Broadline NMR of Structural Ceramics

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1 Introduction

Magic angle spinning (MAS) has become the most widely used NMR technique for the study of inorganic solids. This popularity has come about because MAS removes the effects of chemical shift anisotropy, permitting acquisition of chemical shift spectra in these materials. However, there are two weaknesses to the MAS technique, which are accentuated in the study of structural ceramics.

The first difficulty with MAS is that rotation at the magic angle does not remove the effects of second order quadrupolar broadening of the central $(+1/2 \longleftrightarrow -1/2)$ transition [1]. This has limited the applicability of NMR for half-integral quadrupolar nuclei like ^{27}Al, ^{11}B, ^{17}O, and ^{91}Zr, which are important constituents of ceramics. While recent work has shown that the effects of second order quadrupolar broadening are reduced by working in larger magnetic fields [2], or by employing more sophisticated spinning techniques [3], these solutions can be difficult and expensive to implement.

The other important limitation of MAS, also true of other sample spinning techniques, is that the physical form of the sample is restricted to fine powders, homogeneous cylinders, or chunks of material packed in an NMR inert powder of similar density. All of these forms present problems when working with ceramics. Many ceramics are challenging to machine or grind due to their extreme hardness. Even when grinding is possible, other requirements may limit the use of powders. For example, in determining the effect of long term or repeated heating of a ceramic, heating a powdered sample may provide unreliable data because of surface oxidation. Packing large chunks of sample in a powder with similar density becomes time consuming when a number of samples have to be studied, or the sample is being subjected to heating which changes its chemical or phase composition.

We have used broadline NMR of static samples as an alternative to MAS for samples with large quadrupolar splittings. In favorable cases, the resulting powder pattern, produced by the first order quadrupolar coupling [1], directly yields information about the electronic environment of the nuclei under investigation. Although the broadline technique for quadrupolar nuclei is not new, having been first applied over forty years ago [4], it is a simple, useful technique which is often overlooked. It is generally applicable only to nuclei with large quadrupolar splittings, which provide the most difficulty for MAS; accordingly the broadline technique can serve as a complement to MAS. The work reported here demonstrates that, for many ceramics, broadline spectra can provide useful structural information.

2 Experimental

All spectra were recorded on a Bruker MSL-300 spectrometer, equipped with the BC-131 5 MHz 9 bit digitizer. The spectrometer operates at 96 MHz for ^{11}B, and 78 MHz for ^{27}Al. A standard Bruker multinuclear solenoid probe was used for the broadline spectra. Free induction decays were collected after a single 1 μs pulse. Although the excitation profile of this pulse drops to zero at 1 MHz, reasonable sensitivity is still maintained for satellites 600 to 700 kHz off resonance. The delay time before the start of data collection was typically 5 μs. Usually the first 2 or 4 points of the FID were discarded because of pulse breakthrough. The relatively long deadtime usually prohibits observation of the broad pedestal portion of the powder pattern, but the cusps, which by themselves are sufficient to characterize the quadrupolar splitting, do not appear greatly affected. The width of the spectral window was 2.5 MHz (± 1.25 MHz) for ^{11}B and 1.67 MHz (± 0.833 MHz) for ^{27}Al. A filter bandwidth of 1 MHz, the largest available on the MSL-300 in quadrature mode, was used. Additional data collection parameters used for individual spectra are noted in the figure captions.

Quadrupolar splittings were measured from a point on the outside edge of one satellite, at about 80% of the satellite peak height, to the corresponding point on the other satellite of the pair. The value 80% was obtained by

comparing simulated powder patterns with and without Gaussian broadening. Measurements between the maxima of the satellites give values that are smaller than the true value, because dipolar broadening shifts the position of the maxima toward the central transition.

3   Results and Discussion

The ^{27}Al ($I = 5/2$) resonance in corundum (α-Al$_2$O$_3$) has been observed by a variety of NMR techniques [4], [5]. For comparison, we show an ^{27}Al powder pattern in Figure 1. For this sample, excellent sensitivity is obtained
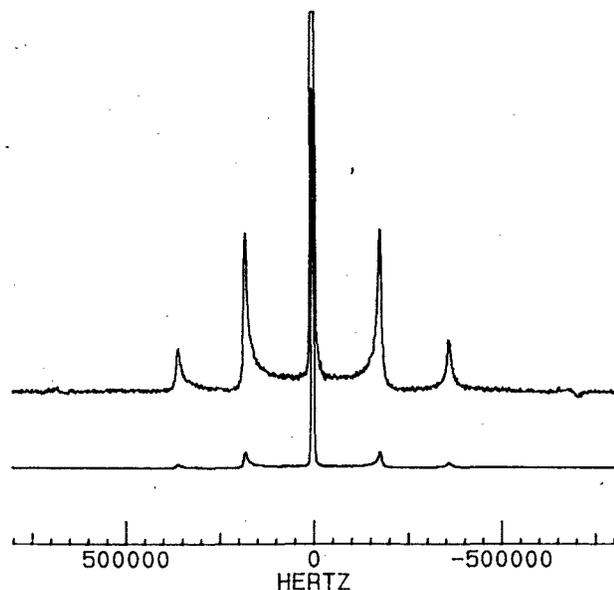

