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Communication

Fast ^{29}Si magic-angle-spinning NMR acquisitions by RAPT-CP ^{27}Al → ^{29}Si polarization transfer

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Abstract

Using enhancement of the ^{27}Al central-transition magnetization by applying RAPT prior to ^{27}Al → ^{29}Si cross-polarization, we demonstrate fast acquisition of ^{29}Si one-dimensional MAS and two-dimensional ^{27}Al–^{29}Si HETCOR spectra on a new sialon phase $Ba_2Al_3Si_9N_{13}O_5$.

Keywords: Cross-polarization; RAPT; Half-integer spin quadrupolar nuclei; Magic-angle-spinning; Sialons

1. Introduction

Since the demonstration of Vega and Naor [1] that satellite inversion increases the population differential across the central-transition (CT) of a half-integer spin quadrupolar nucleus in a static single crystal, modifications of frequency swept schemes appeared for achieving CT signal enhancements in static and rotating single crystals and powders [2–5]. A similar approach, rotor assisted population transfer (RAPT) [6], consists of a series of fast amplitude modulated pulses (FAM) [7] and leads to an increased CT signal under magic-angle-spinning (MAS) conditions, either by first inverting or equalizing the satellite populations prior to the excitation of single-quantum coherences. For a spin-I nucleus, the CT polarization enhancement by RAPT (FAM) or frequency swept schemes amounts to $2I$ (satellite inversion), or $I + 1/2$ (satellite saturation) [6]. In practice, a mixture of them is obtained and experimental optimization is required on the given sample. Various applications and modifications of RAPT include efficient excitation of one-dimensional MAS spectra of various half-integer spins [8–10], measuring quadrupolar coupling constants [11], selective excitation based on the size of the quadrupolar interaction [12], and combination of RAPT with QCPMG [13].

Sialons constitute framework structures, usually comprising mixed $Si(O,N)_4$ and $Al(O,N)_4$ tetrahedra and occasionally five and six coordinated Al. Due to the similar scattering factors of the pairs Al/Si and O/N, solid state NMR is a useful complement to X-ray diffraction for identifying coordination environments in these technologically important materials [14–16]. However, ^{29}Si NMR acquisitions are usually very time-consuming due to long spin–lattice relaxation times [17], and the relatively low natural abundance (~4.7%) of the isotope.

This communication has a dual purpose: first, we demonstrate fast acquisitions of ^{29}Si MAS spectra of the sialon $Ba_2Al_3Si_9N_{13}O_5$ by transferring magnetization from surrounding ^{27}Al by cross-polarization (CP), thereby exploiting the latter's significantly shorter T_1. While CP involving at least one quadrupolar spin species is becoming increasingly exploited, there are relatively few reports involving ^{27}Al and ^{29}Si, despite their occurrences in a wide range of natural and synthetic materials. Current demonstrations of ^{27}Al → ^{29}Si polarization transfers include alumino-silicates in the contexts of minerals [18], glasses [19], and zeolites [20],

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and to our knowledge CP has not yet been demonstrated on a sialon compound. Second, we show that polarization transfers from quadrupolar nuclei under MAS conditions may be improved significantly by first enhancing the CT polarization using RAPT prior to CP. Haase et al. [3] introduced the idea of CT enhanced heteronuclear polarization transfer for static samples and demonstrated it in the context of $^{27}Al \rightarrow {}^{17}O$ transfer, preceded by adiabatic radio-frequency sweeps to achieve the same effect as RAPT employed here.

The combination of RAPT and CP, dubbed RAPT-CP, is demonstrated on $Ba_2Al_3Si_9N_{13}O_5$, a compound belonging to the novel family of barium S-phases. They conform to the general formula $Ba_2Al_xSi_{12-x}N_{16-x}O_{2+x}$, of which the members $x = 0$ and $x = 2$ was recently reported and characterized [21].

