Silicon-29 Magic-Angle Spinning Nuclear Magnetic Resonance Study of Some Lanthanum and Yttrium Silicon Oxynitride Phases

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The preparation and ^{29}Si magic-angle spinning nuclear magnetic resonance spectra of the main phases in the LaSiON system and some related phases in the YSiON system are described. The silicon-29 chemical shifts for most of the LaSiON phases were found to fit well with expected values on the basis of silicon nearest-neighbor coordination, although in general they are more negative than those observed for the analogous YSiON phases. The N-apatite phase of expected composition $La_5Si_3O_{12}N$ is found to give a spectrum indistinguishable from that of the oxyapatite $La_{9.33}Si_6O_{26}$, and therefore doubt is cast on the formulation of this phase. The phase $LaSi_3N_5$ is shown to give rise to an anomalously negative chemical shift when compared with values obtained from other silicon nitride phases.

Ceramics based on silicon nitride and related systems are currently under intensive investigation for use as high-temperature engineering materials.[1] These consist of a matrix of the main silicon nitride phase plus a grain boundary region of a glassy or crystalline oxynitride phase. Until recently, the main methods used to study the crystal structures of these compounds were powder X-ray diffraction (XRD) and transmission electron microscopy (TEM), but in the past 3 years, several multinuclear magic-angle spinning magnetic resonance (MAS NMR) studies have been reported for the quaternary SiAlON system,[2-4] silicon carbides,[5,6] and glass ceramics.[7] Dupree et al.[8] have also studied the YSiON system by ^{29}Si MAS NMR (see Table I). This article describes the ^{29}Si MAS NMR spectra of phases in the related LaSiON system and compares them with those of the YSiON system.

The primary aim of ^{29}Si MAS NMR studies to date has been to correlate isotropic chemical shifts with various structural features influencing them, most notably silicon nearest- and next-nearest-neighbor coordination.[9] Silicon coordinated mainly to oxygen tends to resonate at a lower frequency than when coordination is mainly to nitrogen. Silicon-29 NMR can thus be used as a probe of structural features not readily accessible by other physical methods.

Table I. ^{29}Si Chemical Shifts and Line Widths for Some LaSiON and YSiON Phases

phase	proposed environment	YSiON		LaSiON	
		δ_{Si}/ppm	fwhh[a]/Hz	δ_{Si}/ppm	fwhh[a]/Hz
M_2SiO_5	SiO_4–Q^0	−79.8[b]	80	−83.5[c]	200
$M_2Si_2O_7$	SiO_4–Q^1	−92.8[b,d]	~50	−83.8[e]	200
$M_{9.33}Si_6O_{26}$ (apatite)	SiO_4–Q^0			−78.4	300
$M_5Si_3O_{12}N$ (N-apatite)	SiO_4–Q^0	−74.8[b]	210		
	SiO_3N–Q^0	−67.5[b]	250	−77.9	290
$M_4Si_2O_7N_2$ (N-YAM)	SiO_3N–Q^1	−74.4[b]	320	−83.8	250
$MSiO_2N$ (N-wollastonite)	SiO_2N_2–Q^2	−65.3[b]	400	−72.6	135
		−65.0	130		
$M_2Si_6O_3N_8$ (new phase)				−57.3[f]	330
				−68.2[f]	260
$M_2Si_3O_3N_4$ (N-melilite)	SiO_2N_2–Q_3, –Q_4	−56.7[b]	430		
		−56.6	330		
MSi_3N_5	SiN_4	−45.5[b]	140	−57.3[g]	330
		−42.3[b]	140	−65.4[g]	250
$M_6Si_3N_{10}$	SiN_4	−36.0	120		
		−38.5	130		

[a] Full width at half-height. [b] Taken from ref 8. [c] X_1 type. [d] γ type. [e] β type. [f] Intensity ratio 3:1. [g] Intensity ratio 1:2.

