31}P NMR spectra (Fig. 1), which are shown on the depolymerisation of phosphate chains. The spectrum of the parent glass of the composition $50PbO\text{-}10B_2O_3\text{-}40P_2O_5$ contains two close NMR signals at −18.2 ppm and −9.9 ppm, corresponding to Q^2 and Q^1 structural units, respectively. With the increasing TeO_2 content, these two signals merge into one signal, and its maximum shifts downfield to a chemical shift value around –(12–13) ppm. Within the concentration range of $x = 0.4$–0.7, its position changes only slightly, which indicates that the coordination environment of the phosphorus atoms is not substantially changed in this compositional range.

The ^{11}B MAS NMR spectra were measured not only for the $(1-x)[50PbO\text{-}10B_2O_3\text{-}40P_2O_5]\text{-}xTeO_2$ glass series (Fig. 2), but also in two glass series $(1-x)[50PbO\text{-}yB_2O_3\text{-}(50-y)P_2O_5]\text{-}xTeO_2$ with the constant TeO_2 content of 20 and 60 mol% TeO_2 and with the ratios of B_2O_3/P_2O_5 corresponding to values of $y = 5$, 10 and 15 (Figs. 3 and 4). The ^{11}B MAS NMR spectra measured with the NMR spectrometer at 18.8 T reveal a better resolution than the studies conducted at a lower magnetic field since the quadrupolar effect of ^{11}B (nuclear spin = 3/2) is scaled down at a high field. The obtained NMR spectra are provided

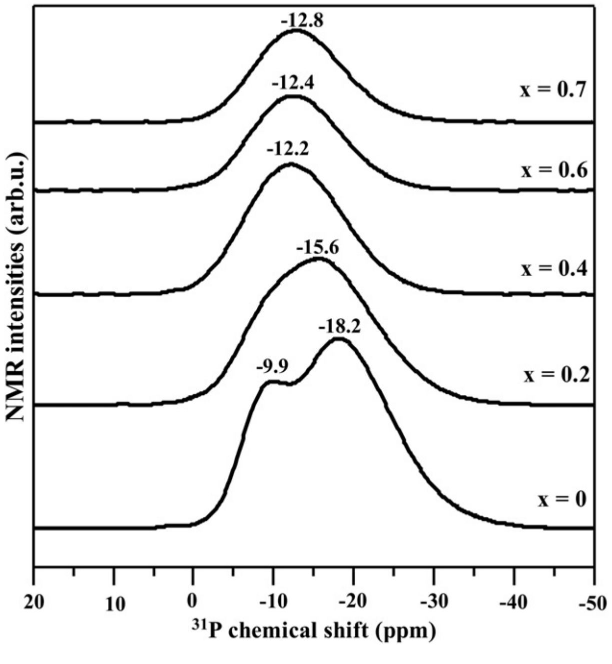

Fig. 1. ^{31}P MAS NMR spectra of $(1-x)[50PbO\text{-}10B_2O_3\text{-}40P_2O_5]\text{-}xTeO_2$ glasses.