Ultra-high Magnetic Field (21.8 T) Solid-state Nuclear Magnetic Resonance for Inorganic Materials

Keiji Shimoda,*[1] Koji Kanehashi,[1] Moriaki Hatakeyama,[1] Yasuhiro Tobu,[1] Tadashi Shimizu,[2] and Koji Saito[1]
[1]*Advanced Technology Research Laboratories, Nippon Steel Corporation, 20-1 Shintomi, Futtsu 293-8511*
[2]*National Institute for Materials Science, 3-13 Sakura, Tsukuba 305-0003*

(Received March 27, 2007; CL-070328; E-mail: shimoda.keiji@nsc.co.jp)

We hereby report that ultra-high magnetic field (21.8 T) solid-state nuclear magnetic resonance (NMR) spectroscopy is very useful in studies of quadrupolar nuclides in inorganic materials. The increase in signal sensitivity, especially for species with large quadrupolar products, and the decrease in signal width become significant with increasing magnetic field strength. An ^{27}Al 5QMAS spectrum of a refractory mortar was considerably resolved at 21.8 T compared with 16.4 T, suggesting the effectiveness of the ultra-high field NMR in clarifying the local structures in complex materials.

Solid-state NMR spectroscopy is one of the very useful techniques for detailed structural analyses of inorganic materials because of its element-specific nature. However, since almost all target elements are quadrupolar nuclides (ca. 70% of NMR-detectable nuclides), which often result in second-order quadrupolar broadening of the central transition, its practical applications have been limited. In addition, it is very difficult for low-γ (i.e., low resonance frequency) nuclei to obtain signals with a reasonable signal-to-noise (S/N) ratio at conventional magnetic field ($\leq$11.7 T). Recently, available high field magnets ($\geq$16.4 T) improve such shortcomings relating to resolution and sensitivity in NMR spectra. Stebbins and co-workers[1,2] have reported ^{17}O magic angle spinning (MAS) NMR spectra of certain crystalline materials at different magnetic fields of up to 21.1 T and showed the signal narrowing with an increasing field. They also successfully observed broad signals for low-γ nuclei, ^{39}K and ^{73}Ge.

Very recently, an ultra-high field superconductor magnet (21.8 T: ^{1}H frequency of 930 MHz) has been available to perform solid-state NMR.[3,4] The advantage of the ultra-high field multiple quantum magic angle spinning (MQMAS) technique has been revealed when applied to low-γ quadrupolar nuclei, ^{25}Mg and ^{43}Ca.[5,6] In this letter, we quantitatively examine the ^{27}Al sensitivity enhancement of inorganic materials with a magnetic field increasing up to 21.8 T. We also demonstrate the ^{27}Al quintuple-quantum (5Q) MAS spectra of an industrial refractory mortar (Al_2O_3: 92 wt %; MgO: 7 wt %; CaO 1 wt %), which is very complex and multiphased material, at 16.4 and 21.8 T, to show the effectiveness of resolution enhancement at ultra-high magnetic field.

^{27}Al MAS spectra of inorganic solids were obtained using Chemagnetics CMX-300, Varian INOVA-500, JEOL ECA-700, and ECA-930 (7.4, 11.7, 16.4, and 21.8 T, respectively). The ^{27}Al working frequencies were 78.2, 130.3, 182.4, and 242.4 MHz, respectively. Basic measurement conditions (sample volume, rf conditions, accumulation time, recycle delay, etc.) were almost identical and samples were spun at 16–18 kHz. ^{27}Al chemical shifts were referenced to saturated $AlCl_3$ solution at −0.1 ppm. In 5QMAS experiments, the z-filter sequence was applied.[7,8]

One of our main purposes is the effective application of solid-state NMR techniques to practical inorganic materials with complex compositions and/or structures.[9,10] Figure 1 plots the variations of the S/N ratio for inorganic materials with quadrupolar products, $P_q = C_q\sqrt{(1 + \eta^2/3)}$, where C_q is the quadrupolar coupling constant and η is the asymmetric parameter, as a function of the magnetic field. This indicates a higher sensitivity at a higher field, as expected. Although the high symmetry Al site ($P_q = 0$ MHz) in alum $AlK(SO_4)_2{\cdot}12H_2O$ is along the $B_0^{3/2}$ line (S/N $\propto B_0^{3/2}$, where B_0 is the external magnetic field), the larger-P_q sites in a coal and blast furnace slag deviate significantly from the ideal line. Fu et al.[11] recently reported a similar but smaller S/N improvement for a spin-1/2 ^{15}N. The striking signal enhancement in this study can be attributed to the decrease in the second-order quadrupolar line broadening at higher magnetic fields and suggests that the ultra-high field solid-state NMR will be suitable especially for large-P_q materials.

