Characterization of Local Atomic Environments and Quantitative Determination of Changes in Site Occupancies during the Formation of Ordered Synthetic Cordierite by ^{29}Si and ^{27}Al Magic-angle Spinning N.M.R. Spectroscopy

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Eight distinct tetrahedral sites for silicon can be identified and assigned in freshly crystallized (hexagonal) synthetic cordierite, $Mg_2Al_4Si_5O_{18}$, four in the chain manifold and four in the six-membered aluminosilicate rings, but there are only two sites (one in the rings, the other in the chains) in the aged (orthorhombic) product; Si:Al ratios within each manifold can be determined from the ^{29}Si magic-angle spinning n.m.r. spectra which also permit the course of Si, Al ordering to be charted as thermodynamic equilibrium is approached.

X-Ray crystallographic methods are often of comparatively little value in determining the character and occupancy of sites when the materials in question lack long-range order. This is particularly true of solids formed from glass precursors, where ordering sets in only after prolonged annealing. Magic-angle spinning (m.a.s.) n.m.r. spectroscopy, which is especially
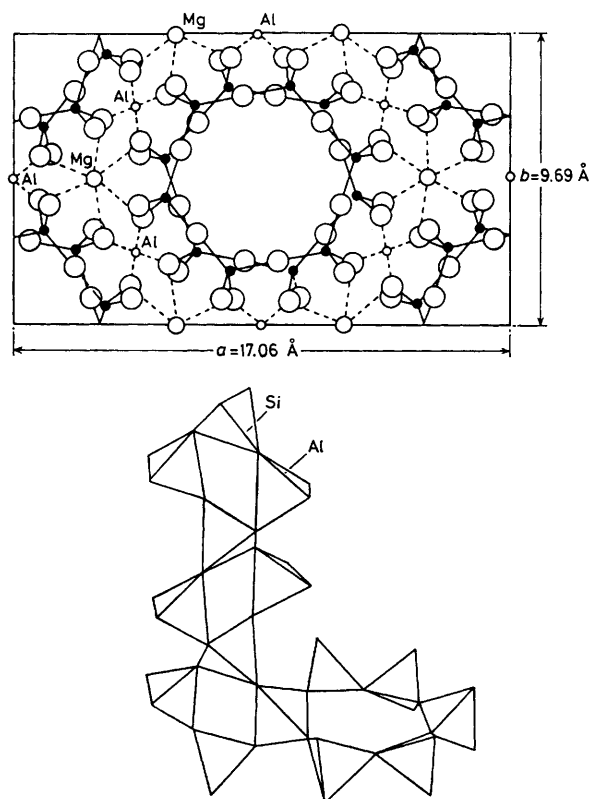
Figure 1. Plan view (upper) of a section of the cordierite structure showing six-membered rings of tetrahedra which are connected to chains of four-membered (tetrahedral) rings as depicted in the elevation view (lower) of part of the structure. No attempt has been made to illustrate the ordering of the Si and Al in the tetrahedra (see the text and Figure 2).

Figure 2. ^{29}Si M.a.s.n.m.r. spectra of synthetic cordierite, $Mg_2Al_4Si_5O_{18}$, at 104.22 MHz, (a) 2 min after crystallization from the melt at 1185 °C, (b) after 23.7 h, and (c) after ca. 2000 h at the same temperature. The freshly crystallized material is hexagonal; that finally produced is orthorhombic.

useful in clarifying the structure of microcrystalline solids not generally amenable to single-crystal X-ray methods, is, however, a potentially viable technique for ascertaining the local atomic environment.[1-3] We have, therefore, been prompted by earlier work on naturally occurring[4] cordierite $(Mn,Mg,Fe)_2Al_4Si_5O_{18}$ and on its synthetic[5] variant, Mg_2Al_4-Si_5O_{18}, to explore the extent to which quantitative studies of local atomic environments could be made by ^{29}Si and ^{27}Al m.a.s.n.m.r. spectroscopy. It transpires that quite far-reaching conclusions pertaining to site occupancies and to the dynamics of site interchange can be drawn from this relatively complicated system.

