GLASS-FORMING ABILITY, THERMAL STABILITY AND CHEMICAL DURABILITY OF LEAD BOROPHOSPHATE GLASSES

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Abstract Borophosphate glasses of the PbO-B2O3-P2O5 system were studied in two compositional series with 50 and 55 mol% PbO. The effect of compositional changes on physical properties of the glasses was investigated. Thermal stability of the glasses was evaluated by a criterion of Hruby using parameters obtained from DTA measurements. Chemical stability corresponds well with the thermal stability. Correlations were made between changes in the physical properties of the glasses and changes in their structure.

INTRODUCTION

Chemical durability of glasses is a very important feature for their practical applications. Phosphate glasses possess a low chemical durability, which is slightly better in the pyrophosphate region than in the ultraphosphate region1. A low chemical durability of phosphate glasses can be improved by the addition of trivalent oxides2. The chemical durability depends also on the type of network modifier. Recently we have studied the structure of lead borophosphate glasses by NMR, Raman and IR spectroscopy3, here we have tried to make a correlation of their properties, stability and chemical durability with their structure.

EXPERIMENTAL PROCEDURE

Borophosphate glasses of the PbO-B2O3-P2O5 system were studied in two compositional series (A) 50PbO-xB2O3-(50-x)P2O5 and (B) 55PbO-yB2O3-(45-y)P2O5. Glasses of the PbO-B2O3-P2O5 system were prepared from PbO, H3BO3 and H3PO4 by heating slowly the reaction mixture up to 1200-1250°C in a Pt crucible. The melt was poured into a copper mould and cooled in air to room temperature. In this way
homogeneous glasses were obtained in the series A for $x = 0-25$ and $45-50$ mol% $B_2O_3$ and in the series B for $y = 0-15$ mol% $B_2O_3$. Glass density, $\rho$, was determined at bulk samples by the Archimedes method using $CCl_4$ as the immersion liquid.

Thermal behavior of the glasses was studied by DTA and TMA. From the obtained values of the glass transition temperature $T_g$, the onset of the first crystallization peak $T_c$ and the onset of the melting peak $T_m$, glass forming ability of the glasses was evaluated using a criterion suggested by Hruby in the form $K_{gl} = (T_c - T_g)/(T_m - T_c)$. The chemical durability of the glasses was evaluated from the dissolution rate of $5x5x5$ mm cubes of glasses at $100^\circ C$ in $100$ cm$^3$ of distilled water. The dissolution rate (DR) was calculated from the relation: $DR = \Delta \omega/St$, where $\Delta \omega$ is the weight loss (g), $S$ is the sample surface area before the dissolution test and $t$ is the dissolution time (min).

RESULTS AND DISCUSSION

Density of the lead borophosphate glasses increases with an increasing content of $B_2O_3$ in both compositional series, whereas their molar volume $V_M$ decreases in both series of glasses (see Fig.1). The observed decrease in $V_M$ gives an evidence for an increase in the bonding forces in the glasses with an increasing $B_2O_3$ content. Whereas lead phosphate glasses possess low $T_g$ values, with an addition of $B_2O_3$ the values of $T_g$
and the dilatation softening temperature, T_d, increase in the glass series A from 257°C to 455°C and in the series B from 336°C to 447°C. On the other side the coefficient of thermal expansion decreases with increasing B_2O_3 content in both glass series.

The compositional dependence of K_gl values (Fig.2) in the glass series A reveals a maximum at the glass with x = 10 mol% B_2O_3, whereas in the glass series B the highest value of K_gl was obtained for the glass with y = 5 mol% B_2O_3.

The chemical durability of the lead borophosphate glasses is very low and the measured values of DR vary within the range of 1x10^-4-9x10^-7 g.cm^-2.K^-1. Its compositional dependence (Fig.3) shows that DR values with an increasing B_2O_3 content decrease at small additions of boron oxide and in the glass series A reach a minimum at the glass with x = 10 mol% B_2O_3. In the glass series B the values of DR reach a minimum at the glass with y = 5 mol% PbO. With a further increase in the B_2O_3 content the dissolution rate increases in both glass series. It means that the chemical durability of the lead borophosphate glasses is the highest at the glasses with the highest glass-forming ability evaluated by the Hruby's criterion.

Structural studies of lead borophosphate glasses revealed that in the glasses of the series A with x = 0-15 mol% B_2O_3, boron atoms form only BO_4 structural units, which make interconnections between phosphate chains and thus increase the dimensionality of the glass structural network, which is reflected in the observed increase in the glass

![FIGURE 2. Variation of the values of Hruby’s criterion K_gl versus B_2O_3 content in the lead borophosphate glasses.](image)
transition temperature and chemical durability of the glasses. In the glasses containing more than 15 mol% B$_2$O$_3$ also trigonal BO$_3$ units appear in their structure and simultaneously chemical durability and glass-forming ability of lead borophosphate glasses decrease.

**SUMMARY**
An increased dimensionality of the glass structure due to interconnections formed by BO$_4$ structural units in the studied glass series 50PbO-xB$_2$O$_3$-(50-x)P$_2$O$_5$ and 55PbO-yB$_2$O$_3$-(45-y)P$_2$O$_5$ results in an improved chemical durability of the glasses with 5-10 mol% B$_2$O$_3$, which is accompanied also by a good thermal stability of these glasses.

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**References**