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Thermomechanical properties and stability of mixed strontium-zinc borophosphate glasses

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Borophosphate glasses of the SrO-ZnO-B_2O_3-P_2O_5 system were prepared in 3 compositional series of 25ZnO-25SrO-xB_2O_3-$(50 - x)P_2O_5$, $(58.3 - x)$ ZnO-xSrO-16.6B_2O_3-33.33P_2O_5 and $(50 - x)$ZnO-20B_2O_3-30P_2O_5 and the changes in their thermomechanical and thermal properties with changes in their composition were investigated. The thermal expansion coefficient α decreases with increasing B_2O_3 content, whereas the values of glass transformation temperature T_g and dilatation softening temperature T_d increase. The replacement of ZnO by SrO increases both T_g and T_d. From the DSC results the value of the the Hruby's criterion K_{gl} was calculated and changes in the glass-forming tendency with changes in glass composition were discussed. © *2000 Kluwer Academic Publishers*

1. Introduction

Phosphate glasses were studied in last years as candidates for various technological applications [1]. One of them is for glass-to-metal seals due to their low melting temperature and low viscosity. The disadvantage of phosphate glasses is their poor chemical durability. Several studies proved that it can be improved either by the addition of trivalent cations (e.g. Al^{3+}, B^{3+}) [2, 3] which results in the crosslinking of their structural network or by addition of cations with high electrostatic field strength (Zn^{2+}, Pb^{2+}) [4, 5] to increase the covalency of P-O-M bonds.

For the glass seals thermal and thermomechanical properties are the most important, because the thermal expansion coefficient should be close to the used metal to avoid internal stresses in the seals. Also their chemical durability is important, because the seals should not be attacked by water. Therefore studies are done on various glassy systems on the effect of various substitutions both on thermal properties and the chemical durability.

The present work deals with the effect of the substitution of zinc metaphosphate glass $Zn(PO_3)_2$ on the cation site by strontium Sr^{2+} and on the anion site by boron B^{3+}. The effect of these substitutions on the glass-forming tendency, thermal and thermomechanical properties and the chemical durability was investigated.

2. Experimental

2.1. Preparation

Samples of the xSrO-yZnO-zB_2O_3-uP_2O_5 were prepared by mixing $SrCO_3$, ZnO and H_3BO_3 in an achate mortar and adding H_3PO_4 in the proper stoichiometric ratio and by subsequent drying and heating the reaction mixture slowly up to 1200–1250°C in a Pt crucible. After 30 min treatment and mixing at this temperature the obtained melt was cooled by pouring on a steel plate. In this way 18 compositions of the SrO-ZnO-B_2O_3-P_2O_5 system were prepared in 3 compositional series of (A) 25SrO-25ZnO-xB_2O_3-$(50 - x)P_2O_5$, (B) xSrO-$(50 - x)$ZnO-20B_2O_3-30P_2O_5 and (C) xSrO-$(58.3 - x)$ZnO-16.6B_2O_3-33.3P_2O_5. The solidified batch of about 50 g formed a thick layer which represented at 13 samples a homogeneous glass.

2.2. Characterization

Glass density, ρ, was determined at the bulk samples by the Archimedes method using CCl_4 as the immersion liquid. The molar volume V_M was calculated using the expression $V_M \equiv \bar{M}/\rho$, where $\bar{M}$ is the average molar weight of the glass composition $xM(\mathrm{SrO})$-$yM(\mathrm{ZnO})$—$zM(\mathrm{B_2O_3})$-$uM(\mathrm{P_2O_5})$ calculated for $x + z + y + u = 1$, where M is the molecular weight of the corresponding compound.

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 linear coefficient of thermal expansion (α) was obtained as a mean value in the temperature range of 50–150°C. The glass transition temperature (T_g) was determined from the change in the slope of the elongation versus temperature plot.