2. Results and discussion

$Ba_2Al_3Si_9N_{13}O_5$ was prepared by spark plasma sintering as described in [21]. The X-ray diffraction powder pattern showed an essentially mono-phasic sample with one weak reflection (1.5% relative intensity) from an impurity.

Fig. 1 displays the ^{27}Al and ^{29}Si MAS spectra of $Ba_2Al_3Si_9N_{13}O_5$, both obtained by direct single-pulse excitation. Both spectra are very similar to those of the corresponding $x = 2$ S-phase $Ba_2Al_2Si_{10}N_{14}O_4$, discussed in detail in [21]. From separate 3QMAS experiments [22], shown for the $x = 2$ phase in [21], and to be discussed elsewhere for the current $x = 3$ phase, we conclude that the main peak at 93.5 ppm in the ^{27}Al MAS spectrum (Fig. 1A) has contributions from two overlapping sites, tentatively assigned to AlN_3O tetrahedra and having ^{27}Al quadrupolar coupling constants ~2.5 and ~4.7 MHz, respectively. In addition, the $x = 3$ phase displays a signal around 60 ppm, typical of AlO_4 coordination environments. This peak probably derives from a minor amorphous phase present in grain boundaries. The ^{29}Si MAS spectrum of $Ba_2Al_3Si_9N_{13}O_5$ ($x = 3$), shown in Fig. 1B, has overlapping signals originating from SiN_4 and SiN_3O units; it is also similar to that of the $x = 2$ phase [21], except from a + 0.5 ppm overall shift of the peak.

Fig. 2B shows the ^{29}Si MAS spectrum of $Ba_2Al_3Si_9N_{13}O_5$, obtained by applying *one* 90° pulse to the magnetization reservoir obtained by waiting 52 min after complete saturation. Fig. 2C shows results using various $^{27}Al \rightarrow {}^{29}Si$ CP transfers, obtained from 64 signal accumulations (amounting to the same acquisition time as that for Fig. 2B) but acquired by the scheme depicted in Fig. 2A. The smallest signal was obtained by applying CP directly after the relaxation interval, with a constant ^{29}Si nutation frequency $\omega^{Si}_{nut}/2\pi = 3.85$ kHz, whereas an increase of 2.17 in the integrated signal intensity resulted by including a linear ramp [23] between $\omega^{Si}_{nut}/2\pi = 3.85 \pm 0.32$ kHz. Ramped CP usually provides more efficient magnetization transfers [23], as also reported in the context of $^{27}Al \rightarrow {}^{29}Si$ [18]. In the present case, we believe the improvements are mainly due to reduced sensitivity to RF inhomogeneity compared to the constant amplitude version. We verified that no ^{29}Si signal was obtained in the CP implementations (Fig. 2A) when the ^{27}Al RF field was turned off.

