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Observation of Four-Coordinate Aluminum Oxynitride (AlO$_{4-x}$N$_x$) Environments in AlON Solids by MAS ^{27}Al NMR at 14 T

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The use of isotropic chemical shifts from magic-angle spinning (MAS) ^{27}Al NMR spectra to characterize the local first- and second-coordination spheres of aluminum atoms in a wide range of amorphous and polycrystalline aluminum−oxygen compounds has been extensively investigated.[1−21] Muller et al.[1] first showed that ^{27}Al NMR exhibits resonances with isotropic ^{27}Al chemical shifts that are dependent upon the Al−O coordination number, with chemical shifts for local six-coordinate AlO$_6$ units occurring in the 0−9 ppm region (relative to Al(H$_2$O)$_6^{3+}$ ion) and four-coordinate AlO$_4$ units in the 55−80 ppm range. Subsequently, ^{27}Al NMR studies of materials containing 5-coordinate AlO$_5$ sites (e.g., barium aluminum glycolate, andalusite, and the dehydroxylated form of the minerals, kaolinite, and pyrophyllite) have shown NMR peaks with isotropic shifts from 30 to 40 ppm.[11,15−18] These studies and others have defined the empirical ^{27}Al chemical shift ranges for 4-, 5-, and 6-coordinate aluminum−oxygen sites based on an extensive range of aluminum systems, including oxides, aluminosilicates, minerals, and zeolites.[1−13,15−18] The use of ^{27}Al chemical shift data to correlate the local second-nearest-neighbor chemical environments in various types of condensed 4-coordinate Al(OX)$_4$ units with neighboring XO$_4$ tetrahedra (X = Si, P) and neighboring XO$_6$ (X = Al) octahedra have also been examined, as summarized by Muller et al.[20] Thus, MAS ^{27}Al NMR also provides a sensitive means to discriminate and assign subtle (i.e., second nearest neighbor) effects in many aluminum−oxygen systems. However, MAS ^{27}Al NMR spectra of aluminates containing variable numbers of nearest-neighbor AlO$_4$ tetrahedra, denoted Q^n, show that such variations do not significantly influence the range of ^{27}Al chemical shifts (76−85 ppm).[20,21]

An empirical relationship between ^{27}Al chemical shifts and the local aluminum coordination environments in solids has recently been reported for four-coordinate AlN$_4$ sites, based on MAS ^{27}Al NMR studies of aluminum−nitrogen compounds such as AlN, β'-SiAlON, β''-SiAlON, and AlON ceramics and powders.[22−25] Butler et al.[23] measured at 9.4 T the ^{27}Al chemical shifts of the AlN$_4$ tetrahedra (110 ppm) in aluminum nitride and the AlN$_4$ tetrahedra (110 ppm) and AlO$_6$ octahedra (3 ppm) in Si−Al−O−N phases. Hayashi et al.[22] subsequently assigned the 100 ppm signal of hydrolyzed AlN powders to AlN$_4$ moieties in unreacted AlN. Dupree and co-workers[24] reported at 8.5 T MAS ^{27}Al NMR studies for AlO$_6$ (12 ppm), AlO$_4$ (65 ppm), and AlN$_4$ (114 ppm) environments in AlON and AlO$_6$ (4 ppm), AlO$_4$ (66 ppm), and AlN$_4$ (104−109 ppm) sites in various β'-SiAlONs and β''-SiAlONs (Mg$_5$AlSi$_3$O$_{11}$N). These studies have suggested that MAS ^{27}Al NMR may be used to distinguish local aluminum oxynitride environments for sites of the AlO$_{4-x}$N$_x$ type in SiAlON materials, although the magnetic field strengths used were insufficient to permit the complete observation or clear resolution of such resonances, presumably due to the large second-order quadrupole contributions to the ^{27}Al line widths at 8.5 T. In addition, these measurements were limited to the observation of only 65% of the total aluminum in AlN, 15% in AlON, and even less for various SiAlON materials. In addition to the work of Butler et al.[23] and Dupree et al.,[24,31] a recent report by Smith has examined the ^{27}Al NMR of various SiAlONs at 11.7 T.[32] That report will be discussed in more detail in relationship to the NMR results reported here.

