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Study of potassium-lead borophosphate glasses

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Mixed potassium-lead borophosphate glasses were prepared and studied in two compositional series $x$$K_2O$-(50-$x$)PbO-10$B_2O_3-40P_2O_5$ and $x$$K_2O$-(50-$x$)PbO-20$B_2O_3-30P_2O_5$ with $x = 0, 10, 20, 30, 40$ and 50 mol% K_2O. The replacement of lead by potassium decreases the density and increases the molar volume of these glasses. On the other hand both glass transition temperature and chemical durability decrease. The observed changes in the properties of these glasses are explained as due to changes in their structure and ionicity of chemical bonds between cations and the anionic network of the glass. The major role is played by differences in the space occupied by cations, differences in electronegativity and the field strength of the corresponding cations.

1. Introduction

Borophosphate glasses are important glassy materials. For example, zinc-calcium borophosphate glasses were studied as candidates for applications as low-melting glass solders or glass seals [1]. Borophosphate glasses of alkaline metals reveal a high solubility [2], whereas zinc borophosphate glasses possess aqueous durability comparable to silicate compositions [3, 4]. For the glasses derived from metaphosphate composition the values of the glass transition temperature T_g increase with increasing B_2O_3 content and reach a maximum at glasses with ~20 mol% B_2O_3. This increase is explained by the transformation of the chain-like structure, characteristic of metaphosphate glasses, into the three-dimensional structure due to the incorporation of boron mostly as BO_4 tetrahedra [3, 5]. Borophosphate glasses containing two different cations were studied in the combinations: ZnO-CaO glasses [1], ZnO-SrO [6] glasses and ZnO-PbO glasses [7]. Recently we have studied the structure of K_2O-PbO borophosphate glasses by NMR, Raman and IR spectroscopy [8], where one Pb^{2+} cation is replace by two K^+ ions, which resulted in interesting changes in the investigated spectra. This paper aims to to study the properties of these glasses and to discuss the relations between the properties and structure of the glasses.

2. Experimental

Samples of the K_2O-PbO-B_2O_3-P_2O_5 glasses were prepared in the batches of 25 g by the reaction of K_2CO_3, PbO, H_3BO_3 and H_3PO_4 and slow heating the reaction mixture up to 1100–1150°C in a Pt crucible. After 30 min reaction and mixing at this temperature, the obtained melt was cooled by pouring into a copper mould of 30 × 50 mm dimensions to form a suitable glass block. The obtained glasses were separately annealed for 15 min at a temperature about their T_g and then slowly cooled to the room temperature. This process was repeated three times to improve glass mechanical properties; T_g was obtained from DTA measurements before the annealing.

The glass density, ρ, was determined at bulk samples by the Archimedes method using CCl_4 as the immersion liquid. The molar volume V_M was calculated as $V_M = \bar{M}/\rho$, where $\bar{M}$ is the average molar weight of the glass composition $w$$K_2O$-$x$PbO-$y$$B_2O_3$-$z$$P_2O_5$ calculated for $w + x + y + z = 1$. The chemical durability of the glasses was evaluated at room temperature from the measurements of the conductivity of a solution obtained by the interaction of 0.3 g of the glass powder (mean diameter of 8 μm) with 100 ml of distilled water for 60 min. For the measurement of thermomechanical properties the cubes with dimensions of 5 × 5 × 5 mm were cut out from the bulk samples.

Thermomechanical properties of glasses were measured on the equipment TMA CX04R (RMI Pardubice) at the heating rate of 5 K/min. From the obtained 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 plot. Thermal behaviour of the glasses was studied with the Perkin Elmer DTA-DSC equipment, model 1700, working in the temperature range of 20–1000°C at a scan rate of $10°C \cdot min^{-1}$ in the DSC mode. The measurement was done on powder samples with mean diameter 8–10 μm placed in sealed vacuum silica ampoules.

3. Results

Two compositional series of borophoshate glasses $x$$K_2O$-(50-$x$)PbO-10$B_2O_3-40P_2O_5$ and $x$$K_2O$-(50-$x$) PbO-20$B_2O_3-30P_2O_5$ with $x = 0, 10, 20, 30, 40$ and

TABLE I Some characteristic parameters of the xK$_2$O-(50-x)PbO-10B$_2$O$_3$-40P$_2$O$_5$ and xK$_2$O-(50-x)PbO-20B$_2$O$_3$-30P$_2$O$_5$ glasses

