Structure and properties of mixed potassium-zinc borophosphate glasses

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Mixed potassium-zinc borophosphate glasses were prepared and studied in two compositional series xK_2O-(50-x)ZnO-$10B_2O_3$-$40P_2O_5$ and xK_2O-(50-x)ZnO-$20B_2O_3$-$30P_2O_5$ with x = 0, 10, 20, 30, 40 and 50 mol% K_2O. The replacement of zinc 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. Structural changes were studied by ^{11}B and ^{31}P MAS NMR and Raman spectra of these glasses, which reveal remarkable differences when replacing ZnO by K_2O. The observed changes in the spectra and properties of the glasses can be ascribed mainly to the differences in the space occupied by cations, the 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[i]. Borophosphate glasses of alkaline metals reveal a high solubility[ii], whereas zinc borophosphate glasses possess aqueous durability comparable to silicate compositions[iii,iv]. For the glasses derived from metaphosphate composition the values of the glass transition temperature T_g increase with an increasing B_2O_3 content and reach a maximum at glasses with ~20 mol% B_2O_3. This increase is explained by a transformation of the chain-like structure, characteristic of metaphosphate glasses, into the three-dimensional structure due to the incorporation of boron in the prevailing form of BO_4 tetrahedra[3,v]. Borophosphate glasses containing two different cations were studied in the combinations: ZnO-CaO glasses[1], ZnO-SrO[vi] glasses and ZnO-PbO glasses[vii]. In this paper, borophosphate glasses containing two cations with different valencies are studied, in this case mixed glasses obtained by the replacement of ZnO by K_2O in borophosphates.

2. Experimental

Samples of the K_2O-ZnO-B_2O_3-P_2O_5 were prepared in the batches of 50 g by the reaction of K_2CO_3, ZnO, H_3BO_3 and H_3PO_4 and heating slowly 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 30x50 mm dimensions to form a suitable glass block. The glasses were separately annealed for 60 min at a temperature of 10K above their T_g and then slowly cooled to the room temperature to improve their mechanical properties.

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 using the expression $V_M = \overline{M}/\rho$, where $\overline{M}$ is the average molar weight of the glass composition wK_2O-$xZnO$-yB_2O_3-zP_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 powder sample of a glass (mean diameter of 8 μm) with 100 ml of water for 60 min.

^{31}P and ^{11}B MAS NMR spectra were measured on a BRUKER AMX400 spectrometer using a pulse length of 2.5 μs for both ^{31}P and ^{11}B MAS NMR spectra. The Larmor frequencies were 161.98 MHz and 128.38 MHz for ^{31}P and ^{11}B, respectively. The recycle delay was 500 ms for ^{11}B MAS NMR and 150s for the ^{31}P MAS NMR measurements.

Raman spectra were measured on a FT IR spectrometer, Bruker model IFS 55, with the Raman attachment, FRA 106, under excitation with a Nd:YAG laser radiation using a slit width of 4 cm^{-1} with the power of 300 mW at the sample surface. The Raman spectra were measured at room temperature on bulk samples using 400 scans.

3. Results

Two compositional series of borophoshate glasses xK_2O-$(50-x)ZnO$-$10B_2O_3$-$40P_2O_5$ and xK_2O-$(50-x)ZnO$-$20B_2O_3$-$30P_2O_5$ with x = 0, 10, 20, 30, 40 and 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. 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 an increasing content of K_2O as can be seen in Fig.2. This increase amounts to more than 30%, when comparing pure zinc borophosphate glasses with the corresponding pure potassium glasses.

The values of the glass transition temperature, T_g, and the dilatation softening temperature, T_d, obtained from the measurements of thermomechanical analysis, decrease in both series of glasses with an increasing potassium content.

The conductivity of the water solution (ϰ) obtained after 60 min interaction of glass powder with water 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 changes only a little with an increasing K_2O content. At a potassium content above 20 mol% K_2O the glasses are more vulnerable to water and the conductivity of the solution, i.e. the amount of ions coming from glass into the solution increases more steeply.

