A ^{11}B and ^{31}P MAS NMR Study of the Impact of Ca^{2+} and Sr^{2+} Network Modifying Cations on the Structure of Borate and Borophosphate Glasses

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Abstract

A detailed qualitative and quantitative analysis into the local- and medium-range order of alkaline-earth binary borate and ternary borophosphate glasses is carried out through the use of ^{11}B and ^{31}P magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. A series of calcium and strontium borate and borophosphate glasses were prepared with a constant P_2O_5:B_2O_3 ratio of 0.4 and varying alkaline-earth loading contents in order to understand the charge compensation characteristics of B and P within the glasses. For the alkaline earth borate glass with loading values up to R = 0.4 (where R is the ratio between alkaline earth metal oxide and borate moieties), the glass network preferentially forms negatively-charged four-coordinate borate units to balance out the cationic charge of the alkaline-earth network modifier. At higher alkaline-earth loading values of R > 0.5 there is a mixture between three- and four-coordinate borate species balancing out the modifier. On the other hand, investigation of the alkaline-earth borophosphate glass series indicates that these compounds form a complex network with depolymerization of the phosphate species while maintaining medium-range connectivity of the borate units within the amorphous solid. At low alkaline-earth loadings, characteristics of BPO_4, clustering is seen, while at high loading values, negatively charged phosphate units are seen bridging to four-coordinate boron species forming a complex mixed former oxide network. Ultrahigh-field ^{11}B MAS NMR helps to determine the varying degrees of ring and non-ring borate species present within these glasses, and confirms the unique structures present in both the binary borate and ternary borophosphate series. The ^{31}P MAS NMR data suggests that calcium prefers a phosphate chemical environment at high R, whereas strontium appears to maintain higher N_4 values over the same composition range.

1. Introduction

Our interest in borophosphate glasses at the moment primarily focuses on the two active components of B_2O_3 and P_2O_5 and their resulting effects on the glass structure-property relationships. Phosphate-based multicomponent glasses are seen to have interesting chemical and physical properties[1] such as lower dissolution rates[2] and optical properties,[3] while the addition of B_2O_3 is seen to markedly increase durability.[4] The addition of other network-modifying oxides such as alkali and alkaline-earth metals (i.e., Li, Na, K, Ca, Sr) extend their potential use to other applications including nonlinear optical (NLO) materials,[5] hermetic sealing substances,[6] and ion conductors.[7] Additionally, the biocompatibility of these compounds leads to their applications as biomaterials in the health and dental fields, since calcium is a prominent ion in promoting hydroxyapatite formation and strontium is a component in drug bases used in efforts to combat osteoporosis.[8,9,10] However, principal structural knowledge of low phosphate-containing borate glasses remains elusive, as the addition of phosphate to boron oxide produces a mixed network-forming glass that lacks long-range periodic order, and thus is very difficult to study under traditional X-ray diffraction techniques. Moreover, the addition of alkaline-earth network modifiers impacts the local structure of the glass, making irregular local environments too complex to observe by many ordinary spectroscopic means.[11] Solid-state nuclear magnetic resonance (NMR) spectroscopy on the other hand is one of the few characterization tools (e.g., X-ray absorption spectroscopy, neutron diffraction, vibrational spectroscopy, etc.) capable of measuring the local and medium-range structural units of these amorphous materials.[12,14] ^{11}B and ^{31}P are highly sensitive NMR-active nuclei due to their favorable gyromagnetic ratio and high natural abundance. Hence, the far-reaching ability of ^{11}B and ^{31}P NMR spectroscopy can reveal important correlations between atomic-level structures within a variety of glass networks.[15,16]

For example, the three- ($^{[3]}$B) and four-coordinate ($^{[4]}$B) boron chemical environments can be clearly distinguished under ^{11}B magic-angle spinning (MAS) NMR with suitable magnetic field strengths of 11.7 T or higher.[17] Closer examination of the peaks ascribed to the $^{[4]}$B region can lead to an understanding of the medium-range structure as the ^{11}B isotropic chemical shift is sensitive to phosphate neighbours, while ultrahigh magnetic fields and advanced NMR techniques such as multiple-quantum magic-angle spinning (MQMAS) can lead to the delineation of varying $^{[3]}$B environments.[18,19] NMR methods for the determination of medium-range homonuclear and heteronuclear distances and connectivity has evolved over the last two decades using various one- and two-dimensional techniques further assisting in understanding glass structure.[20, 21,22,23,24,25] ^{31}P MAS NMR offers additional insight into the degree of depolymerization of the phosphate network such as the transformation from bridging to non-bridging oxygens that may lead to the elucidation of neighbouring network formers.[26] ^{43}Ca and ^{87}Sr are typically not studied due to their challenging NMR properties including low natural abundance, low gyromagnetic ratio and moderately sized quadrupole moments.[27, 28, 29, 30] In addition to these problematic NMR properties, the structural disordered and low concentration of network modifying cations leads to further complications due to the limitations in sensitivity.