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In this communication, we report the first experimental observation of resolvable MAS ^{27}Al NMR resonances, measured at 14 T, in the spectral region between the chemical shifts of resonances for four-coordinate AlO_4 (ca. 66 ppm) and AlN_4 (114 ppm) sites in synthesized AlON ceramic powdered materials.[26-30] The observed ^{27}Al NMR resonances are empirically assigned to four-coordinate aluminum oxynitride ($AlO_{4-x}N_x$) environments, thus providing experimental evidence for a relationship between the ^{27}Al chemical shift and chemical environment over a range of local $AlO_{4-x}N_x$ environments in these ceramic powders. ^{27}Al spin-counting measurements carried out on the 35.7 mol % AlN sample show that 98.9% of the ^{27}Al spins were observed based on comparison of the integrated intensity of the spectral peaks of a weighed sample with the single peak for an alum (potassium aluminum sulfate dodecahydrate, $KAl(SO_4)_2 \cdot 12H_2O$) sample.

The AlON ceramic powders were prepared by pressureless sintering of AlN and α-Al_2O_3 at various AlN/Al_2O_3 reaction ratios from 16.7 to 88 mol % AlN. The reaction mixtures were slurried in *n*-butanol under N_2 flow, and then prereacted at <20 mTorr on a vacuum line for 1 h at 110 °C and at 300 °C for 2 h. The prereacted samples were sintered for four hours at 1200 °C and for 1 h at 1800 °C under 2 psig N_2 flow in a Centorr M60 furnace. Solid-state ^{27}Al MAS NMR spectra were obtained at 156.4 MHz on a Bruker AM-600 NMR spectrometer using a "home-built" MAS probe, with 18–20 kHz sample spinning. The ^{27}Al NMR chemical shifts were externally referenced to a 1 M $AlCl_3 \cdot 6H_2O$ solution assigned as 0.0 ppm.

The ^{27}Al MAS NMR spectra of AlON ceramic powders of different AlN/Al_2O_3 reaction ratios from 16.7 to 88 mol % AlN are shown in Figure 1. In addition, the reference ^{27}Al NMR spectra of the reactants, AlN, and a low surface area Al_2O_3, are also shown. The 16.7% AlON sample displays ^{27}Al NMR peaks at 65 and 14 ppm attributed to AlO_4 and AlO_6 sites, respectively. The 14 ppm peak is asigned to 6-coordinate AlO_6 sites of unreacted Al_2O_3 (Figure 1a), while the 65 ppm peak is due to AlO_4 sites similar to those in γ-Al_2O_3. An AlN_4 peak at 114 ppm analogous to the spectrum of AlN (Figure 1g) is not observed, since AlN is completely absent in this region of the phase diagram.[27] The 35.7% sample shows four resolved peaks: an intense asymmetric peak skewed to the high-shielding side at 14.5 ppm, a broad resonance at 66.3 ppm, a broad partially resolved resonance at 106 ppm and a weak-intensity peak at 114 ppm. This sample corresponds to the reaction ratio of AlN/Al_2O_3 needed to produce γ-AlON.[27] Comparison of this spectrum, attributed to γ-AlON, with the ^{27}Al NMR spectrum of γ-alumina (not shown; peaks at 9.4 and 66.6 ppm) indicates that these materials both show peaks in the 10–14 ppm region and in the 66–67 ppm region, probably due to AlO_6 and AlO_4 aluminum sites, respectively.[8] These two spectral features are common for spinel-type γ-alumina samples, although the octahedral/tetrahedral ratios of the peak intensities are different, i.e., 3.27 for γ-AlON and 2.52 for γ-alumina for the conditions under which these spectra were obtained. In addition to these two peaks, the ^{27}Al NMR spectra of the AlON prepared at 35.7 mol % AlN also shows a peak at 114–117 ppm that is assigned to the AlN_4 sites in unreacted AlN, and a resolved, low-intensity peak skewed to the high-shielding side of the 114–117 ppm peak at 106 ppm. XRD analysis of the 35.7% AlON sample shows a mean AlN content of 3.6%, which supports the assignment of the 114 ppm peak to AlN_4 sites of unreacted AlN in the 35.7% AlON (compared to 4.4% peak area for the 114 ppm NMR peak, Figure 1). The 106 ppm peak is in a chemical shift region between that observed for local AlO_4 and AlN_4 aluminum atom environments and is tentatively assigned to AlN_3O sites. This chemical unit may be a structural unit of γ-AlON or an $O_3Al{-}O{-}AlN_3$ interfacial unit formed between reacted aluminum nitride and aluminum oxide particles.

