^{29}Si NMR Characterization of α- and β-Silicon Nitride

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Abstract: Fine structure in the ^{29}Si MAS NMR spectra of Si_3N_4 has been observed, prompting a reevaluation of the current interpretation of Si_3N_4 spectra. On the basis of variable field studies, this fine structure indicates the presence of quadrupole-perturbed residual dipolar coupling to ^{14}N. This is apparently the first such observation in ^{29}Si NMR. The peaks in the spectra of α- and β-Si_3N_4 are shown to arise from differences in the non-nearest-neighbor environments. Arguments based on a "sphere of influence" approach appear to be an attractive interpretive tool for these and similar ceramic materials. Some speculation is also presented concerning the relationship between the ^{29}Si–^{14}N splitting and the structure of Si_3N_4. The magnetic field dependence of Si_3N_4 spectra emphasizes the point that high fields are important in the study of ceramics, even for nuclides that are spin $^1/_2$.

High-performance ceramics are an important class of engineered materials due to their excellent mechanical and thermal properties. Among the most important of these is silicon nitride (Si_3N_4). Si_3N_4 ceramics exhibit high strength at high temperatures, good thermal stress resistance, and relatively good resistance to oxidation. Efforts to optimize these properties have largely centered on advanced processing techniques.[1] However, the need to relate performance with atomic level chemistry and structure is becoming increasingly important.[2]

Solid-state NMR has proven to be both powerful and versatile in the characterization of ceramic materials.[3-5] NMR is capable of identifying crystalline and amorphous phases, determining the structure of such phases, and studying the chemistry of these phases at the atomic level. For example, early ^{29}Si NMR studies of Si_3N_4 revealed that NMR can readily distinguish the crystalline forms,[6,7] accurately quantitate the amorphous content,[7] and monitor the effects of sintering.[8]

One of the most attractive features of NMR is its sensitivity to the local environment about the nucleus being observed. The most common NMR parameter indicative of this sensitivity is chemical shift. As a result, a number of correlations[9-17] between chemical shift and structural features such as bond angle[9-12] and type of nearest[13-15] and non-nearest-neighbor environments[17] have been derived for solid inorganic systems. The sensitivity of NMR to local structure, however, is not merely limited to chemical shift effects. In fact, subtle structural details are also available in NMR data such as spin–spin couplings and relaxation phenomena. For example, when a spin $^1/_2$ nucleus experiences dipolar coupling to a quadrupolar nucleus, an NMR line splitting is observed. The size of this splitting is dependent upon, among other things, the distance between the two nuclei.[18,19] Detailed analyses of NMR data such as chemical shift and coupling constants hold considerable promise for the structural analysis of new ceramic phases and amorphous systems.

The purpose of this paper is to present a detailed examination of α- and β-Si_3N_4 by ^{29}Si NMR, including the first reported observation of ^{29}Si–^{14}N residual dipolar coupling. This observation has prompted a reevaluation of the current spectral interpretation of Si_3N_4 and has suggested an attractive interpretive tool for the NMR characterization of ceramic phases. Finally, this work demonstrates the need to study many ceramic systems, including spin $^1/_2$ nuclides, at high magnetic fields.

Experimental Section

Silicon-29 NMR spectra were acquired under magic-angle spinning (MAS)[20-22] conditions with single 70–90° pulses and pulse delays of 1

h. Pulse delays of 1 h were required to ensure total magnetization recovery and, therefore, accurate quantitative data.[7] All spectra were externally referenced relative to TMS at 0 ppm. The spectra presented in the text were acquired on a Varian XL200 (39.6 MHz), a Chemagnetics CMX 300 (59.5 MHz), and a Bruker MSL400 (79.5 MHz). The sample of α-Si_3N_4 was a previously studied,[7] commercially available powder (GTE SN502). The sample of β-Si_3N_4 was also a comercially available powder (UBE SNWB). The 79.5-MHz spectra presented in Figures 2 and 3 were digitally manipulated with a 5-Hz resolution enhancement. This was done to reveal more effectively the nature of the fine structure and resulted in a negligible decrease in signal to noise and no additional peaks. The spectra presented in Figure 1 were digitally manipulated with 10–20-Hz exponential line broadening, as has been used in the past.[7]

