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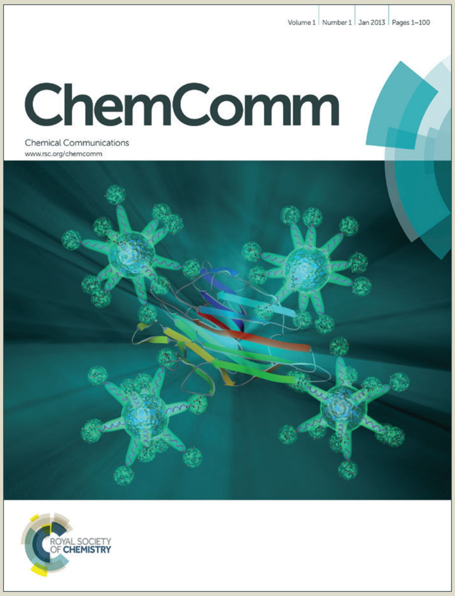

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P-O-B^3 linkage in borophosphate glasses evidenced by high field ^{11}B/^{31}P correlation NMR.

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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The long-standing debate about the existence of P-O-B^3 linkage in glasses has been solved by high-field scalar-correlation NMR. Previously suggested by dipolar-NMR methods, the presence of such species has been definitively demonstrated by ^{11}B(^{31}P) J-HMQC NMR techniques. The results indicate that borophosphate networks contain P-O-B^3 bonds and present thus a higher degree of atomic homogeneity than previously thought.

Growing interest in borophosphate based glasses has been observed during the last decades because of their potential applications in new energy sources as low temperature sealing glasses, all-solid batteries electrolytes or radioactive waste confinement matrices.[1-5] It is well-established that the excellent properties of B_2O_3-P_2O_5 based glasses result from the association between the phosphate and the borate species, giving rise to mixed units that stabilise the glass network and induce an interesting non-linear evolution of macroscopic properties known as the 'mixed glass former effect'. Within the glass network, P^{5+} ions always adopt tetrahedral configuration whereas boron can be found in four- (B^4) and three-fold (B^3) coordination states, the first and second species being dominant at low- and high-B_2O_3 contents, respectively. The extent of mixing between these three structural units is a key parameter for monitoring the global network topology and understanding the particular properties of these materials. While the association between P and B^4 has been demonstrated and extensively studied by vibrational and magic angle spinning solid state nuclear magnetic resonance (MAS-NMR) spectroscopies,[5-15] direct and unambiguous conclusions about the mixing between P and B^3 are still lacking. In 2005, state of the art NMR methods (^{11}B(^{31}P) Rotational Echo Double Resonance (REDOR)[7] and ^{31}P(^{11}B) Cross Polarisation HETeronuclear CORrelation[6]) were employed to tackle this issue. While the 2D correlation maps edited by Jäger et al. did not show any P/B^3 interaction (due to the pulse sequence's ineffectiveness in handling both B^3 and B^4 signals simultaneously), the REDOR technique afforded evidence of a non-zero P/B^3 interaction.[6-7] However, the weak dephasing can be interpreted either as a long distance interaction between unconnected B^3 and P sites,[7] or as an indirect evidence of P-O-B^3 linkages.[8] Therefore, no definitive model is available from through-space correlation NMR and it was still debated if the borophosphate glass network was *homogeneous* and formed by interconnected P, B^4 and B^3 units or *heterogeneous* and composed by (i) interconnected B and P tetrahedra and (ii) domains in which B^4 units are exclusively linked to B^3 moieties.

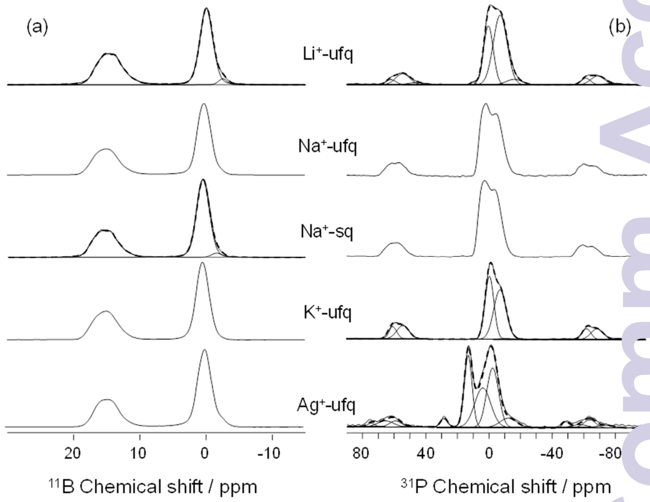

Figure 1. (a) ^{11}B and (b) ^{31}P MAS-NMR spectra of the 45M_2O-35B_2O_3-20P_2O_5 glass series obtained at 18.8 T with a 3.2-mm probehead operating at a spinning frequency of 20 kHz. The ^{11}B spectra have been acquired with 10° pulses of 0.7 µs, 64 transients and a recycle delay (rd) of 4 s. The ^{31}P spectra have been recorded with 30° pulses of 1.7 µs, 32 transients and a rd of 120 s. The spectra are accompanied with representative deconvolutions in dotted lines.