Fig. 1. ^{27}Al powder pattern of α-Al$_2$O$_3$. 32 scans were co-added, using a recycle delay of eight seconds. The upper trace is a magnification of the lower trace by ten.

with about four minutes of signal averaging. From the splitting of each pair of satellites, we find e^2qQ/h = 2.42±0.02 MHz and η = 0.0, in fair agreement with the values determined by Pound [4]. The slight reduction in precision of these numbers, as compared with Pound's work, is offset by the speed and ease with which the results can be obtained on a standard solids NMR spectrometer.

One of the many applications for NMR of ceramics is to follow high temperature phase changes and reactions. We have studied the calcination of gibbsite (Al(OH)$_3$) to form α-Al$_2$O$_3$, which is a complex and poorly understood process [6]. Results of preliminary work to determine the applicability of broadline NMR to this problem are shown in Figure 2. The ^{27}Al spectrum of the unheated material (determined by X-ray diffraction to be at least 90% gibbsite) shows five pairs of satellite transitions, with splittings of 96 kHz, 397 kHz, 517 kHz, 608 kHz, and 960 kHz. The peaks near ±700 kHz, which appear in many ^{27}Al spectra, are probably artifacts. Assuming three sites are present, the splittings can be paired as follows: 397 and 608 kHz, from a site with e^2qQ/h = 2.1 MHz and
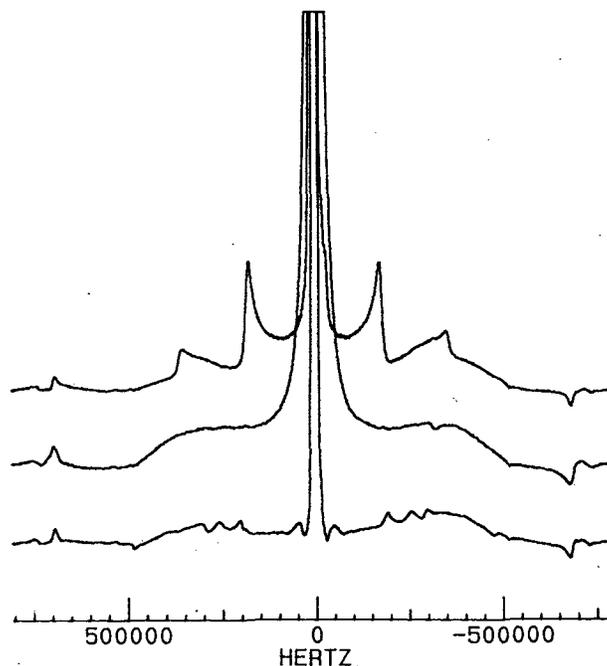

Fig. 2. ^{27}Al powder patterns of gibbsite (Al(OH)$_3$) before heating (lower trace), after heating at 700 C for 35 minutes (middle trace), and after further heating at 1070 C for 16 hours (upper trace). Each trace represents 1 to 2 hours of signal averaging, with a one second recycle delay.

η = 0.5; 517 and 960 kHz, from a site with e^2qQ/h = 3.2 MHz and η = 0.2. The other possible pairing gives one site with e^2qQ/h = 1.8 MHz (η = 0.7) and one with e^2qQ/h = 3.3 MHz (η = 0.5). Only one pair of satellites from the remaining site is visible, with a splitting of 96 kHz. Two possibilities may explain this absence of a second pair. If e^2qQ/h = 0.36 MHz and $\eta \sim 1$, the second pair of satellites will overlap the observed pair. If e^2qQ/h = 0.32 MHz and $\eta \sim 0$, the second pair will have a splitting of about 48 kHz, and will not be resolved from the central transition. An accurate quantification of the relative population of the three sites from this data is difficult, but one can say the three sites are roughly equally populated. The nuclei with the larger couplings are probably in octahedral environments, as expected from the reported structure, in which all the aluminum nuclei are in octahedral environments [7]. The relatively large values of η can be attributed to hydrogen bonding, which distorts the octahedral symmetry of the aluminum sites in gibbsite. The smaller quadrupolar coupling is about an order of magnitude less than that typically observed for octahedral sites (*cf.* α-Al$_2$O$_3$), so is probably due to a slightly distorted tetrahedral site. From a simulation of MAS results at 6.35 T [2], it appears that only two sites are observed by MAS, both of which are octahedral.

