

NMR Methods for Study of Waste Glasses.

Kristian E. Barnsley^a, Prashant Rajbhandari^b, Neil C. Hyatt^b and John V. Hanna^a
 University of Warwick ^a and University of Sheffield ^b



Project Outline and Motives

An NMR based investigation into structure and speciation in borosilicate glass-ceramic waste forms has been undertaken. This is part of a wider project in collaboration with a research group at The University of Sheffield as well as other institutions in the USA. This is motivated by the discovery of considerably higher waste loading rates being obtainable if these glass-ceramic phases are targeted (45 mass% as opposed to 18 mass%)^[1].

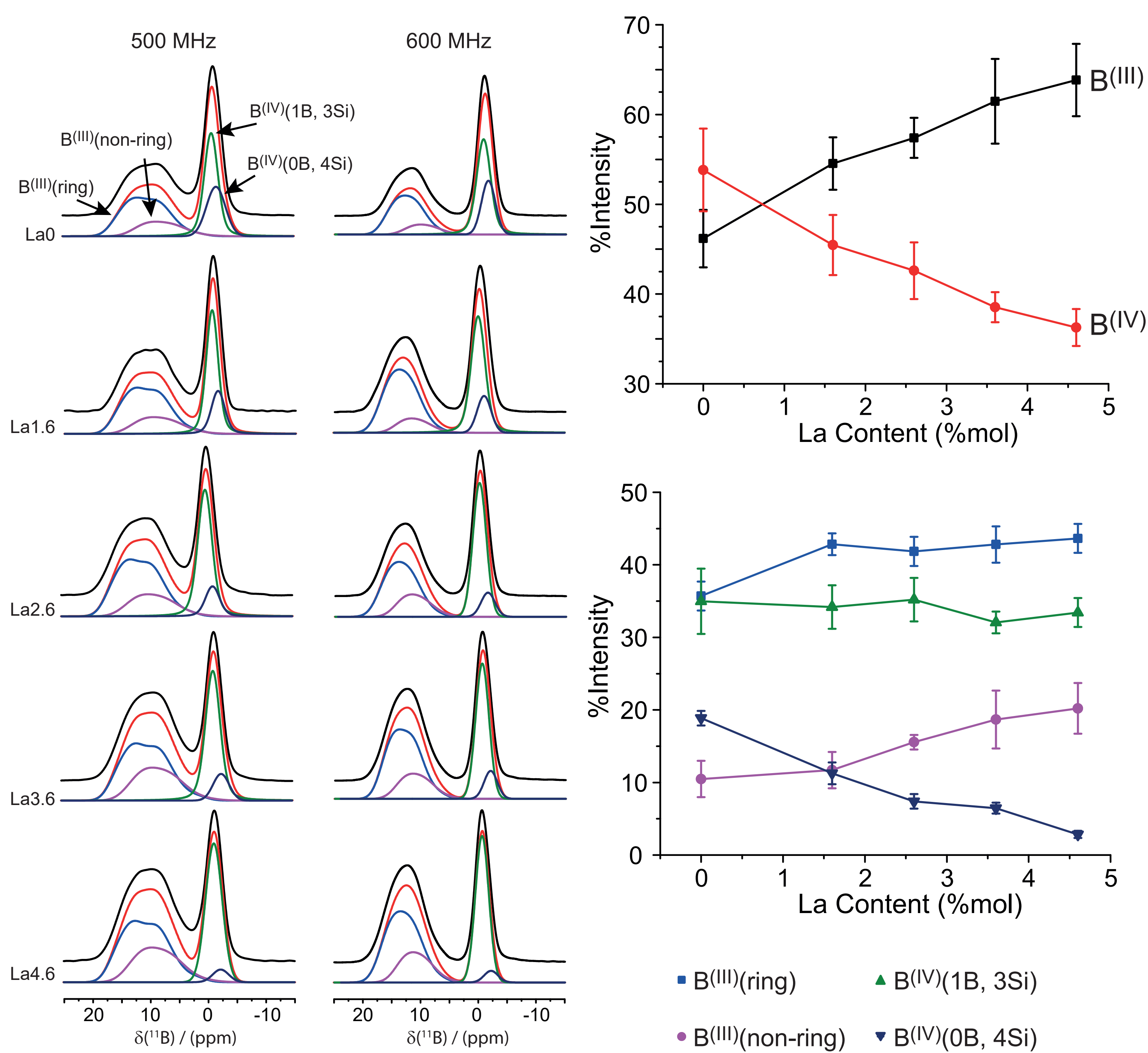
This poster explores the NMR techniques used in this investigation. What information can be gained and how the nature of the waste glass form can present experimental challenges, compared to simpler 'model' glasses.

