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# $^{11}B$–$^{11}B$ Two-dimensional Correlation Nuclear Magnetic Resonance on Sodium Borosilicate Glass

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To study microstructure of $Na_2O$–$B_2O_3$–$SiO_2$–$Al_2O_3$ glass, which is a starting material for preparing porous glass, $^{11}B$ one-dimensional (1D) magic-angle spinning (MAS) spectra and results of two-dimensional (2D) $^{11}B$–$^{11}B$ homonuclear correlation experiment under MAS are examined at 21.8 T. We conclude that two of the four peaks observed for $^{11}B$ are assigned to borate rings, which we assign as the main components in the boron-rich phase to be removed by acid leaching.

With acid leaching of boron-rich phases in phase-separated sodium borosilicate glass, porous glass, which finds widespread application in industry,[1] can be obtained. Phase separation is controlled by heat treatment as well as the composition of starting materials and kinds of dopants. Structural determination of phase-separated glass is important for investigation of these factors affecting phase-separated processes. So far, considerable solid-state $^{11}B$ NMR work has been done on alkali borosilicate glasses.[2] Recently, with high resolution achieved by using magic-angle spinning (MAS) and application of two-dimensional (2D) NMR techniques such as MQMAS,[3,4] it has been shown that a $^{11}B$ MAS spectrum of sodium borosilicate glass consists generally of four or five peaks,[5–7] two peaks with appreciable second-order quadrupolar broadening are attributed to trigonal boron species and the other two or three without significant quadrupolar broadening are ascribed to tetragonal borons. Further, one of the two trigonal boron sites has been attributed to boron in boroxol rings (hereafter, B[3,ring]) and the other one to boron in nonring sites (B[3,nonring]). For the tetragonal boron sites, Du and Stebbins assigned them to tetragonal borons with four Si as its next neighbors (B[4,4Si]), with three Si and one B (B[4,3Si,1B]), and with two Si and two B (B[4,2Si,2B]).[7]

In contrast to these boron species suggested so far by solid-state NMR, the existence of borate rings (triborate, tetraborate,...) in alkali borate glasses especially for glasses with high sodium content has long been postulated.[8,9] In fact, borate rings in phase-separated sodium borosilicate glass were suggested by examining Raman spectra.[10] By combining $^{11}B$ MAS and MQMAS and $^{17}O$ MQMAS results, Du and Stebbins suggested that B[4] and B[3,nonring] tend to mix with silicate units, while B[3,ring] is mainly connected to borate groups.[11,12] A borate ring contains tetragonal boron with two or more trigonal borons as its nearest neighbor; however, such tetragonal boron in a borate ring has not been assigned in a $^{11}B$ MAS spectrum of sodium borosilicate glass. In this work, we investigate $^{11}B$ MAS NMR spectra of sodium borosilicate glass at high magnetic fields of 11.7 and 21.8 T in order to reduce the second-order quadrupolar broadening. To examine $^{11}B$–$^{11}B$ connectivity, we measure $^{11}B$–$^{11}B$ spin diffusion by using the conventional three pulse sequence[13] for two-dimensional (2D) homonuclear exchange NMR, which we have applied recently to study mesoporous BCN[14] and boron-doped diamond.[15]

One of the two glass samples (hereafter, Sample-1) examined is a heat-treated glass sample with the composition of $7.4Na_2O$–$24.9B_2O_3$–$66.3SiO_2$–$1.3Al_2O_3$ (mol %). Appropriate amounts of starting materials were mixed and melted at 1480 °C for 8 h. The glass was quenched by pouring the melt on a brass plate. The obtained glass was heat-treated at 540 °C for 43 h. The other sample (Sample-2) was purchased from Iwaki Glass, Japan. The composition of Sample-2 is $4.0Na_2O$–$12.7B_2O_3$–$80.9SiO_2$–$2.3Al_2O_3$ (mol %) and used as received without further heat treatment.

$^{11}B$ MAS NMR spectra were recorded at 21.8 T on a JEOL ECA 930 spectrometer with a JEOL 4 mm MAS probe and at 11.7 T on a JEOL ECA 500 spectrometer with a Chemagnetics 3.2 mm MAS probe. The $^{11}B$ resonant frequency at 21.8 and 11.7 T were 298.2 and 160.5 MHz, respectively. The MAS frequency was 15–22 kHz in each experiment. The $^{11}B$ chemical shift is referenced to $BF_3 \cdot (C_2H_5)_2O$ at 0 ppm. All one-dimensional (1D) spectra were observed by using a single 30° pulse. The rf strength at 21.8 T was ca. 132 kHz and at 11.7 T ca.139 kHz.

The $^{11}B$ 2D exchange NMR experiment was done using the conventional three $\pi/2$-pulse sequence.[13] Since the apparent flip angle of a rf pulse depends on the quadrupolar coupling constant,[16] it is difficult to find a common $\pi/2$-pulse length for each peak of the samples. In this work, a pulse width of 1.2 μs was used, which corresponds to a flip angle of $\pi/2$ for the peaks of trigonal boron and ca. $\pi/2.7$ for the peaks of tetragonal boron.

