

## Effect of Substituting $B_2O_3$ for $P_2O_5$ in Conductive Vanadate Glass

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### ABSTRACT

In this study, we verified the relationship among the electrical conductivity, chemical durability, and structure of conductive vanadate glass in which  $BO_3$  and  $BO_4$  and  $V^{4+}$  and  $V^{5+}$  coexist simultaneously. We prepared samples of vanadium borophosphate glass with various compositions, given by  $50V_2O_5-xB_2O_3-(50-x)P_2O_5$  ( $x = 0 \sim 20$  mol%) and  $70V_2O_5-xB_2O_3-(70-x)P_2O_5$  ( $x = 0 \sim 10$  mol%), and analyzed the electrical conductivity, chemical durability, FT-IR spectroscopy, thermal properties, density, and molar volume. Substituting  $B_2O_3$  for  $P_2O_5$  was found to improve the electrical conductivity, chemical durability, and thermal properties. From these results, we can draw the following conclusions. First, the electrons shift from the electron rich  $V^{4+}$  to the electron deficient  $BO_3$  as the  $B_2O_3$  content increases. Second, the improvement in chemical durability and thermal properties is attributed to an increase in cross-linked structures by changing from a  $BO_3$  structure to a  $BO_4$  structure.

**Key words :** Glass, Electrical conductivity, Chemical durability, Structure

### 1. Introduction

Vanadate glasses containing large amounts of  $V_2O_5$  have multivalent ions of various states mixed in their structure. These glasses have been developed for infrared transmission and for atomic-exchange electro-conductive glasses using electron conduction. Studies focusing on improving the performance of these glasses involve changing the electrical conduction properties through low valency ( $V^{4+}$ ) to high valency ( $V^{5+}$ ) metal-ion electron hopping<sup>1)</sup> and changing the catalytic properties for the oxidation reaction by altering the valency change between  $V^{4+}$  and  $V^{5+}$ <sup>2)</sup>, and by examining the correlation between the glass composition and its characteristics while focusing on the type and condition of V ions or the type and the amount of alkali or alkaline earth metals<sup>3-7)</sup>.

Vanadium phosphate glasses have the excellent properties of phosphate-based glass, such as high thermal expansion, low melting point, and high ultraviolet transmittance. In addition, the reduced glass forming ability of vanadium phosphate glass is supplemented by the glass former  $P_2O_5$ . However, vanadium phosphate glass has a reduced chemical resistance.<sup>8)</sup> In 2012, we substituted  $B_2O_3$  for  $P_2O_5$  to improve the chemical resistance and electrical conductivity of vanadium phosphate-based glasses, and we were able to investigate the significance of the correlation between the resulting structure and the electrical, thermal, and chemical properties. However, the effect of the substitution was

insignificant.

In our previous research, five  $V_2O_5$ - $B_2O_3$ - $P_2O_5$  glass specimens were prepared and investigated with the goal to improve their conductivity and stability. However, because the  $V_2O_5$  content remained fixed and  $B_2O_3$  was simply substituted for  $P_2O_5$ , we cannot be sure that the results are applicable to every  $V_2O_5$ - $P_2O_5$  binary system. This paper therefore expands on this previous research by identifying the minimum and maximum  $V_2O_5$  concentration within the vitrification range of  $V_2O_5$ - $P_2O_5$  glasses, and subsequently using these values to investigate the broader effect of replacing  $P_2O_5$  with  $B_2O_3$ . The aim of this study was to understand the effect of  $B_2O_3$  substitution on the structure and properties of  $V_2O_5$ - $P_2O_5$  glass systems, and to understand the effect of the  $V_2O_5$  concentration on the electrical conductivity of  $V_2O_5$ - $P_2O_5$ - $B_2O_3$  glass systems.