High-Field ¹¹B MAS NMR

¹¹B MAS NMR spectra were recorded at multiple fields for all of the samples at 12 kHz MAS. The spectra from the Lanthanum series are presented below, with the experimental data in black and simulated data in red. The trends in relative intensities are also presented below.

The spectra were simulated using QuadFit, accounting for the expected disorder of the glass network. The BO^(III) and BO^(IV) peaks were both fitted to two sites. For the BO^(IV) peak this was justified by two clear separate sites in the 2D MQMAS. For the BO^(III) peak there was not sufficient resolution to distinguish between sites, however a combination of literature and the inability to fit it to one peak suggested there were also two sites of BO^(III).^[2]

The multiple field study was used to constrain the ¹¹B NMR parameters.



Trends in ¹¹B NMR Parameters

Interesting changes in the relative intensities of the line shapes are seen as the Lanthanum content is increased, as can be seen from the above two plots.

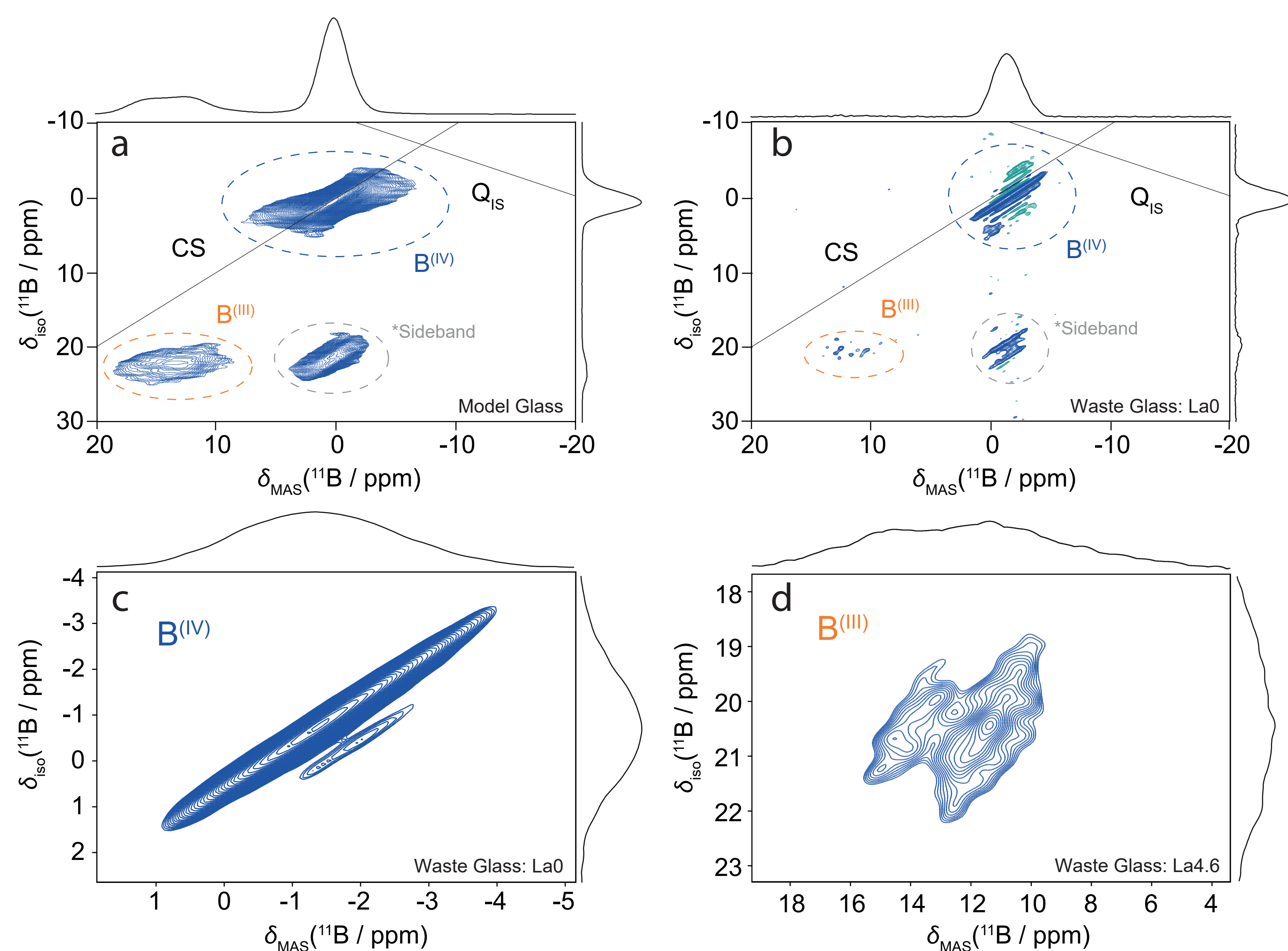
A clear shift from tetrahedral orientation (BO^(IV)) to trigonal planar orientation (BO^(III)) can be seen as Lanthanum content increases. Taking a closer look shows that it is the BO^(IV)(0B, 4Si) species that is being lost. The intensity (and therefore population) first appears to move to the BO^(III)(ring) species up until a Lanthanum content of 1.6 before then levelling off and moving into the non-ring species.