Background

There are two crystalline forms of silicon nitride, α and β.[23-26] The α phase is converted to β during liquid-phase sintering. In both structures each silicon is tetrahedrally bound to four nitrogens. In addition, both structures consist of interleaved sheets of 8- and 12-membered rings of silicon and nitrogen. In the α form, each alternate sheet is inverted and offset slightly with respect to the underlying sheet, creating two crystallographically unique silicon

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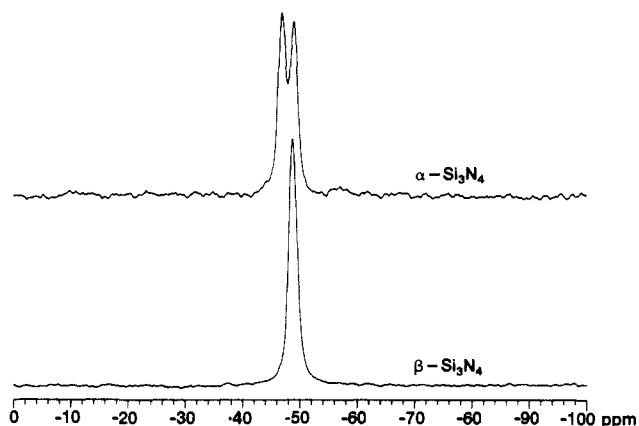‖ Present address: Washington Research Center, W. R. Grace & Co., 7379 Route 32, Columbia, MD 21044.

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Figure 1. ^{29}Si MAS NMR spectra of α- and β-Si$_3$N$_4$ obtained at 59.5 MHz (300-MHz ^{1}H frequency).

sites.[23-26] A ^{29}Si NMR spectrum of α-Si$_3$N$_4$, obtained at 59.5 MHz (300-MHz ^{1}H frequency), is given in Figure 1. The spectrum consists of two peaks centered at roughly –46.8 and –48.9 ppm. Early ^{29}Si NMR studies[5-9] of α-Si$_3$N$_4$ have assigned these two peaks to the presence of mixtures or to slight differences in the SiN$_4$ tetrahedra.

In the β form of silicon nitride, the interleaved sheets of Si and N are stacked in a regular manner. The result is that there is only one unique Si site.[23-26] As can be seen in Figure 1, there is only one peak in the ^{29}Si NMR spectrum of β-Si$_3$N$_4$ with a ^{29}Si chemical shift of roughly –48.7 ppm. Note that the chemical shifts for the α and β structures are similar, reflecting the similarities in nuclear environment.

Observation of Fine Structure

As discussed above, the ^{29}Si MAS NMR spectrum of α-silicon nitride (α-Si$_3$N$_4$) contains two major peaks. However, a careful and thorough analysis of the NMR data reveals that the two main peaks of the α-Si$_3$N$_4$ spectrum show additional fine structure. ^{29}Si MAS NMR spectra of α-Si$_3$N$_4$ obtained at three fields are given in Figure 2. The three fields used in this study are 39.6 MHz (200-MHz ^{1}H frequency), 59.5 MHz (300-MHz ^{1}H frequency), and 79.5 MHz (400-MHz ^{1}H frequency). The spectra presented in Figure 2 (and Figure 3) represent high signal-to-noise data with no digitally added line broadening. Note the existence of substantial fine structure. At 39.6 MHz, this fine structure effectively eliminates the distinction between the major resonances. One potential explanation for the fine structure is the presence of microdomains that have the effect of slightly shifting the isotropic resonance. If this were the case, each spectrum would represent a superposition of spectra from four or five different microdomains. In addition, the position of the lines would be field independent since they would result from a "chemical shift" effect. However, a detailed comparison of the spectra in Figure 2 reveals a field dependence. This is best seen by comparing the downfield region where the resolution is the greatest. With use of only the resolved downfield peaks, the splitting was found to be 32 Hz at 39.6 MHz, 29 Hz at 59.5 MHz, and 24 Hz at 79.5 MHz.