### 2. Experimental Procedure

#### 2.1. Glass preparation

The glass samples used were all in the  $V_2O_5$ - $B_2O_3$ - $P_2O_5$  ternary system with specific compositions obtained by adjusting the  $P_2O_5$  and  $B_2O_3$  contents for fixed  $V_2O_5$  concentrations at 50 and 70 mol. %. The raw materials for this were prepared by mixing the appropriate amounts of reagent grade  $V_2O_5$ ,  $NH_4H_2PO_4$ , and  $B_2O_3$  (JUNSEI Chemical Co. Japan) in an alumina crucible to produce a variety of compositions with the specific details presented in Table 1. These mixtures were heated at 200°C for 1 h (first calcination), then at 500°C for 2 h (second calcination), and finally at 800°C for 2 h. The final melt was quenched between two stainless-steel plates, and then annealed at its glass transition temperature ( $T_g$ ) + 50°C for 1 h.

The glass samples used in the experiments (Thermal Mechanical Analysis (TMA), chemical durability, electrical

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**Table 1.** Molar Concentration of V<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub> and State of Vitrification

Glass Code	Composition mol%			Vitrification
	P <sub>2</sub> O <sub>5</sub>	V <sub>2</sub> O <sub>5</sub>	B <sub>2</sub> O <sub>3</sub>	
PV5	50	50	0	O
PV5-1	45	50	5	O
PV5-2	40	50	10	O
PV5-3	35	50	15	O
PV5-4	30	50	20	O
PV5-5	25	50	25	X
PV7	30	70	0	O
PV7-1	25	70	5	O
PV7-2	20	70	10	O
PV7-3	15	70	15	X

conductivity, density, and molar volume) were in the shape of rectangular parallelepipeds with the surfaces polished using SiC paper. A sub- 325 mesh powder sample of each glass was used for X-ray diffraction (XRD) and Fourier-transform infrared (FT-IR) analyses.

### 2.2. Property measurements

The glass samples produced were classified as either transparent or crystalline depending on their transparency and crystallization, which was re-confirmed by XRD (Rigaku X-ray diffractometer, Cu-K $\alpha$ , 30 KV at 20 mA).

The densities of the various glass samples,  $\rho$ , were determined at room temperature with the Archimedes' method (AND GH-200), in which water was used as the immersion liquid. The molar volume,  $V_M$ , was calculated with the expression  $V_M = M/\rho$ , where  $M$  is the average molar weight of the glass.

The thermomechanical properties of the glasses were measured with a model Q400 thermal mechanical analyzer (TA Instrument) at a heating rate of 10°C/min. From the curves obtained, the linear coefficient of thermal expansion,  $\alpha$ , was determined as the mean value within a temperature range of 100 - 250°C. The glass transition temperature,  $T_g$ , was determined from the change in the slope from the plot of elongation versus temperature. Finally, the softening temperature,  $T_d$ , was obtained from the maximum value of the expansion trace.

Chemical durability measurements were done by dissolving a rectangular parallelepiped glass sample in distilled water at 50°C for 12 h. The dissolution rate,  $DR$ , was calculated with the expression  $DR = \Delta w/St$ , where  $\Delta w$  is the weight loss (g);  $S$  is the surface area (cm<sup>2</sup>) prior to dissolution, and  $t$  is the dissolution time (min)<sup>9</sup>.

Structural changes were investigated by FT-IR spectroscopy (Spectrum GX, Perkin Elmer) with the powdered samples that were mixed with KBr and formed into pellets. Room temperature IR spectra were recorded from 400 to 1400 cm<sup>-1</sup>.

Electrical conductivities were obtained by Hall-effect mea-

surements (HMS-3000).

