Phases occurring in the Si_3N_4–YN system

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A method is described for synthesising complex silicon lanthanide nitrides by carbothermal reduction and nitridation (CRN) of both SiO_2–Ln_2O_3 mixtures and elemental Si–Ln_2O_3 mixtures at 1400–1450 °C. Syntheses in the Si_3N_4–YN system confirm the existence of the compounds YSi_3N_5 and $Y_2Si_3N_6$, which can be prepared virtually free of oxygenated impurity phases from mixtures containing SiO_2 rather than from mixtures containing elemental Si. A third compound was also prepared in this system, with an XRD pattern corresponding to that reported for $Y_6Si_3N_{10}$; mass change data and EDX analyses suggest, however, that this phase is much less Y-rich than $Y_6Si_3N_{10}$, with an apparent composition nearer $Y_3Si_6N_{11}$. X-Ray powder diffraction data and ^{29}Si and ^{89}Y solid-state MAS NMR spectra are reported for all three phases. The NMR results suggest the presence of at least three Si sites in each phase, and at least two types of Y site, one of which, characterised by a resonance at δ 490–510 (ref. YCl_3), is common to all three compounds.

The phase relationships in the Y–Si–Al–O–N system have been researched extensively.[1–6] The Si_3N_4-rich corner of the phase diagram is of special interest as this contains phases such as α- and β-sialon, which are important for tailoring engineering ceramics.[7] The β-sialon phase, $Si_{6-z}Al_zO_zN_{8-z}$ coexists with α-sialon, $Y_xSi_{12-(m+n)}Al_{m+n}O_mN_{16-n}$, which forms in a restricted two-dimensional compositional area in the plane Si_3N_4–Al_2O_3 : AlN–YN : 3AlN (Fig. 1). The Si_3N_4 corner of the illustrated Jänecke prism contains, in addition to the two sialon phases, the nitrogen-rich phases N-melilite and JEM. Melilite solid solutions, $Ln_2Si_{3-x}Al_xO_{3+x}N_{4-x}$, have been found to form with Y and in Ln-sialon systems with lanthanides of atomic number $Z=58$–66.[8,9] Recent studies have revealed a new N-rich phase called JEM with a composition $LnAl(Si_{6-z}Al_z)(N_{10-z}O_z)$. This has so far been found to form only with Ln ions of atomic number $Z=57$–62; a corresponding Y-JEM phase has not been found.[10,11]

The possible formation of other N-rich compounds is difficult to assess because of the difficulty of synthesising pure nitrides in the Si_3N_4–YN–AlN system. Silicon and aluminium nitride powders inherently contain some oxygen, and yttrium nitride powder is a very sensitive starting material which hydrolyses readily unless manipulated in a dry-box, and even at moderate temperatures is oxidized rapidly. Further, the reaction rate between YN and covalently bonded nitrides is very low even at high temperature.

No phase has been reported along the Si_3N_4–AlN tie line, and in the interior of the Si_3N_4–YN–AlN system the α-sialon phase has an extended linear solid solution $Y_{y/3}Si_{12-y}Al_yN_{16}$. The extent of this solid solution range has been variously reported as $y=1.8$–3.4 at 1750 °C[1] or $y=1.3$–2.4 at 1800 °C.[5]

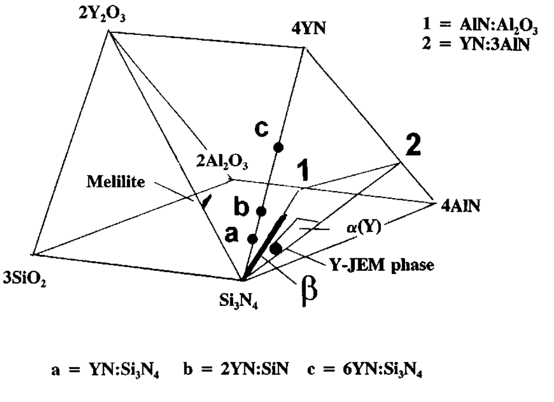

Fig. 1 Schematic illustration of the Jänecke prism for Ln–Si–Al–O–N systems where Ln = Y or the rare-earth elements. All the N-rich phases in the Si_3N_4 corner are marked, but note that melilite, α-sialon and JEM form only with a limited number of Ln elements, see text.