In this study, we examine the impact of altering the calcium and strontium ratios within borate and borophosphate glasses on the network forming roles of borate and the impact phosphate incorporation has on the local structure. Two series of calcium- and strontium-modified glasses were examined while maintaining a constant P_2O_5:B_2O_3 ratio, K, where K = 0 or 0.4. These compositions provide a comparison on how P substitution affects glass polymerization as the concentration of network modifying cations (Ca or Sr) is varied. Results from ultrahigh-field ^{11}B MAS NMR (21.1 T) also provide clear evidence of distinct $^{[3]}$B ring

formation within high alkaline-earth borophosphates, a feature not observed for alkaline-earth borate glasses with comparable alkaline-earth modifier concentrations.

2. Materials and Methods

2.1 Synthesis: Binary alkaline-earth borate and ternary alkaline-earth borophosphate glasses were prepared from reagent-grade (>98% pure) calcium or strontium carbonate, boric acid, and phosphorus pentoxide obtained from Sigma Aldrich. The following chemical reactions describe the preparation of the binary and ternary glasses respectively:

$$R\mathrm{MCO_3} + 2\mathrm{H_3BO_3} \xrightarrow{\Delta} R\mathrm{MCO} * \mathrm{B_2O_3} + R\mathrm{CO_2} + 3\mathrm{H_2O} \quad (1)$$

$$R\mathrm{MCO_3} + 2\mathrm{H_3BO_3} + K\mathrm{P_2O_5} \xrightarrow{\Delta} R\mathrm{MCO} * \mathrm{B_2O_3} * K\mathrm{P_2O_5} + R\mathrm{CO_2} + 3\mathrm{H_2O} \quad (2)$$

where M is either calcium or strontium, R is the alkaline-earth oxide to boron trioxide molar ratio (R = $\mathrm{MO/B_2O_3}$) and K is the phosphorous pentoxide to boron trioxide molar ratio (K = $\mathrm{P_2O_5/B_2O_3}$). The glass samples were synthesized in 500 mg batches (to bypass the onset of crystallization) by combining the proper ratios of alkaline-earth carbonate, boric acid, and phosphorus pentoxide in a platinum(95%)/gold(5%) crucible (Laval Labs, Quebec, Canada). The starting materials were kept in an oven set to 110 °C prior to weighing out the reactants; once combined the crucible was pre-treated at 600-700 °C for 15 minutes to ensure decarbonation was complete, and once the mass loss was confirmed the crucible was placed into a preheated high-temperature box furnace (Carbolite Gero Ltd., Hope Valley, UK) between 1200 and 1300 °C for 1 to 2 hours. All final glasses were within ≤3% of the expected final masses. The melts were rapidly quenched to room temperature by dipping the crucible in cooled deionized water. All glasses were characterized based on their translucent nature, as well as with powder X-ray diffraction (XRD) to ensure that no crystallinity was present. Note: Only the parent 0.4 $\mathrm{P_2O_5}$:$\mathrm{B_2O_3}$ glass, identified as $\mathrm{BPO_4}$, displayed considerable crystallinity,

111 with minor impurities observed in the R=0.05 calcium and strontium borophosphate samples.
112 Glass samples were packed into glass vials sealed with Parafilm and stored under dry
113 atmosphere in a dessicator.

114 2.2 *Powder X-ray diffraction*: The glasses were ground into a fine white powder in an agate
115 mortar and pestle before being mounted on a single crystal quartz (SiO_2) background sample
116 holder and analyzed using a Bruker PLATFORM diffractometer, CCD detector, Mo K_α source.
117 All data were acquired at room temperature with a 2θ range of 5° - 80° and 0.029° increments.