## 3. Results and Discussion

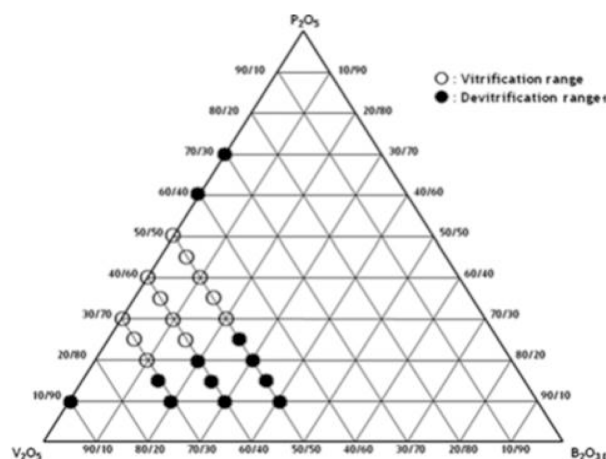
### 3.1. Glass preparation

Figure 1 shows the vitrification range of the V<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub> system. Although binary glasses of P<sub>2</sub>O<sub>5</sub>-V<sub>2</sub>O<sub>5</sub> were formed, in which the atomic concentration of P<sub>2</sub>O<sub>5</sub> varied from 20 to 50%, glass compositions of 50V<sub>2</sub>O<sub>5</sub>-50P<sub>2</sub>O<sub>5</sub> and 70V<sub>2</sub>O<sub>5</sub>-30P<sub>2</sub>O<sub>5</sub> were selected to compare the structures and properties for both extremes of the vitrification range. The concentration of V<sub>2</sub>O<sub>5</sub> was therefore fixed at either 50 or 70 mol%, and P<sub>2</sub>O<sub>5</sub> was progressively replaced with B<sub>2</sub>O<sub>3</sub>.

Figure 2 shows the XRD pattern of a 50V<sub>2</sub>O<sub>5</sub>-x B<sub>2</sub>O<sub>3</sub>-(50-x)P<sub>2</sub>O<sub>5</sub> glass system (PV5 series) and 70V<sub>2</sub>O<sub>5</sub>-x B<sub>2</sub>O<sub>3</sub>-(30-x)P<sub>2</sub>O<sub>5</sub> glass system (PV7 series). From this, it can be seen that in the case of the PV5 series, ternary glasses are formed when 0 ≤ x ≤ 20, whereas for PV7, they are formed only when 0 ≤ x ≤ 10.

### 3.2. Structural properties

The FT-IR spectra in Fig. 3 show the transmittances of the PV5 and PV7 series glasses between 400 and 1400 cm<sup>-1</sup>. The peak at around at 1200 - 1300 cm<sup>-1</sup> is assigned to the (PO<sub>2</sub>) asymmetric stretching of the non-bridging oxygen, whereas that at around 995 cm<sup>-1</sup>, which is present in all the glasses, is attributable to the V-O vibrations of the VO<sub>5</sub> units. Those peaks at around 940 - 960 cm<sup>-1</sup> and 760 - 785 cm<sup>-1</sup> were, respectively, assigned to the vibrations of the P-O and V-O bonds of the connected VO<sub>5</sub> and phosphate groups<sup>10</sup> with both peaks seen in all the glasses. Finally, the peak at around 680 cm<sup>-1</sup> is related to the P-O-B bonds of the connected phosphate and therefore, attributable to the Vs(O-B-O) of the BO<sub>4</sub> unit. Replacing P<sub>2</sub>O<sub>5</sub> with B<sub>2</sub>O<sub>3</sub> results in an increase in the number of VO<sub>5</sub> and metaphosphate bonds and the number of bonded oxygen atoms, and results in the formation of a symmetrical structure. Borophosphate networks are consequently formed through the phosphate and



**Fig. 1.** Vitrification range of the V<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub> glass systems.

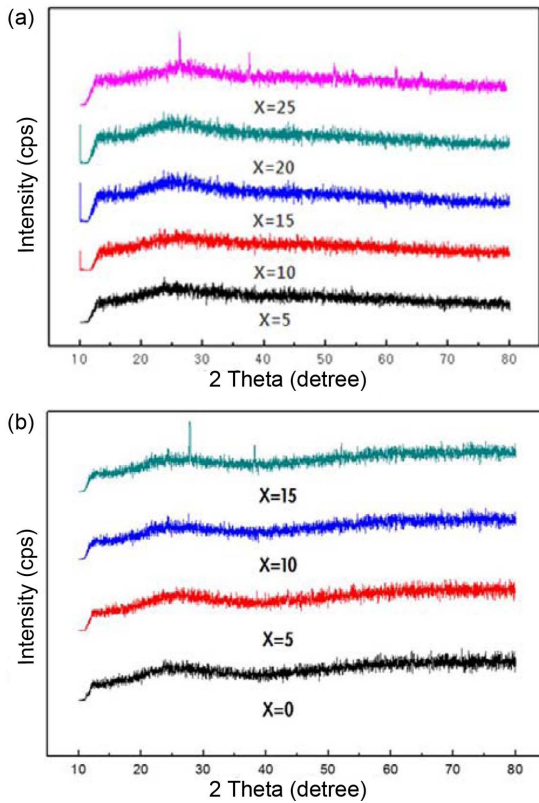


Fig. 2. XRD patterns of (a)  $50\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(50-x)}\text{P}_2\text{O}_5$  and (b)  $70\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(30-x)}\text{P}_2\text{O}_5$  glass systems.

