Structural Analysis of Boron Carbide Using 2D ^{11}B-MQMAS NMR

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2D ^{11}B-multiple quantum magic angle spinning NMR spectra of boron carbide were measured in order to eliminate the second-order quadrupole interaction of ^{11}B in B_4C. Judging from the line width of MQMAS spectrum, not only the second-order quadrupole interaction but also the B-B dipole-dipole interaction was found to cause the line broadening of B_4C in ^{11}B-MAS NMR. They affect the line width in the ratio about 1.3 : 1 at spinning rate of 17 kHz.

The crystal structure of boron carbide (B_4C) shows rhombohedral unit cell and consists of the icosahedral unit of boron atoms (B_{12}) and the linear chain of three carbon atoms (Figure 1).[1,2] Boron atoms are situated in two different sites; bonded to carbon atom ($6h_1$) and bonded to neighboring boron atom ($6h_2$). The ratio $6h_1 : 6h_2$ is 1 : 1.

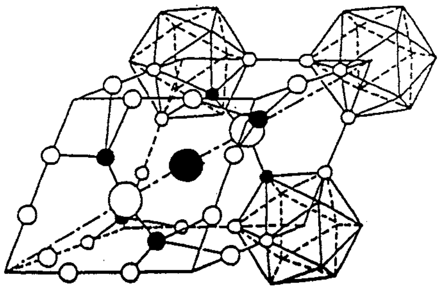

Figure 1. Crystal structure of boron carbide. ●: Boron-$6h_1$, ○: Boron-$6h_2$, ●: Carbon-1b, ○: Carbon-2c.

The ^{11}B-NMR spectra of B_4C have been measured and assigned by several groups.[3-7] Judging from its ideal crystal structure, boron atoms have two nonequivalent sites, $6h_1$ and $6h_2$. However, some groups suggest the presence of B substituted for the center of C-C-C chain site, ($B_{11}C$)(CBC) model by ^{11}B and ^{13}C-NMR. And quadrupole coupling constants, $Cq = e^2qQ/h$, of icosahedral B and B in the C-B-C chain were reported by ^{11}B-static NMR.[3-5,7]

In the NMR measurement of quadrupole nuclei, it is known that peak position generally shifts from essential value. Moreover the peak become asymmetric and broad because of the second-order quadrupole interaction.

It has been proposed that two-dimensional multiple quantum NMR with magic angle spinning (2D MQMAS NMR) is possible to remove the second-order quadrupole broadening of the central transition $\langle m/2, -m/2 \rangle$ of half integer nuclear spins.[8]

We aim to eliminate the second-order quadrupole interaction of ^{11}B in B_4C using MQMAS NMR and extract the essential ^{11}B spectrum.

B_4C was purchased from DENKI KAGAKU KOGYOU KABUSIKI KAISHA. The ^{11}B-NMR spectra were performed at 96.423 MHz on a Chemagnetics CMX-300 NMR spectrometer. The ^{11}B-NMR spectra were measured using MAS and MQMAS methods. MAS spectra were measured with 4 mm probe. A single pulse sequence was used in MAS method. The measurement of spin-lattice relaxation time (= 0.4 s) of ^{11}B in B_4C was carried out using the saturation recovery method. MQMAS spectrum was measured with simple two-pulse sequence and hypercomplex method given in Massiot et al.[9] to obtain pure absorption mode two-dimensional spectrum. π Pulse length (2.2 μs) was used in the first and second pulse lengths. The 2D spectrum was obtained after the shearing transformation. All ^{11}B-NMR spectra were referenced to H_3BO_3 solution, 18.8 ppm.

Figure 2 shows the ^{11}B-MAS spectra at spinning rate of 6 kHz and 17 kHz. The main peak was appeared at – 6.8 ppm with wide-range spinning sidebands. This peak is assigned to the icosahedral B ($6h_1$ and $6h_2$), which is consistent with earlier works.[7] The peak is almost symmetrical, two boron sites are not distinguished in the main peak.

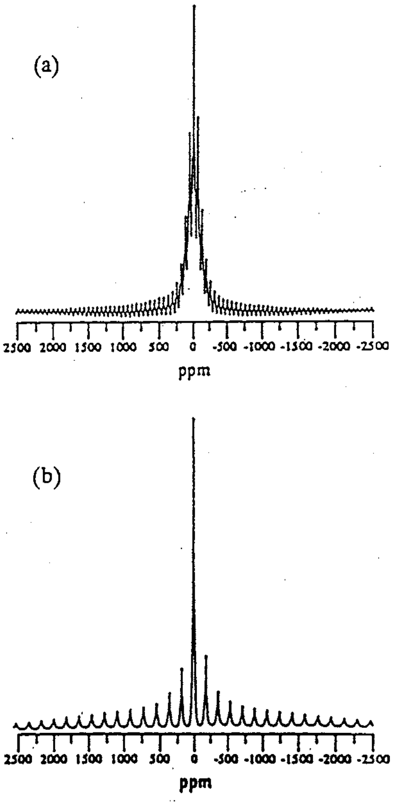

Figure 2. ^{11}B-MAS spectrum of B_4C. (a) spinning rate: 6 kHz, (b) spinning rate: 17 kHz. pulse delay time: 2 s, acquisition number: 16.