Magic-angle spinning[20-22] is widely applied in solid-state NMR to remove sources of inhomogeneous line broadening such as chemical shift anisotropy, heteronuclear dipolar coupling, and first-order quadrupolar effects. This technique is often not entirely efficient. A common example occurs with a spin $^1/_2$ nucleus experiences dipolar coupling to a quadrupolar nucleus. The failure of MAS to remove this interaction is related to the introduction of geometrical factors other than $(\theta - 1)$, for which the magic angle is no longer "magic". Residual dipolar coupling is field-dependent and scales inversely with respect to field strength.[18,19] The most common example is for a ^{13}C adjacent to nitrogen.[18,19,27-35] In
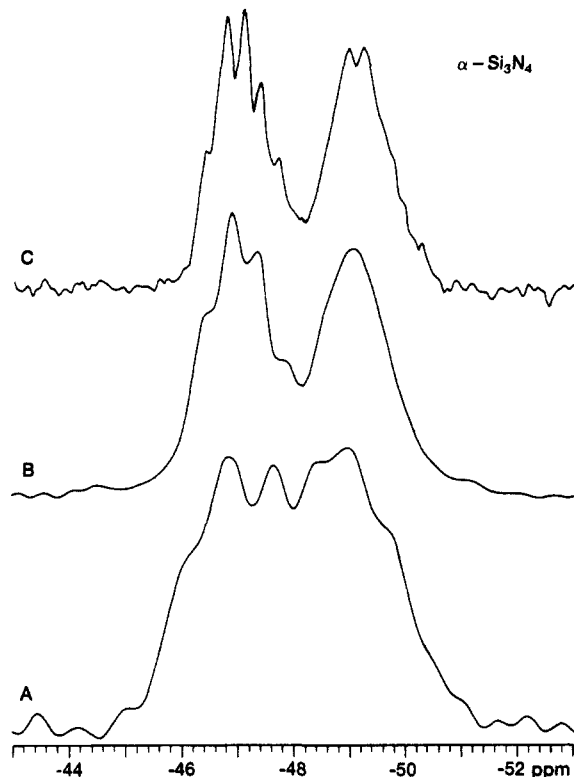

Figure 2. ^{29}Si MAS NMR spectra of α-Si$_3$N$_4$ obtained at (A) 39.5, (B) 59.5, and (C) 79.5 MHz (200-, 300-, and 400-MHz ^{1}H frequency).
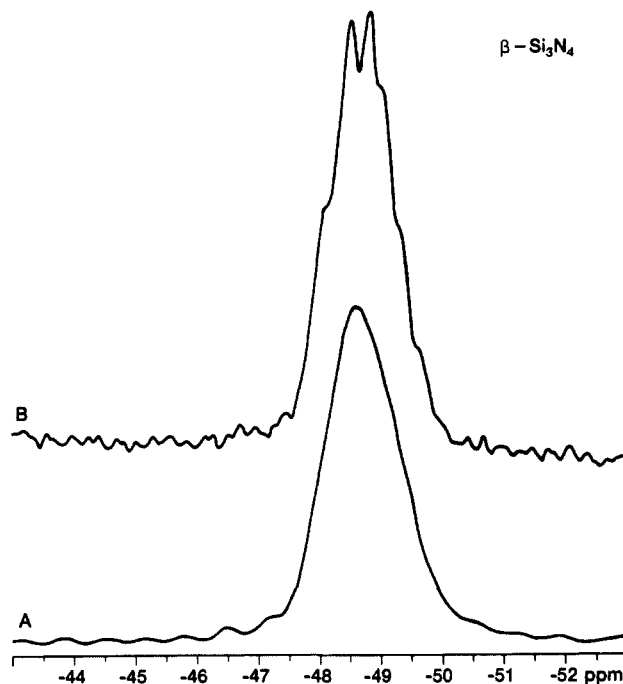
Figure 3. ^{29}Si MAS NMR spectra of β-Si$_3$N$_4$ obtained at (A) 59.5 and (B) 79.5 MHz (300- and 400-MHz ^{1}H frequency).

general, the ^{14}N effect typically broadens the NMR line or creates an asymmetry. However, distinct resolvable splittings are observed,

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for example, in crystalline small organic molecules and peptides.