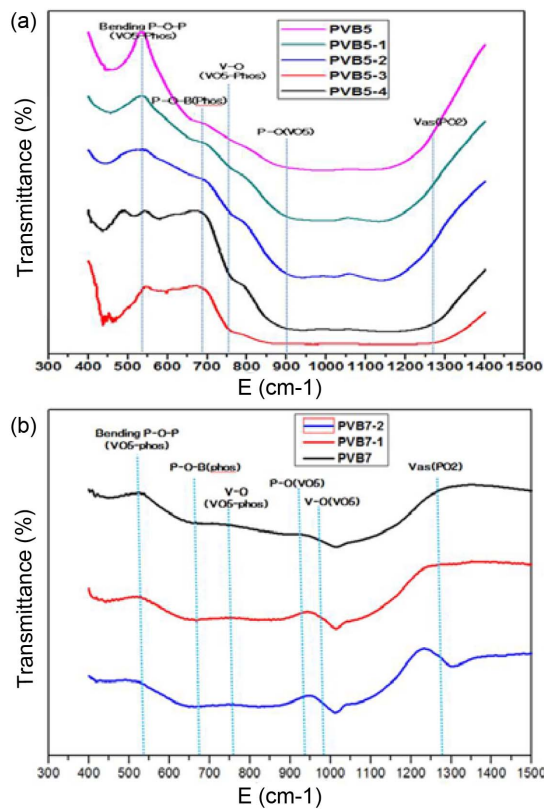


Fig. 3. Infrared spectra of (a)  $50\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(50-x)}\text{P}_2\text{O}_5$  and (b)  $70\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(70-x)}\text{P}_2\text{O}_5$  glass systems.

borate networks combining via the tetrahedral boron, resulting in a highly crosslinked structure that is thought to increase the chemical durability of the glass. Even when the  $\text{V}_2\text{O}_5$  content is varied, the location and trend of the various peaks remain quite similar.

### 3.3. Physical properties

Figure 4 shows the densities and molar volumes ( $V_M$ ) for the various compositions of  $50\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(50-x)}\text{P}_2\text{O}_5$ , where  $0 \leq x \leq 20$ , and  $70\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(70-x)}\text{P}_2\text{O}_5$ , where  $0 \leq x \leq 10$ . In either instance, an increase in the  $\text{B}_2\text{O}_3$  concentration produces an increase in the density of  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5$  and a decrease in its molar volume. Given this, we can expect that replacing  $\text{P}_2\text{O}_5$  with  $\text{B}_2\text{O}_3$  will increase the density of the glass structure by forming the highly crosslinked structure that is thought to strengthen the structural bonds. This result is in good agreement with the structural properties presented in chapter II. Similarly, the  $70\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(70-x)}\text{P}_2\text{O}_5$  glass system should achieve a higher degree of structural bond strengthening for a given  $\text{B}_2\text{O}_3$  concentration.

### 3.4. Electrical conductivity

For both compositions shown in Fig. 5, the replacement of  $\text{P}_2\text{O}_5$  with  $\text{B}_2\text{O}_3$  increases the electrical conductivity of the glass. As the C value decreases, one would expect a decrease in conductivity<sup>6,11,12</sup>. The  $\text{B}_2\text{O}_3$ -containing glasses were found to have lower metal ion ratios, known as the C value ( $C = ([\text{V}^{4+}]/([\text{V}^{4+}]+[\text{V}^{5+}]))$ ), than the corresponding pure  $\text{V}_2\text{O}_5$ -