Glass composition (mol%)				$\rho \pm 0.1$	V_M	$T_g \pm 2$	$T_d \pm 2$	$\alpha \pm 1$	$T_c \pm 2$	κ
K_2O	PbO	B_2O_3	P_2O_5	($g \cdot cm^{-3}$)	(cm^3)	(°C)	(°C)	($ppm \cdot K^{-1}$)	(°C)	($\mu S \cdot cm^{-1}$)
0	50	10	40	4.90	35.8	379	413	14.4	555	10
10	40	10	40	4.27	38.0	356	385	17.5	453	18
20	30	10	40	3.73	40.0	332	362	18.6	443	72
30	20	10	40	3.30	41.4	329	368	18.9	411	620
40	10	10	40	2.83	43.7	318	370	23.1	381	1540
50	0	10	40	2.42	45.9	–	–	–	–	2680
0	50	20	30	5.21	32.3	468	491	13.3	533	15
10	40	20	30	4.51	34.4	436	466	15.8	484	34
20	30	20	30	3.91	36.4	415	459	17.9	442	54
30	20	20	30	3.38	38.3	388	400	20.8	421	630
40	10	20	30	2.89	40.4	375	411	25.1	420	1870
50	0	20	30	2.46	42.2	–	–	–	–	3020

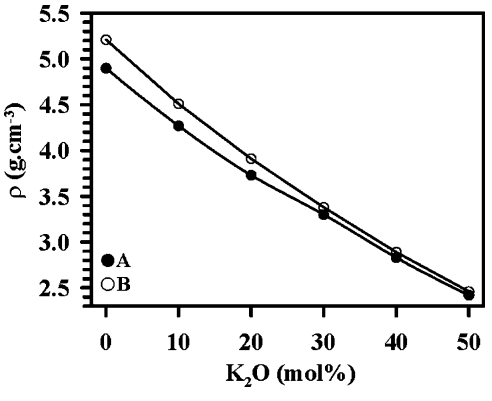

Figure 1 Compositional dependence of density in the glass series xK$_2$O-(50-x)PbO-10B$_2$O$_3$-40P$_2$O$_5$ (A) and xK$_2$O-(50-x)PbO-20B$_2$O$_3$-30P$_2$O$_5$(B).

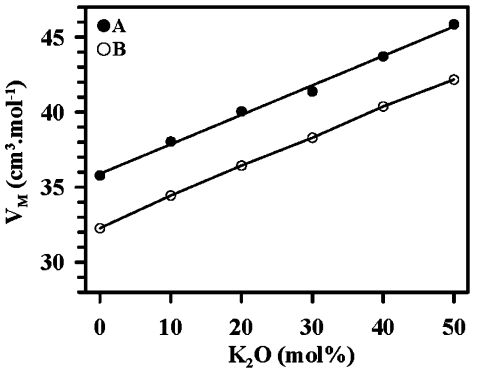

Figure 2 Compositional dependence of molar volume, V_M, in the glass series xK$_2$O-(50-x)PbO-10B$_2$O$_3$-40P$_2$O$_5$ (A) and xK$_2$O-(50-x)PbO-20B$_2$O$_3$-30P$_2$O$_5$(B).

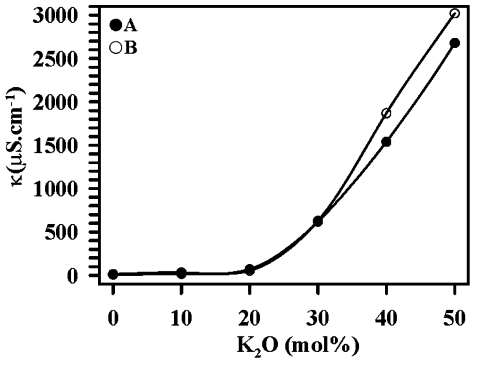

Figure 3 Compositional dependence of conductivity, κ, of water extracts in the glass series xK$_2$O-(50-x)PbO-10B$_2$O$_3$-40P$_2$O$_5$ (A) and xK$_2$O-(50-x)PbO-20B$_2$O$_3$-30P$_2$O$_5$(B).

50 mol% K_2O were synthesized and studied. All the prepared glasses were transparent and homogeneous. The compositional dependencies of the glass density, ρ, for both series of glasses are shown in Fig. 1 and the corresponding data are given also in Table I. As can be seen from this figure, the density of the studied glasses decreases with an increasing content of potassium oxide in both series of glasses. On the other hand, the molar volume, V_M, in both series of glasses increases with increasing content of K_2O as can be seen in Fig. 2. This increase amounts about 25%, when comparing pure lead borophosphate glass with the corresponding pure potassium glass.

The compositional dependence of the conductivity (κ) of water extract obtained after 60 min interaction of glass powder with distilled water at room temperature is shown on Fig. 3. From this figure it can be seen, that at a low potassium content up to 20 mol% K_2O, the chemical durability of the mixed glasses is relatively high and the amount of ions extracted from glass into the solution is very small, because κ changes only a little with increasing K_2O content. At the potassium content above 20 mol% K_2O the glasses are more vulnerable to water and the conductivity of the water extract increases very steeply, i.e., the amount of ions coming from glass into the solution is much higher.