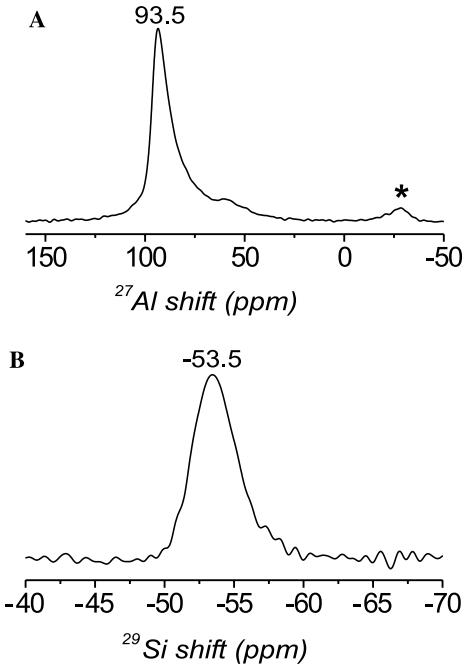

Fig. 1. (A) ^{27}Al MAS spectrum of $Ba_2Al_3Si_9N_{13}O_5$, recorded at an external magnetic field of 9.4 T and spinning frequency $\omega_r/2\pi = 13.1$ kHz, using a filled 4 mm zirconia rotor on a Varian/Chemagnetics Infinity-400 spectrometer. The spectrum is a result of 80 signal transients, using 120 s relaxation delays and 9° pulses, measured with respect to 1 M Al^{3+}(aq), also used as external chemical shift reference. The asterisk indicates a spinning sideband. (B) ^{29}Si MAS spectrum at $\omega_r/2\pi = 5.0$ kHz, using a filled 6 mm zirconia rotor (500 mg of sample) and a double-resonance H-X probehead. The spectrum is the result from 52 transients, using 45° pulses with 45 min relaxation delays, and 3.5 h of equilibration prior to start of acquisition. Chemical shifts are reported relative to TMS. 50 Hz Lorentzian line-broadening was applied to the spectrum in (A), and no apodization was used for that in (B).

An additional improvement by 2.28 in the signal intensity was obtained using RAPT prior to CP, with $n = 100$ and pulse and inter-pulse durations equal to 1.48 and 1.0 μs, respectively. This CP enhancement corresponded well to that found from direct RAPT optimization of the ^{27}Al MAS spectrum (not shown). In all cases, the following ^{27}Al CT nutation frequencies $\omega^{Al}_{nut,CT}/2\pi$ were used: 1.92 kHz during CP, 20.3 kHz for the central-transition selective 90° pulse, and 82.6 kHz for FAM [7] and saturation pulses. The CT nutation frequency $\omega^{Al}_{nut,CT}/2\pi$ is three times larger than that of non-selective pulses [24], i.e., the nutation frequency

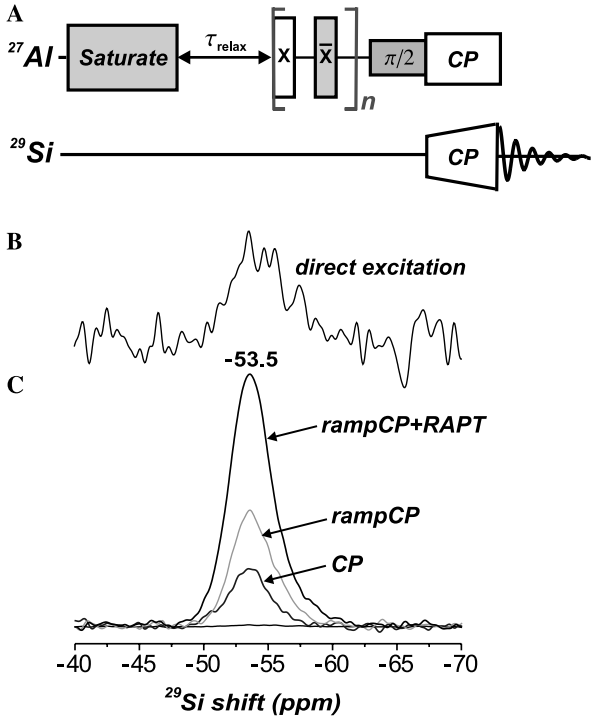

Fig. 2. (A) Pulse sequence incorporating RAPT-CP. The experiment starts with saturation of ^{27}Al to ensure reproducible results, followed by RAPT-CP and detection of the ^{29}Si MAS signal. A slight "ramp" of the ^{29}Si RF field was used during cross-polarization [23]. Note that the RF pulse amplitudes and delays are not drawn to scale. (B) ^{29}Si MAS spectrum at $\omega_r/2\pi = 7.00$ kHz, recorded by first saturating the ^{29}Si magnetization, and signal acquisition following after a delay of 52 min and *one* 90° pulse. (C) ^{29}Si MAS spectra of $Ba_2Al_3Si_9N_{13}O_5$, using different versions of the pulse scheme in (A), with $\omega_r/2\pi = 7.00$ kHz, 200 ms CP contact time, $\tau_{relax} = 50$ s and repetition rate of 2 s between each of the 64 co-added signal transients. Other parameters are given in the text. The spectra were acquired using a Varian/Chemagnetics triple-resonance 6mm probe, manufactured for use at 4.7 T, but modified to tune to $\omega_0^{Al}/2\pi = -104.292$ MHz and $\omega_0^{Si}/2\pi = 79.504$ MHz at 9.4 T.

