Synthesis and Magic-Angle Spinning Nuclear Magnetic Resonance of ^{15}N-Enriched Silicon Nitrides

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Received December 1, 1989

The synthesis of α-$Si_3{}^{15}N_4$ by nitridation of silicon powder using a $^{15}N_2/H_2$ mix and the conversion to β-$Si_3{}^{15}N_4$ are described. The ^{15}N NMR spectra of these two solid phases have been obtained, and they broadly correlate with the crystal structures. The ^{15}N shift range for the α-polymorph covers nearly 25 ppm, suggesting that the sensitivity of the ^{15}N chemical shift to structural factors may be greater than that of ^{29}Si shifts. The ^{15}N spin-lattice relaxation times for β-$Si_3{}^{15}N_4$ were also measured, and were shown to be very long ($\sim$3000 s), with implications for optimization of experimental conditions. Silicon-29 spectra show that, contrary to expectations, unaveraged (^{29}Si,^{14}N) coupling is not the primary cause of line broadening in these phases.

Introduction

Silicon-29 and aluminum-27 magic-angle spinning (MAS) NMR studies have provided structural information on local environment in a range of nitrogen-containing ceramic phases, including those in the Si-Al-O-N,[1-3] Y-Si-O-N,[4] La-Si-O-N,[5] and La-Si-Al-O-N[6] systems, and in some glass ceramic phases.[7] The short-range nature of the influences on NMR spectra means, however, that little information on nitrogen environment has been gleaned and that direct observation of nitrogen in these systems would be desirable. There have been a number of $^{14}N(I=1)$ studies on solid materials,[8] but $^{15}N(I=^1/_2)$ is far preferable for the majority of systems once problems associated with the low natural abundance (0.4%) have been overcome.

Solution-state ^{15}N NMR has for many years provided structural information on a wide range of systems.[9-11] Recently, there have also been several solid-state, natural-abundance studies on inorganic[12,13] and organic/polymeric[8,14] systems using cross-polarization (CP)[15] from protons to enhance sensitivity. For inorganic systems in which no protons are present (and thus CP cannot be used), the long spin-lattice (T_1) relaxation times and low sensitivity of the ^{15}N nucleus generally require isotopic enrichment if spectra are to be acquired in reasonable times (see Figure 1), although a natural-abundance spectrum of aluminum nitride has been reported.[16]

Bunker et al.[17] have recently presented an extensive study of ^{15}N-enriched phosphorus oxynitride glasses in which two-coordinate and three-coordinate nitrogen can clearly be distinguished. Turner et al.[18] describe the ^{15}N spectra of a ^{15}N-enriched impure sample of silicon nitride and of a Mg-Si-Al-O-N glass.

In this article we report the synthesis of pure, ^{15}N-enriched α- and β-Si_3N_4, important precursors for a wide range of nitrogen ceramics, and the ^{15}N and ^{29}Si MAS NMR spectra of these phases.

Experimental Section

Samples of α-Si_3N_4 are generally prepared by the nitridation of silicon powder seeded with α-Si_3N_4 in a flowing, mixed N_2/H_2 atmosphere.[19] However, the cost of $^{15}N_2$ precludes the use of a flowing atmosphere, and so it was imperative to design a synthesis in a static atmosphere in which as little $^{15}N_2$ as possible was wasted.

The equipment used is shown in Figure 2. The rate of reaction is found to depend on both temperature and pressure.[20] If too high an initial temperature is used, then nitridation, although initially rapid, stops before the reaction is completed. If too low an initial temperature is used, then reaction is too slow. At very low nitrogen pressures, nitridation is extremely slow, especially when nearly complete.

With these factors in mind, the following method was devised: Silicon powder (1 g, 0.0356 mol), seeded with 5 wt % α-Si_3N_4, was placed in a BN-lined alumina crucible in a vertical tube furnace (volume 1.2 L) and heated in vacuo to 1240 °C. $^{15}N_2$ (99.8% enriched in ^{15}N, from Isogas Ltd; 0.032 mol) and H_2 were then admitted to the furnace chamber in the initial ratio of 10:1

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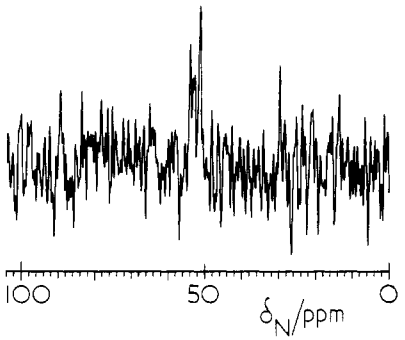

Figure 1. Nitrogen-15 MAS spectrum of α-Si_3N_4 obtained at natural abundance (2000 transients).