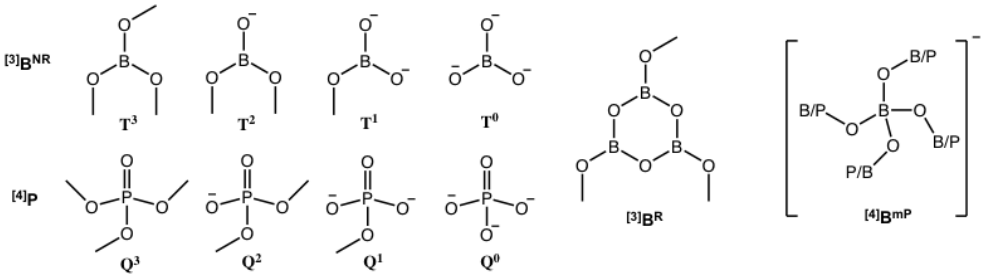
118 *2.3 Solid-state nuclear magnetic resonance spectroscopy:* ^{11}B and ^{31}P NMR spectra were
119 acquired on an Agilent/Varian VNMRS 600 MHz spectrometer equipped with an Oxford
120 magnet (B_0 = 14.1 T). All spectra were acquired using a 3.2 mm triple resonance Varian MAS
121 probe. Powdered samples were placed into ZrO_2 rotors (3.2 mm o.d., 22 μL, 30 to 40 mg)
122 equipped with Torlon drive and top caps. All data were acquired using a spinning frequency of
123 16 kHz. ^{11}B NMR experiments used a short 0.4 μs Bloch excitation pulse (9° tip angle, $\gamma B_1/2\pi$
124 = 62.5 kHz), 4 s recycle delay, 16 dummy scans and 512 co-added transients. All spectra were
125 referenced using boric acid ($H_3BO_{3(aq)}$, 0.1 M) as a secondary reference, set to +19.6 ppm
126 (BF_3Et_2O, δ_{iso} = 0 ppm). ^{31}P NMR experiments were acquired using a Bloch pulse set to 1.6 μs
127 (45° tip angle, $\gamma B_1/2\pi$= 71 kHz), 120 s recycle delays, 4 dummy scans and 64 co-added
128 transients. Phosphoric acid ($H_3PO_{4(aq)}$, 85%) was used as a primary reference, set to 0.0 ppm.
129 Recycle delays were checked for each glass series to ensure quantification.

130 Ultrahigh field ^{11}B NMR spectra (ν_L=288.6 MHz) were acquired on a Bruker Avance II
131 900 (21.1 T) spectrometer at the Canadian National Ultrahigh-Field NMR Facility for Solids
132 (Ottawa, Canada). ^{11}B MAS NMR spectra were acquired on selected samples using a home-
133 built 2.5 mm double resonance boron-free MAS NMR probe with a spinning frequency of 20

kHz. Single pulse (Bloch) experiments used a short 0.4 μs pulse (9° tip angle, $\gamma B_1/2\pi$ = 62.5 kHz), 5 s recycle delays, 4 dummy scans and 512 co-added transients. 3QMAS spectra were acquired using a three-pulse MQMAS experiment with a zero quantum filter and a π/2 selective pulse ($\gamma B_1/2\pi$= 62.5 kHz, where p1 and p2 were optimized for maximum sensitivity).[31,32] All 3QMAS NMR experiments were acquired under identical conditions using a 6 s recycle delay, 48 scans and 256 t_1 increments with an increment of 12.5 μs (4 rotor periods). Spectra were referenced to 0.1 M boric acid (19.6 ppm, with respect to BF_3Et_2O, δ_{iso} = 0 ppm). All spectra were processed using either TopSpin 3.5b (Bruker), VnmrJ4.2a (Agilent) or SpinWorks 4.2 (K. Marat, UManitoba) software packages. MQMAS spectra were processed using the shearing function as implemented within TopSpin. Exponential line broadening between 10 and 50 Hz was applied to all spectra. ^{11}B MAS NMR spectra were simulated using the STARS[33] software within VnmrJ to determine the quadrupolar coupling constants, isotropic chemical shifts and to deconvolute the $^{[3]}B^{R}$ and $^{[3]}B^{NR}$ chemical environments. The N_4 values were determined by peak integration of the 14.1 T data and corrected following the Massiot et al.[34] method. Correction factors of 0.96 $^{[3]}$B and 1.07 ($^{[4]}$B) were used based on our ^{11}B MAS NMR experimental methods and determined quadrupole coupling parameters by examining the central and satellite transitions of the borate and borophosphate glasses.