If the fine structure observed in Figure 2 is due to $^{29}Si-^{14}N$ residual quadrupole-perturbed dipolar coupling, then the size of the splitting should be inversely proportional to field strength.[18,19] An examination of the data reveals that the correlation between the splitting at 79.5 MHz (24 Hz) and 59.5 MHz (29 Hz) provides a reasonable fit. The splitting at 39.6 MHz (32 Hz), however, does not correlate as well. In α-Si_3N_4 each ^{29}Si is tetrahedrally bound to four ^{14}N, resulting in a complex splitting pattern. This pattern is expected to contain as many as 16 lines depending on the size and sign of the coupling, as well as potential peak overlap.[18] Thus, the ^{29}Si NMR spectrum of α-Si_3N_4 containing quadrupole-perturbed residual dipolar coupling is expected to be a superposition of 32 lines. In addition, some scalar J coupling may also be present. As a result, the measured splittings may be complicated, especially at 39.6 MHz where overlap is expected to be the most severe. In spite of this limitation, it is reasonable to attribute the changes in fine structure to the presence of residual dipolar coupling to ^{14}N for two reasons: (1) the expected dominance of this interaction for a Si tetrahedrally bound to four nitrogens and (2) the observed spectral changes with varying field strength (Figures 2 and 3), especially between 59.5 and 79.5 MHz. While the effects of residual dipolar coupling to quadrupolar nuclides have been extensively observed for ^{13}C in organic systems,[18,19,27-35] similar effects for other spin $^1/_2$ nuclides have only been rarely reported.[36-38] This appears to be the first for ^{29}Si.

A more detailed examination of the ^{29}Si NMR spectrum of β-Si_3N_4 reveals a nonsymmetric line shape at 59.5 MHz and a clear splitting at 79.5 MHz. This is illustrated in the spectra given in Figure 3. The splitting observed at 79.5 MHz was found to be 24 Hz. Unfortunately, it was not possible to obtain a similar spectrum at 39.6 MHz. Because of the strong structural similarities between the α and β forms, it is reasonable to attribute the observed changes in splitting and line shape to the presence of $^{29}Si-^{14}N$ residual dipolar coupling.

The observation of residual $^{29}Si-^{14}N$ dipolar coupling in the ^{29}Si MAS NMR spectra of α- and β-Si_3N_4 has important implications for the study of ceramic systems by NMR. As seen in Figure 2, this coupling can effectively remove desired resolution among the chemically inequivalent sites in spectra acquired at too low a field. On the basis of the data presented here, at least a 59.5-MHz operating frequency appears to be necessary to maintain discrimination among different sites in Si/N ceramic materials. The drive toward higher fields for analysis of ceramic materials can thus be justified on three grounds: increased sensitivity, reduction of quadrupolar effects even for nonquadrupolar nuclides, and an increased spread in chemical shift for discrimination among different sites.

Interpretation of Si_3N_4 Spectra

The ^{29}Si NMR spectrum of highly crystalline silicon nitride can be considered as a superposition of three major chemically shifted lines: two from the α phase and one from the β phase. On the surface, one can easily account for the number of observed peaks on the basis of the number of crystallographically distinct sites. However, a more thorough investigation is required to explain the spectra in terms of local Si environments and to account for the differences between the α and β forms. Such an understanding is pivotal for future studies of related systems and of the effects of processing on Si_3N_4 local atomic structure.

For the purpose of this discussion, the two unique Si sites in α-Si_3N_4 will be referred to as $Si\alpha1$ and $Si\alpha2$ (from the identities given in ref 24). The unique site in β-Si_3N_4 will be simply referred to as $Si\beta$. Consider first, the two-peak pattern observed for α-Si_3N_4. Previous studies[6,7] have attributed this pattern to small
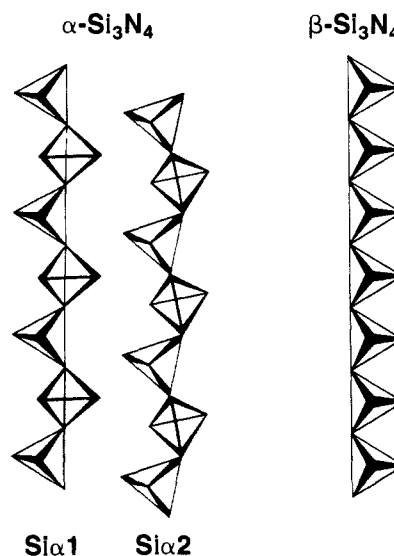
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Figure 4. Schematic representation of the SiN_4 tetrahedra stacking sequences in α- and β-Si_3N_4.
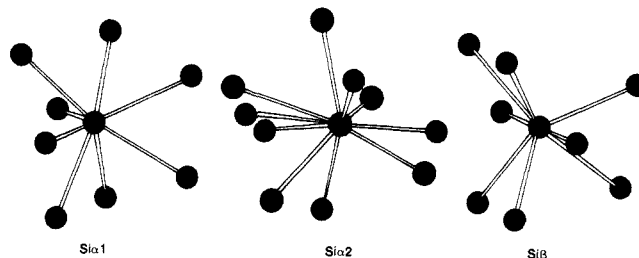