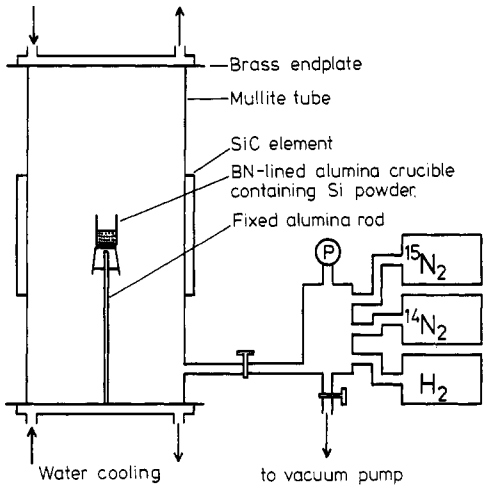

Figure 2. Schematic diagram of the apparatus used for the preparation of ^{15}N-enriched α-Si_3N_4.

by volume. Reaction was allowed to proceed for 16 h, after which time approximately 80% of the $^{15}N_2$ had reacted. Nitridation was completed by heating the sample at 1400 °C for 24 h under $^{14}N_2/H_2$. A total enrichment of 60% ^{15}N was estimated for this process by consideration of the volumes of gases reacting in the furnace chamber. The sample of β-$Si_3{}^{15}N_4$ was prepared by firing a pellet of α-$Si_3{}^{15}N$ premixed with 1 wt % MgO[21] at 1750 °C for 2 h in a carbon resistance furance under an N_2 atmosphere.

Unenriched samples of both polymorphs were prepared by identical routes for the purpose of comparison. In all cases, sample purity was checked by powder XRD using a Hagg-Guinier focusing camera and Cu $K\alpha_1$ radiation. Both α-Si_3N_4 samples were estimated to contain approximately 5% β-Si_3N_4. No other crystalline phases (including unreacted silicon) were detected. Since the resonances from silicon could also not be seen in the ^{29}Si MAS NMR spectra of the samples, it was assumed that nitridation had gone to completion. No crystalline phases apart from β-Si_3N_4 were observed on the photographs of this polymorph.

Nitrogen-15 and silicon-29 MAS NMR spectra were obtained at 30.4 and 59.6 MHz, respectively, by using a Varian VXR 300 spectrometer. Samples were packed in zirconia rotors and spun at 3–4 kHz during acquisition. Nitrogen-15 chemical shifts are quoted relative to the ammonium resonance of solid NH_4NO_3 (δ_N = 0). However, it may be noted that ^{15}N shifts are sometimes quoted relative to the nitrate peak of solid NH_4NO_3 (δ_N = +353.4). Among other referencing materials, CH_3NO_2(l) has been used by many authors: the ^{15}N resonance occurs at δ_N = +358.2 on our scale. See ref 10 for a full discussion on referencing of ^{15}N spectra. Silicon-29 chemical shifts are quoted relative to the signal for TMS (δ_{Si} = 0). The ^{29}Si and ^{15}N spectra were acquired using short (25–70°) radiofrequency pulses and long recycle delays (120–900 s), except for the ^{15}N spectrum of α-$Si_3{}^{15}N_4$ (Figure 3). No line-broadening was applied prior to Fourier transformation.

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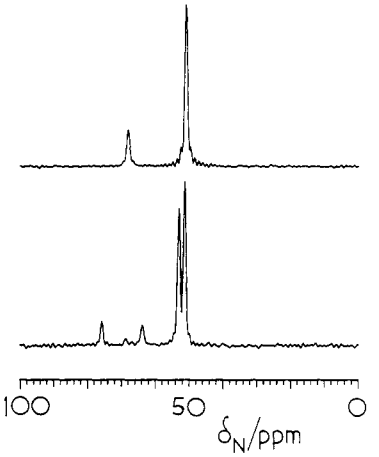

Figure 3. Nitrogen-15 MAS spectra of (bottom) α-(11 transients, 90° pulses, 3600-s recycle delay) and (top) β-$Si_3{}^{15}N_4$ (192 transients in the top spectrum). The ringing observed at the base of the most intense peak arises from slight truncation of the free induction decay; for other conditions, see text.