3. Results and Discussion

3.1 Boron and Phosphorus Speciation: The local speciation within borates and phosphates can be made up from short- and medium-range structural units.[13,14,35] To highlight these structural changes caused by alkaline-earth network modifiers, the short-range structure is defined by the oxide coordination environment and how that network is made up of either bridging or non-bridging oxygens. Borate short-range units may be $^{[3]}$B in a trigonal planar structure comprised of zero non-bridging oxygens (T^3) to all non-bridging oxygens (T^0). It can also be in the form of $^{[4]}$B units, whereby a negative charge is delocalized over the whole structural unit in a pseudo-tetrahedral chemical environment. Phosphorus atoms are four-coordinate ($^{[4]}$P) quaternary units defined as Q^n units, where n defines the number of bridging oxygens, from three for all bridging oxygens (Q^3, $[O{=}PO_3]^0$) to zero for three non-bridging oxygens (Q^0, $[O{=}PO_3]^{3-}$). Medium-range structural information can also be obtained by careful assessment of NMR line shapes and isotropic chemical shifts, including an ability to identify borate rings ($^{[3]}B^R$) or non-ring ($^{[3]}B^{NR}$) units, and bridging boron-phosphorus neighbours to four-coordinate boron environments, $^{[4]}B^{mP}$, where m denotes the number of bridging phosphate neighbours ranging from zero (all bridging borate neighbours, $^{[4]}B^{0P}$) to four (all bridging phosphate neighbours, $^{[4]}B^{4P}$). Scheme 1 summarizes the structural units discussed here.



Scheme 1: Short- and Medium-Range Structural Units in Borates and Phosphates

3.2 Binary Borates: The K = 0 series of calcium and strontium alkaline-earth borate glasses were first measured with ^{11}B MAS NMR to deduce the fraction of four-coordinate boron (N_4). Figure 1 reveals resolution of two main boron environments at 14.1 T, the higher frequency resonance (5 to 20 ppm) is assigned to $^{[3]}$B with a characteristic quadrupolar coupling constant, C_Q= 2.5 to 2.7 MHz, typically observed in borates.[36,37] The unique lineshape features for $R \leq 0.2$ are associated to $^{[3]}B^R$ and $^{[3]}B^{NR}$ borate units.[38] The ultrahigh-field ^{11}B MAS NMR of the three-coordinate boron provides greater resolution of this region as the contribution to the spectrum from the second-order quadrupole broadening scales inversely with magnetic field strength, providing improved clarity to this region.[38] Figure 1c reveals contributions from two ^{11}B resonances where the $^{[3]}B^R$ and $^{[3]}B^{NR}$ have isotropic chemical shifts of δ_{iso} = 18.0 ± 0.5 and 14.5 ± 0.5, respectively. The lower frequency four-coordinate resonance (5 to −5 ppm) is much narrower due to its higher symmetry pseudo-tetrahedral chemical environment ($C_Q \approx$ 250 to 500 kHz) with evidence of only a single BO_4 species.[12,14,38] Evaluating these spectra, the overall N_4 value with respect to R can be evaluated by peak integration of the 14.1 T data, where differences in the quadrupole coupling constants were corrected following the method described in detail by Massiot et al.[39] As seen in Figure 2 there is an approximately linear relationship for the plot of N_4 vs R both the calcium and strontium borate series, typical behaviour among other borate glasses with cationic modifiers,[14,4042] in which the equation that $N_4 = R$ holds up until R = 0.5 (correlation coefficients of 0.96 and 0.97 for CaB and SrB, respectively). This effect is commonly observed in borates as the $^{[3]}$B will convert to $^{[4]}$B carrying a negative charge to compensate for the excess positive charge introduced through the modifying Ca^{2+} or Sr^{2+} cations. Up to this point, the charge compensation mechanism of the calcium and strontium borate glass has been the formation of BO_4^- units, which balances out the positive cationic alkaline-earth network modifiers. Above an alkaline-earth loading of

