

Natural Abundance Solid-state ^{25}Mg MQMAS NMR Studies on Inorganic Solids at a High Magnetic Field of 16.4 T

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An application of a high magnetic field (16.4 T) with a specialized high power radio frequency (rf)-resistant probe that produces a very short 90° pulse enabled measurement of natural abundance ^{25}Mg multiple quantum magic angle spinning (MQMAS) spectra of complex inorganic materials, such as minerals and steel-making slag with the large quadrupolar coupling constant (C_Q) (≈ 10 MHz).

Magnesium is an important element in various materials, such as minerals, glasses, and ceramics, as well as biological systems. ^{25}Mg NMR is expected to provide useful atomic scale structural information on both crystalline and noncrystalline materials. However, solid-state ^{25}Mg NMR of these materials often suffers from low sensitivity and the large second-order quadrupolar broadening of the central transition ($1/2 \leftrightarrow -1/2$) of ^{25}Mg , because ^{25}Mg has a low Larmor frequency (ex. 18.4 MHz at a widely used magnetic field of 7.0 T), low natural abundance (10.13%), and moderate nuclear quadrupole moment (nuclear spin $I = 5/2$, $Q = 2.2 \times 10^{-29} \text{ m}^2$). In spite of these difficulties, one-dimensional (1D) ^{25}Mg NMR studies in solids have been reported on a variety of compounds, such as inorganic compounds,¹⁻⁷ glasses,⁸⁻¹⁰ and an organometallic compound.¹¹

Two-dimensional (2D) multiple quantum magic angle spinning (MQMAS)¹² is a very effective method for obtaining intimate structural information on half-integer quadrupolar nuclei, such as ^{11}B ,¹³ ^{27}Al ,¹⁴ and ^{17}O ¹⁵ in solid materials by virtue of averaging the second-order quadrupolar broadening. Recently, ^{25}Mg MQMAS studies on inner-sphere Mg^{2+} binding complexes¹⁶ and magnesium(II) adenosine 5'-triphosphate¹⁷ both of which were isotropically enriched by ^{25}Mg to enhance signal intensity have been reported. These studies clearly succeeded in distinguishing different Mg sites whose peaks were completely overlapped in ^{25}Mg MAS spectra. However, some solid materials, especially natural minerals and slag that is by-products of the steel-making process, cannot be enriched by ^{25}Mg technically. To the best of our knowledge, only one report on 2D high-resolution natural abundance ^{25}Mg NMR spectra has been published; Dowell et al. very recently showed natural abundance ^{25}Mg satellite transition magic angle spinning (STMAS) spectra of some minerals at 9.4 T.¹⁸ However, the crystal structures of these minerals have already been defined, and application of STMAS is often technically limited, because STMAS requires the spinning axis to be very precisely on the magic angle. Therefore, measurement of natural abundance (not enrichment) ^{25}Mg MQMAS spectra has been strongly desired.

In the present paper, we demonstrated natural abundance ^{25}Mg MQMAS NMR of several inorganic solids at a magnetic field of 16.4 T together with a high power radio frequency (rf)-resistant probe. We applied ^{25}Mg MQMAS to a relatively simple

mineral ($\text{Mg}(\text{OH})_2$), followed by a very complicated industrial material (steel-making slag) whose structure was unknown. On the basis of these MQMAS spectra, we succeeded in estimating the isotropic chemical shift (σ_{iso}) and the quadrupolar coupling constant (C_Q) of individual Mg species.

All Mg samples had natural abundance of ^{25}Mg (not enriched). MgO and $\text{Mg}(\text{OH})_2$ were purchased from Aldrich Chemical Company Inc. Two slag samples (slag A: magnesium content, 9.1 mass %; slag B: magnesium content, 8.9 mass %) that have low crystallinity, were produced as by-products of the steel-making process.

^{25}Mg NMR spectra were acquired on a JEOL model JNM-ECA700 spectrometer with an 16.4 T ($^1\text{H} = 700$ MHz) narrow-bore magnet at a resonance frequency of $^{25}\text{Mg} = 42.9$ MHz. A home-built 4-mm MAS probe that endures a very high power rf field and produces quite a short 90° pulse ($= 3.8 \mu\text{s}$ at 1110 W (probe-in)) of ^{25}Mg in MgO ($C_Q \approx 0$ MHz) was used. All samples were spun at a rate of 18 kHz. The spin-echo sequence proposed by Kunwar et al.¹⁹ was used for ^{25}Mg MAS spectra to avoid ringing from the transmitter and the probe. In MQMAS, a triple quantum excitation was applied. The three-pulse sequence with z -filter that is a selective 90° pulse at low rf power was applied for the symmetric coherence transfer, yielding a nondispersive line shape.²⁰ A typical rf field strength of $\nu_1 = 66$ kHz was used for both the triple quantum excitation pulse and the conversion pulse, whereas a weaker rf field strength of $\nu_1 = 12.5$ kHz was used for the z -filter selective pulse. ^{25}Mg chemical shifts were referenced to saturated aqueous MgSO_4 solution at 0 ppm.