Figure 2 presents the ^{27}Al MAS spectra of a refractory mortar at different magnetic fields. At the lowest 7.4 T, the MAS spectrum shows only broad two peaks at ca. 10 ppm and 80 ppm, which are assigned to octahedral and tetrahedral coordination Al species, respectively. On the other hand, additional

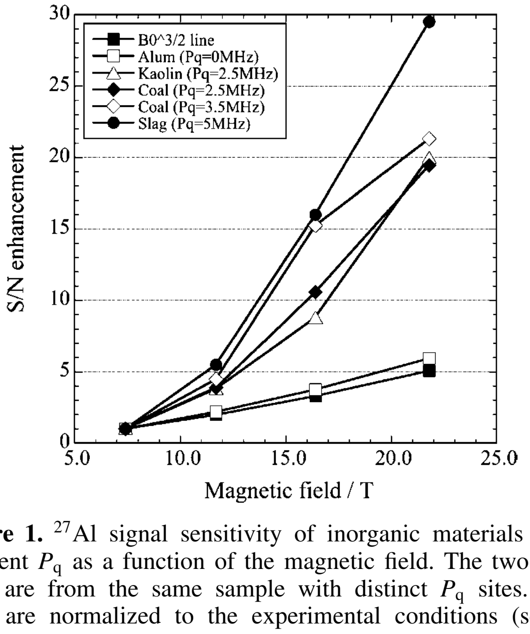

Figure 1. ^{27}Al signal sensitivity of inorganic materials with different P_q as a function of the magnetic field. The two coal plots are from the same sample with distinct P_q sites. The plots are normalized to the experimental conditions (scans, recycle delay, MAS speed, rotor volume, and broadening factor) for individual sample and to be unified at 7.4 T.

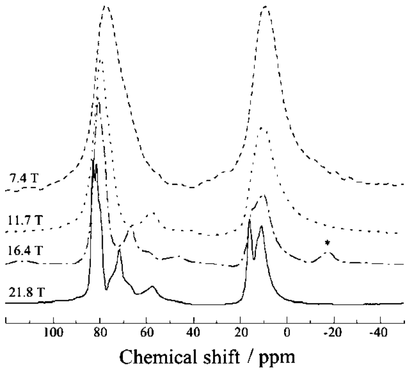

Figure 2. The ^{27}Al MAS NMR spectra of an industrial refractory mortar at different fields. The horizontal axis indicates the relative frequency in ppm. The asterisk is a spinning side band.

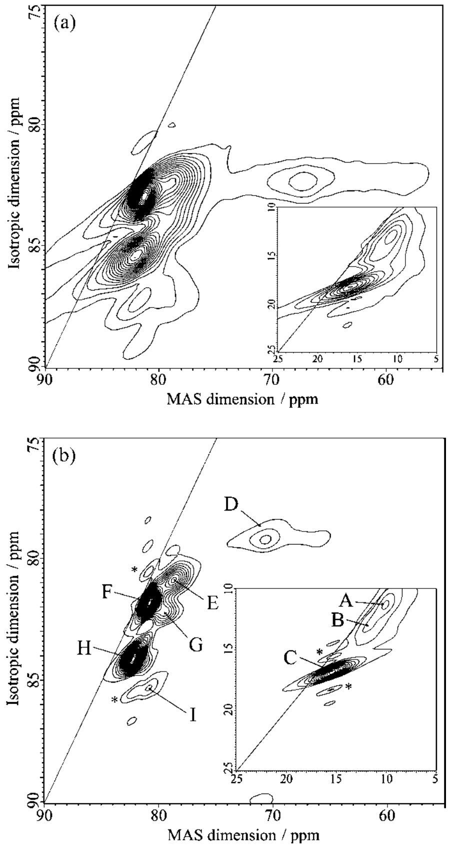

Figure 3. The ^{27}Al 5QMAS NMR spectra of an industrial refractory mortar at (a) 16.4, and (b) 21.8 T, respectively. The excitation and conversion pulses optimized for the refractory were 3.2 and 1.5 µs at 16.4 T, and 3.0 and 1.6 µs at 21.8 T, respectively. 80 scans with a recycle delay of 8 s were collected for 64t_1 increments at 16.4 T, and 120 scans with the delay of 18 s were for 128t_1 at 21.8 T. It should be noted that there are ghost peaks along the isotropic dimension (with asterisks) at 21.8 T, owing to the incomplete acquisition of long-tailed t_1 FID signal. Inspection of the 3QMAS spectrum (not shown) suggests that the site I is not a ghost. The insets envelop the octahedral Al region.