The dilatation softening temperature (T_d) was obtained from the maximum of the expansion trace. This maximum results from the onset of the viscous deformation of the glass sample, which is subjected to a small compressive force (50 mN) in the equipment. T_d values are dependent on the applied force and only useful for comparison between various glass compositions. 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 $10^{\circ}\text{C}\cdot\text{min}^{-1}$ in the DSC mode.

The chemical durability of the glasses was evaluated from their dissolution rate in distilled water at 25°C (for 24 hr) and at 100°C in boiling water (for 1 hr). Samples in the form of cubes 5 × 5 × 5 mm were immersed in 100 cm^3 of water. Before and after the dissolution test the samples were dried at 80°C. The dissolution rate (DR) was calculated as a weight loss in grams of the glass surface of 1 cm^2 after 1 min as:

$$DR = \frac{\Delta\omega}{St},$$

where $\Delta\omega$ is the weight loss (g), S is the area before the dissolution test and t is the dissolution time (min.).

3. Results and discussion

The samples of the $SrO-ZnO-B_2O_3-P_2O_5$ system were prepared in 3 compositional series. The first one with a constant MO content of 50 mol% as (A) $25ZnO-25SrO-xB_2O_3-(50-x)P_2O_5$, and the other two with a constant P_2O_5/B_2O_3 ratio and with 50 mol% MO as (B) $(50-x)ZnO-xSrO-20B_2O_3-30P_2O_5$ and with 58.3 mol% MO as (C) $(58.3-x)ZnO-xSrO-16.6B_2O_3-33.33P_2O_5$. The prepared samples were checked visually on the homogeneity and crystallinity, because glasses were clear and transparent and crystalline samples were opaque. Under experimental conditions described above homogeneous glasses were not obtained in the first series of glasses only at the sample A4 with $x = 30$ mol.% B_2O_3. In the other glass series crystalline samples were formed at a high Sr content. The composition of the obtained homogeneous glasses is given in Table I together with the determined values of density (ρ) of the glasses, the molar volume (V_M) calculated from the values of density and the dissolution rate. In the series A the density slightly increases with the replacement of P_2O_5 by B_2O_3 and the molar volume decreases. It seems that the incorporation of borate structural units BO_3 and BO_4 into the phosphate network results in a more compact structure of the glass. In the series of B and C the replacement of Zn by Sr results in a slight increase both in density and the molar volume with the replacement of a lighter and smaller Zn atoms by bulky and heavy Sr atoms.

The obtained data on the dissolution rate of the Sr-Zn borophosphate glasses show, that the studied borophosphate galssses are relatively stable in water at low temperatures. The dissolution rate was higher in boiling water than at room temperature. Pure Zn phosphate and borate glasses revealed a tendency to crack in boiling water, borophosphate glasses were more stable. Mixed Sr-Zn borophosphate glasses are less soluble in boiling water than pure Zn borophosphate glasses. Also the glasses with higher $MO/(P_2O_5 + B_2O_3)$ content reveal higher chemical stability.

Study of Sr-Zn borophosphate glasses by thermomechanical analysis gave the values of thermal expansion coefficient, α, of the studied glasses and their glass transition temperatures, T_g, and dilatation softening temperatures, T_d, are presented in Table II. In Fig. 1 there is shown the dependence of the values of T_g and T_d on the content of B_2O_3 in the glass series A with a constant content of 25 mol.% ZnO and 25 mol.% SrO. Both T_g and T_d increase abruptly at small additions of B_2O_3 and reach a maximum at about 40 mol.% B_2O_3 in the glasses. These changes undoubtedly correspond to the changes in the nature of bonding in the structural network.