Figure 1, top, shows the crystalline phases and phase relationships in the $Ce^{III}SiON$ system.[10] A similar diagram has not been constructed for the LaSiON system, but extensive studies[11-13] indicate that analogous phases are present in this system, although doubt has been cast on the existence of the N-melilite phase, $La_2Si_3O_3N_4$.[11] A tentative phase diagram for this system is shown in Figure

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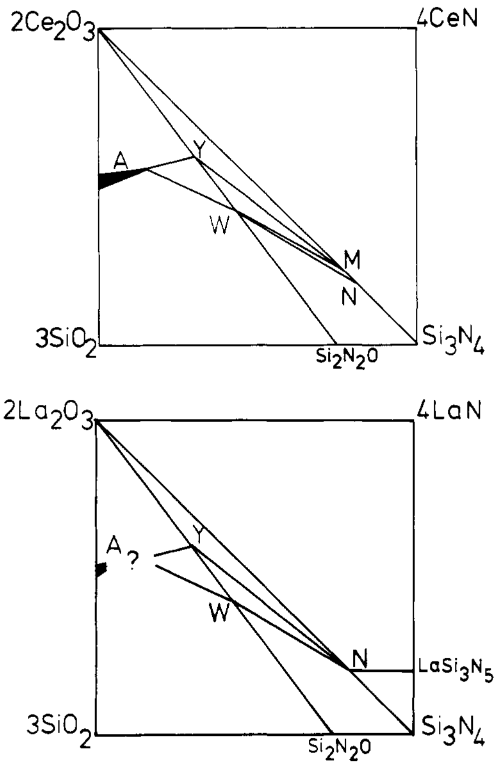

Figure 1. Top: crystalline phases and phase relationships in the Ce^{III}SiON system[10] at 1700 °C. Bottom: Proposed diagram for the LaSiON system at 1700 °C. (A = apatite, W = N-wollastonite, Y = N-YAM, M = N-melilite, N = new phase.) Oxide phases are not shown.

1, bottom. Of the nitrogen-containing phases, only the structures of the N-wollastonite, $LaSiO_2N$,[14] and the nitride $LaSi_3N_5$[15] have been fully determined.

Experimental Section

Samples of all the LaSiON phases were prepared by firing pellets of La_2O_3, α-Si_3N_4, and SiO_2 premixed in the correct proportions and embedded in BN in a graphite crucible, at temperatures in the range 1500–1800 °C for 0.5–2 h in a graphite resistance furnace under N_2. To prepare pure nitride phases, a mixed carbothermal reduction/nitridation route was developed in which pellets containing carbon were placed on a bed of BN in an open crucible to allow free flow of gases around the pellet during firing. $LaSi_3N_5$ was prepared by reduction of $La_2Si_6O_3N_8$:

$$N_2(g) + La_2Si_6O_3N_8 + 3C \xrightarrow[1\ \text{h}]{1800\ ^\circ\text{C}} 2LaSi_3N_5 + 3CO(g)$$

$Y_6Si_3N_{10}$ was prepared by carbothermal reduction of a mixture of Y_2O_3 + 2α-Si_3N_4 + 3C at 1800 °C for 1 h. In this case, $Y_2Si_3O_3N_4$ and SiC were significant impurities.

Sample purity was checked by powder XRD using a Hägg–Guinier focusing camera and Cu Kα_1 radiation, and all samples except those of $LaSi_3N_5$ ($\sim$75%) and $Y_6Si_3N_{10}$ ($\sim$50%) were estimated to be >95% pure. Cell dimensions were determined by accurate measurements of XRD photographs and were refined by using a least-squares fitting program.