Previous studies of the pseudo-binary Si_3N_4–YN system have mainly concentrated on very high temperature reactions between the nitrides. Three phases, YSi_3N_5, $Y_2Si_3N_6$ and $Y_6Si_3N_{10}$, were reported by Thompson,[1] but in a later work only $Y_2Si_3N_6$ was found, the XRD patterns reported for the other two nitrides by Thompson being assumed by the subsequent authors[5] to be a mixture of N-melilite and other oxygen-containing phases. It should be stressed, however, that the later paper[5] reports only five preparations in the Si_3N_4–YN system, all of which include at least one oxygen-containing phase in addition to $Y_2Si_3N_6$; the additional oxygenated phases were typically N-melilite ($Y_2Si_3O_3N_4$), J-phase ($Y_4Si_2O_7N_2$) or even Y_2O_3.[5]

Discrepancies in the literature seem to be due, at least in part, to difficulties in achieving an absolutely oxygen-free environment when working with nitride starting materials. Alternative lower-temperature synthesis techniques include carbothermal reduction of silica and yttria at about 1400 °C accompanied by simultaneous nitridation, or a similar reaction in which silica is replaced by elemental silicon. The use of very fine grained carbon will initiate reduction of the oxides, and in the presence of an excess of nitrogen gas, the reaction will produce Si–Y nitrides with compositions depending on the ratios of the starting materials. A small excess of carbon assures an oxygen-free reaction environment.

Although carbothermal reduction and nitridation (CRN) has been used for the preparation of β-sialon powders from natural clays and minerals,[12,13] the technique has not been reported previously for syntheses in the Si–Y–N system. In the synthesis of sialons, the CRN process involves a complex reaction sequence which depends on the character of the precursors and the process parameters. It is generally accepted that gas-phase reactions involving SiO and CO are involved in sialon formation. A number of possible reactions have been suggested, which may proceed at different temperatures, sometimes even parallel to each other.[13–15]

This paper describes the phase relationships in the system Si_3N_4–YN, deduced from samples prepared by the CRN technique, using both SiO_2–Y_2O_3 mixtures and elemental Si–Y_2O_3 mixtures, both in combination with carbon. We report X-ray powder diffraction data for the product phases YSi_3N_5, $Y_2Si_3N_6$ and $Y_3Si_6N_{11}$, and also their ^{89}Y and ^{29}Si solid-state MAS NMR spectra.

Experimental

The compositions of the present CRN samples were calculated so as to lie along the Si_3N_4–YN tie line. Mixtures were prepared corresponding to Si_3N_4:YN ratios of 2:1, 1:1, 1:2, 1:3 and 1:6. The starting materials were carbon (Degussa Lampblack), SiO_2 (Silica Superfine, $d_{50} = 1.45$ µm, Commercial Minerals Ltd), elemental Si (Sicomill, grade 4D, $d_{50} = 4.6$ µm, KemaNord Industrikemi, Sweden) and Y_2O_3 (Fine, grade C, H. C. Starck, Berlin). The amount of carbon added corresponded to the calculated amounts for complete reaction plus an excess of 10%. The samples were heated in alumina crucibles placed in an alumina boat in a horizontal tube furnace (40 mm i.d.). The dynamic reaction atmosphere was nitrogen (high-purity, oxygen-free), flow rate 100 ml min^{-1}. The holding temperature (1400–1450 °C) was approached at a heating rate of 10 °C min^{-1} with the holding time at the final temperature varying from 8 to 48 h. A small amount (*ca.* 70 µmol g^{-1}) of Eu_2O_3 was added before heating to the samples prepared for examination by MAS NMR spectroscopy. The purpose of this addition, which did not change the phase composition of the products, was to increase the relaxation rate of both ^{89}Y and ^{29}Si and enable these spectra to be acquired.[16]

