

Effect of B₂O₃ addition on microhardness and structural features of 40Na₂O–10BaO–x B₂O₃–(50–x)P₂O₅ glass system

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Abstract. Phosphate glasses having composition, 40Na₂O–10BaO–x B₂O₃–(50–x)P₂O₅, where x = 0–20 mol% were prepared using conventional melt quench technique. Density of these glasses was measured using Archimedes principle. Microhardness (MH) was measured by Vicker's indentation technique. Structural studies were carried out using IR spectroscopy and ³¹P and ¹¹B MAS NMR. Density was found to vary between 2.62 and 2.77 g/cc. MH was found to increase with the increase in boron content. ³¹P MAS NMR spectra showed the presence of middle Q² groups and end Q¹ and Q⁰ groups with P–O–B linkages. FTIR studies showed the presence of BO₃ and BO₄ structural units along with the depolymerization of phosphate chains in conformity with ³¹P MAS NMR. ¹¹B NMR spectra showed increase in BO₄ structural units with increasing boron content. The increase in MH with B₂O₃ content is due to the increase of P–O–B linkages and BO₄ structural units as observed from MAS NMR studies resulting in a more rigid borophosphate glass networks.

Keywords. Phosphate glass; microhardness; FTIR; MAS NMR.

1. Introduction

Phosphate glasses like sodium phosphate (Moustafa and El-Egili 1998) and sodium barium phosphate (Wilder 1980) are reported to have high thermal expansion coefficients and electrical conductivity with low glass transition and melting temperatures as compared to sodium borate glasses. However, their poor chemical durability with respect to water limits their practical use. Earlier studies indicate that the chemical durability of phosphate glasses can be improved by the addition of trivalent ions like Al³⁺, B³⁺, Bi³⁺, etc (Tsuchiya and Moriya 1980; Magistris *et al* 1983; Chioldelli *et al* 1986; Constantini *et al* 1994; Brow 2000). Therefore, borophosphate glasses having improved durability are among the multicomponent glasses studied for various interesting applications. Alkali and silver borophosphate glasses have been developed for fast ion conducting applications (Kaushik and Hariharan 1987; Coppo *et al* 1996); zinc–calcium borophosphate glasses were studied as candidates for applications as low-melting glass solders and glass–to–metal (GM) seals (Ma *et al* 1993; Harish Bhat *et al* 2001). The properties of these glasses can be controlled by changing their compositions and this gives us an opportunity to use them in different applications.

Studies related to the structure of borophosphate glasses were carried out mostly by NMR methods (Yun and Bray 1978; Ducler *et al* 1994; Zeyer-Dusterer *et al* 2005) and by Raman and infrared (IR) spectroscopy (Scagliotti *et al* 1987). Yun and Bray (1978) studied the structure of borophosphate glasses by NMR spectroscopy and found that both BO₃ and BO₄ structural units are present in the glass structure. They also succeeded in finding the fraction of BO₄ units in the glasses. Ducler *et al* (1994) in their NMR study of (1 – x)NaPO₃–xNa₂B₄O₇ glasses found that in the phosphate rich part (x < 0.1) almost all the boron atoms are in tetrahedral coordination, but with increasing boron content the fraction of BO₄ tetrahedra abruptly decreases. Such structural studies of borophosphate glasses show that difference in coordination number affects properties of the glasses.

Sodium barium phosphate glasses studied by Wilder (1980) yielded thermal expansion coefficients (TEC) > 200 × 10⁻⁷/°C and glass transition temperatures, T_g, below 400°C which could be hermetically sealed to aluminium alloys. Sodium borophosphate glass studies show an increase in T_g and decrease in TEC for y = B/(B + P) = 0 – 0.5 (B = boron content in mol%, P = phosphorus content in mol%), where BO₄ units dominate over BO₃ units. The results for y > 0.6, where BO₃ units dominate over BO₄ units, show a decreasing trend in T_g whereas the TEC remains unaffected. The maximum TEC reported for sodium borophosphate glasses is 199 × 10⁻⁷ for y < 0.5. Therefore, it seems interest-

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ing to study the effect of B_2O_3 addition in sodium barium phosphate glass where $y < 0.5$. In this work, we report the preparation, microhardness and structural features of $40Na_2O-10BaO-xB_2O_3-(50-x)P_2O_5$ glass ($x = 0-20$ mol%). To the best of our knowledge, this work represents first reported data of microhardness and its dependence on the structural features of mixed sodium barium borophosphate glass series. We have prepared a vacuum seal using glass composition, $x = 10$ mol% with Al metal, withstanding 10^{-6} Torr pressure and also carried out glass-to-metal interface study.