The peaks at 85 and 130 ppm which were assigned to boron atoms substituted for carbon atoms in the C-C-C chain site, were appeared in ^{11}B-MAS spectra besides the large peak near 0 ppm by Kirkpatrick et al..[6] Instead of these peaks, other peaks were observed at 37 and – 60 ppm which are assumed to correspond to CB$\underline{B}$, BBB chain as well as 4B cluster in Harazono's work.[7] No peak corresponding to C-B-C was observed in our spectrum. Even if boron atoms replaced by carbon atoms in the C-C-C chain exist, they are thought to be few and buried under spinning sidebands.

The faster the spinning rate, the weaker the intensity of spinning sidebands is, because of the decrease of the chemical shift anisotropy. The full width at half maximum (FWHM), however, hardly changed between 6 kHz and 17 kHz.

The resonance in the isotropic projection in ^{11}B-MQMAS NMR spectrum showed in – 2.8 ppm (Figure 3). Only one cross peak of 2D MQMAS spectrum was observed. The projection of 2D spectrum along the isotropic axis is almost symmetrical and similar to the triple quantum filtered single quantum MAS cross-section. So the isotropic chemical shifts of two nonequivalent sites of 6h$_1$ and 6h$_2$ in boron atoms are practically same. Therefore, those boron atoms are found to situate in the nearly same environment electronically.

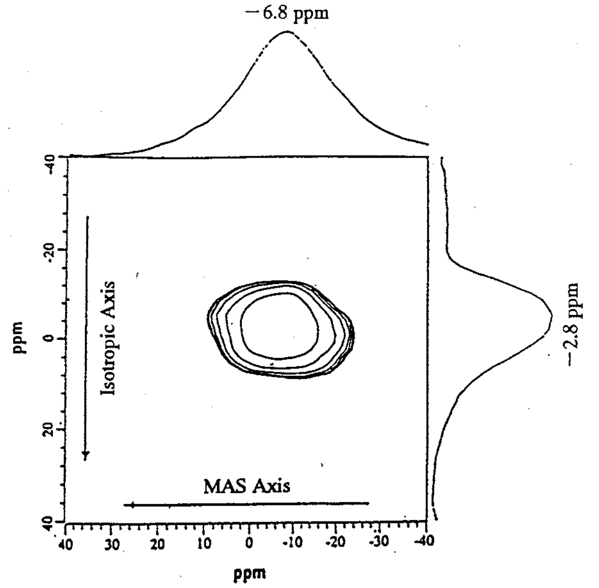

Figure 3. 2D ^{11}B-MQMAS (triple quantum-single quantum) spectrum of B$_4$C. spinning rate: 17 kHz, pulse delay time: 2 s, acquisition number: 60, t_1 increment: 58.8 μs, data point: 32×64 ($t_1 \times t_2$).

Next, the isotropic chemical shift, $\Delta\sigma$, and the quadrupole coupling constant, C_q, were given by Eqs 1 and 2 for the spin I=3/2, respectively.

$$\Delta\sigma = (8/27)\,\omega_{iso} + (10/27)\,\omega_G \qquad (1)$$

where ω_{iso} is the position of the resonances (in ppm) in the isotropic projection, ω_G is the weighted average of single quantum frequency (in ppm).

$$\omega_{iso} = (17/8)\,\Delta\sigma + (10^6/8)(\omega^2_Q/\omega^2_0)((\eta^2/3)+1) \qquad (2)$$

where $\omega_Q = 2\pi\nu_Q = 6\pi C_q/2I(2I-1)$, ω_0 is the Zeeman frequency, η is the asymmetry parameter.[9]

In Eq. 2, η was regarded as zero according to the previous paper.[3] $\Delta\sigma$ was found to be –3.4 ppm, and C_q was 1.1 MHz. It was reported that C_q of the icosahedral B was (0.2–1.3) MHz[3], (0–1.06) MHz[4] using ^{11}B-cw NMR and (<0.69–1.20) MHz[5] by solid echo method. Our value of C_q is good agreement with these data.

The line width of the projection along the isotropic axis became narrow compared to the triple quantum filtered single quantum MAS cross-section because of the elimination of the second-order quadrupole interaction.

Several groups[3,6,7] studied the cause of the line broadening. Silver et al. concluded that the quadrupole interaction was the dominant perturbation by ^{11}B-cw NMR.[3] On the other hand, Harazono et al. concluded that the line broadening of ^{11}B-static spectrum is not the second-order quadrupole interaction but the B-B dipole-dipole interaction.[7] The cause of line broadening of ^{11}B are thought to be the chemical shift anisotropy, the dipole-dipole interaction and the quadrupole interaction. The range of chemical shift of ^{11}B is about 200 ppm (= 19.2 kHz), which is negligibly small compared to the C_q = 1.1 MHz. So there is hardly the contribution of chemical shift anisotropy to line broadening. The FWHM of the isotropic chemical shift is 1035 Hz considering scaling factor (Table 1). Since the FWHM of the projection along the MAS Axis is 2400 Hz, the dipole-dipole interaction and the second-order quadrupole interaction affect the line width of ^{11}B-MAS spectrum in B$_4$C, in the ratio about 1 : 1.3 respectively at spinning rate of 17 kHz. It is necessary to spin the sample faster than now in order to cancel the line broadening caused by the B-B large dipole-dipole interaction of icosahedral boron atoms.[6]

Table 1. Comparison of the FWHM between the projection along the isotropic axis and that along MAS axis.

	FWHM / Hz
MAS shift	2400
Isotropic shift	2200 (with scaling factor)[a] ↓ 1035 (considering scaling factor)

[a] The position of the resonances in the isotropic projection of MQMAS spectrum contain the scaling factor of 17/8 (see Eq. 2 in the text).

References and Notes

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