

^{31}P and ^{11}B nuclear magnetic resonance investigations of borophosphate glasses: correlations between structure and chemical and physical properties

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Abstract

Results of ^{31}P and ^{11}B nuclear magnetic resonance of glasses of composition $(1-x)\text{NaPO}_3-x\text{Na}_2\text{B}_4\text{O}_7$ are summarized. The proposed structural models show the progressive change from random ramification phosphate network to the borate network with increasing x . The physical and chemical properties are correlated with these different structures.

1. Introduction

In a previous paper, glasses with composition $(1-x)\text{NaPO}_3-x\text{Na}_2\text{B}_4\text{O}_7$ were prepared. Physical and chemical properties such as glass transition T_g and crystallization T_c temperatures, molar volume V , solubility in water S and cut-off wavelength in the UV region λ_c were measured [1]. These properties are strongly modified, mainly in the borate-poor glass domain.

Recently, these vitreous compositions have been studied by ^{31}P magnetic angle spinning (MAS) and ^{11}B nuclear magnetic resonance (NMR) [2].

This paper summarizes the NMR results of these borophosphate glasses and correlates the structural interpretation with physical and chemical properties.

2. Experimental details

The glassy samples studied in this work (Table 1) with composition $(1-x)\text{NaPO}_3-x\text{Na}_2\text{B}_4\text{O}_7$ were obtained from the vitreous domain of the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{B}_2\text{O}_3$ ternary system. In Fig. 1 the glass samples (small circles) correspond to the composition $(1+x)/(1+2x)\text{Na}_2\text{O} + (1-x)/(1+2x)\text{P}_2\text{O}_5 + 4x/(1+2x)\text{B}_2\text{O}_3$ (broken line) enclosed in the vitreous domain (solid line). One notes the presence of a small glassy domain in the Na_2O -rich part of the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ binary system.

The NMR and the physical and chemical characterizations are described in detail in refs. 1 and 2, respectively.

3. Nuclear magnetic resonance

3.1. ^{31}P MAS nuclear magnetic resonance

Figure 2 shows a schematic evolution of the ^{31}P MAS NMR spectra of the glass samples studied (Table 1). The ^{31}P spectra are referenced to H_3PO_4 . The peaks labelled (a), (b), etc. in this figure were assigned by comparison with those identified in silver and lithium borophosphates [3] and crystallized polyphosphates [4]. The peaks (a), (b), (c), (d), and (e) correspond respectively to the MP, MB_1 , then progressively to the MB_2 , EP, EB, and MO phosphate units. The structural formulae and symbols for these phosphate units are reported in Table 2.

3.2. ^{11}B nuclear magnetic resonance

The integrated experimental ^{11}B NMR spectra consist of a central narrow peak and a broad line superposition, due respectively to boron atoms in BO_4 (called B_{IV}) and BO_3 (called B_{III}) units. Using a deconvolution method and area measurements [2], the percentage of BO_4 units could be determined vs. the glass composition, as seen in Fig. 3 (curve a).

The excess of negative charge of BO_4 units may be compensated for either by the excess of positive charge of PO_4 units or the Na^+ cation modifiers forming the C_P and C_{Na} units respectively (see Fig. 3, curve a).

Determination of the unit fraction of C_{Na} [2], the only form existing in borate glasses with composition $y\text{Na}_2\text{O}-(1-y)\text{B}_2\text{O}_3$ (Fig. 3, curve b), allows the unit fraction of C_P in the sodoborophosphate glasses to be estimated. This is possible if the equilibrium between

TABLE 1. Composition and $[\text{B}]/[\text{B} + \text{P}]$ ratio corresponding to glass samples $(1-x)\text{NaPO}_3-x\text{Na}_2\text{B}_4\text{O}_7$ studied by NMR

x	0	0.02	0.05	0.10	0.13	0.17	0.20	0.33	0.50	0.66	0.91	1.00
$[\text{B}]/[\text{B} + \text{P}]$	0	0.075	0.167	0.308	0.374	0.444	0.500	0.667	0.800	0.889	0.968	1.000