All samples were carefully weighed before and after the reaction, and the reaction products were stored in a desiccator before examination by X-ray powder diffraction (XRD) in a dry flowing nitrogen atmosphere using a Philips PW1700 computer-controlled diffractometer with graphite monochromator, Co-Kα radiation and APD1700 software. Selected specimens were examined using a Huber 620 Guinier X-ray camera and Y:Si ratios were determined on the bulk material by EDXA (the materials were too fine-grained to permit analysis of the individual particles). The room-temperature ^{89}Y and ^{29}Si MAS NMR spectra were acquired at 11.7 T using a Varian Unity 500 spectrometer with a 5 mm Doty MAS probe spinning at 10–12 kHz, under the following conditions: ^{89}Y: 20 µs $\pi/2$ pulse, recycle delay 3 s, 170 µs ringdown delay between excitation and sampling, shifts referenced to aqueous 1 mol dm^{-3} YCl_3 solution; ^{29}Si: 6 µs $\pi/2$ pulse, recycle delay 30 s, shifts referenced to tetramethylsilane.

Results and Discussion

Regardless of the starting mixture, all the CRN samples experienced a mass loss 3–5% higher than the theoretical loss, due to the removal from the sample of gaseous SiO, which condensed as a fine wool-like material on the cooler downstream furnace tube walls. XRD showed this condensed material to be amorphous; solid-state ^{29}Si NMR studies indicated a preponderance of Si—O bonds, with evidence of some Si—C bonds also, probably formed by the presence of CO gas during SiO condensation. This migration of material made it difficult to predict the final composition of the product, which, however, proved in all cases to be a Y–Si nitride with a Y content slightly elevated over the batched composition. Once formed, the Y–Si nitride appeared to be stable under prolonged heating in nitrogen and did not decompose with time.

In the preliminary experiments, the odour of ammonia was sometimes detected during grinding of the products in air, denoting the presence of hygroscopic nitrides. All subsequent preparations were therefore immediately desiccated and the XRD traces obtained under dry nitrogen. Further investigations showed that the samples were only hygroscopic when YN or a small amount of amorphous nitride (probably YN) was indicated by XRD. The different crystalline Y–Si nitrides, once formed, proved to be fully stable to ambient air.

It proved difficult to obtain oxygen-free products by CRN reaction of Si–Y_2O_3 mixtures; the products at 1400 °C always contained, in addition to the Y–Si–N phases, significant amounts of J-phase ($Y_4Si_2O_7N_2$) and sometimes even unreacted Y_2O_3 (where the yttria content was very high). Raising the temperature to 1450–1475 °C increased the degree of nitridation, making it possible to prepare mixtures of YSi_3N_5 and a phase with the XRD pattern reported[1] for $Y_6Si_3N_{10}$. However, single-phase preparations were not achieved using elemental Si and, surprisingly, $Y_2Si_3N_6$ was never formed in this system.

By contrast, CRN reactions in mixtures of SiO_2 and Y_2O_3 produced phases with the XRD patterns[1] of YSi_3N_5, $Y_2Si_3N_6$ and $Y_6Si_3N_{10}$, and, in some samples, even YN. It was possible to prepare almost pure $Y_2Si_3N_6$ from a starting mix of the appropriate composition; EDXA indicated the bulk Y:Si ratio of this phase to be 0.65, in good agreement with the theoretical ratio of 0.66.

