JOURNAL OF MATERIALS SCIENCE LETTERS 4 (1985) 393–395

Co-ordination of Si atoms in silicon-oxynitrides determined by magic-angle-spinning NMR

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A relatively new technique of high-resolution magic-angle spinning (MAS) NMR spectroscopy is capable of defining local coordination for specific types of atom. The technique has been used to resolve ambiguities in crystal structure analysis of silicates and has overcome the problem of similarity in X-ray scattering factors for silicon and aluminium atoms. The purpose of rapid (kHz) sample spinning at the "magic angle" ($54^0 44^1$) with respect to magnetic field direction is to achieve the required resolution of NMR spectral lines which, for solids, are normally too broad to identify characteristic chemical shifts due to specific atomic coordination.

In a previous publication (Butler *et al.* [1]) we have demonstrated the application of MAS-NMR to crystallographic problems in the Si–Al–O–N system. The distinction between tetrahedral and octahedral site symmetry for aluminium atoms in a polytypoid phase has been demonstrated with reference to characteristic shifts in standard specimens (AlN and Al $(H_2O)_6^{3+}$) with unambiguous site symmetries. In addition to ^{27}Al nuclei sharp MAS–NMR spectral lines were reported for ^{29}Si in Si–Al–O–N phases. The purpose of this communication is to demonstrate the sensitivity of chemical shifts in MAS–NMR to small changes in site symmetry and chemical environment for silicon atoms in Si–Al–O–N structures and hence to provide structural information not previously attainable via X-ray, neutron or electron diffraction.

Crystal structures in the Si–Al–O–N system are predominantly based on differing arrangements of (Si, Al) $(O, N)_4$ tetrahedra. In the terminal nitride Si_3N_4 each nitrogen atom is linked to three silicon atoms in planar arrays which are stacked parallel to the basal plane of an hexagonal-symmetry unit cell. Two alternative hexagonal structures have been completely determined by X-ray diffraction; α-Si_3N_4 with stacking sequence ABCD and β-Si_3N_4 with an ABAB sequence and consequent halving of the hexagonal c lattice parameter. A projection of the α-structure on to the basal (0 0 1) plane (Fig. 1) illustrates the tetrahedral framework structure with sites 1 and 2 for silicon atoms identified by small differences in tetrahedral bond-length and symmetry. In the β structure all tetrahedra have the same dimensions.

α and β Si_3N_4 were first used as standards for SiN_4 tetrahedral coordination in MAS–NMR spectra. α-Si_3N_4 was a commercial powder produced from two sources by nitriding silicon, β-Si_3N_4 was produced by phase transformation during hot-pressing of the α-powder in the presence of a liquid sintering aid and is the basis of the well-known high-temperature ceramics [2, 3]. NMR spectra were obtained from the nitrides in particulate form using a Bruker WH-400 spectrometer and MAS probe with spinning frequency ~3 kHz. Chemical shifts were measured in relation to tetramethylsilane (TMS) as a reference standard. The MAS–NMR spectra (Fig. 2) demonstrate the characteristic SiN_4 shift to be in the range −48 to −50 ppm with respect to TMS. β-Si_3N_4 has a single, well resolved, line at −48.5 ppm consistent with a unique tetrahedral co-ordination symmetry whereas the α-Si_3N_4 spectral peak is split into two at −48.0 and −49.7 ppm. The peak splitting is well resolved and reproducible and hence may be ascribed to the small differences in Si(1) and Si(2) tetrahedral sites. Alternative explanations such as silicon within a surface oxygen-rich layer or the presence of interstitial silicon can be dismissed in relation to both the magnitude of the shift and the relative amplitudes of the pair. Si(1) and Si(2) have equivalent occupancy, consistent with the similar peak amplitudes. The absence of a visible peak associated with surface oxygen or interstitial sites is due to their small concentrations and the suggestion of α-stabilization via interstitials [4]

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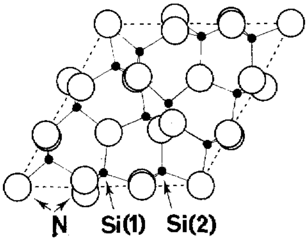

Figure 1 Projection of the α-Si_3N_4 structure on to (0 0 1) showing the two silicon site symmetries: Si(1) and Si(2).