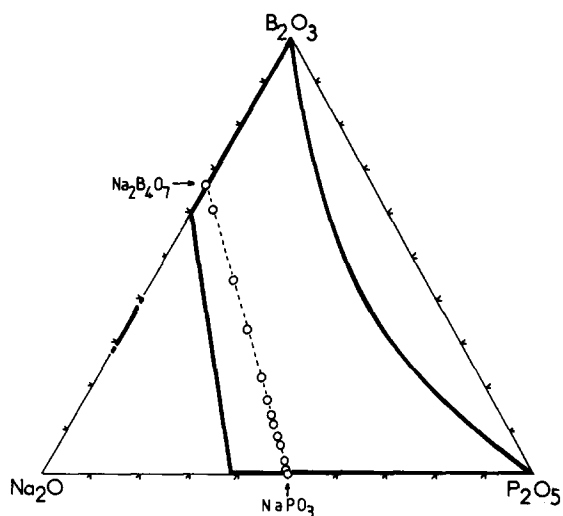


Fig. 1. Vitreous domain (solid line) and glass samples (○) studied by NMR.

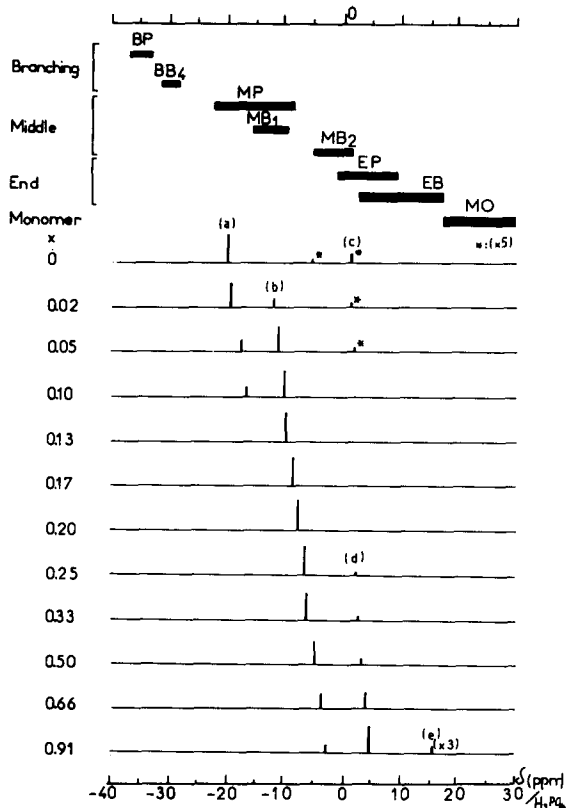
Fig. 2. Schematic representation of ^{31}P MAS NMR spectra vs. glass composition x . Comparison with the values of isotropic chemical shifts (δ referenced to H_3PO_4) corresponding to the phosphate units (see Table 2) previously identified in ref. 3.

TABLE 2. Structural formulae and symbols of phosphate units identified in ref. 3

Symbol	Structural entity
BP	$\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \diagup \quad \diagdown \\ \text{O}-\text{P} \end{array}$
BB ₄	$\begin{array}{c} \text{B}-\text{O} \\ \diagup \quad \diagdown \\ \text{P} \\ \diagdown \quad \diagup \\ \text{B}-\text{O} \end{array}$
MP	$\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \diagup \quad \diagdown \\ \text{P}-\text{O} \quad \text{O}-\text{M}^+ \end{array}$
MB ₁	$\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \diagup \quad \diagdown \\ \text{B}-\text{O} \quad \text{O}-\text{M}^+ \end{array}$
MB ₂	$\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \diagup \quad \diagdown \\ \text{B}-\text{O} \quad \text{O}-\text{B} \end{array}$
EP	$\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \diagup \quad \diagdown \\ \text{P}-\text{O} \quad \text{O}^- \text{M}^+ \end{array}$
EB	$\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \diagup \quad \diagdown \\ \text{B}-\text{O} \quad \text{O}^- \text{M}^+ \end{array}$
MO	$\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \diagup \quad \diagdown \\ \text{M}^+ \text{O} \quad \text{O}^- \text{M}^+ \end{array}$

the formation of C_{Na} and BO_3 units is the same in the two glasses. It mainly depends on the concentration of Na_2O , and is therefore not affected by the presence of phosphorus.

