Alkali borophosphate glasses are of interest for their uses as biomaterials, ionic conductors and optical materials. The intermixing of borate and phosphate glass networks improves chemical durability while maintaining low processing temperatures. A significant body of research has focused on structure and properties in lithium and sodium phosphate glasses with low levels of added boron. We turn our attention to the borate-rich compositional regime, where properties such as dissolution and ionic conductivity are expected to be quite different. We are also interested in the network-modifying behaviour of the less-studied heavier alkali cations (K, Rb and Cs), which appear to have a different structural role than Li and Na.

Figure 1 shows the $^{11}$B MAS NMR spectra of three low-alkali cesium borophosphate glasses. The remarkable resolution afforded by high field permits clear separation between neutral three-coordinate ($\text{BO}_3$, ca. 15 ppm) and anionic four-coordinate ($\text{BO}_4^-$, ca. 0 ppm) boron species, and allows a correspondingly straightforward quantification of their ratio. Figure 2 shows the total fraction of $\text{BO}_4^-$ as a function of alkali content, indicating that there must be two charge-balancing mechanisms: alkali cations and positively charged phosphate units. While the latter species are seldom found in pure phosphate glasses, they are known to form in strict alternation with anionic $\text{BO}_4^-$ to result in the crystalline phase, $\text{BPO}_4$. 

**Figure 1**: $^{11}$B MAS NMR spectra collected at 21.1 T of cesium borophosphate glasses, where $\text{P}_2\text{O}_5/\text{B}_2\text{O}_3 = 0.2$ and $\text{Cs}_2\text{O}/\text{B}_2\text{O}_3 = 0.05$ (a), 0.1 (b), 0.2 (c).
The use of ultrahigh-field NMR reduces peak overlap between the three-coordinate boron in rings and those not in rings, revealing ratio at low alkali content similar to that of pure B₂O₃. Furthermore, three distinct types of four-coordinate boron are observed in the high-field ¹¹B MAS NMR spectra, suggesting that connectivity to neighbouring phosphate network-formers can be determined from their intensities. Quantum chemical calculations and ¹¹B{³¹P} double-resonance NMR experiments confirm that these peaks are distinguished by the number of phosphate neighbours, with greater phosphate connectivity shifting the peaks to more negative frequencies. With the help of charge-balance calculations, we find that only clustering into non-crystalline BPO₄-like regions can account for these observations.

These results provide a picture of low-alkali borophosphate glasses in which phosphorus is preferentially bound to anionic borate units, leaving an undermodified phosphate-poor borate phase. This work helps define the homogeneous glass-forming region of alkali borophosphates and provides valuable information on the suitability of such materials for practical applications.

References