about R = 0.5, a negative deviation occurs such that the excess charge from the cationic input is compensated not only by the $^{[4]}$B site, but also by the formation of non-bridging oxygens (NBOs) in the local structure of the glass, in the form of T^2 units, as shown in Scheme 1. The ratio of $^{[4]}$B units and T^2 $^{[3]}$B units can be obtained from a charge balance calculation such that they balance the cationic charge. Using a sample case of R = 0.5 in the strontium borate series, with an N_4 value of 0.44, there is still a fraction of 0.06 excess cationic charge left within the system, which must be balanced, requiring the creation of negatively charged T^2 units with anionic non-bridging oxygens.[14,43] Thus the overall fraction of local units in the structure can be calculated by means of the N_4 value, with 44% being the $^{[4]}$B unit, 6% from the T^2 three-coordinate site, and 50% based on the neutral trigonal T^3 units. Indeed, a careful analysis reveals that increasing the R value further to a value of 0.6 leads to a steeper negative deviation from the linear N_4 relationship, indicating increasing preference towards forming NBOs in the form of T^2 units to charge balance rather than the BO_4^- four coordinate site as the alkaline-earth loading is increased. This driving force in forming T^2 units above R = 0.5 is often attributed to the avoidance of $^{[4]}$B-O-$^{[4]}$B whereby it is energetically unfavorable to have two negatively charged anions bridged by the same oxygen.[42] Both the Ca^{2+} and Sr^{2+} samples exhibit similar behaviour over the whole compositional range as the modifying concentration increases above R=0.5, the N_4 fraction decreases as it begins to depolymerize forming NBOs (< 15%, based on charge balance arguments).

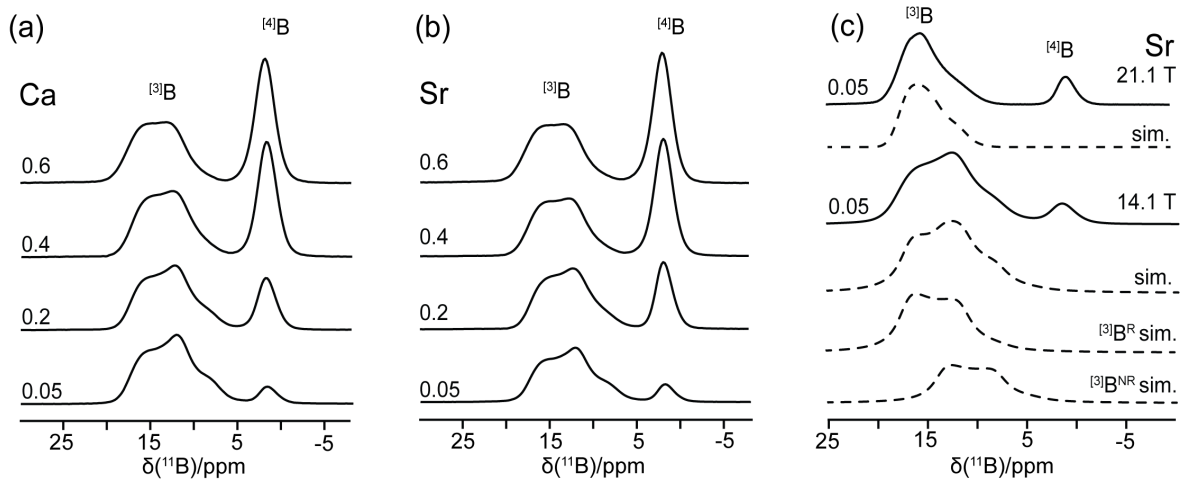


Figure 1: ^{11}B MAS NMR spectra of (a) calcium and (b) strontium borates. (c) Strontium borate, R=0.05 glass revealing the ring and non-ring contributions of the [3]B region at 14.1 and 21.1 T. Simulations are shown as dashed lines.

3.3 Ternary Borophosphates: The calcium and strontium K = 0.4 borophosphate glass series (CaBP and SrBP) were also analyzed using ^{11}B MAS NMR spectroscopy to identify the fraction of four-coordinate boron. Figure 2 compares the borophosphate (K = 0.4) glass series over the same compositional range of Ca and Sr modifier (R = 0.05 to 0.6). As discussed above, both [3]B and [4]B are present, with the N_4 increasing as the Ca or Sr modifier is added. What is unique about the ^{11}B NMR spectra is their remarkable sensitivity to the medium-range glass structure, markedly changing with the addition of network forming P_2O_5 as seen in alkali and alkaline-earth borophosphates.[44] Notably, at higher alkaline-earth loading, the ring contributions in the [3]B region of the borophosphate spectra remain high whereas those for the borates quickly lose this feature above R = 0.2, which is shown in Figure 3. This effect has been observed in other ternary composition glasses such as borosilicates whereby the depolymerization of the silicate units into non-bridging oxygens occurs to some extent, accommodating the excess charge prior to the formation of T^2 borate units.[38]