2. Experimental

2.1 Glass preparation

Glasses having composition, $40Na_2O-10BaO-xB_2O_3-(50-x)P_2O_5$, where $x = 0-20$ mol% were prepared by conventional melt-quench technique as reported earlier (Shah *et al* 2003). Analytical grade reagents with no water of crystallization, $NaNO_3$, $Ba(NO_3)_2$, B_2O_3 and $NH_4H_2PO_4$, were used as starting materials in such proportions that the O/P ratio changed from 3.0 to 4.33. The initial charge (30–40 g) was thoroughly mixed and ground for 30–40 min in a mortar pestle and then calcined in an alumina crucible for 18–20 h by heating in a predetermined manner considering the decomposition temperatures of individual compounds at the maximum temperature of $600^\circ C$. This charge was reground and calcined again at $600^\circ C$ for 4 h in the same manner. The calcined charge was then melted in a platinum crucible using lowering and raising hearth furnace (Model OKAY 70R 10, M/s Bysakh and Co., Kolkata) and held at temperatures ranging from $750-800^\circ C$ depending on the composition for 2 h for thorough mixing in air ambient. When the melt was thoroughly homogenized and attained the desirable viscosity, it was poured either onto a metal plate and pressed by a graphite disc or into graphite moulds. The glass was then annealed at appropriate temperatures (between 350 and $400^\circ C$) for 3 h and stored in a desiccator prior to evaluation.

2.2 Glass characterization

Powder XRD patterns of the glasses were recorded on JEOL 3080 Diffractometer using $Cu-K_\alpha$ radiation to ascertain the glassy nature of the samples. Density (ρ) of glass samples was measured at room temperature using Archimedes principle with an accuracy of ± 0.03 g/cm^3 . Microhardness of glass samples was measured by indentation technique using Vicker's indenter on a microhardness tester (Leica model VMHT30M). Before measurements, the sample was polished with $0.3 \mu m$ alumina powder to get good polished surface. Indentation was obtained by applying 50 g load for 10 s. An average of at least 10 indentations was taken as the value of MH.

Fourier transform infrared (FTIR) absorption spectrum of samples (0.5% as KBr pellets) under evacuation in the region $400-4000$ cm^{-1} was recorded using a BOMEM DA8 FTIR spectrometer at a resolution of 4 cm^{-1} using a Globar infrared source (bonded silicon carbide rod), KBr beam splitter and deuterated triglycine sulphate (DTGS) detector. For each spectrum, about 50 scans were recorded to get good signal to noise ratio. Transmittance spectrum was calculated with reference to background spectrum taken with blank KBr pellet. ^{31}P and ^{11}B MAS NMR spectra were measured on a BRUKER AMX400 spectrometer using a pulse length of $2.5 \mu s$ 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 150 s for the ^{31}P MAS NMR measurements. The spinning speed was 12.5 kHz; the chemical shifts were referenced to 85% phosphoric acid (H_3PO_4) and boric acid (H_3BO_3).

3. Results and discussion

We have obtained bubble free glass samples in all the cases. XRD patterns for different glass samples are presented in figure 1. These patterns confirm the glassy nature of the samples with broad peaks around $20-30^\circ$ and $40-50^\circ$ (2θ values). Density was found to vary between 2.62 and 2.77 g/cm^3 . Dependence on microhardness on glass composition is shown in figure 2. It is seen that microhardness increases with the increase in the boron content indicating the formation of more rigid structure. The results are summarized in table 1.