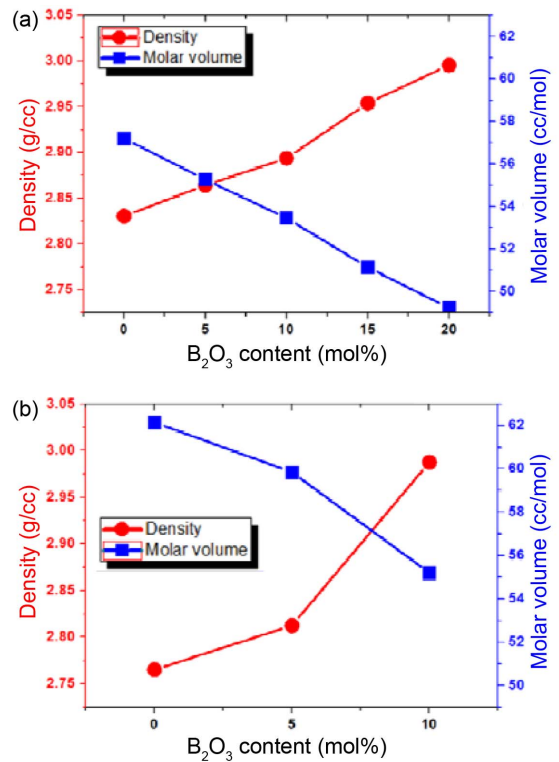


Fig. 4. Density and molar volume of (a)  $50\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(50-x)}\text{P}_2\text{O}_5$  and (b)  $70\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(70-x)}\text{P}_2\text{O}_5$  glass systems.

P<sub>2</sub>O<sub>5</sub> glasses. A possible reason for this difference in behavior is that electron-deficient or coordinatively unsaturated BO<sub>3</sub> units are attracted to the electron-rich V<sup>4+</sup> species with a subsequent electron transfer from V<sup>4+</sup> to BO<sub>3</sub> leading to the formation of BO<sub>4</sub> structural units and V<sup>5+</sup>. This is supported by the appearance of a peak at around 680 cm<sup>-1</sup>, which is from this BO<sub>4</sub> structural unit. In other respects, the 70V<sub>2</sub>O<sub>5</sub>-xB<sub>2</sub>O<sub>3</sub>-(70-x)P<sub>2</sub>O<sub>5</sub> glass system consistently has a higher conductivity than that of the 50V<sub>2</sub>O<sub>5</sub>-xB<sub>2</sub>O<sub>3</sub>-(50-x)P<sub>2</sub>O<sub>5</sub> glass system, both before and after substituting B<sub>2</sub>O<sub>3</sub>. This proves that V<sub>2</sub>O<sub>5</sub> greatly enhances the electrical conductivity by electron transfer<sup>13,14</sup>. Electrical-conductive glasses containing transition metal oxide (TMO) have been widely studied for their electrical-conduction mechanism.<sup>15,23</sup>

**3.5. Chemical durability**

In general, phosphate glasses are sensitive to moisture because their P-O linkages, which are not bonded to cations, can react with moisture to form phosphoric acid, thereby spoiling/reducing the durability of the material<sup>24</sup>. However, the addition of B<sub>2</sub>O<sub>3</sub> has been reported to enhance the chemical durability<sup>25,26</sup>. Fig. 6 shows the dissolution rates of the various glass systems, which decrease with an increasing B<sub>2</sub>O<sub>3</sub> concentration in a number of instances. This is explained by the increase in the number bonds with the B<sub>2</sub>O<sub>3</sub> addition, resulting in a two-dimensional network of phosphate glass taking on a more highly crosslinked B(PO)<sub>4</sub>