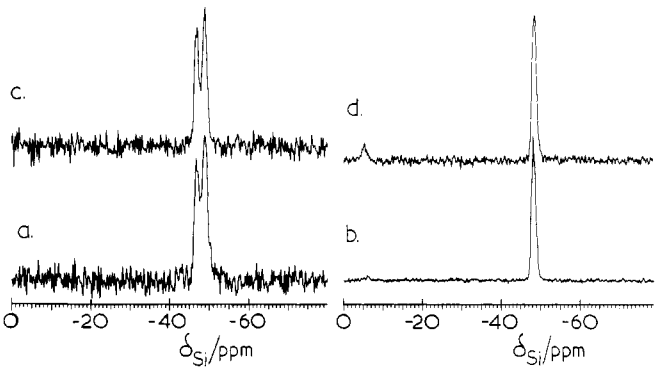

Figure 4. Silicon-29 MAS spectra of (a) α- and (b) β-$Si_3{}^{14}N_4$ and (c) α- and (d) β-$Si_3{}^{15}N_4$. The numbers of transients are 472, 606, 500, and 500 for a–d, respectively.

Table I. NMR Data for Silicon Nitrides

	δ_{Si}/ppm	fwhh/Hz[a]	δ_N/ppm	fwhh/Hz[a]	intensity[c]
α-$Si_3{}^{14}N_4$	−49.0				
	−47.1				
α-$Si_3{}^{15}N_4$	−49.0		49.0	~50[b]	} 35
	−47.1		50.8	~50[b]	
			61.4	50	2.5
			73.5	55	3
β-$Si_3{}^{14}N_4$	−48.5	75			
β-$Si_3{}^{15}N_4$	−48.5	75	51.5	30	25
			68.7	35	6

[a] Full width at half-height. [b] Measurement difficult because of overlap. [c] Not necessarily quantitative.

Relaxation times (T_1) were measured by using an inversion recovery method[22] in which a 4-h relaxation delay was employed. A total of five points was recorded.

Results

The ^{15}N spectra of α- and β-$Si_3{}^{15}N_4$ are shown in Figure 3, and the ^{29}Si spectra of α- and β-$Si_3{}^{14}N_4$ and $Si_3{}^{15}N_4$ in Figure 4. Chemical shift and line-width data are summarized in Table I. Spin–lattice relaxation times for ^{15}N in β-$Si_3{}^{15}N_4$ were determined as 2700 ± 400 s for the 51.5 ppm resonance and 3000 ± 600 s for the 68.7 ppm resonance. These values imply that the sample should be kept in the magnet for the order of 5 h before pulsing begins

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Table II. Silicon and Nitrogen Environments in Silicon Nitrides

	Si atoms	ratio	N atoms[a]	ratio
α-Si_3N_4	Si(1)	1	N(1)*	1
	Si(2)	1	N(2)*	1
			N(3)†	3
			N(4)†	3
β-Si_3N_4	Si(1)	1	N(1)*	1
			N(2)†	3

[a] The atoms indicated by asterisks are on 3-fold axes; those marked by daggers are not on 3-fold axes.

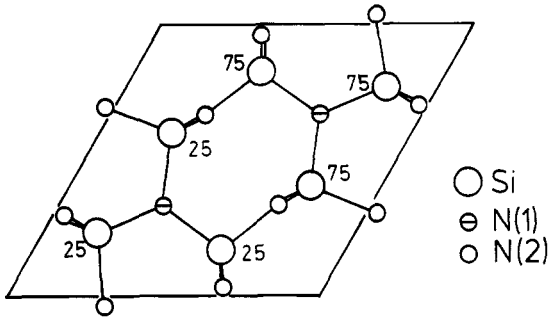

Figure 5. Hexagonal crystal structure of β-Si_3N_4, projected along the c axis. The z coordinates of the Si atoms (only) are given as $100z/c$.

and that short pulses plus long recycle delays must be used when acquiring spectra. The T_1 results are the first to be determined for ^{15}N in a ceramic system. The ^{29}Si T_1 relaxation time for α-Si_3N_4 was also determined as 3000 ± 300 s.

Note that the ^{15}N spectrum obtained by Turner et al.[18] clearly shows that β-$Si_3{}^{15}N_4$ is present in their sample, with chemical shifts of 68.9 (ascribed by the authors to an impurity) and 51.6 ppm. A third peak at 40.6 ppm may be assigned to Si_2N_2O.

