New Limits of Silicon-29 Solid-state N.M.R. Chemical Shifts

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Sodalites characterised by high resolution ^{29}Si n.m.r. spectroscopy exhibit a single resonance over a wide range of chemical shifts dependent upon composition; the resonance frequency correlates well with the geometry of the $Si(OAl)_4$ tetrahedron and with the lattice parameter, both determined by powder neutron diffraction.

Sodalites are an unusual group of aluminosilicates in that they contain within the framework anionic species such as Cl^-, SO_4^{2-}, and SCN^-. They are of the general formula $M_8(SiAlO_4)_6.X$ where M may be sodium, lithium, silver, or more rarely other monovalent or divalent cations and X represents one divalent or two monovalent anions. The structure is based on a simple truncated octahedral cage linked in three dimensions.[1] Exchange of the cations, which occurs readily, allows the synthesis of sodalites of a variety of compositions; the flexibility of the aluminosilicate framework, through changes in the Si–O–Al bond angle, enables a wide range of ion sizes to be incorporated within the cavities. Ramdas and Klinowski[2] have interpreted variations in ^{29}Si resonance frequencies in a range of zeolites in terms of changes in Si–O–Al bond angles. However for their limited range of $Si(OAl)_4$-type structures only average bond angles were estimated. We have recently prepared a range of sodalite derivatives for powder neutron diffraction and ion conduction studies. As part of this work we have obtained high resolution solid-state n.m.r. spectra, and present here the analysis of this data which shows that current views of the range of resonance frequencies associated with $Si(OAl)_4$ species should be modified. In addition, more accurate atom positions, particularly for oxygen from neutron diffraction, for a series of a materials of the same structural type enables us to relate resonance frequency to Si–O–Al bond angle in a less empirical fashion.

The materials were synthesised by literature methods.† In each case the products were shown to consist of a single phase by powder *X*-ray diffraction. The materials synthesised are summarised in Table 1 along with their refined lattice constants (determined from the neutron diffraction data). N.m.r. spectra were obtained using sample spin speeds of 4000 Hz, sufficient to give high-resolution spectra with low-intensity spinning side bands. High-resolution powder neutron diffraction data were collected for some of the materials using the ISIS and ILL facilities. A full-profile Rietveld refinement[6–8] program was used to determine atomic positions and hence the Si–O–Al bond angles; the details of this work and the structures will be published elsewhere.

Table 1. Lattice parameters (a_o), ^{29}Si chemical shifts, and Si–O–Al bond angles.

Material	a_o/Å	$-^{29}Si$ δ (p.p.m.)	Si–O–Al angle (°)
$Li_8(AlSiO_4)_6Cl_2$	8.457(1)	76.73	124.6
$Li_{3.85}Na_{4.15}(AlSiO_4)_6Cl_2$	8.683(1)	81.68	131.9
$Li_{1.40}Na_{6.60}(AlSiO_4)_6Cl_2$	8.812(1)	85.10	
$Li_{1.60}Na_{6.40}(AlSiO_4)_6Cl_2$	8.834(1)	85.22	
$Na_8(AlSiO_4)_6Cl_2$	8.881(1)	85.34	138.1
$Na_8(AlSiO_4)_6Br_2$	8.927(1)	86.70	140.4
$Na_8(AlSiO_4)_6I_2$	9.032(1)	89.13	144.5
$K_{0.75}Na_{7.25}(AlSiO_4)_6Cl_2$	8.905(2)	87.16	141.9
$K_{4.30}Na_{3.70}(AlSiO_4)_6Cl_2$	9.086(2)	91.03	146.2
$Na_8(AlSiO_4)_6(NO_2)_2$	8.906(1)	86.60	
$Na_{7.38}Al_{5.4}Si_{6.6}O_{24}Cl_2$	8.885(1)	85.47	139.3
$Na_8(AlSiO_4)_6(SCN)_2$	9.086(2)	90.36	
$Na_8(AlSiO_4)_6CrO_4$	9.114(1)	91.40	148.6
$Na_8(AlSiO_4)_6MoO_4$	9.119(1)	91.87	
$Na_8(AlSiO_4)_6WO_4$	9.121(2)	91.47	

For the majority of the materials a single resonance was observed in the ^{29}Si spectrum consistent with the ordered array of silicon and aluminium and the sole existence of $Si(OAl)_4$ environments expected in these compounds with a Si : Al ratio of 1 : 1. Exceptions were $Na_8(SiAlO_4)_6{\cdot}MO_4$ (M = Cr, Mo, or W), where four closely spaced resonances were observed. This is due to the partial filling of the sodalite cavities and orientational ordering of the tetrahedral anions which we have observed in our structure refinements of these compounds. A more complicated spectrum was also observed for a sodalite synthesised from zeolite Linde 13X (B.D.H.), which was readily interpreted in terms of the various silicon environments expected for this material with a silicon-to-aluminium ratio of 1 : 0.82. For these materials an average resonance frequency was taken.