^{11}B and ^{31}P NMR spectra were obtained for the glass series of the composition xK_2O-$(50-x)ZnO$-$20B_2O_3$-$30P_2O_5$. The ^{11}B MAS NMR spectra of zinc-rich borophosphate glasses are composed of two peaks at δ = -3 and –5 ppm and a BO_3 signal at about 10 ppm. With an increasing potassium content the strength of the first peak increases, whereas the strength of the latter peak decreases. In the ^{31}B NMR spectra of potassium-rich glasses there is only one BO_4 peak with the maximum at δ = -1 - (-2) ppm. The ^{31}P MAS NMR spectra of pure zinc borophosphate glass of the composition $50ZnO$-$20B_2O_3$-$30P_2O_5$ reveal one broad signal with the maximum at δ = -18 ppm, i.e. in the region characteristic for the presence of both Q^1 and Q^2 units[viii]. With an increasing potassium content the peak shifts downfield and at potassium-rich glasses it splits into two signals at δ = -1 and – 9 ppm.

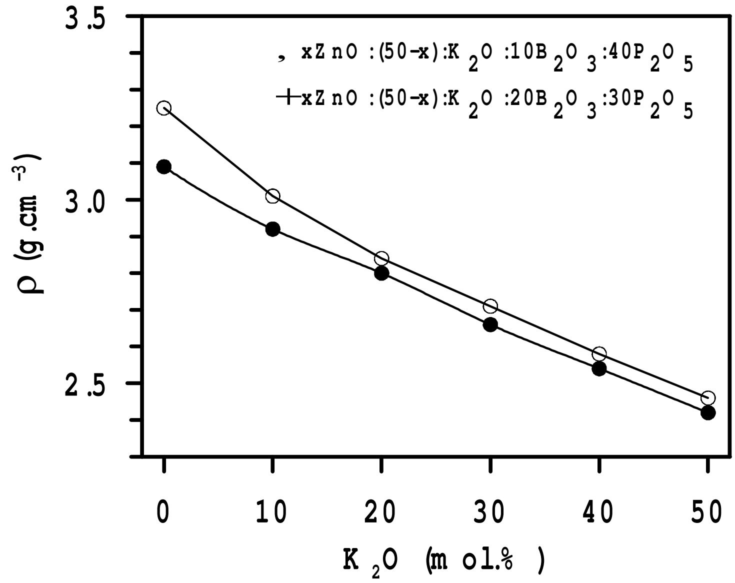

Fig.1. Compositional dependence of the density of potassium-zinc borophosphate glasses.

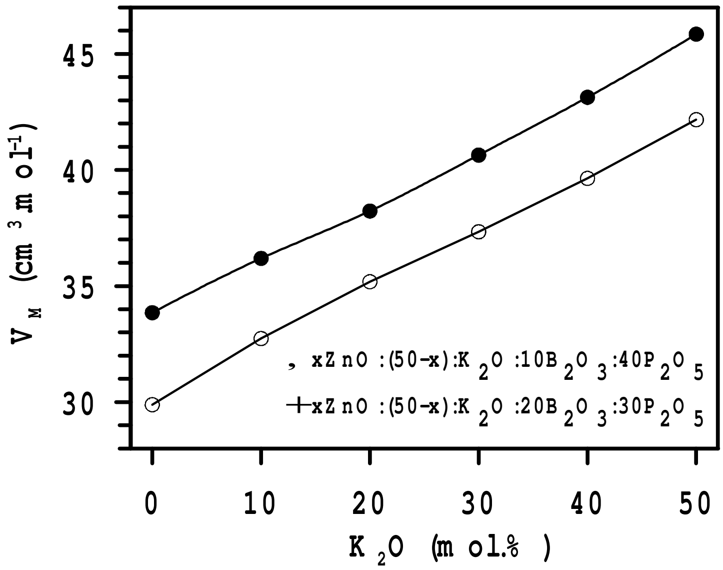

Fig.2. Compositional dependence of the molar volume of potassium-zinc borophosphate glasses.