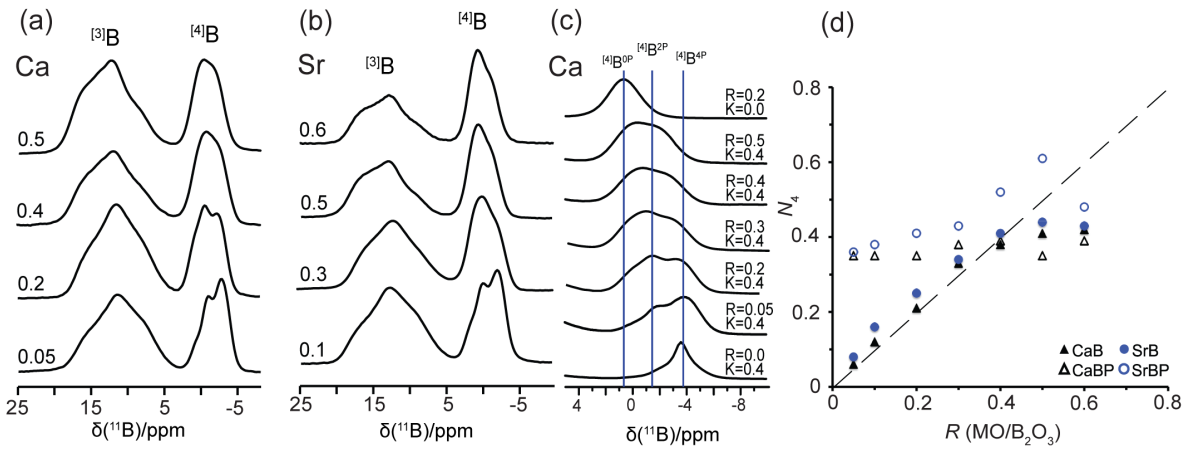


Figure 2: ^{11}B MAS NMR spectra (11.7 T) of (a) calcium borophosphates and (b) strontium borophosphates with *K* = 0.4 and varying *R* values. (c) Ultrahigh-field (21.1 T) spectra comparing the $^{[4]}$B regions of binary calcium borate (*K* = 0) to calcium borophosphates with varying *K* and *R* values. (d) Plot of N_4 *vs R* for all binary and ternary alkaline-earth borates and borophosphate glasses (dashed line is a guide set to 1:1).

There are multiple overlapping $^{[4]}$B resonances for the borophosphate series, representing various degrees of phosphate connectivity in the glass network, in contrast to the single peak observed for the corresponding spectra of the Ca and Sr borate glass series. As seen in Figure 2, the ^{11}B MAS NMR spectra indicate that there are two to three different $^{[4]}$B environments with varying degrees of P neighbours, as seen in other borophosphate glass series.[17] The peaks shift to higher frequency with higher alkaline-earth content, indicating a change in the medium-range structure from $^{[4]}$B rich with P neighbours converting to a $^{[4]}$B with B neighbouring environments. From past borophosphate studies utilizing crystalline models, quantum chemical calculations and dipolar recoupling approaches, the ^{11}B site with $\delta_{iso} \approx 1$ ppm is due to $^{[4]}B^{0P}$ while the peak to lowest frequency ($\delta_{iso} \approx -3.5$ ppm) is due to $^{[4]}B^{4P}$

with each P substitution for a B neighbour shifting the data to higher frequency by ~0.7 ppm.[17,38]

