

## Structure and Properties of Borophosphate Glasses

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Glasses in the system  $x\text{B}_2\text{O}_3-(60-x)\text{P}_2\text{O}_5-40\text{Na}_2\text{O}$  ( $x = 0$  mol. %, 10 mol. %, 20 mol. %, 30 mol. %, 40 mol. %) were prepared and characterized by measuring their density ( $\rho$ ), molar volume ( $V_M$ ), glass transition/softening temperature ( $T_g/T_d$ ), thermal expansion coefficient ( $\alpha$ ) and chemical durability (DR). All of these values were found to vary with the  $\text{B}_2\text{O}_3$  content of the glasses. The results were interpreted on the basis of the structural data. The Raman and infrared spectra confirmed these structural changes.

**Keywords:** borophosphate glasses, thermophysical properties, chemical durability, glass structure

### 1. INTRODUCTION

Phosphate glasses have a wide range of technical applications.<sup>[1]</sup> However, it is well known that a pure phosphate network is very hygroscopic and therefore not very stable. It has been demonstrated that the addition of  $\text{B}_2\text{O}_3$  to a phosphate network improves the chemical durability as well as the thermal and mechanical stability of pure phosphate glass.<sup>[2,3]</sup> The properties of mixed glasses are specific to the mixture, being distinct from the properties of either the pure phosphate or borate networks. The basic units of pure amorphous phosphate glasses are  $\text{PO}_4$  tetrahedra linked through covalent bridging oxygens, whereas the basic units of pure amorphous borate glasses are trigonal  $\text{BO}_3$  groups. In recent years, a large family of glasses based on a combination of both  $\text{B}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  with various network modifiers has been developed for widespread applications, including hermetic sealing materials<sup>[4,5]</sup> and fast ion conductors in solid state batteries.<sup>[6]</sup> The addition of a modifier oxide to phosphate and borate networks has differing effects. In the phosphate network, it has a depolymerizing effect; the extra oxygen atoms introduced by the modifier oxides form negative non-bridging oxygen sites, whose charge is compensated for by the positive charge of the modifier cations. In a borate network, the addition of a modifier oxide has the opposite effect, i.e. it increases the degree of polymerization: given the acidic Lewis character of  $\text{B}_2\text{O}_3$ , the boron coordination changes from trigonal to tetrahedral and the basic units change from  $\text{BO}_3$  to  $\text{BO}_4$ .<sup>[7,8]</sup> We note that pure phosphate and borate networks can be classified depending on the way the tetrahedra

are linked to each other.

In the present work, the primary objective was to verify the data on glass formation in the  $\text{P}_2\text{O}_5\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$  system and to characterize the obtained homogeneous glasses in this system using thermophysical, chemical and spectral methods.

### 2. EXPERIMENTAL PROCEDURE

Glass samples from the system  $x\text{B}_2\text{O}_3-(60-x)\text{P}_2\text{O}_5-40\text{Na}_2\text{O}$  ( $x = 0$  mol. %, 10 mol. %, 20 mol. %, 30 mol. %, 40 mol. %) were prepared using  $\text{B}_2\text{O}_3$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ , and  $\text{Na}_2\text{CO}_3$ , all with purities higher than 99.9%. All of the prepared chemical powders were finely mixed for ten minutes. Each batch was melted in a platinum crucible in an electrical furnace at 1300 for 30 min. These melts were quenched on steel plates and annealed in an electrical furnace at 400°C for two hours to release the thermal stress in the glasses.

The density of the glass samples,  $\rho$ , was determined at room temperature by the Archimedes method (AND GH-200), with water as the immersion liquid. The molar volume was calculated using the expression  $V_M \equiv \bar{M}/\rho$ , where  $\bar{M}$  is the average molar weight of the glass.<sup>[9]</sup> The thermophysical properties of the glasses were measured on a model TMA-60H thermal mechanical analyzer (Shimadzu) at a heating rate of 10°C/min. From the obtained curves, the linear coefficient of thermal expansion ( $\alpha$ ) was obtained as the mean value in the temperature range of 100°C to 300°C. The glass transition temperature ( $T_g$ ) was determined from the change in the slope of the elongation vs. temperature plot. The softening temperature ( $T_d$ ) was obtained from the maximum of the expansion trace. The chemical durability of the glasses was evaluated from their dissolution rate in distilled water at

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50°C. The glass cubes were put in distilled water for 12h. The dissolution rate, DR, was calculated from the expression  $DR = \Delta w / St$ , where  $\Delta w$  is the weight loss (g), S is the sample area (cm<sup>2</sup>) before the dissolution test and t is the dissolution time (min). The infrared spectra were recorded with an FT-IR spectrometer (Bruker IFS 66). Also, the Raman spectra were obtained with a Raman spectrometer (FRA 106).