Discussion

The crystal structures of α- and β-Si_3N_4 have been determined,[23,24] and the silicon and nitrogen environments in the two phases are summarized in Table II. The crystal structure of β-Si_3N_4 is shown in Figure 5. The α-form has a unit cell with the c dimension roughly twice that in the β-form. The top half of the cell is related to the bottom half by reflection through a plane parallel to c, followed by translation by $c/2$. Distortions in bond lengths and angles mean that the symmetry of this transformation is not preserved and each Si or N environment in β-Si_3N_4 gives rise to two environments in α-Si_3N_4.

Nitrogen-15 Spectra. Comparison of the intensity data in Table I and the crystallographic data in Table II for β-Si_3N_4 demonstrates unequivocally that the peak at 68.7 ppm in the ^{15}N spectrum of that phase can be assigned to nitrogen atoms on a 3-fold axis (N(1)*) and the peak at 51.6 ppm to nitrogen atoms not on a 3-fold axis (N(2)†). The intensity ratio of the two peaks is rather more than 3:1. The measured T_1 values for β-$Si_3{}^{15}N_4$ demonstrate, however, that both resonances are saturated during acquisition and that the N* atoms probably have a somewhat longer T_1 relaxation time and hence are differentially saturated.

The two resonances from β-$Si_3{}^{15}N_4$ are separated by 17.4 ppm. Both nitrogen environments are planar, NSi_3 coordinated, although the Si–N–Si bond angles are unequal at the N(2)† site (113.5°, 121.3°, 125.1°), whereas they are all equal at the N(1)* site (120.0°). There is a similar variation in Si–N bond lengths at the two sites. It is thus clear that ^{15}N chemical shift values are very sensitive to local coordination geometry and more so than ^{29}Si shifts (even when account is taken of the lower Larmor frequency for ^{15}N) though differences in the range of structures so far studied imply that caution should be exercised in this conclusion.

The structure of α-$Si_3{}^{15}N_4$ is related to that of β-$Si_3{}^{15}N_4$ as discussed above. Little change is seen in the chemical shifts of the N† atoms, which are clearly in very similar environments to the N† atoms in the β-polymorph. The N* atoms, which are still on 3-fold axes, however, are clearly in rather different environments, both to each other and to the N* environment in β-Si_3N_4. The N*(2) site is no longer in a planar coordination environment, with an Si–N–Si angle of 117.3°, whereas the N(1)* site is still nearly planar. In addition, the N(2)–N(2) distance is roughly twice both the N(1)–N(1) distance and the corresponding N(1)–N(1) distance in β-Si_3N_4. Thus it is not surprising that the chemical shifts of nitrogen atoms in the two environments are very different, but the crystallography of the two phases might lead one to predict that only one of the two peaks would be significantly shifted from the N(1)* resonance in β-Si_3N_4, whereas in fact, both are so shifted. As with β-$Si_3{}^{15}N_4$, predicted and observed intensity ratios for the four peaks do not agree. Although no T_1 measurements have been made for ^{15}N in α-$Si_3{}^{15}N_4$, it is to be expected that similar influences are at work. All attempts to correlate ^{15}N chemical shifts with N–Si–N bond angles[25-27] were unsuccessful.

The observed ^{15}N T_1 relaxation times in β-$Si_3{}^{15}N_4$ are of a similar order of magnitude to ^{29}Si T_1 times measured in this study and by Carduner et al.,[28] indicating that similar but as yet uncharacterized relaxation processes are occurring. The absence of motions and the relative weakness of internuclear dipolar coupling are the principal reasons for the long T_1 values.

Silicon-29 Spectra. The ^{29}Si spectra all agree with previous results reported for the two polymorphs.[2,28] Most authors have believed that broadening of ^{29}Si resonances in nitrogen ceramics is due, at least partially, to unaveraged (^{29}Si,^{14}N) coupling,[4,5] and therefore we expected to find that ^{29}Si lines in the two ^{15}N-enriched samples would be significantly narrower than in the unenriched analogues. This was found not to be the case. There was a marginal narrowing in the case of α Si_3N_4 (see Figure 3), but it seems that line broadening is due to other sources. Possible origins include the presence of paramagnetic centers, which may give rise to T_2 broadening but because of the absence of motion do not lead to fluctuating magnetic fields at the Larmor frequency, and small variations in bond angles.