Previous studies have shown[5,6] that there is a constant overall composition (Si : Al = 1.25) in synthetic, so-called high cordierite, which has a hexagonal structure, the broad features of the framework of which are well known.[7] This disordered polymorph transforms on annealing to an orthorhombic structure in which Si and Al are ordered within the chain and ring manifolds (see Figure 1).[4,5]

Figure 2 shows the ^{29}Si high-field m.a.s.n.m.r. spectra, obtained using equipment previously described,[3,8] for synthetic cordierite after various times of annealing following crystallization from the glass at 1185 °C. At this temperature crystallization is complete within less than a minute, and X-ray diffractograms confirm the formation of hexagonal cordierite. M.a.s.n.m.r. peaks of the crystals first formed are very narrow, indicative of appreciable local, short-range Al, Si order. But, whereas the X-ray diffractograms remain essentially unchanged after 100 h, when long-range Al, Si order becomes established, there are noteworthy changes in the m.a.s.n.m.r. spectra [only two of which are shown in Figure 2(a) and 2(b)].
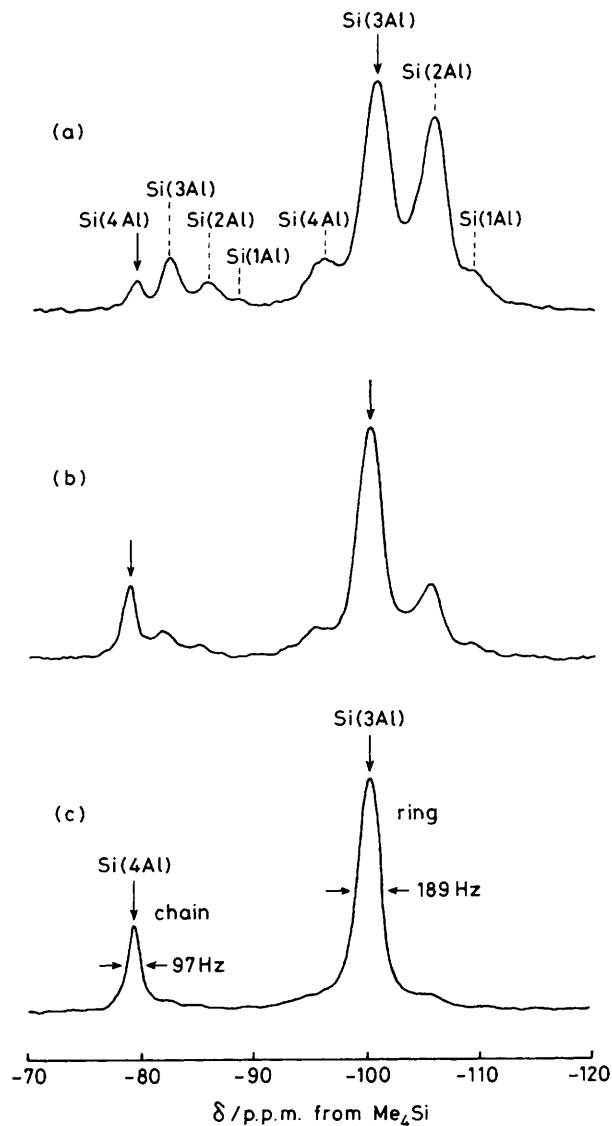
In each spectrum recorded for the hexagonal structure there are two distinct groups of peaks with chemical shifts (from Me_4Si) in the ranges -79 to -88 p.p.m. and -95 to -109 p.p.m. From previous m.a.s.n.m.r. spectra[2] of a wide range of aluminosilicates we conclude that both these groups of peaks signify tetrahedrally bonded Si (six-co-ordinated Si in stishovite, e.g., falls[9] at -191.3 p.p.m.). The first range is characteristic of chain structures, the second of ring structures. For each of these two groups a maximum of five peaks is theoretically possible [$Si(OAl)_4$, $Si(OAl)_3(OSi)$, $Si(OAl)_2(OSi)_2$ etc. designated Si(nAl) where $n = 0, 1 \ldots 4$]. It is to be noted that, within a few minutes of crystallization from the glass [Figure 2(a)], eight of these ten possible peaks are discernible, and it is not surprising that no $Si(OSi)_4$ groupings are found for highly aluminous materials such as cordierite, the probability of the occurrence of such groupings being 0.0016 for Si : Al = 1.25. In the orthorhombic form, [Figure 2(c)], which approaches the thermodynamically stable state, there are but two peaks : one corresponding to silicon in a 'chain' site, the