3.1 FTIR spectra

FTIR spectra for different phosphate glasses are shown in figure 3. The fundamental and strong broad absorption

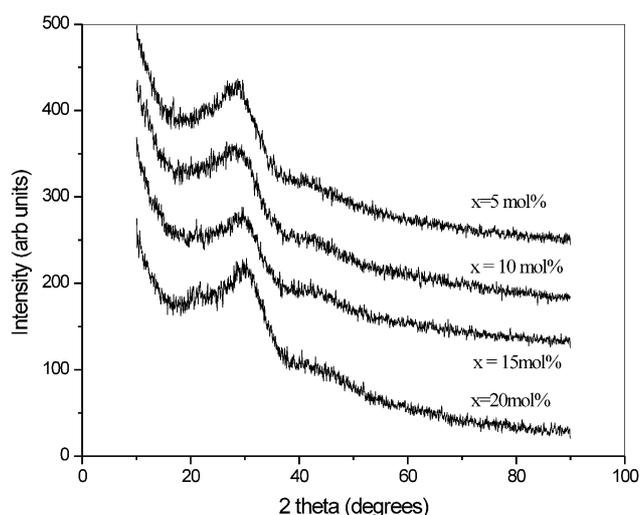
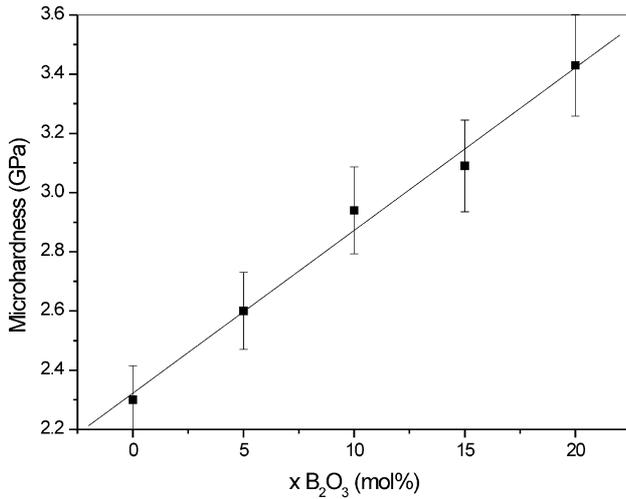
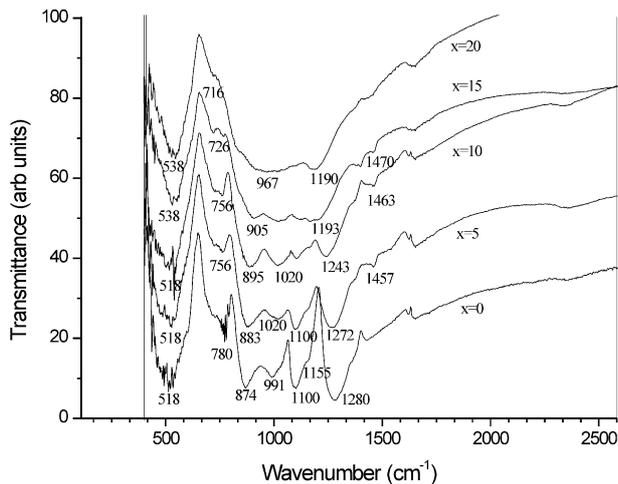


Figure 1. XRD plots of different glass samples having nominal composition, $40Na_2O-10BaO-xB_2O_3-(50-x)P_2O_5$, where $x = 0-20$ mol%.

Table 1. Composition, density and microhardness of 40Na₂O–10BaO–x B₂O₃–(50–x) P₂O₅ glass system.

Composition (nominal) x (mol%)	O/P ratio	$n = P/M^*$	$y = B/B + P$	Density (g/cm ³) (± 0.03)	MH (GPa) (± 0.05)
0	3.0	1.25	0	2.69	2.3
5	3.22	1.125	0.1	2.62	2.6
10	3.5	1.0	0.2	2.73	2.94
15	3.85	0.875	0.3	2.77	3.09
20	4.33	0.75	0.4	2.69	3.43

M* = alkali content in mol%.

**Figure 2.** Microhardness of different glass samples having composition, 40Na₂O–10BaO–x B₂O₃–(50–x) P₂O₅, where $x = 0$ –20 mol%.**Figure 3.** Infrared spectra of different glass samples having composition of 40Na₂O–10BaO–x B₂O₃–(50–x) P₂O₅, where $x = 0$ –20 mol%.

band around 1280 cm⁻¹ of glass sample having $x = 0$ is attributed to P=O asymmetric stretching vibrational mode.

