Magic-angle-spinning NMR at 30 T with a Hybrid Magnet

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Solid-state NMR measurements at 30 T have been performed with a hybrid magnet of National Institute for Materials Science. Spectral resolution less than 3 ppm was confirmed by ^{79}Br magic-angle-spinning (MAS) NMR measurements of a reference material KBr. A small sample and an aluminum metal shield were used to reduce the effects of field inhomogeneity and fluctuation. As an example of application for an industrial material, ^{27}Al MAS NMR of a refractory mortar was demonstrated.

NMR plays important roles in analytical chemistry. NMR spectrum gives information of local field at nucleus used as a probe. This feature enables us to investigate a material from a microscopic point of view. In general, NMR measurements at higher magnetic fields are desired, because sensitivity and resolution increase with increasing the external magnetic field. Especially for quadrupole nuclei having nucleus spins larger than a half ($I > 1/2$), NMR measurement at higher field is one of the most effective method to obtain higher-resolution NMR spectrum, because the line width due to quadrupolar interactions becomes narrower with increasing the magnetic field.[1,2] Many inorganic materials such as catalysts, slags, glasses, ceramics, and rubber contain quadrupole nuclei such as ^{11}B, ^{17}O, ^{23}Na, ^{27}Al, and ^{33}S. High-field solid-state NMR measurements of these quadrupole nuclei would give detailed information about structure and/or chemical properties those are difficult to obtain by other experimental method.

NMR measurement is usually performed with a superconducting magnet (SCM). Remarkable progress in a SCM technology makes it possible to operate a SCM at 21.8 T in a persistent mode.[3,4] The strength of a magnetic field generated by a SCM, however, will soon reach its upper limit unless new materials with higher critical fields become available. Steady magnetic fields more than 25 T are available only with the help of a resistive magnet. A hybrid magnet consisting of a SCM and a resistive magnet is a promising candidate to generate a steady field for NMR measurements over 25 T. A resistive magnet, however, has a disadvantage in its field stability originated from a power source. Field fluctuations make it difficult to average NMR signals directly and cause extrinsic line width in NMR spectra. Field inhomogeneity is also responsible for additional line width. The performance of the hybrid magnet installed in the National Institute for Materials Science (NIMS) for NMR measurements was previously reported.[5,6] It was revealed that a size of sample and a shield for field fluctuations are crucial to obtain a higher-resolution NMR spectrum. In this study we will demonstrate a potential of the hybrid magnet for a practical solid-state NMR measurement at 30 T. As an example of application for an industrial material, ^{27}Al MAS NMR of a refractory mortar was performed. The refractory mortar (Al_2O_3: 92 wt %, MgO: 7 wt %, and CaO 1 wt %) is very complex and amorphous-mixed material.[7] The investigation of the local environment of Al ion is in progress.[7]

Fourier transform (FT) NMR measurements were performed for KBr and the refractory mortar at room temperature without an NMR lock nor a shim system. A 4-mm MAS sample tube was used. A spherical sample holder with 2 mm in diameter was used for KBr, and a cylindrical holder with 2.6 mm in diameter and 4 mm in length was used for the refractory mortar. Speed of MAS was 15 kHz. The sample position was precisely adjusted to minimize the NMR line width. A pipe of aluminum metal with 2 mm in thick and 250 mm in length was used as a shield to reduce field fluctuation. The aluminum shield is effective for the field fluctuation with the frequency higher than of the order of 1 kHz. Thus, the effect of the field fluctuation on the line width is reduced. The magnetic field, however, still fluctuates with lower frequency, resulting in the fluctuation of the resonance frequency. Figure 1 shows the time dependence

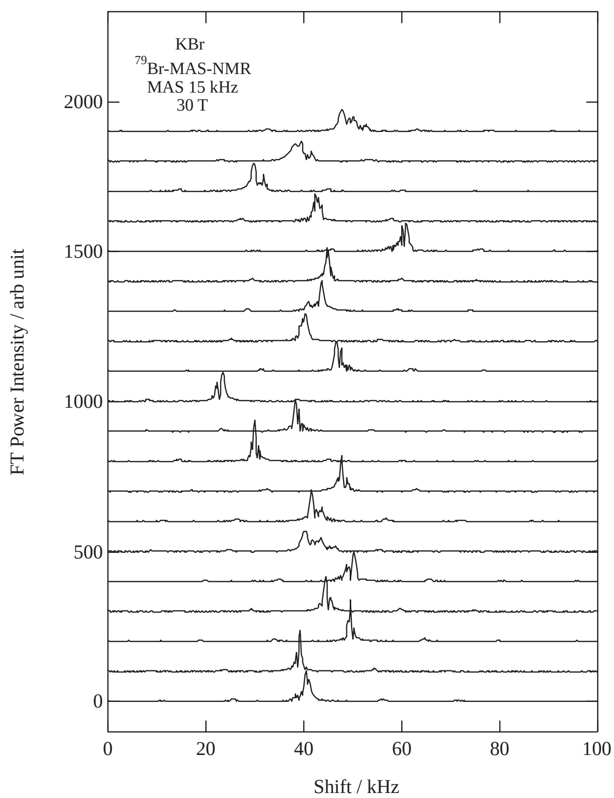

Figure 1. Time dependence of the ^{79}Br MAS NMR spectra of KBr at 30 T. Repetition time was 1 s. Horizontal axis is a shift from the operating frequency of 324.4 MHz.