Figure 5. Schematic representation of the neighboring silicon environments for each silicon type in α- and β-Si_3N_4 within 3.80-Å sphere of influence (see text).

differences in the SiN_4 tetrahedra between $Si\alpha1$ and $Si\alpha2$. For example, the average Si–N bond length is 1.747 Å at $Si\alpha1$ and 1.740 Å at $Si\alpha2$. With this argument, the chemical shift differences would arise from a spatial difference of only 0.007 Å. This difference is probably not significant since it is smaller than the error limits of even the most careful X-ray structure determination. In addition, the average Si–N bond length in α-Si_3N_4 is 1.732 Å. If bond length was the dominant chemical shift determining interaction, then we would not expect to find the $Si\beta$ (1.728 Å) peak coincident with one of the two α-Si_3N_4 (1.740, 1.747 Å) resonances, as observed in Figure 1. Similar arguments can also be used to eliminate average bond angle from consideration. In light of these simple discrepancies, we were led to find alternative chemical shift interpretations based on non-nearest-neighbor environments.

Since each silicon in both phases is tetrahedrally bound to four nitrogens, it is reasonable to assume that any differences in non-nearest-neighbor environment would be related to the arrangement of surrounding silicon nuclei. This is, in fact, the case. In β-Si_3N_4, the SiN_4 tetrahedra are oriented such that the edges are in a straight line parallel to the unit cell c axis. In α-Si_3N_4, there are two types of stacking sequences that are distorted with respect to one another by about 60–70° around the c axis. Schematic representations of the SiN_4 tetrahedra stacking sequences in α- and β-Si_3N_4 are given in Figure 4. One can see, by inspection, that the surrounding network is different for $Si\alpha1$, $Si\alpha2$, and $Si\beta$.

Using figures such as these and the available crystallographic data,[23-26] we find that all three silicon types have eight Si neighbors within a sphere of 3.00 ± 0.12 Å. For $Si\alpha1$ and $Si\beta$, the next nearest silicon neighbor(s) resides at an outer surface of 3.80 ± 0.07 Å. The $Si\alpha2$ nucleus also has a neighbor residing on the 3.80-Å surface. However, between the 3.00- and 3.80-Å surfaces are two additional silicon neighbors at 3.60 Å. These additional neighbors are absent for the cases of $Si\alpha1$ and $Si\beta$. Thus, within

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a 3.80-Å "sphere of influence", Siα1 and Siβ have eight neighboring silicons while Siα2 has ten.

The silicon environments within the 3.8-Å sphere of influence for each silicon type are illustrated in Figure 5. The fact that Siα1 has eight neighbors and Siα2 has ten can be used to explain the two-peak spectrum shown in Figure 1. Using the above argument, we would expect the chemical shifts of Siβ and Siα1 to be the same, since they both have eight silicon neighbors. In fact, the Siβ peak (-48.7 ppm) is virtually coincident with one of the two α-Si3N4 peaks (-46.8, -48.9 ppm). Thus, we are led to the conclusion that in α-Si3N4 the peak at -48.9 ppm can be assigned to Siα1 and the peak at -46.8 ppm to Siα2. The sphere of influence approach outlined above has resulted in the first chemical shift assignments for α- and β-Si3N4.