cannot be disproven on this basis. The assignment of the Si(1)–Si(2) peak shift to differences in near-neighbour (N) coordination and not to next-near-neighbour (Si) atoms is reinforced by the insensitivity of shifts for tetrahedral SiN_4 in highly substituted β-Si_3N_4 described below. The sensitivity of the MAS–NMR technique is, however, emphasized by the small differences in Si–N bond length between Si(1) and Si(2) tetrahedral sites given in Table 1. SiO_2 polymorphs have also been reported to exhibit small shifts for ^{29}Si resonances; a change in O–Si–O bond angle from 146.4 to 143.6 (cristobalite to α-quartz) corresponds to a shift from -108.3 to -107.1 ppm [7].

Changes in coordination number and chemistry have a much greater influence on NMR peak positions. The oxynitride compound Si_2N_2O is a convenient reference for the substitution of one oxygen atom for nitrogen in the SiN_4 coordination tetrahedra. The structure [8] has orthorhombic symmetry with SiN_3O tetrahedra linked by Si–O–Si bonds perpendicular to the *a*-axis. Si–N tetrahedral bond lengths are 1.70, 1.71 and 1.75 ± 2 [8], similar to Si_3N_4, with a shorter Si–O distance of 0.162 nm. The oxygen substitution produces a large shift in NMR peak from -48 to -63 ppm (Fig. 3c), the singular symmetry giving a well-resolved peak. The subsidiary peaks near -48 ppm are due to ~5% each of impurity α- and β-Si_3N_4.

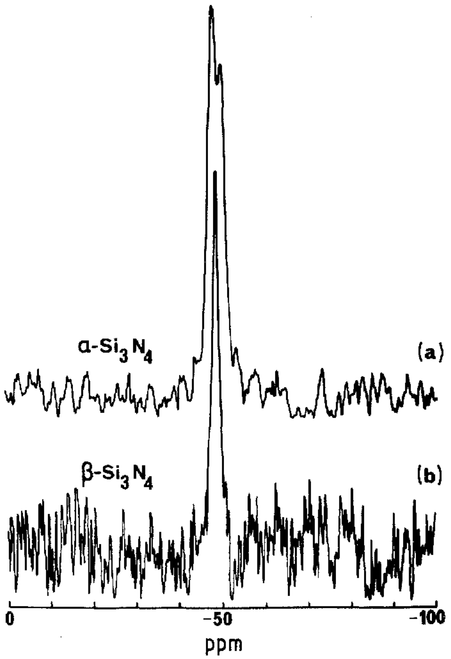

Figure 2 MAS–NMR spectra from α- and β-Si_3N_4.

Si_2N_2O and β-Si_3N_4 have been used as NMR standards in exploring structural ambiguities in the substitutes β' form of β-Si_3N_4 which has a general formula $Si_{3-x}Al_xO_xN_{4-x}$ where x has a maximum of ~2. X-ray neutron or electron diffraction provides no evidence for specific site occupancy of substitutional aluminium and oxygen but simply an expansion of the hexagonal unit cell. NMR–MAS spectra have been collected from a series of nominally single-phase hot-pressed β' ceramics with substitution levels $x \sim 0.5$, 1 and 2. These have previously been well characterized microstructurally via X-ray diffraction and electron microscopy and compositionally via electron-probe microanalysis. ^{29}Si spectra are exemplified for $x = 2$ and $x = 0.5$ ceramics in Fig. 3a and b. Throughout the range of substitution only SiN_4 tetrahedra are present, the inference being that substitutional oxygen is strictly coupled to $Al(O, N)_4$ tetrahedra. The SiN_4 chemical shift remains constant at 48 ± 0.5 ppm regardless of substitution level. There is, however, a significant increase in spectral line width with substitution level; the FWHM increases from ~1 ppm (β-Si_3N_4) typical of good crystals with singular site symmetry to 3.5 ppm ($x = 0.5$) and 5.5 ($x = 2$). This is indicative of a small spread in nm bond length or angle together with a change in local field which accompanies substitution in n.n.n. sites. This is unlike the behaviour of ^{29}Si in framework silicates in