This structural model, undebated for almost 10 years, has been re-investigated in this contribution in the light of new evidences provided by (i) high magnetic field (18.8 T) NMR, allowing for highly resolved ^{11}B spectral analysis with well separated B^3/B^4 regions; (ii) 1D/2D dipolar- but also scalar- mediated NMR pulse sequences performed with a prototype 3.2mm $^{11}B/^{31}P$ measurement probe on (iii) a glass series with different network former species having the composition $45M_2O-35B_2O_3-20P_2O_5$ with M=Li, Na, K or Ag. The samples have been prepared through the melt-quenching method at 1100°C with standard quenching (sq: 10^2 K.s^{-1}) for M=Na and ultra-fast twin roller quenching (ufq: 10^6 K.s^{-1}) conditions for M=Li, Na, K and Ag, according to previously published procedures.[10,12]

The local order has been investigated with ^{31}P and ^{11}B 1D MAS-NMR spectra (Fig. 1). The ^{11}B spectra (Fig. 1a) show resolved B^4 and B^3 regions at 0 and 18 ppm. As determined from the spectra deconvolution (Tab. 1), the samples contain B^4 and B^3 species in close proportions. The constant NMR parameters (Tab. 1) of B^3 and B^4 units suggest a minor influence of the surrounding cations and indicate that B^4 is mainly present as $B(OP)_1(OB)_3$ species.[14] The ^{31}P spectra (Fig. 1b) present broad and asymmetric features resulting from the superimposition of different signals with close chemical shifts.[8-10,12-15] Two major components can be identified from the spectral deconvolution (Tab. 1, ESI) indicating that the glass network is mainly composed by Q^0_1 and Q^0_2 species, i.e. P^{5+} attached to 1 and 2 B^{3+} species (m=1,2 in the Q^n_m notation), respectively, without any connectivity with other P^{5+} ions (n=0 in the Q^n_m notation). Only the Ag-sample presents an additional signal assigned to a P connected to B species (Fig. 1, ESI). Altogether, the 1D MAS-NMR results indicate a similar local order in all the samples, independently of the nature of the M cation or the quenching method.

Table.1 : ^{11}B NMR parameters : chemical shift (δ_{iso} in ppm, +/- 0.1), full width at half maximum (fwhm in ppm, +/- 0.2), quadrupolar coupling constant (Cq in MHz, +/- 0.1), asymmetry parameter (η_Q, +/- 0.1) B^4/B^3 relative proportions (Rel. Prop. in %, +/- 2), second moment ($M_2(^{11}B(^{31}P)$ in 10^6 rad^2.s^{-1},+/- 10%).

Sample	B^4 δ_{iso} ; fwhm	B^3 δ_{iso} ; C_Q ; η_Q	Rel. Prop. B^3 ; B^4 / %	$M_2(^{11}B/^{31}P)$ B^4 ; B^3
Li-ufq	0.1 ; 2.3	17.5 ; 2.7 ; 0.5	53.2 ; 46.8	5.0 ; 1.7
Na-ufq	0.4 ; 2.3	17.9 ; 2.7 ; 0.5	53.3 ; 46.5	5.2 ; 1.6
Na-sq	0.4 ; 2.3	18.2 ; 2.7 ; 0.5	53.0 ; 47.0	4.9 ; 1.7
K-ufq	0.5 ; 2.1	18.1 ; 2.6 ; 0.5	53.3 ; 46.7	4.9 ; 1.5
Ag-ufq	0.1 ; 2.3	17.4 ; 2.6 ; 0.5	61.8 ; 38.2	4.8 ; 1.5

The medium range order has been analysed in a first step using dipolar correlation NMR, which is sensitive to spatial proximity. These first ever reported high resolution 2D $^{11}B/^{31}P$ through space correlation maps have been generated at 18.8 T using the recently developed $^{11}B(^{31}P)$ dipolar Heteronuclear Multiple Quantum Coherence (D-HMQC) method (Fig. 2a, ESI).[15-16] The 2D map obtained on the Li-containing sample (Fig. 2a) has been acquired in 7 hours. Two separate correlation signals can be observed indicating spatial proximity between both borate species (B^4 and B^3) and the phosphate units, in a good agreement with the correlation map obtained at lower field (9.4 T) on a similar sample.[10] The REDOR[17-18] curves obtained on the 5 samples are presented in Fig. 2b, accompanied with representative parabolic fits used to derive the dipolar second moment ($M_2(^{11}B\{^{31}P\})$) values for the B^3 and B^4 species. While the B^4 curves present a stronger dephasing than the B^3 curves, a comparison between the five glass samples indicates that the REDOR curves for the B^4 species are all very similar to each other, and the same is true for the B^3 REDOR curves. These results suggest that the P/B organisation is similar in the five samples. The M_2 values derived from the parabolic fits are reported in Tab.1 and support the previously reported conclusions. In the case of the B^4 units, the M_2 value (5×10^6 rad^2.s^{-2}) indicates the presence of about one B-O-P linkage (on average) per unit[8,10,13,14] suggesting the dominant presence of $B^4(OP)_1(OB)_3$ groups within the glass structure, consistent with the chemical shift analysis reported above. The low M_2 values associated with the B^3 units (1.6 10^6 rad^2.s^{-2}) agree with previously found results obtained in other borophosphate glasses. However, interpretation of these results as evidence of P-O-B^3 linkage is still questionable as these techniques can only provide through-space information.