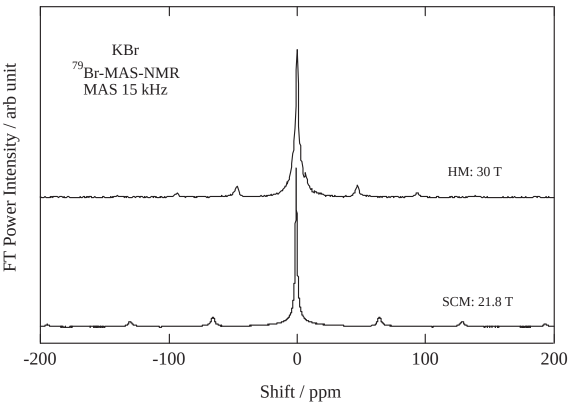

Figure 2. ^{79}Br MAS NMR spectra of KBr at 30 T with a hybrid magnet and at 21.8 T with a superconducting magnet. The spectrum at 30 T is obtained by summing 20 single-shot spectra after alignment of the central peak at a relative chemical shift of 0 ppm.

of the ^{79}Br MAS NMR spectra of KBr at 30 T with an operating frequency of 324.4 MHz. Each spectrum was obtained from a single-shot measurement of a free-induction-decay (FID) signal. The FID signal was digitized with a sampling rate of 781.25 kHz for 4096 points. The resolution of the FT spectrum was 190 Hz, i.e., 0.6 ppm. The width of the excitation pulse was 2 µs. The repetition time was 1 s. The resonance frequency varies in every measurement by the slow field fluctuation and the spectral shapes change due to the remains of the fast field fluctuation.

In order to average the spectra shown in Figure 1, the position of the central peak was aligned at a relative chemical shift of 0 ppm. Figure 2 shows the NMR spectrum obtained by summing up the 20 spectra after alignment. The spinning side band (SSB) peaks can be seen to the second order. The full width at half of the maximum (FWHM) of the central peak is 2.9 ± 0.6 ppm. The FWHM can be reduced to 1.8 ± 0.6 ppm by applying the deconvolution method using an induced electromotive force signal.[8] The ^{79}Br MAS NMR spectrum of KBr obtained at 21.8 T with a SCM at MAS speed of 15 kHz is also shown in Figure 2 for comparison. The spectrum was obtained by averaging four scans. The FWHM of the spectrum with a SCM is 1.5 ± 0.1 ppm. The positions of the SSB peaks were different between the two spectra, because the operating fields of the spectra were different and the horizontal axis is in ppm. The observation of the SSB to the second order and an achievement of a spectral resolution less than 3 ppm indicate that the hybrid magnet is capable for a practical solid-state NMR measurement both in sensitivity and in resolution. In the following, we demonstrate ^{27}Al MAS NMR of the refractory mortar as an example of application for an industrial material.

Figure 3 shows the ^{27}Al MAS NMR spectrum of the refractory mortar at 30 T. The operating frequency was 337.4 MHz. The width of the excitation pulse was 1 µs. The repetition time was 5 s. The spectrum was obtained by summing four single-shot measurements after alignment of peak positions. A splitting around 80 ppm was 2.8 ± 0.6 ppm. This spectrum is consistent with a result obtained by using a 930 MHz (21.8 T) spectrometer.[7]

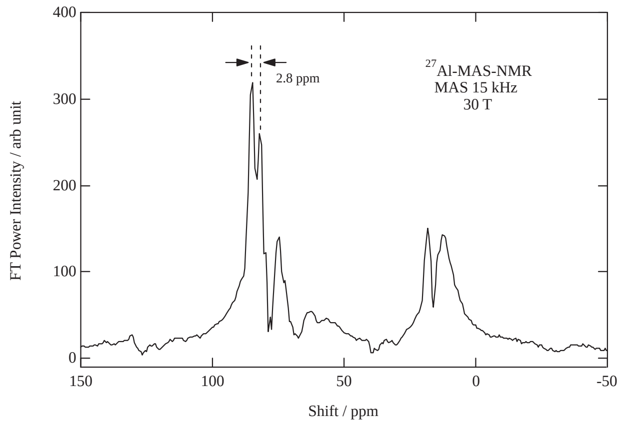

Figure 3. ^{27}Al MAS NMR spectrum of a refractory mortar at 30 T obtained by summing four single-shot spectra after alignment of the peak positions.

In summary, we have performed solid-state NMR measurements at 30 T with a hybrid magnet. Resolution of a spectrum less than 3 ppm was confirmed by ^{79}Br MAS NMR measurements of a reference material KBr. As an example of application for an industrial material, ^{27}Al MAS NMR of a refractory mortar was demonstrated. NMR spectrum which is consistent with a result obtained by using a 930 MHz spectrometer, was obtained at 30 T with a hybrid magnet. These results indicate that the hybrid magnet has a potential for a practical solid-state NMR measurement at 30 T. In order to average NMR signals directly, improvement of a power source for the hybrid magnet is in progress.[9]

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