Silicon-29 MAS NMR spectra were obtained with a Varian VXR300 spectrometer operating at a frequency of 59.6 MHz. Samples were packed in zirconia rotors and spun at 3–4 kHz during acquisition. Chemical shifts are quoted relative to the signal for tetramethylsilane (δ_{Si} = 0) via measurements on 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (δ_{Si} = 1.18 ppm). Spectra were acquired by using 90° radio frequency pulses (5 μs) and 120-s recycle delays unless stated otherwise. Line broadening of ca. 100 Hz was applied prior to Fourier transformation. Static ^{139}La spectra were obtained at 42.4 MHz by using a spin–echo sequence to overcome the problems of probe ringing.[16]

Results

Our ^{29}Si MAS NMR results are summarized in Table I. In no cases were significant spinning sideband patterns observed, even at modest rotation speeds. Analysis of powder patterns obtained from static samples to obtain shielding anisotropy was not possible because of the poor signal-to-noise ratio. Because ^{29}Si relaxation times are long, the spectra are not quantitative. There is significant overlap between the spectra of $LaSi_3N_5$ and $La_2Si_6O_3N_8$. Since these two phases are often present together, the spectra of the samples were also recorded under quantitative conditions by using short pulse lengths (π/10) and long recycle delays (900 s). The spectra were essentially unchanged.

The lanthanum-139 spectra were all very broad, with line widths in the region 150–200 kHz. The spectra were indistinguishable from each other.

Discussion

The three lanthanum silicates La_2SiO_5, $La_2Si_2O_7$, and the apatite phase $La_{9.33}Si_6O_{26}$ all have resonances in the region expected for structures containing SiO_4 tetrahedra.[6] In La_2SiO_5 and $La_{9.33}Si_6O_{26}$, silicon is present in a Q^0 environment,[17] while in $La_2Si_2O_7$ it is[18] of type Q^1.

The NMR spectra of the two apatite phases $La_{9.33}Si_6O_{26}$ and that with target composition $La_5Si_3O_{12}N$ are indistinguishable, and thus it seems unlikely that the two phases have significantly different compositions. The spectra also show single peaks, unlike the yttrium analogue, $Y_5Si_3O_{12}N$, which shows two peaks, assigned to SiO_4 and SiO_3N tetrahedra. The cell dimensions of the two lanthanum phases were determined, giving a = 9.701 Å, c = 7.255 Å for the N-apatite and a = 9.711 Å, c = 7.211 Å for oxide apatite. These compare with literature values of a = 9.721 Å, c = 7.258 Å for N-apatite[11] and a = 9.713 Å, c = 7.194 Å for oxide apatite.[18] This suggests that neither of the two phases prepared for this study correspond exactly to phases reported in the literature, and that a homogeneity range occurs that has not been studied in detail. The NMR spectra suggest that the phase of supposed composition $La_5Si_3O_{12}N$ contains little or no nitrogen, and it seems likely that the range of homogeneity of the apatite phase does not extend as far as this composition.

The phases $LaSiO_2N$ and $YSiO_2N$ have similar three-membered ring structures, with essentially identical silicon environments (SiO_2N_2–Q^2). The resonances observed from these two phases are significantly narrower than those described by Dupree et al.[3] Line widths in these systems depend on a variety of factors, including the amounts of paramagnetic impurities present in the precursor α-Si_3N_4[19] and residual dipolar coupling between ^{29}Si and ^{14}N (which is not necessarily in Zeeman states).[20] It is unlikely that significant conclusions can be drawn from accurate measurement of line widths. A difference of 7 ppm is noted between the chemical shifts of the two phases, and a similar difference is observed for the $M_4Si_2O_7N_2$ (N-YAM, M = La and Y) compounds (9.6 ppm), the lanthanum derivative again giving the lower frequency. No satisfactory

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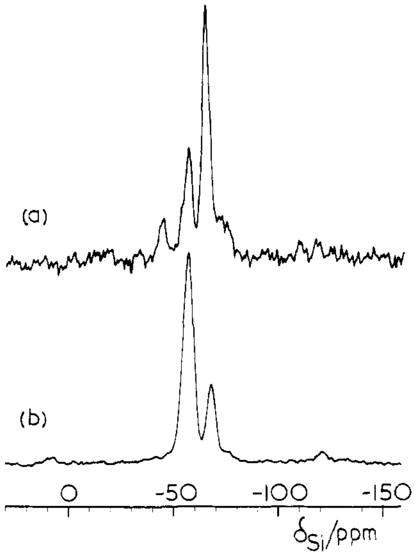

Figure 2. ^{29}Si MAS NMR spectra of (a) $LaSi_3N_5$ (210 transients) and (b) $La_2Si_6O_3N_8$ (580 transients).

explanation of these differences has yet been proposed.