Thermoanalytical curves obtained from DTA analysis of the glass powders in the temperature range of 50–700°C revealed two distinct enthalpic peaks—the exothermic crystallization peak and the endothermic melting peak. Most of the studied glasses crystallize at heating within the temperature range of 380–620°C. In Fig. 4, as an example, there are shown DTA curves of glasses of the series xK$_2$O-(50-x)PbO-10B$_2$O$_3$-40P$_2$O$_5$. In this figure it can be seen that with increasing K_2O content the onset of the crystallization peak, T_c, shifts towards lower temperatures. The change in the heat capacity at the glass transformation temperature, T_g, is relatively small and the determination of T_g can not be done precisely, so for its determination we have applied TMA measurements. The endothermic

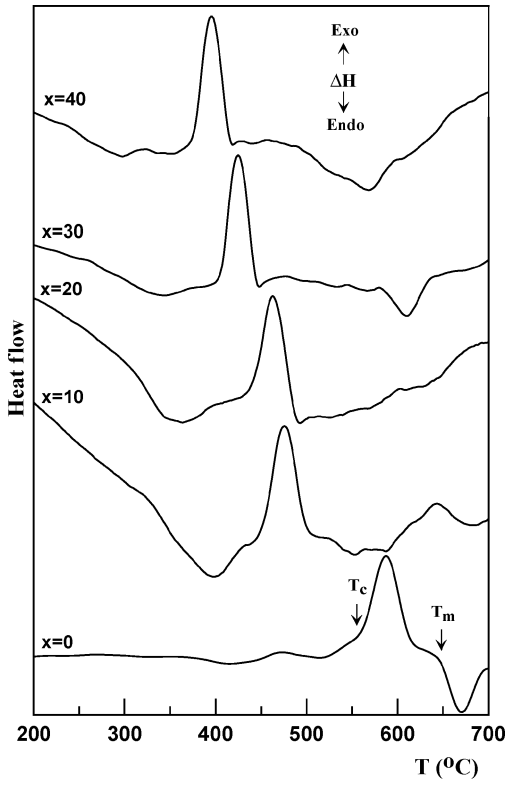

Figure 4 DSC curves of glasses of the series $x$$K_2O$-(50-$x$)PbO-$10B_2O_3$-$40P_2O_5$.

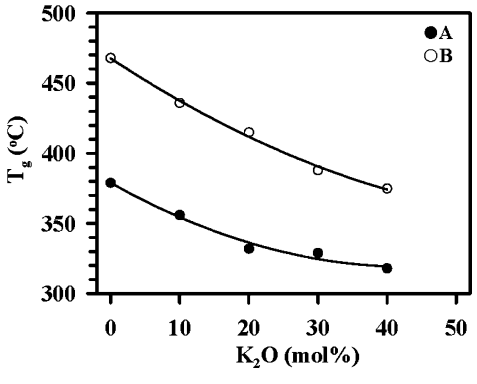

Figure 5 Compositional dependence of the glass transition temperature, T_g, of the glass series $x$$K_2O$-(50-$x$)PbO-$10B_2O_3$-$40P_2O_5$ (A) and $x$$K_2O$-(50-$x$)PbO-$20B_2O_3$-$30P_2O_5$(B).

melting peak (its onset is shown in Fig. 4 at the lead borophosphate glass as T_m) was observed within the studied temperature range only at some samples and therefore the data on T_m are not covered in Table I.

Study of K_2O-PbO borophosphate glasses by thermomechanical analysis gave the values of glass transition temperatures, T_g, and the dilatation softening temperature, T_d, of the studied glasses and also their thermal expansion coefficient α; their values are given in Table I. The compositional dependence of T_g for both series of glasses are shown in Fig. 5. As can be seen from this figure, the glass transition temperature decreases with increasing content of K_2O in both series of borophosphate glasses. Thermal expansion coefficient α (see Table I) in both series of the borophosphate glasses increases monotonously with increasing K_2O content.