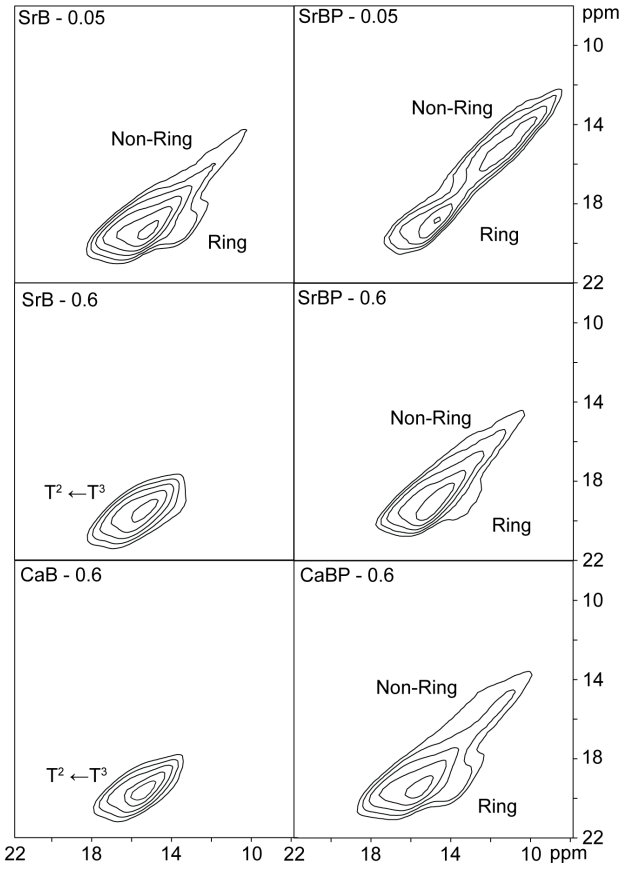


Figure 3: ^{11}B 3QMAS NMR spectra (B_0 = 21.1 T) of the $^{[3]}$B region showing the presence of ring and non-ring contributions for selected calcium or strontium containing borate (K = 0, left hand side) and borophosphate (K = 0.4, right hand side) glasses. Contour base levels were set to 10% of maximum intensity and incremented by a factor of 1.45.

Closer examination of the fraction of four-coordinate boron (Figure 2d) shows a large positive deviation from the $N_4 = R$ relationship as seen in the $K = 0$ series. The glass structure changes markedly with the addition of phosphates to the network, as this gives another avenue by which the cationic alkaline-earth modifiers can be charge compensated. Notably, at lower alkaline-earth loading, a positive deviation from the supposed $N_4 = R$ relationship

suggests drastic medium-order structural changes. As charge compensation requires, this excess of anionic charge coming from the $^{[4]}$B sites can only be balanced by the formation of a positively charged local unit by the phosphate, PO_4^+ (Q^4), as is apparent from the crystalline BPO_4.[17,45,46] X-ray diffraction and NMR spectroscopy of K = 0.4 and R = 0 (data not shown) reveal the presence of amorphous and crystalline BPO_4 analogues, with $\delta_{iso}(^{11}B) = -3.3$ and $\delta_{iso}(^{31}P) = -30$ ppm.[47,48]

^{31}P NMR spectroscopy provides information on the phosphate chemical environment, in particular aiding in the assessment of the depolymerization of chains with alkaline-earth loading. In the ^{31}P MAS NMR spectra for the calcium and strontium borophosphate series shown in Figure 4, there is a remarkable change in the centre-of-gravity shift (δ_{cgs}) of the ^{31}P MAS NMR resonance indicating a breakdown of the bridging oxygens within the phosphate linkages. Previous ^{31}P NMR studies of phosphate glasses and crystals have shown that the isotropic chemical shift generally trends to increase as quaternary phosphate units depolymerize from bridging oxygens (Q^3) to orthophosphate, non-bridging units (Q^0).[49] As seen from the ^{31}P NMR spectra of the higher R-value glasses (Figure 4), there is almost no overlap of the peak from the Q^3 region (−30 ppm), and in fact Ca and Sr strongly favour Q^2 and/or Q^1 units. The N_4 values also agree with this, as between an R value of 0.5 and 0.6, there is a crossover from positive deviation about the linear relationship $N_4 = R$ to a negative one. This result indicates a change in the charge balancing behaviour in these glasses whereby the positive cationic charge is being compensated by delocalized negatively charge $^{[4]}$B units and localized negatively charged NBOs located on Q^2 and Q^1 phosphate units.