The weak band at 1155 cm⁻¹ has been assigned to symmetric stretching modes, ν_s (PO₂)⁻¹ of metaphosphate chains (Almeida and Mackenzie 1980). The strong band at 1100 cm⁻¹ is attributed to asymmetric stretching of PO₃ groups in (PO₄)³⁻ units. The weak band at 1020 cm⁻¹ is assigned to symmetric stretching mode of PO₃ units. The band at 883 cm⁻¹ is attributed to the asymmetric vibrations, ν_{as} (P–O–P), of bridging oxygen atoms in phosphate chains, which confirms the chain structure of metaphosphate glass. The broad band at 763 cm⁻¹ may be attributed to symmetric stretching vibrations, ν_s (P–O–P), of bridging oxygen atoms. The broad band at 518 cm⁻¹ belongs to the bending vibrations of basic structural units of phosphate glasses (Dayanand *et al* 1996). When B₂O₃ is added to sodium barium phosphate glass, FTIR spectra will have overlapping bands arising due to B₂O₃ with those of P₂O₅. The bands appearing in the region 860–1100 cm⁻¹ are due to B–O bond stretching of tetrahedral BO₄ units, which are overlapped with phosphate bands. These bands are assigned to the vibration of tetraborate (triborate and pentaborate) groups of BO₄ units (Kamitsos *et al* 1986; Julien *et al* 1989). The bands appearing in the region 1150–1450 cm⁻¹ are attributed to the B–O bond stretching of trigonal BO₃ units (Kamitsos *et al* 1990). The band at 1020 cm⁻¹ is a characteristic absorption of BO₄ structural units and the band observed at 1457 cm⁻¹ is a characteristic absorption of BO₃ structural units in the glass. As B₂O₃ concentration increases in the glass the stretching frequencies of P–O bonds systematically gets shifted to lower wave numbers indicating the depolymerization of phosphate network.

3.2 ³¹P MAS NMR

³¹P MAS NMR spectra of the glass series, 40Na₂O–10BaO–x B₂O₃–(50–x) P₂O₅, where $x = 0$ –20 mol% are presented in figure 4. This spectra shows a broad peak around –16 ppm for $x = 5$ mol% glass sample. The peak shifts towards more positive values with increasing O/P ratio and B₂O₃ concentration.

Based on ³¹P MAS NMR studies of phosphate and borophosphate (Villa *et al* 1987) glasses, the peak around –16 ppm observed for $x = 5$ mol% can be attributed to the Q² structural units of P (P, having two bridging oxygen

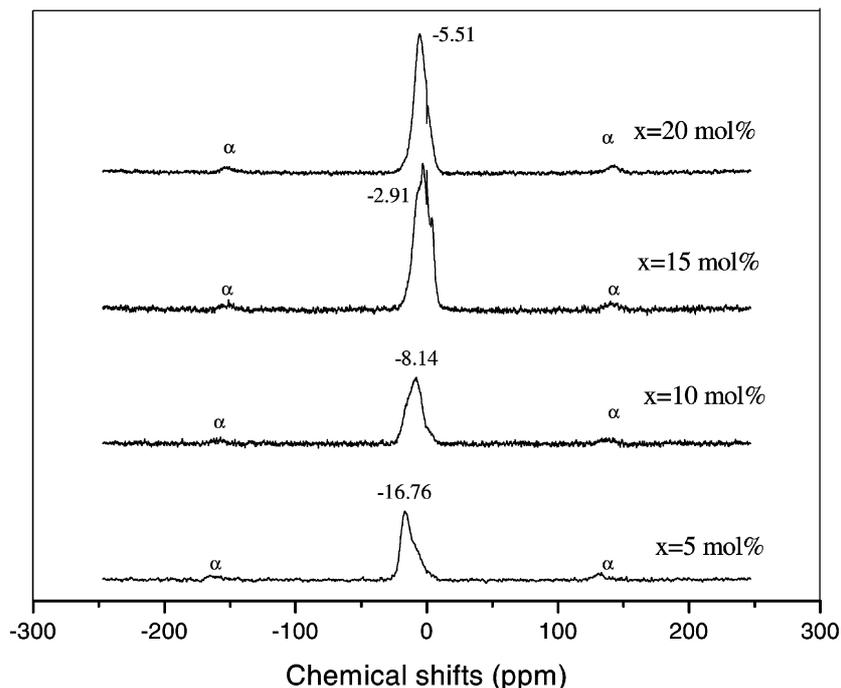


Figure 4. ^{31}P MAS NMR spectra of $40\text{Na}_2\text{O}-10\text{BaO}-x\text{B}_2\text{O}_3-(50-x)\text{P}_2\text{O}_5$, where $x = 0-20$ mol%, glass samples (α = spinning side bands).