The chemical shifts observed for these materials (Table 1) cover a much larger range than has been recorded previously for silicon in an $Si(OAl)_4$ environment. Klinowski[9] quotes values between −82 and −89 p.p.m.;[4] we observe values in the range −76 to −93 p.p.m.

The ^{29}Si chemical shift has been shown to depend upon the Si–O–Al bond angle by several workers;[2,9] however such analyses have been restricted in value in that materials with different structural elements were compared and accurate structural information was lacking. In the sodalite structure bond angles are related to lattice parameters if it is assumed that the framework bond lengths are constant; Figure 1 shows a reasonably good correlation between these two quantities.

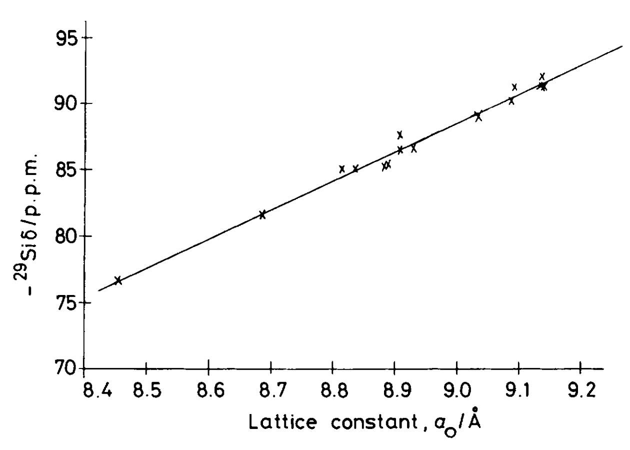

Figure 1. Variation of ^{29}Si resonance frequency with lattice parameter.

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† The sodalites $Na_8(SiAlO_4)_6{\cdot}X$ with X = Cl_2, Br_2, I_2, CrO_4, MoO_4, or WO_4 were synthesised from zeolite 4A;[3] with X = $(NO_2)_2$ and $(SCN)_2$ direct precipitation from aluminate solution was employed .[4] Ion-exchanged materials $Na_{8-x}M_x(SiAlO_4)_6{\cdot}X$ were prepared by the method of Taylor.[5]

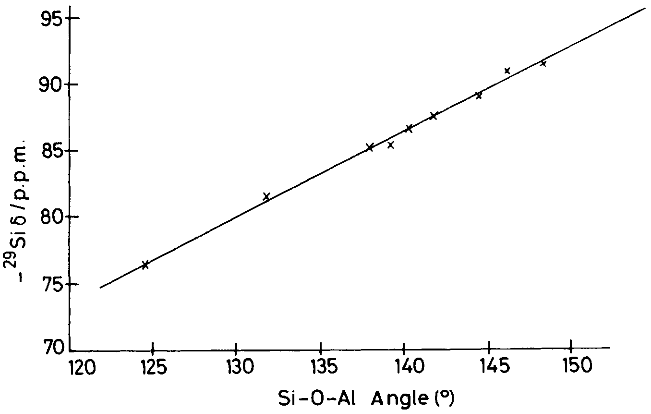

Figure 2. Correlation of the Si–O–Al bond angle, determined by powder neutron diffraction, with ^{29}Si resonance frequency.

Atomic positions for silicon, aluminium, and oxygen determined accurately by powder neutron diffraction show a marked variation in the Si–O–Al bond angle (Table 1) for the nine materials studied. Indeed, notable variations in the Si–O bond length between 1.63 and 1.67 Å were observed; previous analyses of n.m.r. data have assumed this value to be constant.

The variation of ^{29}Si resonance frequency with Si–O–Al bond angle(θ) determined by neutron diffraction (Figure 2) can be fitted accurately by the expression (i); thus the framework geometry in this class of materials can be determined even when the compounds are of poor crystallinity.

$$\delta_{Si} = 1.89 - 0.631\theta \tag{i}$$

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