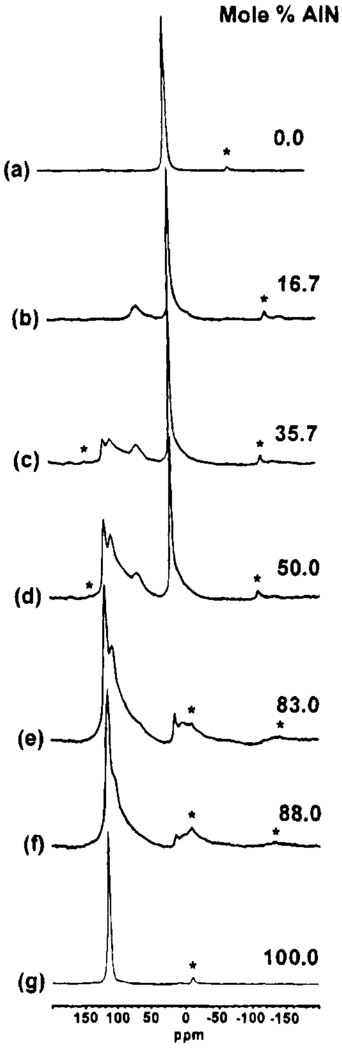

Figure 1. ^{27}Al MAS NMR at 14 T of various AlON powders prepared at different AlN/Al_2O_3 reaction ratios. Mole % AlN: (a) 0.0, (b) 16.7, (c) 35.7, (d) 50.0, (e) 83.0, (f) 88.0, and (g) 100.0 (* denotes spinning sidebands).

The 50.0 and 83.0 mol % AlON samples (excess AlN region of the phase diagram[27]) also yield ^{27}Al NMR peaks at 115–117, 106, 67–68, and 14 ppm, which are assigned to AlN_4, AlN_3O, AlO_4, and AlO_6, respectively. The 88 mol % sample also shows peaks at 115, 106, and 14 ppm attributed to AlN_4, AlN_3O, and AlO_6 sites, respectively, but no 67–68 ppm peak; instead, a peak at 77 ppm is seen that is assigned to $AlNO_3$ sites. In addition, the various AlON samples all show some resonance intensity in the 10 to −10 ppm region that may be due to the effects of second-nearest-neighbor

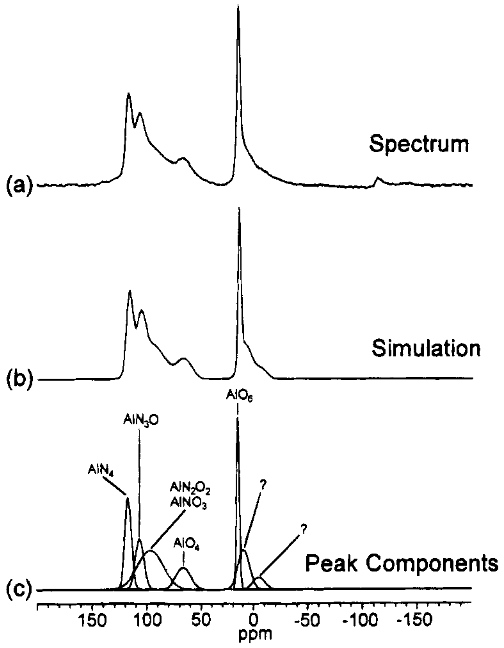

Figure 2. ^{27}Al MAS NMR results at 14 T for AlON powders prepared at 50 mol % AlN: (a) experimental spectrum, (b) simulated spectrum, and (c) peak components from deconvolution analysis.