other to silicon in a 'ring' site. These sites can be identified in all three spectra, and are arrowed in Figure 2(a)—(c). The diminution in number of m.a.s.n.m.r. peaks in proceeding from the embryonic hexagonal to the aged orthorhombic form is what would be expected if Si,Al ordering is pronounced in the latter. The ratio of intensities of the 'chain' to 'ring' absorptions is 0.192:0.808, in good agreement with the expected ratio of 0.200:0.800 based on the X-ray structure[4] of the ordered form of (low) cordierite. Moreover, we would expect, if there were no site preferences and there was a statistically random distribution of Si and Al amongst all nine (three 'chain' and six 'ring) tetrahedral sites, a ratio of 0.333:0.666 at the very earliest stages of crystallization from the melt. In actual fact the ratio of 'chain' to 'ring' tetrahedral sites after 2 min [Figure 2(a)] is 0.122:0.878, there being even greater preference for 'ring' sites at this early stage of crystallization than at the final, near-equilibrium stage [Figure 2(c)].

The intensity ratio of the two peaks in the final, orthorhombic (low) cordierite structure [Figure 2(c)] is almost exactly what would be expected on the basis of the X-ray established ordering scheme. For every Si atom in a chain site there are four in ring sites. Moreover, the X-ray structure shows the 'chain' silicon to possess a local environment of $Si(OAl)_4$ and the 'ring' silicon of $Si(OAl)_3(OSi)$. Taking these assignments as a point of departure, the other peaks in Figure 2(a) and 2(b) may also be assigned with internal self-consistency. (That being so, we note in passing that the kinetics of site population and depopulation may now be followed from time-lapse m.a.s.n.m.r. measurements.[10]) Furthermore, the nature of the disordered, hexagonal structure may be elucidated by estimating the Si:Al ratios from ^{29}Si m.a.s.n.m.r. intensities (as described previously[3,11]). Thus, although it is known that the global Si:Al ratio remains unchanged at 1.25 throughout the course of ordering amongst the tetrahedral sites, the values computed, on the assumption that there are no Al–O–Al linkages, are, after 2 min at 1185 °C, 1.46 in the chain manifold, 1.54 in the rings, and 1.53 overall, and, after ca. 2000 h at the same temperature, 1.07, 1.33, and 1.27, respectively.

The fact that, in the early stages of annealing, the Si:Al ratios computed from m.a.s.n.m.r. spectroscopy exceed the known value points strongly to the existence of Al–O–Al linkages. Such linkages are, however, progressively eliminated as the degree of ordering increases, and in the final, orthorhombic state no two AlO_4 tetrahedra are adjacent.

The ^{27}Al m.a.s.n.m.r. spectra show very distorted and rather ill defined peak profiles. When the samples are spun off the magic angle (54 ° 44′ to the magnetic field) essentially all of the Al atoms are seen to be in tetrahedral environments (the small percentage that are not, appear to be a trace impurity). From the anisotropy of the spectrum it is concluded that the AlO_4 tetrahedra are rather distorted. In the ^{27}Al spectra corresponding to the samples the ^{29}Si spectra of which are shown in Figure 2(a)—(c) there is a gradual change in the peak position [from ca. 49.6 to ca. 40.3 p.p.m. from $Al(H_2O)_6{}^{3+}$] in proceeding from the 2 min to the 2000 h samples.

A fuller treatment of the results along with further details as to how m.a.s.n.m.r. spectroscopy may profitably be used quantitatively to monitor and delineate site symmetry and site occupancy changes during solid-state transformations will be given elsewhere. In conclusion, we note that m.a.s.n.m.r. spectroscopy as a technique has shown itself capable of elucidating the course and nature of local environment changes when other techniques, such as X-ray diffraction, are largely insensitive to such changes.

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