The phases $La_2Si_2O_7$ and $La_4Si_2O_7N_2$ give rise to indistinguishable chemical shifts. In both of these phases, the principal structural unit is the Si_2X_7 group (X = O, N). As Dupree et al. point out,[8] Pauling's second crystal rule (PSCR) predicts that in the $M_4Si_2O_7N_2$ oxynitrides, nitrogen should be directly bonded to silicon. The only arrangement of nitrogen atoms consistent with both PSCR and the ^{29}Si MAS NMR spectra involves them occupying nonbridging sites. Thus, in this case, silicon in an Si_2O_7 unit ($La_2Si_2O_7$) and a $[Si_2O_5N_2]$ unit give rise to the same chemical shift. However, silicon chemical shifts in such units are very sensitive to bond angles and other structural parameters,[9] as can be seen by comparing the shifts observed for γ-$Y_2Si_2O_7$ (−92.8 ppm) and β-$La_2Si_2O_7$ (−83.8 ppm). In both structures the main unit is $[Si_2O_7]$, but in $Y_2Si_2O_7$, the OSiO bond angle is 180°, whereas in $La_2Si_2O_7$ it is closer to 140°. Of course there is no direct proof that in $M_4Si_2O_7N_2$ nitrogen bonds directly to silicon, but it seems unlikely that PSCR is violated.

The spectra of $La_2Si_6O_3N_8$ and $LaSi_3N_5$ are the most difficult to interpret. The two spectra are superimposed in Figure 2. The peaks at −46 and −65 to −70 ppm are thought to result from impurities because they are not observed from impure samples prepared by other means. The two compounds have identical La/Si ratios and are difficult to prepare in isolation from each other. Nevertheless, the XRD pattern indicates that the $La_2Si_6O_3N_8$ is >95% pure and is not contaminated with any $LaSi_3N_5$. The $LaSi_3N_5$ is less pure; some lines in its XRD pattern could not be identified and are possibly due to another lanthanum silicon nitride.

The crystal structure of $La_2Si_6O_3N_8$ has not yet been determined. The ^{29}Si NMR spectrum suggests that two distinct silicon environments are present in the ratio 3:1, presumably either SiN_4 and $SiON_3$ or (more likely, given the chemical shifts and stoichiometry) $SiON_3$ and SiO_2N_2. Figure 2 shows that the minor peak in the spectrum of $La_2Si_6O_3N_8$ cannot arise from impurity $LaSi_3N_5$ as suggested by preliminary results from Dupree et al.[21]

The crystal structure of $LaSi_3N_5$ has not been published in full,[15,22] but an examination of an incomplete list of coordinates suggests that three distinct silicon environments may be identified, namely, SiN_4-Q^5, -Q^6, and -Q^7. If it is assumed that this phase contains no oxygen, the peak at −65.4 ppm can certainly be assigned to at least two of the environments, but whether the peak at −57.3 ppm arises from the third environment or from an impurity is not clear. This observed chemical shift is by far the most negative seen for an SiN_4 environment and compares with −36.0/−38.5 ppm for $Y_6Si_3N_{10}$ and −42.3/−45.5 ppm for YSi_3N_5. In fact it is more characteristic of an $SiON_3$ than an SiN_4 environment.

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Registry No. Y, 7440-65-5; La, 7439-91-0; O_2, 7782-44-7; N_2, 7727-37-9; Si, 7440-21-3; $La_5Si_3O_{12}N$, 57034-89-6; $LaSi_3N_5$, 79304-71-5.

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