Conversion of Al(OH)$_3$ to α-Al$_2$O$_3$ involves several intermediate phases such as boehmite, χ-Al$_2$O$_3$, γ-Al$_2$O$_3$, κ-Al$_2$O$_3$, δ-Al$_2$O$_3$, and θ-Al$_2$O$_3$, with formation of α-Al$_2$O$_3$ reportedly occurring at 1140 C [6]. The middle

trace in Figure 2 shows the effect of heating gibbsite at 700 C for 35 minutes. The satellites attributed to gibbsite have disappeared, and the central transition is flanked by broad features indicative of amorphous material. The width of the central transition, which may be attributed to the second order quadrupolar interaction, corresponds to values of e^2qQ/h ranging up to 4.4 MHz. After further heating for 16 hours at 1070 C, the upper spectrum in Figure 2 was obtained. The sharp features indicate a substantial amount of amorphous material has converted to α-Al_2O_3. This contradicts the notion that conversion to α-Al_2O_3 occurs only at temperatures above 1140 C. However, the conversion is quite sluggish at 1070 C. These broadline spectra demonstrate conversion of gibbsite to α-Al_2O_3, but unfortunately information on the intermediate phases cannot be obtained from these spectra. Chemical shift spectra obtained with sample spinning will probably not be useful in determining which phases are present in the amorphous intermediate stage, considering the large quadrupolar couplings which appear to be present.

Another problem of interest is the oxidation of ceramics at high temperatures. When boron nitride (BN) is heated in an oxidizing environment, conversion to boron oxide gradually takes place. Since both BN and B_2O_3 have large quadrupole couplings [8], [9], one can expect difficulty in resolving the signals from the two materials in MAS spectra. In fact, the second order quadrupolar broadening is on the order of 50 ppm, based on a Larmor frequency of 96 MHz, which is a significant fraction of the expected range of chemical shift for ^{11}B. To demonstrate that broadline NMR may prove more useful in monitoring the oxidation of BN, we prepared a mixture of roughly equal amounts of BN and $B(OH)_3$. Boric acid was used instead of boron oxide because the fine powder required for MAS work is not hygroscopic, as is the B_2O_3 powder, and the boric acid was readily available. Boric acid has a quadrupolar splitting of 1282 kHz, similar to that of B_2O_3 (1308 kHz).

^{11}B ($I = 3/2$) MAS and broadline spectra of the boron nitride/boric acid mixture were recorded, and are shown in Figures 3 and 4 respectively. From the MAS spectrum, one can see that the single peak observed is a composite of several resonance lines. However, one would have difficulty determining which boron species are present in the sample, or even how many species there are. This spectrum should be contrasted with the broadline spectrum shown in Figure 4. One immediately sees that two boron sites are present, with quadrupolar splittings of 1462±10 kHz and 1256±10 kHz. By comparison with previous work [8], [9] the species are identified as boron nitride and boric acid respectively. Based on this model mixture, we expect to be able to monitor the oxidation of boron nitride.

A variety of approaches, including double-rotation (DOR), dynamic-angle-spinning (DAS) [3], and MAS in larger static fields [2], have been used to improve the
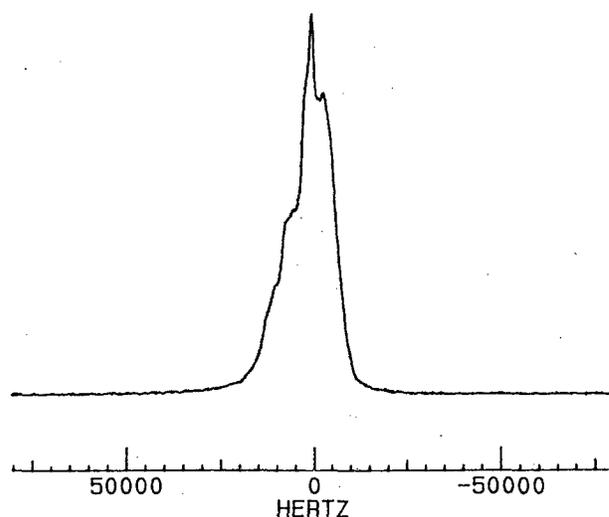

Fig. 3. MAS spectrum of ^{11}B in a mixture of boron nitride and boric acid, with a 5 kHz spinning rate. 2296 scans were collected, with a recycle delay of one second.

resolution of chemical shift spectra beyond that attainable by conventional MAS. Broadline NMR may compare less favorably with these new techniques than it does with MAS. However, these techniques have not been widely exploited in materials research, and, like MAS, they suffer from the physical limitations imposed on the sample as discussed in the Introduction.