4. Discussion

The substitution of PbO by K_2O means that two K^+ ions compensate the charge of one Pb^{2+} ion. The consequence of this replacement is that the space occupied by cations in these glasses substantially increases. In a first approximation we can suppose that bonding of Pb atoms in these glasses possess a covalent character, so we can take into account covalent radius for Pb(II) in these glasses, which is 0.147 nm [9]. In potassium glasses, we can consider more ionic character of K–O chemical bond, so we can take into account rather the ionic radius of K(I) being 0.133 nm [8]. In this way in a first approximation we can calculate the ratio of the molar volumes for the boundary compositions $50PbO\text{-}10B_2O_3\text{-}40P_2O_5$ and $50K_2O\text{-}10B_2O_3\text{-}40P_2O_5$ as

$$R(V_{KBF}/V_{PbBF}) = \frac{100V(K_{ion}) + 20V(B_{cov}) + 80V(P_{cov}) + 280V(O_{cov})}{50V(Pb_{cov}) + 20V(B_{cov}) + 80V(P_{cov}) + 280V(O_{cov})}.$$

The calculated ratio using the covalent volumes of the corresponding atoms given in [9] for these (A) series of glasses with 10 mol% B_2O_3 amounts 1.20 and for the (B) series of glasses amounts 1.22. The observed increase in V_M of 25% is close to the values calculated using in a first approximation the covalent radius for Pb(II) and ionic radius for K(I). The actual radii will be changed a little, because the Pb–O bonds have a covalent-ionic character with about 26% ionicity and K–O bonds possess 82% ionicity, estimated from the difference of electronegativity values of corresponding elements [8].

The differences in the chemical durability of the glasses of series A and B are small. We assume that the observed steep decrease in the chemical durability of potassium-rich K-Pb borophosphate glasses is associated with changes of structure and the character of bonding interactions between the cations and anionic network. As the molar volume increases due to the incorporation of bulky potassium cations K^+, the glass network becomes more opened and the ionicity of M–O bonds increases. Therefore cations can be easily extracted from K-rich glasses by water, which explains an increase in the conductivity of water extracts at the testing of glass durability at room temperature. Nevertheless, a non-linear dependence of the conductivity of water extracts (Fig. 3) shows that in Pb-rich glasses K^+ ions remain closed inside the network and only when the structure is sufficiently opened then the cations can be efficiently dissolved.

The observed decrease in T_g is associated with a decreasing strength of chemical bonds inside the structural network. As can be seen in Fig. 5, glasses with higher content B_2O_3 have higher values of T_g. In lead borophosphate glasses generally T_g values increase with increasing B_2O_3 content within the range 0–20 mol% B_2O_3 [5]. This increase in T_g is ascribed to the incorporation of BO_4units between the metaphosphate chains resulting in a transformation of chain structure into the 3-dimensional network structure with higher bonding forces [5].

The observed increase in the thermal expansion coefficient, α, with the replacement of PbO by K_2O is associated mostly with the weakening of bonding forces in the structural network of the glasses, as evidenced by decreasing T_g. The increased ionicity of the chemical bonds in these glasses contributes also to the increase of α.

All the observed changes in the properties of mixed K-Pb borophosphate glasses are related mainly to the changes in the glass structure and bonding interactions in the disordered network. The study of the structure of these glasses by NMR, Raman and infrared spectroscopy [8] revealed that the glass network is formed by PO_4 tetrahedra and predominantly by BO_4 tetrahedra. Only in the glasses with 20 mol% B_2O_3, a small part of boron atoms forms also BO_3 units. The increased volume of the space occupied by cations in potassium-rich glasses results also in the interruption of some bonds in the anionic network of the glass structure and its reorganization, which is also reflected in the observed changes in NMR and Raman spectra. The ^{31}P MAS NMR spectra revealed also that with the replacement of PbO by K_2O a shortening of phosphate chains takes place and the number of Q^1 units increases [8]. Also the Raman spectra of potassium-rich borophosphate glasses reveal the increased strength of Raman bands ascribed to the vibrations of pyrophosphate-type structural units.

5. Conclusion

Study of the properties of mixed potassium-zinc borophosphate glasses of two compositional series $x K_2O$-(50-x)PbO-10B_2O_3-40P_2O_5 and $x K_2O$-(50-x)PbO-20B_2O_3-30P_2O_5 revealed that with the replacement of PbO by K_2O a higher ionicity of bonds between cations and the anionic network is associated with a decrease in the strength of bonding interactions in the structural network. Stronger P–O–Pb bonds are replaced by $P–O^- \cdots K^+$ bonds. Weakening of chemical bonds in the network results in a decrease in the glass transformation temperature and chemical durability of the potassium-rich borophosphate glasses. Because one lead atom (PbO) is replaced by two bulky potassium atoms (K_2O), molar volume of glasses increases with increasing K_2O content and also the thermal expansion coefficient increases. The glasses with a higher boron content have a higher crosslinking of network structure due to BO_4 groups interconnecting phosphate PO_4 groups and thus the glasses of the series with 20 mol% B_2O_3 have also higher values of the glass transition temperature than the glasses with lower B_2O_3 content.

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