atoms). As B_2O_3 concentration increases at the expense of P_2O_5 , Q^2 structural units get converted to Q^1 and Q^0 structural units of P (P, having one and zero bridging oxygens, respectively). For $x = 20$ mol% sample, mainly Q^0 structural units exist and B_2O_3 acts as the main network former. Normally the chemical shift values of Q^2 and Q^1 structural units of P exist at -20 ppm and -10 ppm, respectively for binary alkali phosphate glasses (Brow 2000). The slight positive increase of the chemical shift values of Q^2 (-16 ppm) and Q^1 (-8 ppm) structural units of P in these samples can be attributed to the presence of P–O–B linkages and the chemical shift observed at -5.51 ppm for $x = 20$ mol% is thought to be associated with P–O–B along with P–O–H linkages.

Brow and Tallant (1997) used spectroscopic methods to describe structure of borophosphate glasses and reported formation of tetrahedral $\text{B}(\text{OP})_4$ with increasing B_2O_3 concentration. Ducelet *et al* (1995) and Brow (1996) also characterized borophosphate glasses from MAS NMR and XPS investigations and linked borate and phosphate units through P–O–B bonds. Koudelka *et al* (2002) applied vibrational spectroscopy in combination with ^{31}P and ^{11}B MAS NMR to show the intermixing of borate and phosphate units. In a recent paper, Zeyer-Dusterer *et al* (2005) has shown, from combined ^{17}O , ^{31}P and ^{11}B NMR of both glassy and crystalline borophosphates, that the crosslinking between phosphate and borate groups plays a major role in determining the physical properties. Further, they were also able to distinguish between BPO_4 like units and BO_4

units in sodium borophosphate glasses. Our results are also consistent with the above studies.

The results of FTIR are in conformity with ^{31}P MAS NMR findings. The phosphate units, which progressively disappear as B_2O_3 content or O/P ratio increases, bridge the borate groups. At high B_2O_3 content ($x > 10$ mol%), the bonds get merged and a broad band appears in the region $900-1100\text{ cm}^{-1}$. This feature indicates that the glasses with $x > 10$ mol% are borate rich glasses. The chain-like phosphate glass structure enhances from one dimension to three dimensions with the inclusion of BO_4 structural units.

3.3 ^{11}B MAS NMR

The ^{11}B MAS NMR spectra of the phosphate glasses having nominal composition, $40\text{Na}_2\text{O}-10\text{BaO}-x\text{B}_2\text{O}_3-(50-x)\text{P}_2\text{O}_5$, where $x = 0-20$ mol% are presented in figure 5. ^{11}B MAS NMR patterns were found to be complex due to highly overlapping sharp pattern characteristic of tetrahedrally coordinated boron configurations occurring around 0 ppm and a broad pattern arising due to trigonally coordinated boron structural units. As B_2O_3 concentration increases at the expense of P_2O_5 , there is a systematic increase in the intensity of peak corresponding to BO_4 structural units.

From the results of FTIR and ^{31}P MAS NMR combined with ^{11}B NMR, it is confirmed that BO_4 units increase and P–O–B linkages are formed as B_2O_3 concentration increases at the expense of P_2O_5 . Due to dominance of