The variation of the total B_{IV} fraction $N_{\text{B}_{\text{IV}}}$ and the fraction of B_{IV} in C_{Na} units $N_{(\text{B}_{\text{IV}})_{\text{Na}}}$, in relation to the number of network formers (boron and phosphorus atoms) vs. x are shown in Fig. 3 (curve c). By difference, the variation of the B_{IV} fraction in C_{P} units $N_{(\text{B}_{\text{IV}})_{\text{P}}}$ can be estimated. These units predominate in phosphorus-rich glasses with a maximum value close to $x = 0.2$ and disappear beyond $x = 0.5$.

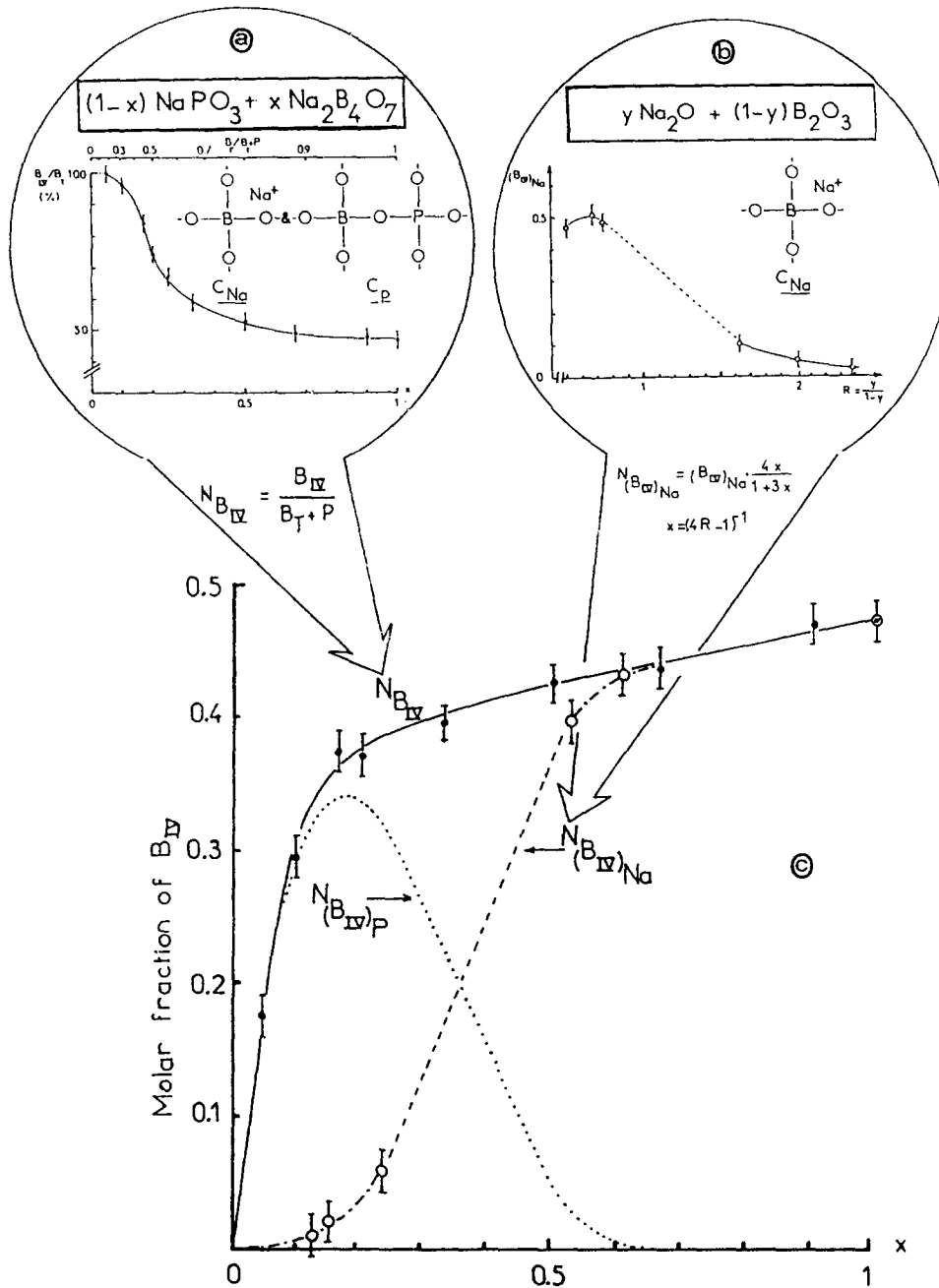


Fig. 3. Evolution of the BO₄ unit fraction in relation to B_T + P vs. sodoborophosphate glass composition (curves c): in C_P and C_{Na} forms, N_{B_{IV}} (—) obtained from curve a; in C_{Na} form, N_{(B_{IV})Na} (-----) obtained from curve c; in C_P form, N_{(B_{IV})P} = N_{B_{IV}} - N_{(B_{IV})Na} (.....).