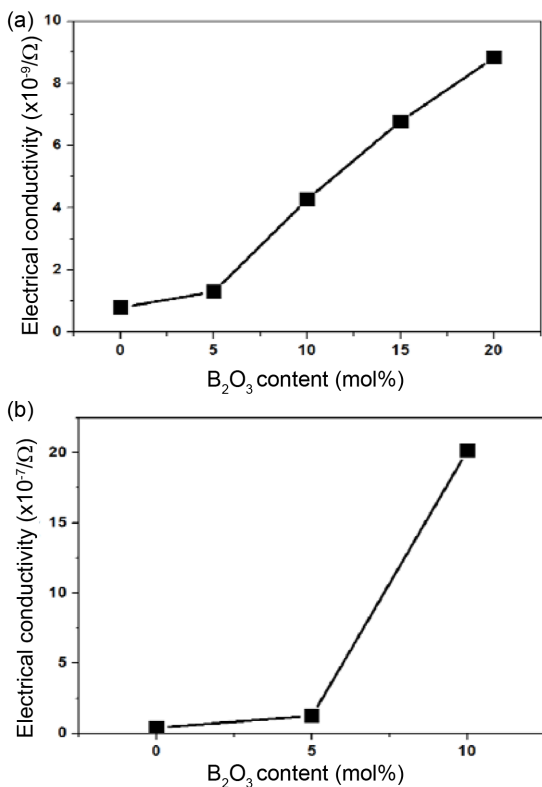


Fig. 5. Electrical conductivity of (a) 50V<sub>2</sub>O<sub>5</sub>-xB<sub>2</sub>O<sub>3</sub>-(50-x)P<sub>2</sub>O<sub>5</sub> and (b) 70V<sub>2</sub>O<sub>5</sub>-xB<sub>2</sub>O<sub>3</sub>-(70-x)P<sub>2</sub>O<sub>5</sub> glass systems.

structure shown in Fig. 7. With regards to the V<sub>2</sub>O<sub>5</sub> concentration, the higher dissolution rate of the 70V<sub>2</sub>O<sub>5</sub>-xB<sub>2</sub>O<sub>3</sub>-(70-x)P<sub>2</sub>O<sub>5</sub> glass systems confirms that while V<sub>2</sub>O<sub>5</sub> does not improve the chemical durability, both P<sub>2</sub>O<sub>5</sub> and B<sub>2</sub>O<sub>3</sub> do improve it.

**3.6. Thermal properties**

Through thermomechanical analysis of the vanadium borophosphate glasses, values were obtained for their thermal expansion coefficients, α, as well as their glass-transition temperatures, T<sub>g</sub>, and softening temperatures, T<sub>d</sub>. Figure 8 shows the dependences of all these variables on the B<sub>2</sub>O<sub>3</sub> content of the glass. With either base composition, α decreases as the contents of B<sub>2</sub>O<sub>3</sub> increase, whereas both T<sub>g</sub>

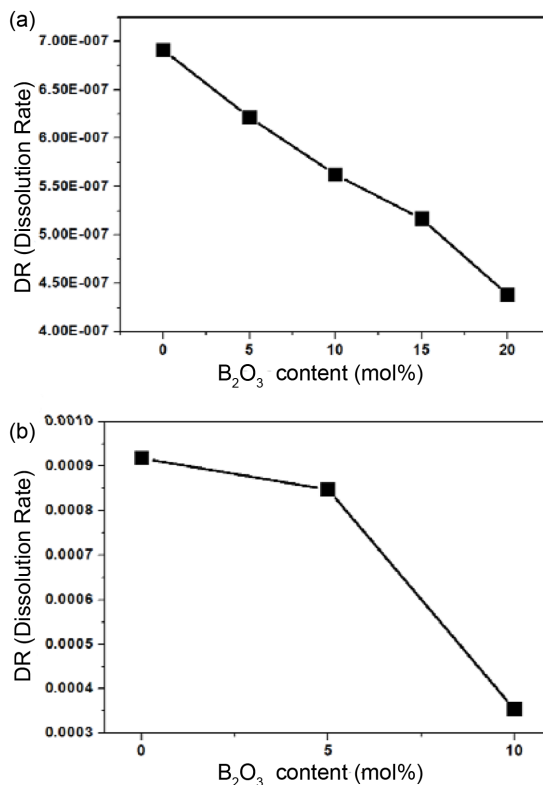


Fig. 6. Dissolution rate of (a) 50V<sub>2</sub>O<sub>5</sub>-xB<sub>2</sub>O<sub>3</sub>-(50-x)P<sub>2</sub>O<sub>5</sub> and (b) 70V<sub>2</sub>O<sub>5</sub>-xB<sub>2</sub>O<sub>3</sub>-(70-x)P<sub>2</sub>O<sub>5</sub> glass systems.