In the phosphate glasses close to metaphosphate composition $Zn_{0.5}Sr_{0.5}(PO_3)_2$, the structural network consists of PO_4 structural units with 2 bridging and 2 non-bridging oxygen atoms. These units are linked into a structural chain via -P-O-P- bridges giving thus $-(PO_3)_n-$ polymer-like structural network. Boron atoms

TABLE I Density, molar volume and dissolution rate of $ZnO-SrO-B_2O_3-P_2O_5$ glasses

Sample	SrO	ZnO	B_2O_3	P_2O_5	ρ	V_M	DR_{25}	DR_{100}
	[mol.%]				$[\text{g}\cdot\text{cm}^{-3}]$	$[\text{cm}^3]$	$[\text{g/cm}^2\cdot\text{min}]$	$[\text{g/cm}^2\cdot\text{min}]$
A1	25	25	0	50	3.05	38.5	0	2.9×10^{-5}
A2	25	25	10	40	3.27	33.6	2.4×10^{-7}	2.0×10^{-5}
A3	25	25	20	30	3.39	30.3	1.2×10^{-7}	0.4×10^{-5}
A4	25	25	30	20	Crystalline			
A5	25	25	40	10	3.39	26.0	1.0×10^{-7}	1.0×10^{-5}
A6	25	25	50	0	3.48	23.3	0	$^{*}28.0 \times 10^{-5}$
B1	0	50	20	30	3.26	29.8	16.8×10^{-7}	$^{*}47.1 \times 10^{-5}$
B2	12.5	37.5	20	30	3.36	29.8	0	0.1×10^{-5}
B3 = A3	25	25	20	30	3.39	30.3	1.2×10^{-7}	0.4×10^{-5}
B4	37.5	12.5	20	30	3.42	30.8	6.9×10^{-7}	3.3×10^{-5}
C1	0	58.3	8.3	33.3	3.50	28.7	0.9×10^{-7}	$^{*}16.0 \times 10^{-5}$
C2	14.6	43.8	8.3	33.3	3.48	29.8	2.5×10^{-7}	1.0×10^{-5}
C3	29.2	29.2	8.3	33.3	3.53	30.4	0	0

*the denoted glasses in the boiling water a white surface film was formed, which gradually split off.

TABLE II Glass transition temperature, Tg, dilatation softening temperature, T_d, and the thermal expansion coefficient α of the SrO-ZnO-B_2O_3-P_2O_5 glasses

Sample	SrO	ZnO	B_2O_3	P_2O_5	T_g [°C]	T_d [°C]	α [ppm·K^{-1}]
	[mol.%]						
A1	25	25	0	50	437	465	7.9
A2	25	25	10	40	513	537	8.0
A3	25	25	20	30	554	574	7.5
A4	25	25	30	20		Crystalline	
A5	25	25	40	10	574	605	6.6
A6	25	25	50	0	567	592	4.3
B1	0	50	20	30	492	516	3.2
B2	12.5	37.5	20	30	517	539	4.2
B3 = A3	25	25	20	30	554	574	7.5
B4	37.5	12.5	20	30	593	607	8.1
C1	0	58.3	8.3	33.3	480	522	5.5
C2	14.6	43.8	8.3	33.3	505	524	4.9
C3	29.2	29.2	8.3	33.3	534	551	5.9

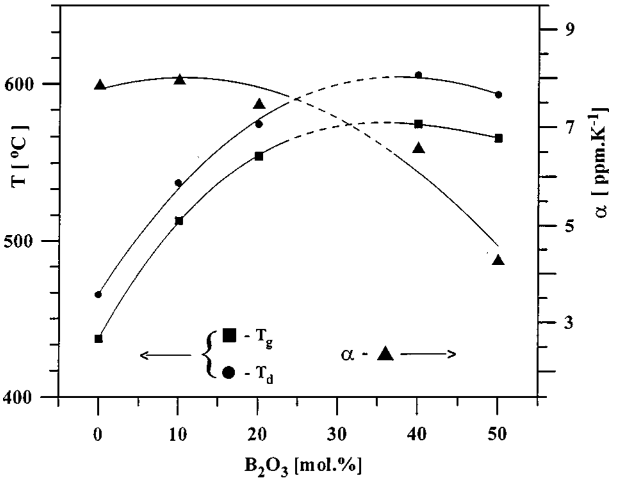

Figure 1 Dependence of the glass transition temperature, T_g, dilatation softening Temperature, T_d, and thermal expansion coefficient, α, on the B_2O_3 content in the glass series 25SrO-25ZnO-$x$$B_2O_3$-$(50 - x)$$P_2O_5$.