Residual Dipolar Coupling

It is beyond the scope of this work to present a detailed analysis of the observed $^{29}Si-^{14}N$ residual dipolar coupling in terms of the structure of Si3N4. However, some brief comments are worthy of note at this time. With the same formalism previously[18] adopted for an isolated $^{13}C-^{14}N$ pair, the size of the splitting (S) is given by

$$S = \tfrac{9}{20}(DX/Z_N)[(3\cos^2(\beta - 1)) + \eta\sin^2\beta\cos 2\alpha] \quad (1)$$

Here, D is the dipolar coupling constant, X is the quadrupole coupling constant, Z_N is the Zeeman frequency of ^{14}N in the applied field, and η is the asymmetry parameter of the electric field gradient (EFG) tensor. β and α are the polar and azimuthal angles that define the orientation of the internuclear vector in the principal axis system of the EFG at the ^{14}N nucleus with respect to the direction of B_0. The dipolar coupling constant (D) is inversely proportional to the cube of the Si–N internuclear distance, r^{-3}.

In Si3N4, each ^{29}Si experiences the effect of four ^{14}N nuclei, with the result of substantially complicating eq 1. However, one should note that the size of the splitting depends upon geometric (β, α, r) and energetic (X, η, Z_N) factors. To a first approximation, it seems reasonable to assume that the energetic factors (X, η, Z_N) are equivalent or similar at Siα1, Siα2, and Siβ for a given applied magnetic field, since the values for X and η should be dominated by interactions associated with the SiN4 tetrahedra and Z_N is constant. This being the case, then differences in the splitting between Siα1, Siα2, and Siβ would be due solely to differences in geometric factors. With this information, it may be possible refine the structural details of Si3N4. This type of analysis has been very successful in organic systems,[18,19,27,30,32-34] and work along these lines for Si3N4 is underway.

Two intriguing observations suggest that such an analysis would provide unique and detailed information. As we have shown above, the chemical shift of Siα2 (-46.8 ppm) is distinct from that of Siα1 (-48.9 ppm) and Siβ (-48.7 ppm). In terms of chemical shift, Siα1 and Siβ form a pair. However, in considering the size of the splitting determined by the separation between maxima at 79.5 MHz, we find that Siα2 (24 Hz) and Siβ (24 Hz) form a pair, while Siα1 (20 Hz) remains distinct. This suggests that the Si–N geometric factors are similar for Siα2 and Siβ but distinct from those for Siα1. The second intriguing observation concerns

the apparent line width of the "unique" resonances in these spectra. The apparent line width of the three major resonances for Siα1, Siα2, and Siβ is not the same at a given field. For example, by comparing the line width of the major resonances at 79.5 MHz in Figures 2 and 3, one can see that the resonance for Siβ is the narrowest. Subtleties in splittings, peak positions, and line width have the clear potential to provide unique structural information in Si3N4 systems.

Finally, it should be noted that the data in Figures 2 and 3 can also be used to provide a rough estimate of the quadrupolar coupling constant. On the basis of the data obtained at 79.5 MHz, we find an estimate for X to be 0.23 MHz.

Sphere of Influence

The chemical shift assignments for α- and β-Si3N4 were determined above from a sphere of influence approach. By examining the non-nearest-neighbor network surrounding each silicon site, we were able to identify the sphere of influence that gave rise to different chemical shifts for nuclei with identical neighbors. It should be noted that a similar approach has also proven successful in the related highly refractory ceramics, LaSi3N5 and SiC. In a separate study, Hatfield and co-workers have shown[39] that this sphere of influence is roughly 4 Å in LaSi3N5. Hartman and co-workers[40,41] have shown that the sphere of influence in SiC is roughly 5 Å. In this study, the sphere about Si3N4 is 3.8 Å. These examples emphasize two important points. The first is that a sphere of influence approach is an attractive interpretive tool for the characterization of ceramic materials containing nuclei with equivalent nearest neighbors. The second, and perhaps more important point, is that in some ceramic materials ^{29}Si chemical shifts can be sensitive to influences as far away as 5 Å. This has major implications for examining the local effects induced by technologically significant forces such as thermal and mechanical stresses.

Conclusions

The features in the ^{29}Si NMR spectra of α- and β-silicon nitride have been shown to arise from a combination of non-nearest-neighbor effects and the presence of residual quadrupole-perturbed dipolar coupling. The NMR results offer a detailed and self-consistent characterization of these technologically important materials and help lay the groundwork for future studies of new ceramic systems. The observation of non-nearest-neighbor-induced chemical shift differences also reveals that ^{29}Si NMR can be used to monitor structural changes on the order of 5 Å.

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