TABLE I

Si in β [5]	0.170 nm	0.173 nm	0.173 nm	0.177 nm
Si(1) in α [6]	0.1736 nm	0.1746 nm	0.1747 nm	0.1759 nm
Si(2) in α [6]	0.1715 nm	0.1740 nm	0.1744 nm	0.1759 nm

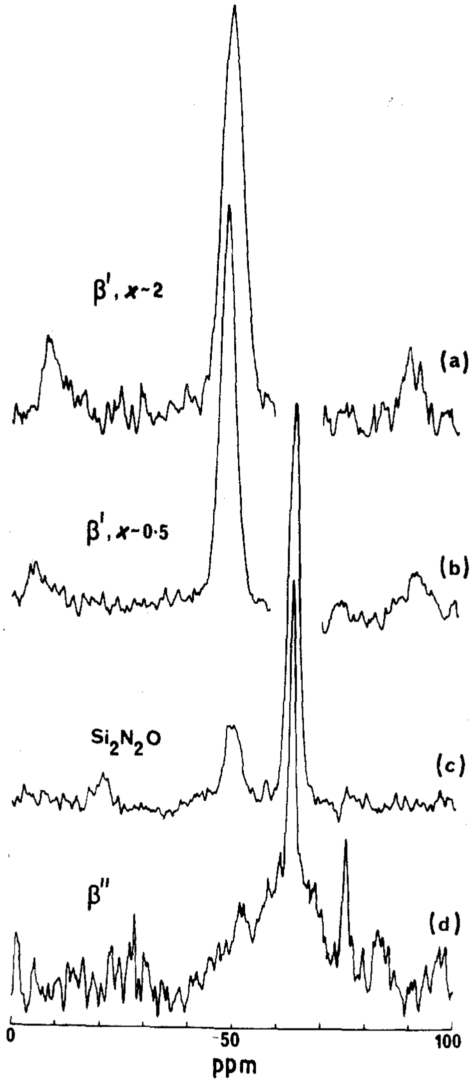

Figure 3 MAS–NMR spectra from substituted (β')Si_3N_4 (a, b), Si_2N_2O (c) and from the Mg + Al-substituted β'' structure (d).

which a large SiO_4 shift (between ~ -85 and -110 ppm) accompanies n.n.n. tetrahedral aluminium substitution. An additional influence of n.n.n. aluminium or oxygen in the nitrides comes from the increased amplitude of spinning sidebands (SSB) with Al + O concentration (Fig. 2a, b). SSB are minor peaks at multiples of the spinning frequency on either side of the main peak which arises from anisotropy in the local field of the nucleus and hence is also influenced by coordination changes.

A final example of a preferred coordination for silicon has been observed on a related but metastable compound β'' in which both magnesium and aluminium substitution occurs [9]. This retains the same crystal structure and metal/non-metal ratio but is much enriched in oxygen with general composition $Mg_xAl_{4-x}Si_2O_{4+x}$, i.e. a magnesium substituted form of the β'' compound, $SiAl_2O_2N_2$ described above. A nearly single phase microstructure of composition $Mg_5AlSi_3O_{11}N$ may be crystallized from the glassy state which gives the MAS–NMR ^{29}Si spectrum of Fig. 2d. The precise correlation of the -63.1 ppm peak with that from Si_2N_2O and the presence of one other discreet peak at -75.5 ppm shows that at such oxygen-rich compositions SiN_4 tetrahedra are absent and SiN_4 tetrahedra are partitional between SiN_3O and a more oxygen-rich coordination tetrahedron (SiO_4, SiO_3N, or $Si_2O_2N_2$). The mean composition would favour SiO_4 but there is no reference shift in silicate structures in view of their sensitivity to n.n.n. coordination chemistry. There is, however, a general trend to reduced (−ve) shift from normal SiO_4 framework sites ($Q_4 \sim 110$ ppm) to those with aluminium substituted n.n.n. ($Q_4 - 4Al \sim 85$ ppm) [10].

The model of preferred n.n. coordination chemistry, as opposed to random site selection for silicon, nitrogen and oxygen is supported by MAS–NMR spectra for $Al(O, N)_4$ tetrahedra in the same compounds. Variations in amplitude of AlN_4 and oxygen-rich Al tetrahedra are observed with substitution level, as anticipated. These will be described in a forthcoming publication.

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Received 19 July
and accepted 30 July 1984