The Raman spectrum of the pure Zn borophosphate glass in the glass series xK_2O-(50-x)ZnO-$20B_2O_3$-$30P_2O_5$ is characterized in the high-frequency region by a broad band with the maximum at 1094 cm^{-1}. With the replacement of zinc by potassium in this glass series this band gradually splits into three narrower bands at 1014, 1114 and 1210 cm^{-1}. The band of 753 cm^{-1} shifts to lower frequencies with an increasing potassium content up to 721 cm^{-1} in pure potassium borophosphate glass. In the glass series xK_2O-(50-x)ZnO-$10B_2O_3$-$40P_2O_5$ the high frequency band at 1166 cm^{-1} in 50ZnO-$10B_2O_3$-$40P_2O_5$ glass with an increasing potassium content also gradually splits into two narrow bands with the maxima at 1064 and 1157 cm^{-1} in $50K_2O$-$10B_2O_3$-$40P_2O_5$ glass.

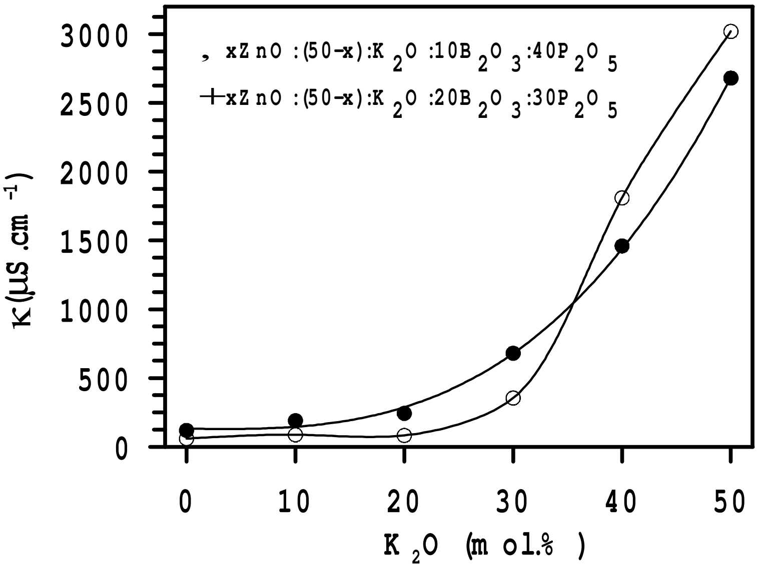

Fig.3. Conductivity of the water solution (κ) after interaction of glass powder with water.

4.Discussion

The replacement of zinc by potassium in the mixed potassium-zinc borophosphate glasses results in substantial changes of their physical properties and also in their NMR and Raman spectra.

The substitution of ZnO by K_2O means that two K^+ ions compensate the charge of one Zn^{2+} ion. The consequence of this replacement is that the space occupied by cations in these glasses substantially increases. We can suppose that bonding of Zn atoms in these glasses possess a high part of covalent character, so we can take into account covalent radius for Zn(II) in these glasses, which is 0.125 nm. In potassium glasses, we can consider more ionic character of bonds between K and O, so we can take into account rather the ionic radius of K(I) being 0.135 nm. Even greater difference in the size we would obtain when comparing atomic radii of Zn (0.138) and K (0.235). Nevertheless both considerations show that one smaller Zn(II) cation is replaced by two bigger K(I) cations. This increase in the space occupied by cations is also reflected in the observed increase of the molar volume of these glasses (see Fig. 2) which amounts to about 33-35% when we compare pure Zn glasses with the corresponding pure K glasses.

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 observed changes in the ^{31}P MAS spectra can be explained by a shortening of phosphate chains and an increase in the number of Q^1 units with the replacement of ZnO by K_2O. Also the Raman spectra reveal the increased strength of spectral bands ascribed to the vibrations of pyrophosphate-type structural units.

Such changes in the connectivity of the network are reflected also in a decrease in the values of the glass transition temperature, T_g, and dilatation softening temperature, T_d, with the replacement of ZnO by K_2O. In this way the glass network becomes also more opened and especially in the potassium-rich glasses, the potassium cations can be easily extracted by water, which explains an increase in the conductivity of solutions at the testing of glass durability in water at room temperature.

5. Conclusion

The structure of inorganic oxide-based glasses consists usually of a disordered network composed of polyhedra formed by glass-forming oxides. The cationic part has usually a slighter effect on their structure, so in the phosphate glasses[ix] the Raman spectra and NMR spectra of the similar glass compositions with different cations are very similar. We have observed that in mixed potassium-zinc borophosphate glasses these differences are much larger, which can be explained by the differences in the cation sizes, electronegativity and also the different field strength of these two different modifying cations.

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