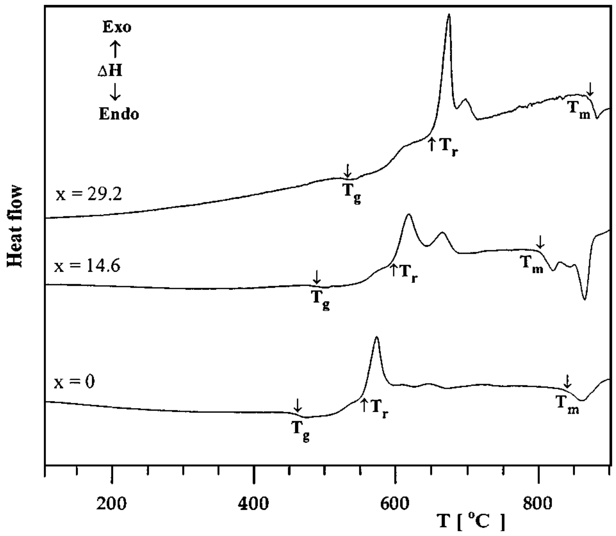

Figure 2 DSC curves of glasses of the series xSrO-$(58.3 - x)$ZnO-16.6B_2O_3-33.3P_2O_5.

form in borate glasses structural units BO_3 with three-coordinated boron atom and BO_4 with four-coordinated boron atom. Their mutual participation in the structure of Zn borophosphate glasses was investigated by ^{11}B NMR studies [4] which showed that in phosphate-rich glasses tetrahedral BO_4 units are preferred. Therefore the incorporation of BO_4 units into the chain-like phosphate glass structure results in the enhancement of dimensionality of the structural network from one-dimensional to three-dimensional and increasing bonding forces within the network.

The replacement of Zn by Sr atoms in the borophosphate glasses of the series of B and C result also in a substantial increase in T_g and T_d by about 100°C with the replacement of 3/4 of Zn by Sr atoms at the series C (see Table I). The effect of Sr replacing Zn atoms on the thermal expansion coefficient is more pronounced in the glasses with a lower cation content (series C), where an increase in the value of α with an increasing Sr content is the most pronounced. In the series A its values are the highest at a low boron content (8×10^{-6} ppm/K), but with a further replacement of phosphate groups by borate groups they decrease.

Thermoanalytical study of the behaviour of borophosphate glasses revealed three temperature values of the characteristic features - the glass transition temperature T_g, the onset of the exothermic crystallization peak T_r and the onset of the endothermic melting peak T_m. The studied glasses at heating crystallize within the temperature region of 600–800°C and mostly in two stages. In Fig. 2, as an example, there are shown DSC curves of the glassy samples of the series B. In this figure it can be seen that with an increasing Sr content both T_g and the onset of the crystallization peak T_r shift toward higher temperatures (both values are given in Table III). The obtained value of T_g determined from DSC curves are mostly close to the values obtained by the TMA method.