measured from an aqueous solution of Al^{3+}. The overall signal improvement by implementing RAPT and ramped CP amounts to 4.66 compared to CP at constant ^{29}Si RF field. Further, if 3.5 h of equilibration prior to start of the ^{29}Si signal acquisition is included in the total experimental time for obtaining the spectrum in Fig. 1B, one may conclude that a comparable spectrum by RAPT-CP allowed for *46 times faster* acquisition. These enhancements should be regarded as approximate *guidelines*, as the spectra were acquired using different probeheads (however, we estimated that both probeheads provide similar S/N ratios).

There should be room for further improvements of the RAPT-CP transfers. It was shown recently that saturation (or inversion) of the outer and inner satellite transitions by consecutive RAPT blocks generally give higher CT enhancements for spins-5/2 [8,9]. However, in our case we could not improve the transfers further using this approach; incidentally, our RAPT enhancement of 2.3 is similar to those obtained for spins-5/2 by employing consecutive RAPT-blocks in [9]. Additionally, by careful optimization over larger ranges of spinning frequencies and RF nutation frequencies, it may be possible to find more beneficial cross-polarization conditions [25–27]. Keeping the spinning frequency constant at 7.00 kHz, we employed a rather narrow search of nutation frequencies around the first-order sideband condition $\omega_{nut,CT}^{Al} + \omega_{nut}^{Si} = \omega_r$ [27]. Interestingly, optimal results were obtained for $\omega_{nut,CT}^{Al}/2\pi = 1.92$ kHz and $\omega_{nut}^{Si}/2\pi = 3.85$ kHz, giving a match slightly below the expected value of $\omega_r/2\pi = 7.00$ kHz. Also, as the ^{27}Al T_1 was estimated to be about 30 s, the CP transfers could not exploit the entire equilibrium ^{27}Al reservoir, and the compromise $\tau_{relax} = 50$ s was used.

It should be noted that *in general*, neither $^{27}Al \rightarrow {}^{29}Si$ CP nor direct ^{29}Si excitation provides quantitative spectra from sialons, when there are several distinct ^{29}Si sites. It is for fundamental reasons in the case of cross-polarization due to the possibility of non-uniform polarization transfers to the various sites. For direct excitation, it may be due to different T_1-relaxation times for inequivalent ^{29}Si spins; in practice, it is difficult to assess the degree of such effects as relaxation times may be in the order of *hours* [17]. The spectra acquired by CP in Fig. 2C do not display line-shape distortions compared to that in Fig. 1B, indicating uniform magnetization transfers. The overall signal improvement depends of course on the number of surrounding Al nuclei available for transfer. However, in order to achieve significant gains compared to direct ^{29}Si excitation, it is not necessary to have a large Al/Si ratio: for our RAPT-CP experiment of the S-phase, as well as the demonstration of CP in the mineral low albite [18], the Al/Si ratio was 1/3. Also, we obtained enhancements by cross-polarization in an S-phase $Ba_2Al_{0.5}Si_{11.5}N_{15.5}O_{2.5}$ having the very low ratio Al/Si ~0.04. A detailed NMR characterization of a series of barium S-phases will be reported elsewhere.