4. Correlations between structure and physical and chemical properties

From interpretation of the NMR spectra and in agreement with the evolution of chemical and physical properties (Fig. 4), it is possible to outline models for structural evolution vs. glass composition. Four structural domains can be distinguished.

Domain 1. This is characterized by a shortening of the average chain length (MP and EP). These short chains are interconnected by BO₄ units inducing the formation of MB₁ or more accurately MB'₁ entities (see Table 3), in the presence of C_P units.

Domain 2. The phosphate chains have disappeared and every PO₄ group becomes more and more bound to boron atoms (B_{III} and B_{IV}). These phosphate

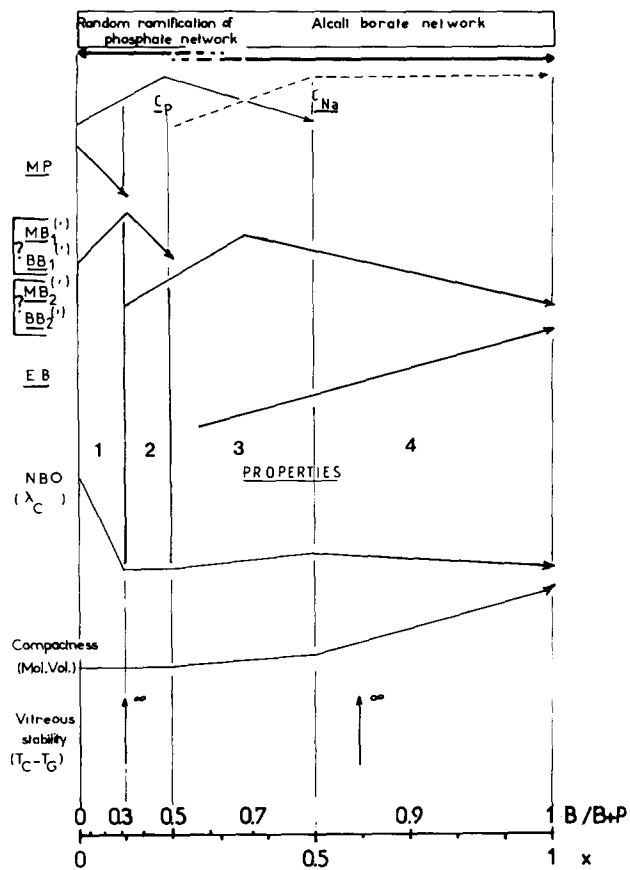


Fig. 4. Schematic representations of the evolution of the structural units identified by NMR and various properties such as cut off wavelength in the UV region λ_c and solubility in water S related to the number of non-binding oxygen atoms (NBO) in the glass network, the molecular volume (Mol. Vol.) corresponding to the compactness of the glass network, and the difference in crystallization and transition temperatures ($T_c - T_g$) corresponding to the vitreous stability.

TABLE 3. Structural formulae and symbols of new phosphate units identified in this work

Symbol	Structural entity
MB_1'	$\begin{array}{c} M^+ \quad O^- \quad O-P \\ \quad \quad \quad \\ \quad \quad \quad P \\ \quad \quad \quad / \quad \backslash \\ B-O \quad \quad O-M^+ \end{array}$
MB_2'	$\begin{array}{c} M^+ \quad O^- \quad O-B \\ \quad \quad \quad \\ \quad \quad \quad P \\ \quad \quad \quad / \quad \backslash \\ B-O \quad \quad O-M^+ \end{array}$

groups correspond to MB_1 and MB_2 or more accurately to the MB_1' , MB_2' entities in the presence of C_p units.

These two structural models agree with evolution of the properties, showing a random ramification of the phosphate network.

Domains 3 and 4. The major entities are now the BO_4 (C_{Na} units) and BO_3 units which bridge the phosphate tetrahedra (MB_2 and/or MB_2' , EB and a few C_p). For high concentrations of boron atoms, C_{Na} and BO_3 units probably form borate groups with some interconnected EB units.

References

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