AlO_4 tetrahedra on the chemical shifts of the AlO_6 octahedra.

A deconvolution analysis of the experimental ^{27}Al NMR spectrum of the 50 mol % AlON sample is shown in Figure 2. The simulated spectrum (Figure 2b) obtained from deconvolution analysis using Gaussian peak components shows two peaks (Figure 2c) with ^{27}Al NMR chemical shifts of 106 and 96 ppm located between the 114 (AlN_4) and 66 ppm (AlO_4) resonances. These two NMR peaks are empirically assigned to local four-coordinate AlN_3O and either AlN_2O_2 or $AlNO_3$ chemical environments. The peaks denoted "?" are not spinning sidebands since they are not shifted in the NMR spectrum with changes in the spinning speed; but rather, their resonance intensities and peak positions are similar to those observed for similar peaks in the ^{27}Al NMR spectrum of γ-alumina. These resonances are probably due to octahedral AlO_6 sites with second-nearest-neighbor aluminum atoms that may be six-coordinate, or more likely are four-coordinate, consistent with the spinel lattice structure of γ-alumina materials. The use of Gaussian deconvolution analysis instead of second-order powder patterns is consistent with the interpretation that chemical shift dispersion, not second-order quadrupolar effects, is the dominant line-broadening mechanism for these AlON measurements at 14 T. The success of this type of simulation (Figure 2) implies that this interpretation may be the correct one.

Table 1. Tentative MAS ^{27}Al NMR Structural Assignments

^{27}Al chemical shift, ppm	structural unit	aluminum materials
14	AlO_6	Al_2O_3 and γ-AlON
66	AlO_4	γ-AlON
96	$AlNO_3$	AlON or Al_2O_3/AlN composite
96	AlN_2O_2	AlON or Al_2O_3/AlN composite
106	AlN_3O	AlON or Al_2O_3/AlN composite
114–117	AlN_4	AlN

A summary of the tentative ^{27}Al NMR spectral assignments is given in Table 1.[7] The results of the ^{27}Al chemical shift assignments for the AlON system of Table 1 differ from the work of Smith[32] on the SiAlON system in several aspects. First, while the assignments of the chemical shifts for the AlO_4 and AlO_6 sites are nearly identical, the resolved peak at 106 ppm assigned to AlN_3O sites in this work at 14 T differs from the 93 ppm (AlN_3O) and 106 ppm (AlN_4 of AlN) peak assignments of Smith[32] at 11.7 T. The agreement between the XRD and NMR AlN content of the 35.7% AlON support our assignment of the AlN_4 resonance between 114 and 117 ppm to AlN_4 sites of AlN, while our assignment of the resolved 106 ppm peak to AlN_3O sites in γ-AlON may be contrasted with the decreased peak resolution of the 11.7 T spectral peaks observed by Smith.[32] Second, the 96 ppm peak in our work is assigned to a mixture of AlN_2O_2 and $AlNO_3$ sites in γ-AlON that are not resolved, presumably due to chemical shift dispersion effects, while the work of Smith[32] assigns shoulder resonances of poorly resolved spectra of SiAlONs materials to AlN_2O_2 (at 89 ppm) and AlO_3N (at 75 ppm) sites. Differences in these assignments are probably a consequence of the field differences in the measurements as well as chemical shift dispersion effects that would be more prominent in SiAlON materials (second-nearest-neighbor Si and Al atoms) relative to the AlON materials (only second-nearest-neighbor Al atoms).

The results of these at 14 T ^{27}Al NMR investigations indicate that sufficient spectral resolution can be obtained via MAS at this field to distinguish and assign four-coordinate aluminum oxynitride moieties in AlON materials. Further studies of these systems are in progress to develop a more detailed chemical understanding of the structural chemistry and MAS ^{27}Al NMR characteristics of these unique ceramic materials.

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