Fig. 3A shows a pulse scheme for acquiring two-dimensional heteronuclear correlation (HETCOR) spectra to establish ^{27}Al–^{29}Si connectivities. It is identical to that of Fig. 2A, except including an additional ^{27}Al evolution interval ("t_1") prior to the CP block. Fig. 3B displays the resulting two-dimensional spectrum from $Ba_2Al_3Si_9N_{13}O_5$.

As RAPT gives uniform enhancements over moderately large ranges of ^{27}Al quadrupolar coupling constants and chemical shifts [9–12], it is likely the spin locking required for CP that primarily may limit this approach. Hence, whenever CP is applicable, RAPT is likely to offer enhancements. More work is required to verify the general applicability of this technique, and it is unlikely that RAPT-CP will replace direct excitation as a *general* means of acquiring ^{29}Si MAS spectra of

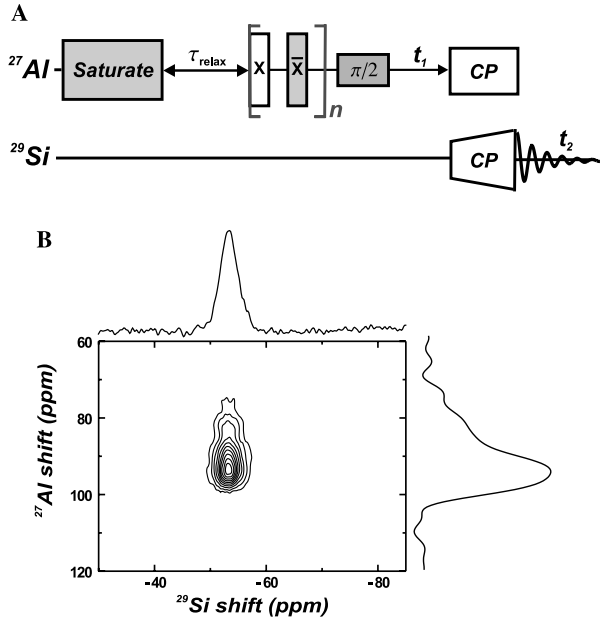

Fig. 3. (A) Pulse scheme for acquiring two-dimensional HETCOR spectra. (B) The result by using the scheme in (A) on $Ba_2Al_3Si_9N_{13}O_5$ with parameters as in Fig. 2, except $\tau_{relax} = 25$ s and 40 transients per t_1-value. Time-points (36×128) were recorded with increments equal to 1/3 and 1 rotational period in the first and second dimensions, respectively, and incorporating TPPI [28]. The total acquisition took 10 h.

sialons or non-protonated alumino-silicates. Rather, we believe that its major merits for structural studies lies in spectral editing applications, and for determining ^{27}Al–^{29}Si internuclear distances. The incorporation of extended RAPT versions [12] may also allow for selective excitation of ^{29}Si spins in close proximity to ^{27}Al sites experiencing *either* weak *or* strong quadrupolar interactions.

3. Conclusions

The combination of RAPT [6,8–12] and $^{27}\text{Al} \rightarrow {}^{29}\text{Si}$ cross-polarization [18–20], was demonstrated for efficient ^{29}Si MAS NMR acquisitions in a novel sialon compound $Ba_2Al_3Si_9N_{13}O_5$. Recording of a one-dimensional ^{29}Si RAPT-CP spectrum was >40 faster than an acquisition using single-pulse excitation. This approach may open new avenues for exploiting multi-dimensional experiments involving ^{29}Si in sialons, as hitherto no applications of advanced, but potentially more informative, NMR techniques have to our knowledge been attempted on these materials. The RAPT-CP method is beneficial whenever the source spin species is half-integer quadrupolar of high natural abundance, with a significantly shorter T_1 than the target spin, and the $T_{1\rho}$ relaxation times of both nuclei allow long enough contact intervals for polarization transfer. Other attractive combinations of nuclei include ^{27}Al–^{31}P, ^{11}B–^{29}Si, and ^{11}B–^{31}P.

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