### 3. RESULTS AND DISCUSSION

#### 3.1. Physical properties

The samples of the B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-Na<sub>2</sub>O system were studied in five compositional series containing 0 mol. % B<sub>2</sub>O<sub>3</sub>, 10 mol. % B<sub>2</sub>O<sub>3</sub>, 20 mol. % B<sub>2</sub>O<sub>3</sub>, 30 mol. % B<sub>2</sub>O<sub>3</sub> and 40 mol. % B<sub>2</sub>O<sub>3</sub>. The homogeneity of the prepared samples was checked visually. Most of the prepared samples were transparent glasses, but the 20 mol.% B<sub>2</sub>O<sub>3</sub> sample had a milky appearance, revealing phase separation. The density values obtained for the glasses are given in Table 1 as are the values of the molar volume,  $V_M$ , calculated from the values of the density. As can be seen from Table 1, the molar volume of the glasses decreases with increasing content of B<sub>2</sub>O<sub>3</sub>. The observed decrease in  $V_M$  shows that the packing of the coordination polyhedra in the structural network of the borophosphate glasses improves with increasing B<sub>2</sub>O<sub>3</sub> content.

#### 3.2. Thermal and Chemical properties

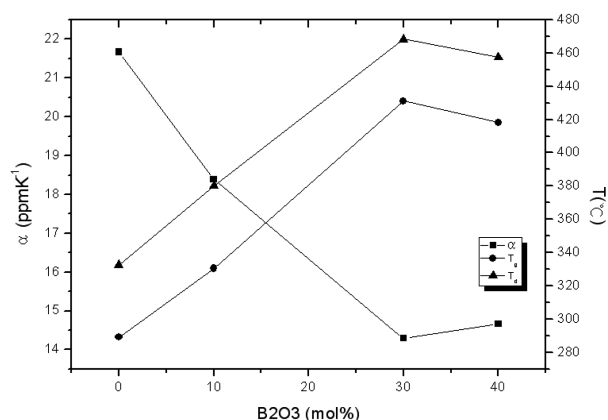
The study of the borophosphate glasses by thermomechanical analysis gave the values of their thermal expansion coefficients,  $\alpha$ , as well as their glass transition temperatures,  $T_g$ , and softening temperatures,  $T_d$ . Figure 1 shows the dependence of the values of  $\alpha$ ,  $T_g$  and  $T_d$  on the content of B<sub>2</sub>O<sub>3</sub> in the glass series. These results show that the thermal expansion coefficient decreases with increasing B<sub>2</sub>O<sub>3</sub> content, whereas the values of the glass transition temperature and softening temperature increase. Both  $T_g$  and  $T_d$  increase abruptly upon addition of B<sub>2</sub>O<sub>3</sub> and reach a maximum at a B<sub>2</sub>O<sub>3</sub> content in the glasses of about 30 mol.%.

The chemical durability of the studied glasses is closely associated with their B<sub>2</sub>O<sub>3</sub> content. This behavior undoubtedly corresponds to some changes in the nature of the bonding in the structural network. The dissolution rate for these glasses steeply decreases within the range of x = 10 mol. %

to 30 mol. %. The decrease in the dissolution rate as the B<sub>2</sub>O<sub>3</sub> content is increased up to 30 mol. % is attributed to the replacement of the P-O-P bonds by P-O-B bonds and is accompanied by an increase in the glass transition temperature and chemical durability. This finding provides evidence for the increasing bonding forces inside the structural network due to the formation of P-O-B bonds. This conclusion is in good agreement with the strength of the chemical bonds in the diatomic molecules of P-O (599.1 KJ/mol) and B-O (808 KJ/mol) determined by spectroscopic methods.<sup>[10]</sup> However, when the B<sub>2</sub>O<sub>3</sub> content is further increased, DR slightly increases. These changes are due to the BO<sub>3</sub> structural units, which weaken the glass structure.