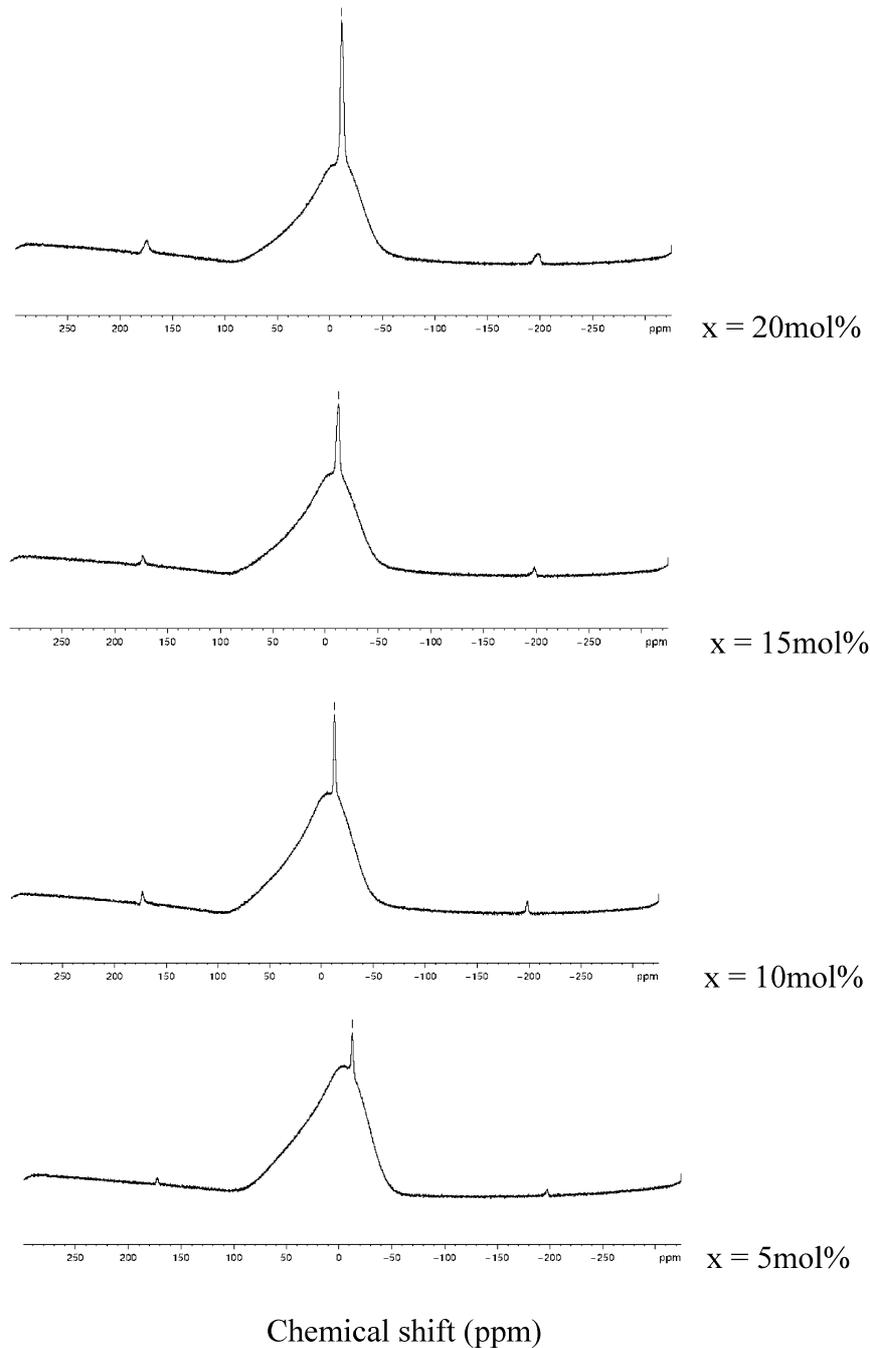


Figure 5. ^{11}B MAS NMR spectra of $40Na_2O-10BaO-xB_2O_3-(50-x)P_2O_5$, where $x = 0-20$ mol%, glass samples.

BO_4 units and formation of P–O–B linkages, improved cross-linking between the phosphate chains creates a more rigid borophosphate network because of increase in stronger O–B linkages. Consequently, microhardness shows increase with increase in B_2O_3 content.

4. Conclusions

Bubble free glasses of sodium barium borophosphate, $40Na_2O-10BaO-xB_2O_3-(50-x)P_2O_5$, were prepared. Mi-

crohardness was found to increase with increase in the boron content. FTIR results showed the depolymerization of phosphate chains and the presence of predominantly four-coordinated boron units, which increased with increase in the boron content. ^{31}P MAS NMR results showed the presence of middle Q^2 group and end Q^1 and Q^0 groups along with P–O–B linkages, which are responsible for more rigid borophosphate glass network thereby increasing MH. ^{11}B MAS NMR results also support this observation.

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