Sample/mol%	SiO ₂	CaO	Na ₂ O	B ₂ O ₃	Al ₂ O ₃	La ₂ O ₃	ZrO ₂
La ₀	52.01	17.14	12.92	11.51	3.14	0.00	3.25
La _{1.6}	51.15	16.86	12.71	11.32	3.09	1.64	3.09
La _{2.6}	50.62	16.68	12.58	11.20	3.05	2.68	3.16
La _{3.6}	50.09	16.51	12.45	11.08	3.02	3.68	3.13
La _{4.6}	49.57	16.34	12.32	10.97	3.00	4.68	3.10

Samples Investigated

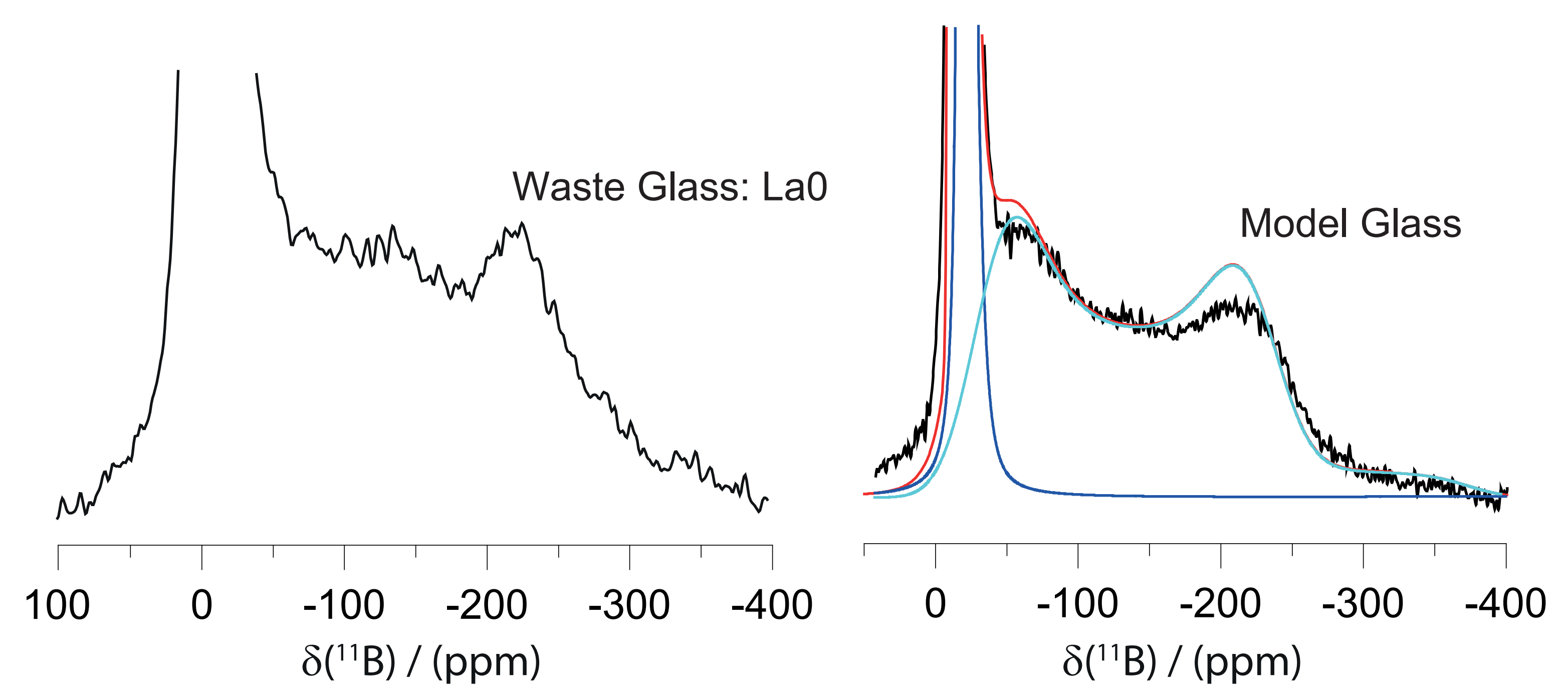
The waste glasses used in this investigation are from a series of samples constructed to investigate the effects of introducing rare-earth elements into the glass network. This poster features spectra from a subset investigating Lanthanum, compositions of which can be found in the table to the bottom left.

The 'model' glass that they are being compared to is a pure borosilicate glass, synthesised with the aim of understanding fundamental behaviours rather than real world applications.



¹¹B MQMAS

For additional information and insight into the different sites within the two orientations, ¹¹B MQMAS spectra were recorded on a 14.1 T spectrometer under 12 kHz MAS, presented above. Here a comparison is drawn between the waste glasses and the model glasses. It is found that it is much harder to achieve sufficient signal and resolution in the B^(III) region of the waste glasses (figure b) than in the model glass (figure a). The B^(IV) region of figure a has been replotted in figure c to clearly show the two separate sites. In an effort to improve resolution in the B^(III) region, the experiment was re-optimised and a sample with higher B^(III) content was used, the results of this are shown in figure d.