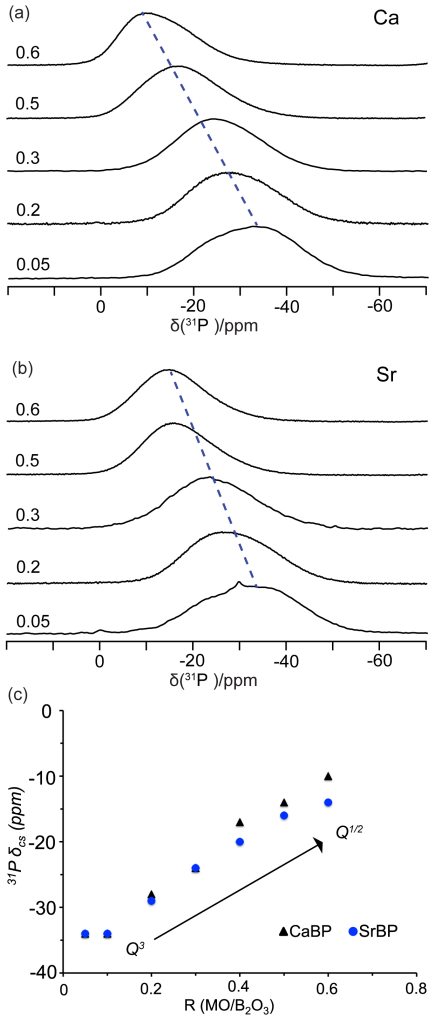


Figure 4: ^{31}P MAS NMR spectra (B_0 = 14.1 T) of Ca (a) and Sr (b) borophosphate glasses K = 0.4) with varying *R* values. Change in the peak maxima of the chemical shift (ppm) as a function of calcium and strontium network modifiers. The dashed lines are a guide for the eye, highlighting the shift in the centre of gravity. The *R* = 0.05 SrBP glass has a small crystalline impurity <2% (30 ppm).

Examination of the δ_{cgs}(^{31}P) values for the strontium-containing K = 0.4 series (Figure 4) shows an increase in chemical shift, indicating the conversion of fully bridging Q^3 (−30 to −50 ppm) units to depolymerized Q^2 (~−20 ppm) units with a single non-bridging oxygen. Combining these observations with the ^{11}B MAS NMR results, there are clear B-O-P units present with the $^{[4]}$B environments, indicating that the neighbouring P species are Q^2 linkages on the borate pseudo-tetrahedra. The calcium borophosphate glasses show similar behaviour

where the formation of non-bridging oxygens occur as Ca loading increases; however the fraction of four-coordinate boron does not change as drastically over the compositional series, while the ^{31}P NMR peaks shift quickly to the Q^1 (~ -10 ppm) region (Figure 4). Although, other explanations are not excluded, we propose that this observation indicates that the Ca^{2+} cations prefer a phosphate chemical environment, thus preferentially interact with the phosphate rather than the borate units, whereas Sr^{2+} does not appear to exhibit this preference as strongly, maintaining higher N_4 values over the same composition range (Figure 2d). This behaviour may be related to the preferential stabilization of charge by NBOs rather than the shared negative charge from $^{[4]}$B, similar to the behaviour of binary borate glasses.[14,21] Other possibilities include that the glass-forming ability improves with Sr, although crystalline features in CaBP were not observed in the XRD analysis. The cation field strength (Sr: 0.29 *vs.* Ca: 0.36) may be important in directing the physical properties within glassy materials, however understanding the property-structure relationship and the impact that field strength may have on direct atomic-level structure (e.g., coordination number, connectivity, etc.) is beyond the scope of the current work, requiring carefully executed systematic studies.[50] What is clear from this data is that Ca prefers NBO environments isolated on PO_4 units over the delocalized negative charge on $^{[4]}$B or localized negative charges found on T^1 or T^2 units. The ^{11}B 3QMAS NMR spectra clearly indicate the presence of borate ring structures even at R = 0.6 Ca or Sr loadings (Figure 3). These findings suggest that the $^{[3]}$B site medium-range structure has a significant amount of ring component within these high R alkaline-earth borophosphate glasses, while the $Q^{1/2}$ phosphate species interact with the tetrahedral borate units to some extent due to the presence of $^{[4]}B^{2P}$ and $^{[4]}B^{1P}$ spectral signatures, *vide supra*.

4. Conclusion

We have focused on the role of alkaline-earth modifiers and their structural implications on a series of binary borate and ternary borophosphate glasses, with emphasis on short- and medium-range structure. The binary calcium and strontium borate series behave similarly to other borate glasses with cationic loading, with a preference for forming T^2 units at alkaline-earth loadings of more than R = 0.5. The aim of this study was to determine the structural differences associated with the use of calcium and strontium oxide modifiers in borophosphate glasses. The calcium cation clearly prefers a phosphate environment for charge compensation, as the N_4 value is markedly lower than that of strontium. This observation is also seen in the stark contrast in the peak positions seen in the ^{31}P MAS NMR spectra, as the changes in δ_{cgs} with each R-value is seen to be much higher, with a resonance within the Q^1 region for the calcium borophosphate glass R = 0.6 than for the strontium series. This behaviour may be related to the preferential stabilization of charge by NBOs rather than the shared negative charge from $^{[4]}$B. The presence of two very distinct medium-range structural units at two primary alkaline-earth loading environments indicates a complexity among the glass forming network that goes beyond the scope of the first coordination sphere. It is apparent that any potential application of borophosphate glasses should be crucially linked to a careful selection of the composition of the glass; a combination of ^{11}B and ^{31}P MAS NMR spectroscopy provides a clear insight into the structure and thus will continue to play a critical role in the advancement of these materials.

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