Figures 1a and 1b show $^{11}B$ MAS NMR spectra of (a) Sample-1 and (b) Sample-2 measured at 11.7 T. The spectra are a sum of characteristic $^{11}B$ MAS second-order quadrupolar lineshapes. Clearly these spectra reflect differences between the two samples. However, the severe signal overlapping makes it difficult to examine, for example, the chemical shift and the quadrupolar couplings of the boron signals included. On the other hand, $^{11}B$ MAS spectra taken at 21.8 T show improved resolution due to reduction of the second-order broadening. Four signal components (peak-a to peak-d as indicated in the figure) are appreciable. According to previous studies, the peak-a to -d are assigned to B[4,4Si], B[4,3Si,1B], B[3,nonring], and B[3,ring], respectively. At 21.8 T, the spectral differences between Sample-1 (Figure 1c) and that of Sample-2 (Figure 1d) are apparent; namely, the intensities of the peak-a (B[4,4Si]) and the peak-c (B[3,nonring]) are significantly smaller in Sample-1. This clearly indicates the usefulness of NMR at high-magnetic field in the characterization of sodium borosilicate glass.

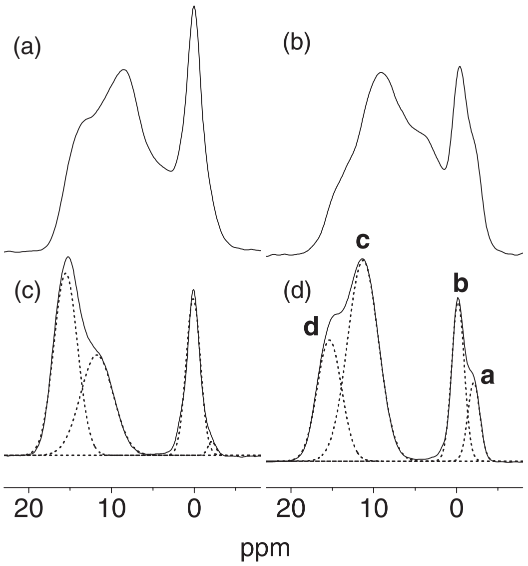

**Figure 1.** $^{11}$B MAS NMR spectra of Sample-1 (a and c), and Sample-2 (b and d). (a) and (b) were observed at 11.7 T. (c) and (d) were observed at 21.8 T (b). The dotted lines in (c) and (d) are four Gaussian lineshapes used to fit the observed $^{11}$B MAS spectra at 21.8 T.

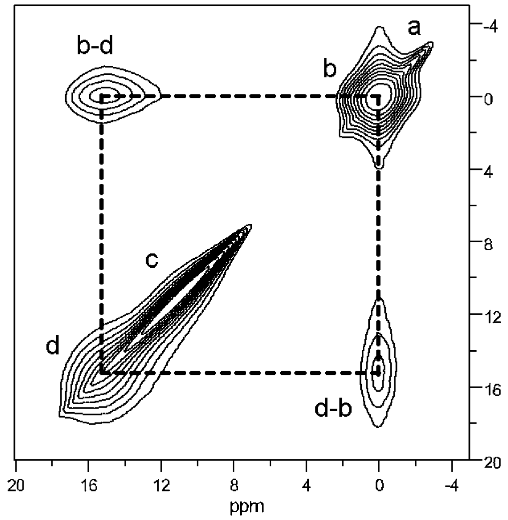

**Figure 2.** $^{11}$B–$^{11}$B 2D homonuclear correlation spectrum of Sample-1 observed at 21.8 T with the mixing time of 2 s.

Figure 2 shows $^{11}$B–$^{11}$B 2D exchange spectrum of Sample-1 at a mixing time of 2 s and MAS spinning speed of 15 kHz. The spectrum exhibits strong cross peaks between peak-b and peak-d, indicating that these borons are in close proximity. Hence, the nearest neighbor boron of B[4,3Si,1B] is B[3,ring] and not B[3,nonring]. Further, the observed cross peak between a trigonal boron and a tetragonal boron is indeed consistent with the borate structures. Hence, the peak-b also contains the signal of tetragonal boron in the borate rings, and the peak-d contains the trigonal boron in the borate rings. To conclude, the peak-a to -d are assigned as follows: peak-a is B[4,4Si], peak-b is B[4,3Si,1B] and the tetragonal boron in a borate ring, peak-c is B[3,nonring], and peak-d is B[3,ring] and the trigonal boron in a borate ring.

The 2D spectrum shows that no cross peaks are observed for peak-a, indicating that B[4,4Si] is isolated from other borons. Further, while the diagonal signals of peak-b and peak-d are roundish due to exchange among these borons, that of peak-c also bears a roundish component, indicating exchange among nearby B[3,nonring] with different local structures. This suggests a domain consists of B[3,nonring]. In Sample-2, the relative ratio of peak-a (B[4,4Si]) is larger than that in Sample-1. This is consistent with the large Si ratio in Sample-2. In the phase-separated Sample-1, the intensity of peak-d is larger than that of peak-c, while peak-c is larger than peak-d in Sample-2. This indicates that B[3,nonring] (peak-c) changes to B[3,ring] (peak-d) by heat treatment.[11,12] Close examination of the spectra shows the relative ratio of peak-b in Sample-1 is larger than that in Sample-2. The above assignments of $^{11}$B signals are prerequisite for investigation of phase-separation process by $^{11}$B NMR, for example, formation of borate rings as well as boroxol rings caused by intrusion of Na ion in the B[3,nonring] domain can be examined by comparing these $^{11}$B signals among various heat-treated samples. Detailed studies on the phase separation are under way and will be published elsewhere.

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