#### 3.3. Structural properties

The infrared spectra of the B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-Na<sub>2</sub>O glasses are shown in Fig. 3. The infrared spectrum of the 60P<sub>2</sub>O<sub>5</sub>-40Na<sub>2</sub>O glass contains three vibrational bands at 1258 cm<sup>-1</sup>, 1017 cm<sup>-1</sup> and 894 cm<sup>-1</sup>. The band at 894 cm<sup>-1</sup> can be ascribed to the asymmetric stretching vibration of the bridging oxygen atoms in the P-O-P bonds,  $\nu_{as}(P-O-P)$ , whereas the other broad band at 1258 cm<sup>-1</sup> belongs to the asymmetric vibrations,  $\nu_{as}(PO_2)$ , of the non-bridging oxygen atoms in the phosphate chains.<sup>[11]</sup> The other band in the infrared spectra at 1017cm<sup>-1</sup> is ascribed to the symmetrical stretching vibration,  $\nu_s(PO_2)$ . The band at 763 cm<sup>-1</sup> is assigned to the symmetric



**Fig. 1.** Variation of the thermal expansion coefficient, glass transition and softening temperature.

**Table 1.** Thermophysical properties of glasses of the xB<sub>2</sub>O<sub>3</sub>-(60-x)P<sub>2</sub>O<sub>5</sub>-40Na<sub>2</sub>O system

Parameter	x = 0	x = 10	x = 30	x = 40
Density, $\rho$ (g/cc)	2.6340	2.5712	2.4663	2.4239
Molar volume, $V_m$ (cc/mole)	41.7449	39.9518	35.7864	33.4288
Transition temperature, $T_g$ (°C)	289.24	330.55	431.19	418.32
Softening temperature, $T_d$ (°C)	332.58	380.11	468.34	457.59
Thermal expansion coefficient, $\alpha$ (ppmK <sup>-1</sup> )	21.67	18.39	14.29	14.67
Dissolution rate, DR (g/cm <sup>2</sup> min)	$7.2338 \times 10^{-7}$	$6.8146 \times 10^{-7}$	$4.2088 \times 10^{-7}$	$6.2004 \times 10^{-7}$

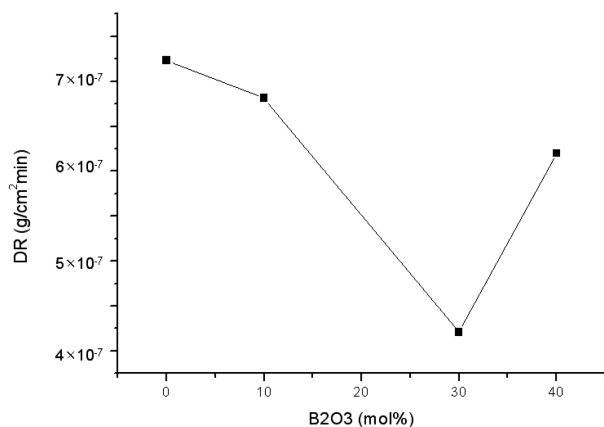


Fig. 2. Variation of the dissolution rate.

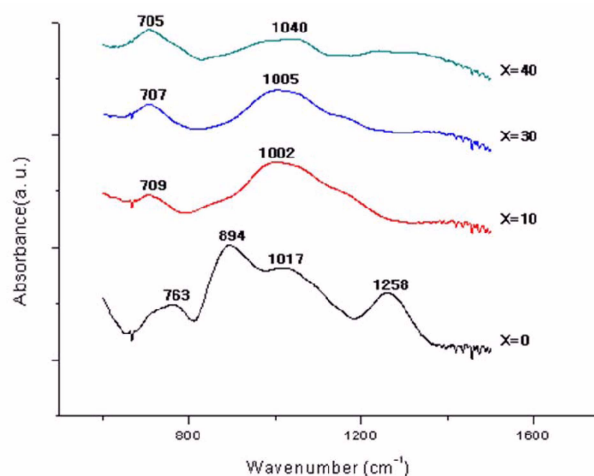


Fig. 3. Infrared spectra of the  $x\text{B}_2\text{O}_3-(60-x)\text{P}_2\text{O}_5-40\text{Na}_2\text{O}$  glasses.

stretching vibrations,  $\nu_s(\text{P-O-P})$ , of the bridging oxygen atoms. With increasing  $\text{B}_2\text{O}_3$  content and decreasing  $\text{P}_2\text{O}_5$  content, a series of changes in the spectra can be observed. The vibrations  $\nu_{\text{as}}(\text{PO}_2)$  at  $1258\text{cm}^{-1}$  become broader and weaker. The decrease in the strength of the vibrations of the non-bridging  $\text{PO}_2$  groups seems to indicate a progressive increase in the connectivity of the glass with increasing  $\text{B}_2\text{O}_3$  content. It is likely that this connectivity is due to the formation of P-O-B links, which replace the P-O-P bonds. The vibrations of the bridging P-O-P groups,  $\nu_{\text{as}}(\text{P-O-P})$ , at  $894\text{cm}^{-1}$  decrease and are almost undetectable in the sample with the highest  $\text{B}_2\text{O}_3$  content. The formation of P-O-B links as  $\text{B}_2\text{O}_3$  is added is suggested by the broadening of the bands in the region of  $894\text{cm}^{-1}$  (which is due exclusively to the B-O stretching of the  $\text{BO}_4$  units).<sup>[12]</sup>