From the results of the thermoanalytical study we also evaluated the glass-forming ability of the studied borophosphate glasses using the criterion suggested by Hrubý [6] in the form

$$K_{gl} = \frac{T_r - T_g}{T_m - T_r},$$

TABLE III The results of thermoanalytical study of ZnO-SrO-B_2O_3-P_2O_5 glasses and the values of Hruby's criterion of glass stability

Sample	SrO	ZnO	B_2O_3	P_2O_5	T_g [°C]	T_r [°C]	T_m [°C]	K_{gl}
	[mol.%]							
A1	25	25	0	50	437	589	688	1.53
A2	25	25	10	40	509	667	899	0.68
A3	25	25	20	30	544	620	854	0.33
A4	25	25	30	20	Crystalline			
A5	25	25	40	10	567	624	838	0.27
A6	25	25	50	0	560	699	828	1.08
B1	0	58.3	8.3	33.3	465	559	829	0.35
B2	14.6	43.8	8.3	33.3	492	615	805	0.65
B3	29.2	29.2	8.3	33.3	527	656	870	0.60
C1	0	50	20	30	479	591	856	0.42
C2	12.5	37.5	20	30	513	643	813	0.77
C3 = A3	25	25	20	30	544	620	854	0.33
C4	37.5	12.5	20	30	583	655	902	0.29

where T_m is the onset of the melting peak. According to Hrubý [6], glasses with higher values of K_{gl} reveal better glass-forming tendency. The criterion gives a numerical expression useful for the evaluation of glass-forming tendency of melts. The values of K_{gl} for the studied Sr-Zn borophosphate glasses calculated from the obtained DSC data are given in Table III.

The observed values of K_{gl} make it possible to discuss glass-forming tendency in all three compositional series. In the series A the most stable glass is the starting Sr-Zn metaphosphate. The replacement of P_2O_5 by B_2O_3 decreases glass-forming tendency which is confirmed by the crystallization of the composition denoted as A4 with 30 mol.% of B_2O_3. With a further increase of B_2O_3 content towards pure metaborate, the glass-forming ability increases again. The observed effect is associated with a change from the polymer-like chain structure of metaphosphate glasses to the three-dimensional structure with dominant tetrahedral BO_4 units connecting phosphate chains, which increases a tendency of the crystallization of BPO_4 from the glass melt [7]. In the glasses with a high B_2O_3 content planar BO_3 units prevail, which reveal higher tendency toward glass formation.

Interesting effect of the replacement of Zn by Sr on the glass forming-ability can be observed in the series of B and C. Small additions of Sr result in an increasing glass-forming tendency due to a higher disorder in the structure with two types of cations - smaller Zn ions and bulkier Sr ions and so the glasses with a low Sr content have higher K_{gl} values than pure Zn borophosphate glasses. Nevertheless with a further increase in the Sr content glass-forming ability decreases, as can be seen from decreasing K_{gl} values and thus at a high Sr content the crystallization of the melt takes place and pure Sr borophosphate glass was not obtained in any of the series B and C.

4. Conclusion

Strontium-zinc borophosphate glasses reveal a relatively high chemical durability, especially those with the molar ratio $MO/(P_2O_5 + B_2O_3) > 1$. The replacement of zinc by strontium changes some of the properties of the parent glasses of the ZnO-P_2O_5-B_2O_3 system. An increase in the glass transition temperature for glasses with a higher Sr content can be due not only to the stronger chemical bonding in the mixed Sr-Zn strontium borophosphate glasses, but also to a change in the coordination of the cation. Recent studies of the coordination of Zn and Sr in metaphosphate glasses by X-ray diffraction measurements [8] showed that Sr atoms are coordinated by 6 oxygen atoms, whereas Zn atoms are coordinated by only 4 oxygen atoms. We believe that similar coordination of both atoms can be assumed also in borophosphate glasses, especially those with the high phosphorus content like those in the composition rows of B and C.

The criterium for glass-forming ability, suggested by Hruby [6] for chalcogenide glasses, reveals to be useful also for borophosphate glasses, because it makes it possible to evaluate the glass-forming tendency in these glasses and its changes with the composition. An increase in the Sr content in the borophosphate glasses results also in a smaller tendency toward glass-forming and in both series B and C a pure borophosphate glasses does not form and at the series B the glass with 75% of Zn atoms replaced by Sr atoms can not be prepared at the cooling rate used in our experiments.

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