Supplementary material for

Zinc borate glasses: properties, structure and modelling of the composition-dependence of borate speciation

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Figure S1. X-ray diffraction patterns for upper and lower ZnO limits of $xZnO-(1-x)B_2O_3$ glasses capable of being prepared in large sample sizes and cooled slowly without crystallizing.



Figure S2. Infrared absorption coefficient spectrum measured from splat quenched x=0.50 zinc borate glass. The vertical lines denote characteristic infrared activity of boric acid. The larger spot size of the infrared beam, relative to Raman measurements discussed in the main text, probes a larger sample area thus capturing both components of the phase separated sample.



Figure S3. DSC scans for binary zinc borate glasses. The glass transition temperature trend is represented by the dotted line while the trend in the onset temperature of crystallization is depicted by the dashed line.



Figure S4. ¹¹B MAS NMR spectra of binary zinc borates taken at 16.4 T on splat quenched glass samples.



Figure S5. ¹¹B MAS NMR spectra of binary zinc borates taken at 16.4 T on annealed glass samples.



Figure S6. ¹¹B MAS NMR spectra of annealed 0.54ZnO- $0.46B_2O_3$ glass measured at 11.7 T and fitted using results from higher field (16.4 T). The fit here gives 24.4% B₃^S, 48.2% B₃^{AS}, and 27.4% B₄.



Figure S7. ¹¹B MAS NMR spectra of 0.54ZnO-0.46B₂O₃ glass measured at 16.4 T for splat quenched (solid black) and annealed (dashed red) glasses.



Figure S8. ¹¹B 3QMAS NMR measurement of splat quenched 0.63ZnO- $0.37B_2O_3$ glass measured at 16.4 T, showing only the spectral region for BO₃. It is difficult to see any distinction in the MAS lineshape (i.e. quadrupolar coupling asymmetry parameter, η) for the different BO₃ signals identified in the isotropic project (curve plotted to the left).