Mixtures with the composition $Y_6Si_3N_{10}$ were found to be not very reactive below *ca.* 1450 °C, while above this temperature, the loss of volatile Si species was too great for the stoichiometry to be maintained. However, mixtures of YSi_3N_5 composition were found to give an essentially pure phase with the reported $Y_6Si_3N_{10}$ XRD powder pattern after reaction at 1475 °C for 8 h. This reaction was accompanied by a mass loss 8–12% greater than the theoretical loss for formation of YSi_3N_5 from this mixture, suggesting the removal of additional Si and the formation of a more Y-rich phase. However, the mean bulk Y:Si ratio determined by EDXA (0.39) indicates that only slight Y-enrichment has occurred, and certainly not to the extent required for the formation of $Y_6Si_3N_{10}$ (Y:Si ratio 2). That this phase is not $Y_6Si_3N_{10}$ is also suggested by the observed mass loss, which is much less than the theoretical value for the conversion of $6YSi_3N_5 \rightarrow Y_6Si_3N_{10}$ (48%). On the basis of the mass change and the EDXA data, a possible composition for this phase may be $Y_3Si_6N_{11}$; this would have a Y:Si ratio of 0.5 and its formation would be accompanied by a mass loss of 19.2%. It should be noted that the original

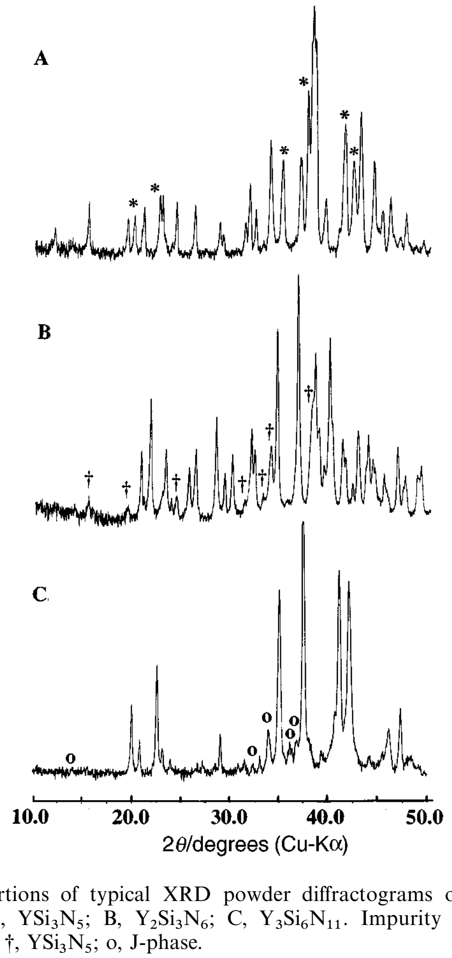

Fig. 2 Portions of typical XRD powder diffractograms of Y–Si–N phases: A, YSi_3N_5; B, $Y_2Si_3N_6$; C, $Y_3Si_6N_{11}$. Impurity phases: *, $Y_3Si_6N_{11}$; †, YSi_3N_5; o, J-phase.

Table 1 XRD powder diffraction data for YSi_3N_5,[a] $Y_2Si_3N_6$[b] and $Y_3Si_6N_{11}$[c]

YSi_3N_5				
h	k	l	d_{obs}/Å	$(I/I_0)_{obs}$
1	0	0	8.48	6
1	0	1	6.63	12
0	0	2	5.32	9
1	1	0	4.905	8
1	0	2	4.509	13
2	0	0	4.249	12
2	0	1	3.946	8
1	1	2	3.607	5
2	0	2	3.320	6
1	0	3	3.272	18
2	1	0	3.212	9
2	1	1	3.074	33
3	0	0	2.833	23
2	1	2	2.749	88
3	0	1	2.737	100
2	0	3	2.722	99
0	0	4	2.659	13
1	0	4	2.638	32
3	0	2	2.5001[d]	2
2	2	0	2.4534	45
2	1	3	2.3805	27
3	1	0	2.3576	2
1	1	4	2.3379	10
3	1	1	2.3012	10
2	0	4	2.2547	2
2	2	2	2.2279	3
3	0	3	2.2136	1
3	1	2	2.1553	1
4	0	0	2.1249	1
1	0	5	2.0638	3
2	1	4	2.0485	9
4	0	2	1.9728	1
3	1	3	1.9633	2
3	2	0	1.9497	1
3	0	4	1.9394	2
3	2	1	1.9173	10
2	0	5	1.9016	2
3	2	2	1.8303	24
4	1	1	1.8268	11
4	0	3	1.8222	3
2	2	4	1.8032	5
2	1	5	1.7734	11
0	0	6	1.7732	
3	1	4	1.7639	2
1	0	6	1.7361	1
3	2	3	1.7082	13
3	0	5	1.7008	20
5	0	0	1.6996	
5	0	1	1.6781	6
1	1	6	1.6675	2
4	0	4	1.6598	1
4	1	3	1.6432	3
2	0	6	1.6361	18
3	3	0	1.6357	
5	0	2	1.6189	14
4	2	1	1.5881	1
3	1	5	1.5793	2
3	2	4	1.5722	17
3	3	2	1.5632	6