Titanium boride (TiB_2) has been presented as a candidate for lightweight armor [10]. The structure consists of alternating planar layers of boron and titanium, with each boron nucleus trigonally bound to three other boron nuclei [11]. To yield the 2:1 stoichiometry, each boron layer contains twice as many nuclei as a titanium layer. The crystal structure suggests only one type of boron site is present, and previous workers have reported only one site, with a quadrupolar splitting of 180±10 kHz [9]. However,
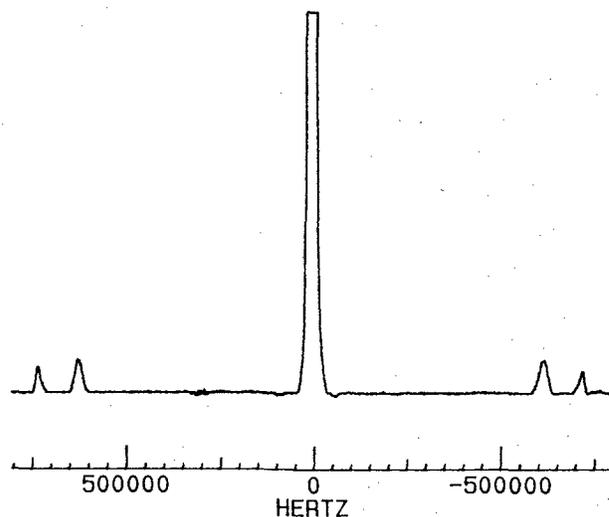

Fig. 4. ^{11}B powder pattern of the mixture examined in Figure 3. This spectrum was obtained after about 16 hours of signal averaging (56989 scans, one second recycle delay).

we see evidence for at least two sites in broadline ^{11}B NMR spectra (Figure 5), with quadrupolar splittings of
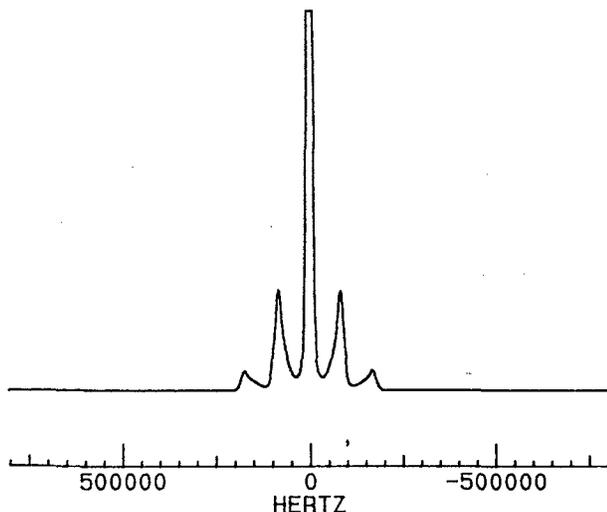

Fig. 5. ^{11}B powder pattern of titanium boride (TiB$_2$), from 324 co-added scans with a recycle delay of one second.

177 kHz and 355 kHz. In addition, a weak, poorly resolved pair of satellites may be present with a splitting of 195 kHz. It appears that roughly four fifths of the boron nuclei are located in the 177 kHz site, one fifth in the 355 kHz sites, with a much smaller fraction in the 195 kHz site.

X-ray diffraction confirmed the sample was greater than 90% TiB$_2$, with most of the remainder consisting of titanium oxides. The general features of the pattern matched that of AlB$_2$, which also has planar layers. The diffraction pattern showed no similarity to patterns from compounds containing puckered boron layers, such as RhB$_2$, TcB$_2$, and Ru$_2$B$_3$. Thus it appears the two sites are in equivalent geometrical positions within the boron plane. The larger quadrupolar splitting could be due to decreased donation of electrons from the titanium atoms to the boron π orbitals in about one fifth of the boron nuclei [9]. This heterogeneity within the boron layers may explain why titanium boride does not fracture along the interface between layers, as does graphite and many other layered materials.

4   Summary

For many ceramics, the second order quadrupolar broadening in MAS spectra exceeds the dispersion provided by the chemical shift. The far greater dispersion from the first order quadrupolar interaction can be used to obtain resolved spectra from these samples. We have provided examples of several structural ceramics for which broadline spectra, obtained with a standard solids spectrometer, yield useful structural information. Thus the technique shows the potential to complement MAS in the study of inorganic materials.

5   References

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