Definitive conclusions about the bond connectivity have been obtained by the scalar-correlation NMR experiment, which exploits indirect spin-spin couplings for the creation of heteronuclear double-quantum coherences. Compared to the dipolar based experiment, $^{11}B(^{31}P)$ J-HMQC[19] (Fig. 2b, ESI) presents a lower sensitivity, due to rather long echo delay required for coherence creation, that results in significant signal losses due to spin-spin relaxation. Typically, 110 h (instead of 7 h in case of the dipolar map) were required to record the 2D map on the Li-sample (Fig. 2c), in spite of the high sensitivity afforded by the high magnetic field used for this experiment. However, in spite of a lower signal to noise ratio, the 2D map perfectly confirms the correlation scheme derived from the dipolar 2D map and delivers the first unambiguous and direct evidence for the presence of P-O-B^3 linkages in borophosphate glasses.

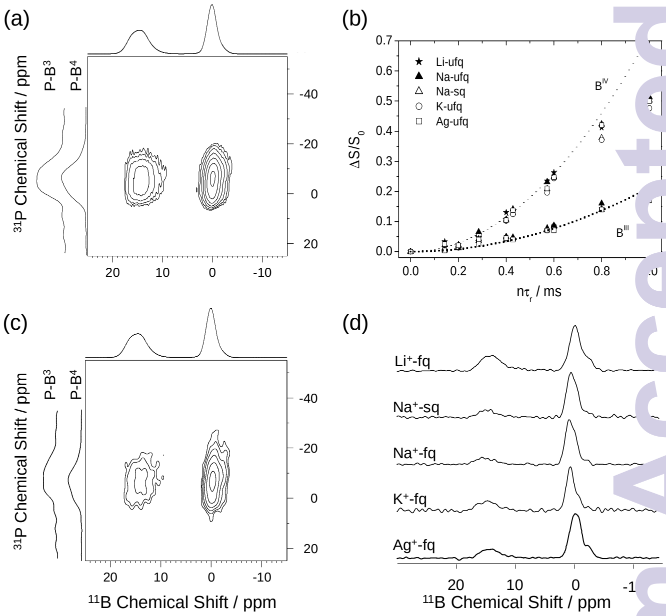

Fig.2: (a) 2D through-space $^{11}B/^{31}P$ correlation map obtained at 18.8 T on the Li- sample (7 h of acquisition : 2474 x 50 data points, 10 and 5 μs ^{11}B and ^{31}P π/2 pulse lengths, 256 transients and 2 ms $SR4^2_1$ dipolar recoupling). (b) $^{11}B(^{31}P)$ REDOR curves obtained at 9.4 T with 10 and 5 μs ^{11}B and ^{31}P π/2 pulse lengths and 32 transients. (c) 2D through-bond $^{11}B/^{31}P$ correlation map obtained at 18.8 T on the Li- sample (110 h of acquisition : 2474 x 50 data points, 10 and 5 μs ^{11}B and ^{31}P π/2 pulse lengths, 2048 transients and 5 ms echo-delay. (d) 1D through-bond $^{11}B(^{31}P)$ J-HMQC spectrum obtained at 18.8 T on the $45M_2O-35B_2O_3-20P_2O_5$ glass series with 2-4 k transients.

Having been evidenced in the Li- and ultra-fast quenched sample, the presence of P-O-B^3 linkage in the other samples was investigated by using the 1D version of the $^{11}B(^{31}P)$ J-HMQC experiment. These DQ filtered ^{11}B spectra are summarised in Fig. 2d and show that both B^4 and B^3 are connected to P^{5+} units in all the glasses. Thus bond connectivity between phosphate units and three-coordinated boron is not dependent on a particular formulation or synthesis procedure and must be considered as a common motif in borophosphate glasses.

The quantitative analysis of the $^{11}B/^{31}P$ dipolar interaction, derived from the REDOR experiment (Fig. 2b), can thus be re-interpreted. Keeping in mind that for each B-O-P linkage an M_2 increment of 4-5 × 10^6 $rad^2.s^{-2}$ is observed,[7,8,14] the M_2 values obtained for the B^3 species (1.5 to 1.7 × 10^6 $rad^2.s^{-2}$), suggest that approximately 30 ±10% of all B^3 units present a B-O-P linkage. The three structural basic units (P, B^3 and B^4) interact altogether to create the mixed glass network and it is now clearly established that the borophosphate glass network presents a good atomic homogeneity even at high B_2O_3 amount.

Notes and references

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Electronic Supplementary Information (ESI) available: [Tab. 1 ^{31}P NMR parameters; Fig. 1 $^{11}B(^{31}P)$ D-HMQC experiment performed on the Ag-sample]. See DOI: 10.1039/c000000x/

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