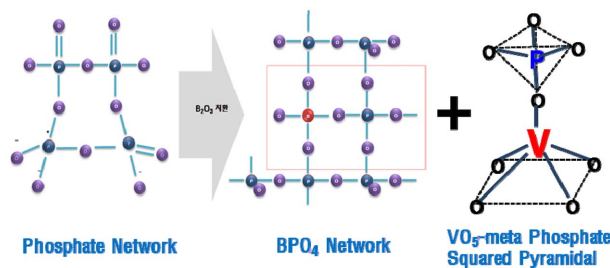


Fig. 7. Effect of B<sub>2</sub>O<sub>3</sub> addition on the formation of a more highly crosslinked B(PO)<sub>4</sub> structure.

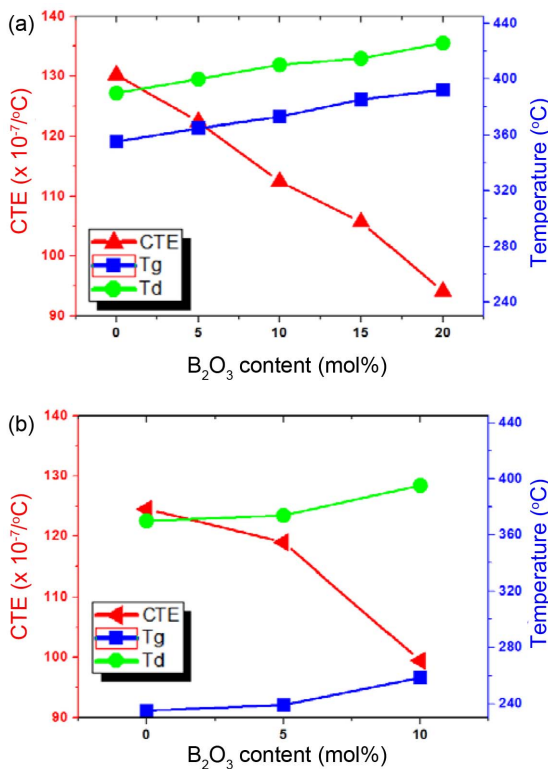


Fig. 8. Thermal properties of (a)  $50\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(50-x)P}_2\text{O}_5$  and (b)  $70\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(70-x)P}_2\text{O}_5$  glass systems.

and  $T_d$  increase as a result of the boron breaking the asymmetrical P-O-P bonds, thereby increasing the number of P-O-B bonds and the strength of the glass structure<sup>27-30</sup>. Moreover, the thermal properties of the  $70\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(70-x)P}_2\text{O}_5$  glass system are worse than those of the  $50\text{V}_2\text{O}_5\text{-xB}_2\text{O}_3\text{-(50-x)P}_2\text{O}_5$  glass systems; that is, the  $\alpha$  value is lower, and the  $T_g$  and  $T_d$  values are higher. This confirms that  $\text{V}_2\text{O}_5$  does not increase the strength of the bonds in the glass structure.

#### 4. Conclusion

We investigated the effect of substituting  $\text{B}_2\text{O}_3$  for  $\text{P}_2\text{O}_5$  on the structure and properties of  $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$  glass systems, as well as the effect of varying their  $\text{V}_2\text{O}_5$  content. For all compositions,  $\text{B}_2\text{O}_3$  substitution was found to increase the density and decrease the molar volume and dissolution rate. This combination increases the chemical durability of the glass, which can be directly correlated to an increase in the mole fraction of  $\text{BO}_4$  structural units present, evidenced by its FT-IR peak at around  $680\text{ cm}^{-1}$ . Similarly, it was shown that increasing the  $\text{V}_2\text{O}_5$  content, at the expense of  $\text{P}_2\text{O}_5$  and  $\text{B}_2\text{O}_3$ , reduces the chemical durability of vanadium borophosphate glasses.

The increase in electrical conductivity observed in the  $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5$  glasses compared to the  $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$  glasses was attributed to a decrease in their C values, which is a result of the partial replacement of  $\text{P}_2\text{O}_5$  by  $\text{B}_2\text{O}_3$ . Furthermore, the increase or decrease in the conductivity with C

can be attributed to the degree of trapping of the charge carriers, which results from a decrease or increase in the number of polarons.

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