The Raman spectra are shown in Fig. 4. It is evident that there is a modification of the structure as the composition changes. The spectrum is characterized by distinct vibrational bands when the content of  $\text{B}_2\text{O}_3$  is 0 mol. %. The strongest band at  $1165\text{cm}^{-1}$  is ascribed to the symmetric

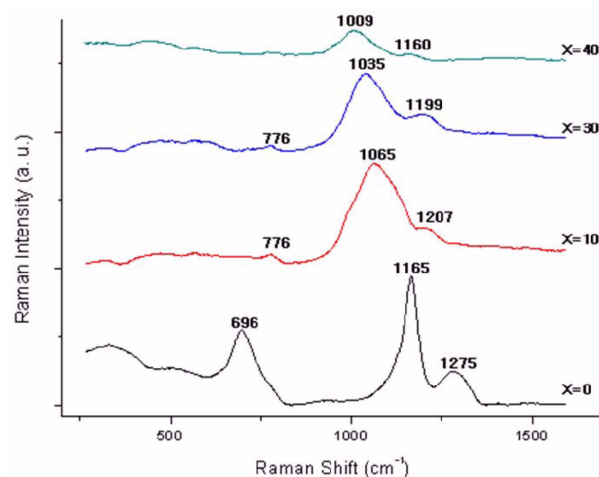


Fig. 4. Raman spectra of the  $x\text{B}_2\text{O}_3-(60-x)\text{P}_2\text{O}_5-40\text{Na}_2\text{O}$  glasses.

stretching vibrations,  $\nu_s(\text{PO}_2)$ , of the  $(\text{PO}_2)$  groups in the phosphate chains, while the intensity of the other strong band at  $696\text{cm}^{-1}$  decreases with increasing  $x$ . The band at  $696\text{cm}^{-1}$  is attributed to the symmetric stretching vibrations  $\nu_s(\text{P-O-P})$  of the bridging oxygen atoms connecting the neighboring  $\text{PO}_4$  tetrahedra.<sup>[13,14]</sup> With increasing content of  $\text{B}_2\text{O}_3$  replacing  $\text{P}_2\text{O}_5$ , the intensity of the bands described above decreases and the position of the main band at  $1165\text{cm}^{-1}$  shifts to lower frequencies. These changes are attributed to the depolymerization of the continuous phosphate network through the incorporation of  $\text{BO}_4$  and  $\text{BO}_3$  structural units into the phosphate chains. Also, there is a distinct band at  $1275\text{cm}^{-1}$  that is assigned to the symmetric stretching vibrations of the P=O bond in the  $\text{PO}_4$  structural units with one nonbridging oxygen atom.

#### 4. CONCLUSION

Homogeneous glasses can be prepared in the series  $x\text{B}_2\text{O}_3-(60-x)\text{P}_2\text{O}_5-40\text{Na}_2\text{O}$  for  $x=0$  mol. % to 40 mol. %. Borophosphate glasses offer the possibility of changeable structure and properties according to changing composition. These changes can be done in either the anionic or cationic networks of the glasses. The addition of  $\text{B}_2\text{O}_3$  increases the dimensionality of the structural network of the parent phosphate glasses. It is known that the structure of  $\text{BPO}_4$  is composed of  $\text{PO}_4$  and  $\text{BO}_4$  tetrahedra interconnected into a network. Therefore, it can be supposed that the borophosphate glasses studied herein contain P-O-B linkages within their structural networks.

Generally, the replacement of P-O-P bonds by P-O-B bonds (formation of  $\text{BPO}_4$  tetrahedral structure : highly cross-linked structure) in the investigated glasses is accompanied by an increase in the glass transition temperatures and chemical durability with increasing  $\text{B}_2\text{O}_3$  content. Up to a

displacement B<sub>2</sub>O<sub>3</sub> quantity of 30 mol. %, the structure of the glass consisted of BO<sub>4</sub> tetrahedra, whereas at quantities of B<sub>2</sub>O<sub>3</sub> above 30 mol. % it changed to a BO<sub>3</sub> based structure, which is known to be weaker.

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