Low-Field ¹¹B MAS NMR

¹¹B MAS NMR spectra were also recorded on a 2.4 T spectrometer under 18 kHz MAS, presented above. This was done since lowering the external field strength increases the relative broadening due to the quadrupolar interaction present at the B^(III) sites.

Normally NMR spectroscopists go to great lengths to narrow their lines to allow for better resolution between signals. But in this case, by allowing the lineshapes to broaden out sufficiently, the different quadrupolar lines become easier to distinguish between than at high-field! This is a technique that has been used to great success on model glasses at The University of Warwick. It is now being applied to waste glasses with moderate success, as can be seen above, the two B^(III) begin to become distinguishable. This method also suffers from the same issue as the MQMAS of lacking signal in the B^(III) region, hence the zoomed y-axis, cutting the B^(IV) peak.

[1] Crum, Jarrod V., et al. "Multi-Phase Glass-Ceramics as a Waste Form for Combined Fission Products: Alkalies, Alkaline Earths, Lanthanides, and Transition Metals." Journal of the American Ceramic Society 95.4 (2012): 1297-1303.

[2] Soleilhavoup, Anne, et al. "Contribution of first-principles calculations to multinuclear NMR analysis of borosilicate glasses." Magnetic Resonance in Chemistry 48.S1 (2010): S159-S170.