Al peaks appear in the 40–70 ppm region above the moderate field of 11.7 T, and finally these peaks are well resolved at 21.8 T. In the octahedral Al region, the single broad peak at 7.4 T becomes well separated into two peaks at 21.8 T. The decrease in the second-order quadrupolar broadening again affects the improvement of signal resolution.

Figure 3 displays the ^{27}Al 5QMAS spectra of the refractory at 16.4 and 21.8 T. The 5QMAS spectra provided detailed site information compared with the corresponding MAS spectra (Figure 2). At 21.8 T, we observed better resolved 9 nonequivalent Al species compared with 16.4 T. Sites A–C (the estimated isotropic chemical shifts δ_{CS} and quadrupolar products P_{q} are as follows;[6] A: 10.9 ppm, 2.7 MHz; B: 12.5 ppm, 2.8 MHz; C: 16.3 ppm, 2.9 MHz) are assigned to octahedral Al species with distinct environments each other, and the sites D–I are to tetrahedral Al species (D: 75.5 ppm, 7.8 MHz; E: 80.1 ppm, 3.7 MHz; F: 81.4 ppm, 2.5 MHz; G: 81.2 ppm, 4.2 MHz; H: 83.4 ppm, 3.4 MHz; I: 83.7 pm, 4.5 MHz). Thus, the present study strongly suggests the power of the ultra-high field MQMAS spectroscopy, from the viewpoint of resolution improvement, at 21.8 T, currently the leading global superconductor magnet.

In summary, the significant advantages of using ultra-high magnetic field solid-state NMR techniques for quadrupolar nuclei were indicated below;

1. The signal sensitivity (or S/N ratio) is drastically improved. In particular, the increase for the complex materials with large P_{q}'s is 4–6 times higher than the $B_0^{3/2}$ line at 21.8 T, showing a good correlation with P_{q} (Figure 1).
2. The signal resolution is also highly improved (Figures 2 and 3), because of the decrease in the second-order quadrupolar broadening.

All the advantages reduce the acquisition time and also allow measurements with low concentration samples or small sample volumes. The practical applications of ultra-high field solid-state NMR spectroscopy are powerful and welcome for detailed analyses of the local structure of quadrupolar nuclides in many complex solids.

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References

1 S. Kroeker, P. S. Neuhoff, J. F. Stebbins, *J. Non-Cryst. Solids* **2001**, *293–295*, 440.
2 J. F. Stebbins, L.-S. Du, S. Kroeker, P. Neuhoff, D. Rice, J. Frye, H. J. Jakobsen, *Solid State Nucl. Magn. Reson.* **2002**, *21*, 105.
3 M. Murakami, T. Shimizu, M. Tansho, A. Vinu, K. Ariga, K. Takegoshi, *Chem. Lett.* **2006**, *35*, 986.
4 Y. Yamamoto, M. Murakami, R. Ikeda, K. Deguchi, M. Tansho, T. Shimizu, *Chem. Lett.* **2006**, *35*, 1058.
5 K. Shimoda, Y. Tobu, Y. Shimoikeda, T. Nemoto, K. Saito, *J. Magn. Reson.* **2007**, *186*, 156.
6 K. Shimoda, Y. Tobu, M. Hatakeyama, T. Nemoto, K. Saito, *Am. Mineral.* **2007**, *92*, 695.
7 L. Frydman, J. S. Harwood, *J. Am. Chem. Soc.* **1995**, *117*, 5367.
8 J.-P. Amoureux, C. Fernandez, S. Steuernagel, *J. Magn. Reson., Ser. A* **1996**, *123*, 116.
9 K. Kanehashi, K. Saito, *Fuel Process. Technol.* **2004**, *85*, 873.
10 M. Hatakeyama, T. Nemoto, K. Kanehashi, K. Saito, *Chem. Lett.* **2005**, *34*, 864.
11 R. Fu, O. Gunaydin-Sen, N. S. Dalal, *J. Am. Chem. Soc.* **2007**, *129*, 470.