Figure 1 shows ^{25}Mg spin-echo MAS spectra of inorganic samples. A single sharp signal is observed at 26.6 ppm in MgO because of the Mg site with high symmetry in cubic lattice, which is the same result as previous reports.^{1,5} In contrast, a ^{25}Mg MAS spectrum of $\text{Mg}(\text{OH})_2$ clearly shows the typical single second-order quadrupolar line shape. Indeed, a natural abundance ^{25}Mg 3QMAS spectrum of $\text{Mg}(\text{OH})_2$ proves that there is

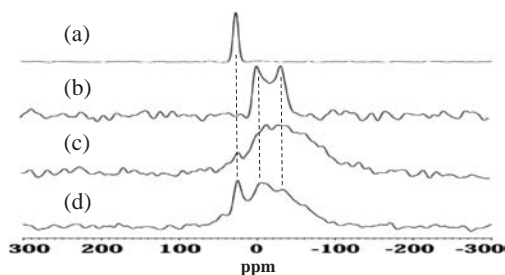


Figure 1. Natural abundance ^{25}Mg spin-echo MAS spectra of (a) MgO , (b) $\text{Mg}(\text{OH})_2$, (c) slag A, and (d) slag B. Pulse repetition times of (a) 150 s, (b) 25 s, (c) 3 s, and (d) 3 s were applied.

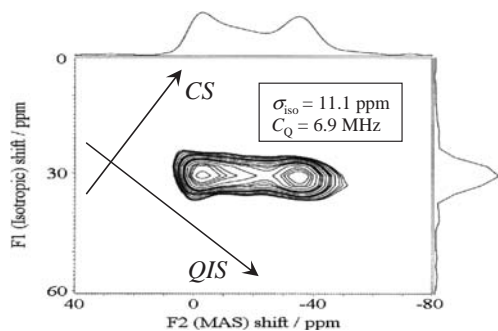


Figure 2. Natural abundance ^{25}Mg 3QMAS spectrum of $\text{Mg}(\text{OH})_2$. The optimized excitation and conversion pulse width was 6.0 and 2.4 μs , respectively. The selective 90° pulse width was 30 μs . A total of 1200 transients were collected for each of 32 t_1 increments with a repetition time of 7 s.

only one Mg site in $\text{Mg}(\text{OH})_2$ (Figure 2). The σ_{iso} (= 11.1 ppm) and the C_Q (= 6.9 MHz; the asymmetric parameter (η) = 0 is assumed) of this Mg site can be easily derived from the peak position in the 2D MQMAS spectrum.²¹

In Figure 1d, the line shape of slag B seems to be mainly composed of MgO and $\text{Mg}(\text{OH})_2$. An IR spectrum of slag B also clearly shows O–H stretching vibration of $\text{Mg}(\text{OH})_2$ at 3696 cm^{-1} . On the other hand, neither MgO nor $\text{Mg}(\text{OH})_2$ is main components of Mg species in slag A. The ^{25}Mg MAS spectrum of slag A indeed shows broad peaks in the region of $\text{Mg}(\text{OH})_2$ signals (Figure 1c); however, O–H stretching vibration of $\text{Mg}(\text{OH})_2$ is not clearly observed in an IR spectrum of slag A. Moreover, signal intensity corresponding to MgO in slag A is weaker than that in slag B. Therefore, Mg species other than $\text{Mg}(\text{OH})_2$ and MgO is supposed to exist in slag A. To confirm the existence of other Mg species, a natural abundance ^{25}Mg 3QMAS experiment was performed. A natural abundance ^{25}Mg 3QMAS spectrum of slag A with a reasonable signal-to-noise ratio was obtained in 9 days (Figure 3). The ^{25}Mg spectrum of slag A clearly shows new Mg sites, whereas the ^{25}Mg MAS spectrum do not provide obvious results. New two Mg sites in Figure 3 have a quite large C_Q (≈ 10 MHz), which suggests that slag A has a disordered, complicated structure, and Mg sites in slag A are situated in the environments with low spherical symmetry.

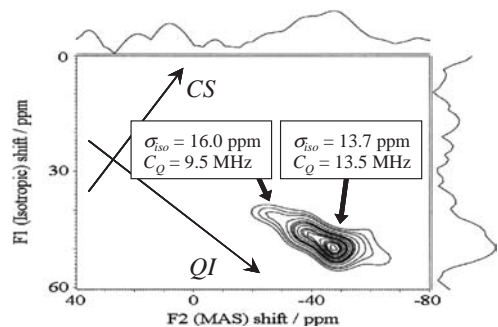


Figure 3. Natural abundance ^{25}Mg 3QMAS spectrum of slag A. The excitation and conversion pulse width was 6.0 and 2.4 μs , respectively. The selective 90° pulse width was 30 μs . A total of 48,000 transients were collected for each of 16 t_1 increments with a repetition time of 0.5 s.

It should be also noted that the line shape of the summation along the F2 (MAS) axis does not resemble the line shape of the ^{25}Mg MAS spectrum. A summed line shape along the F2 axis in MQMAS spectra is generally similar to the MAS spectra; however, no signals are observed in the region of ca. -20 to 20 ppm in Figure 3, though the corresponding MAS spectrum (Figure 1c) shows broad signals in this region. The reason why the summed line shape along the F2 axis partly (not fully) contributes to the MAS line shape is that other Mg species that have the very long spin–lattice relaxation time (T_1) compared with a pulse delay might exist. Magnetization of such Mg species is expected not to be fully recovered; therefore, signal intensity seems to be depressed or invisible.

In conclusion, we successfully obtained natural abundance ^{25}Mg MQMAS NMR spectra with the reasonable signal-to-noise ratio, even if Mg species in the sample have considerably the complicated structure and the large C_Q . Because the z -filter sequence that is most commonly used in MQMAS experiments needs a high power rf field for an effective excitation of multiple quantum coherences and conversion into single quantum coherence, a high power rf-resistant probe that can provide a very short 90° pulse is a very effective tool. Moreover, a high magnetic field overcomes relatively low sensitivity of ^{25}Mg with low γ . Natural abundance ^{25}Mg MQMAS NMR should provide novel, useful information on chemical structures of various Mg-containing solid materials with complex structures.

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