Concluding Remarks

This study has demonstrated the potential of ^{15}N MAS NMR in the structural elucidation of nitrogen-containing ceramic phases. Structural information on nitrogen environments has previously been very difficult to obtain by XRD because most phases also contain oxygen, which has a very similar scattering factor. Silicon nitride is the

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precursor for a range of nitrogen ceramic phases, and further ^{15}N NMR studies on these compounds will resolve some of the remaining questions concerning these structures.

Acknowledgment. M.J.L. is grateful to the U.K. Science and Engineering Research Council for a Research Studentship under the Earmarked Scheme. We thank P. Wilson for technical assistance.

Incommensurate Modulations in the Pb-Doped BiSrCaCuO 221 Superconducting Phase: A Five-Dimensional Superspace Description

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Received January 26, 1990

The new modulation introduced by Pb doping of the 221 BiSrCaCuO superconducting phase has been analyzed by using five-dimensional superspace group theory. The complete X-ray diffraction pattern has monoclinic rather than orthorhombic symmetry and is in agreement with the superspace group $P{:}Aa{:}P1$. In addition to the original modulation with $\mathbf{q}_1 = 0.234\ (1)\mathbf{a}^*$, an extra set of satellites with $q_2 = 0.144\ (3)\mathbf{a}^*$, and "combination" satellites with $q_1 - q_2 = 0.090\ (1)\mathbf{a}^*$ occur. The two modulations differ in the internal translational symmetry. Anomalous dispersion experiments show that both Bi and Pb atoms are affected by each of the modulations, a conclusion confirmed by the diffraction analysis. The displacements of the new modulation are in-phase, rather than out-of-phase, for two adjacent BiO layers. The c-axis displacements of the Bi atoms for the original modulations are significantly reduced, while the amplitudes of the $\mathbf{q}_2$ modulation in this direction exceed 0.3 Å for several of the atoms.

Introduction

The incommensurate modulations in the BiSrCaCu oxides represent structural features that perturb the three-dimensional lattice property of the crystalline materials. As a result their crystal structures cannot be fully described by conventional crystallography. In previous single-crystal studies, we have analyzed the modulations in the 2212 and 221 BiSrCaCuO structures,[1-3] using superspace symmetry theory as developed by De Wolff[4] and De Wolff, et al.[5] The analysis shows displacements of the atoms from their average positions, which are as large as 0.5 Å in the a and c directions of the unit cell. The displacements affect the geometry of all layers in the crystals, including the CuO_2 layers, the geometry of which is crucial for the superconductivity mechanism. Recent studies of commensurate analogues containing Fe and Co rather than Cu are in agreement with the results of our supersymmetry analysis of the superconducting phases and give evidence for the existence of extra oxygen atoms in the Bi–O layers.[6]

As lead doping tends to stabilize the higher T_c phases, the structural details of the lead-doped phases are of importance. The doping also has a dramatic effect on the satellite reflection pattern. As reported,[7-10] Pb doping of the BiSrCaCu oxides induces a second modulation wave in the crystals. In the Ca-containing 221 phase this wave has a modulation vector $\mathbf{q}_2 = 0.144\mathbf{a}^*$, in addition to the modulation with $\mathbf{q}_1 = 0.234\mathbf{a}^*$, which is similar to the undoped 2212 modulation (Table I). It is noteworthy that the modulations in both the undoped and Pb-doped 221 phases are strongly affected by the presence of Ca. The calcium-free Pb-doped 221 sample does not show any satellite reflections in its single-crystal diffraction pattern, as observed by Torardi et al.[11] and confirmed in our experiments. Ramesh et al.[7] report that in the Pb-doped 2223 phase, the 2212-like modulation disappears upon cooling to 88 K while the second modulation is not affected.

Table I. Modulation Wave Vectors for the (Bi and Pb-Doped Bi) 2212 and 221 Phases

phase	wave vector	ref
Bi-2212	$0.210a^*$	1, 2
Bi-221	$0.213a^* + 0.61c^*$	1, 2
Pb-doped Bi-2212	$0.220a^*$ ($\mathbf{q}_1$)	16
	$0.136a^*$ ($\mathbf{q}_2$)	
Pb-doped Bi-221	$0.234\ (1)a^*$ ($\mathbf{q}_1$)	this work
	$0.144\ (3)a^*$ ($\mathbf{q}_2$)	
	$0.090\ (1)a^*$ ($\mathbf{q}_1$–$\mathbf{q}_2$)	

In this paper, we describe an X-ray single-crystal analysis of the two-dimensional modulated structure of the Pb-doped 221 superconductor using the five-dimensional superspace approach. The average structure of the 221

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