$F_3 = 171(0.006,30)$

$Y_2Si_3N_6$				
h	k	l	d_{obs}/Å	$(I/I_0)_{obs}$
2	1	0	6.44*	1
0	0	1	4.975	9
1	0	1	4.754	25
2	2	0	4.441	11
4	0	0	4.034	8
2	1	1	3.935	10
3	0	1	3.653	20
1	2	1	3.546	5
3	1	1	3.456	11
2	3	0	3.249	17
4	2	0	3.218	9
4	0	1	3.136	3
3	2	1	3.012	64
1	3	1	2.844	100
5	2	0	2.762	3
2	3	1	2.721	33
4	2	1	2.702	9
6	0	0	2.691	12
0	4	0	2.661	3
1	4	0	2.626	68
6	1	0	2.609	15
3	3	1	2.546	15
2	4	0	2.527	6
0	0	2	2.4876	3
1	0	2	2.4594	13
5	2	1	2.4142	5
6	2	0	2.4020	15
2	0	2	2.3766	4
6	0	1	2.3674	4
1	4	1	2.3221	4
6	1	1	2.3098	2
3	0	2	2.2585	11
1	2	2	2.2321	2
4	4	0	2.2222	5
2	2	2	2.1705	5
6	2	1	2.1635	3
5	3	1	2.1536	6
7	0	1	2.0939	1
3	2	2	2.0785	16
4	1	2	2.0768	
2	5	0	2.0590	4
1	3	2	2.0213	14
2	3	2	1.9755	13
7	2	1	1.9478	5
5	1	2	1.9386	9
2	5	1	1.9019	5
6	4	0	1.8927	7
8	2	0	1.8871	5
4	5	0	1.8835	6
8	1	1	1.8427	3
0	4	2	1.8180	2
7	3	1	1.8023	10
0	6	0	1.7745	17
4	5	1	1.7608	2
8	3	0	1.7548	9
6	2	2	1.7281	7
3	4	2	1.7223	8
7	0	2	1.6920	2
9	0	1	1.6879	3
5	5	1	1.6745	15
7	1	2	1.6704	5
1	6	1	1.6626	8
0	0	3	1.6585	6
7	4	1	1.6457	3
2	0	3	1.6246	3
10	0	0	1.6146	6
7	2	2	1.6122	
1	5	2	1.6096	
6	5	1	1.5829	2
3	1	3	1.5679	1

$F_{30} = 90(0.006,52)$

$Y_3Si_6N_{11}$				
h	k	l	d_{obs}/Å	$(I/I_0)_{obs}$
1	1	0	5.1583	11
0	2	0	5.1333	
0	0	2	4.9455	4
1	1	1	4.5737	20
0	2	1	4.5563	
1	1	2	3.5699	5
0	2	2	3.5616	
0	1	3	3.1391[d]	4
2	0	0	2.9830	15
1	3	0	2.9685	49
1	1	3	2.7780	100
0	2	3	2.7741	
2	2	0	2.5792	4
2	0	2	2.5543	52
1	3	2	2.5452	
2	2	1	2.4957	31
0	4	1	2.4844	31
1	4	1	2.2935[d]	3
1	0	4	2.2843[d]	3
0	4	2	2.2781[d]	
1	1	4	2.2298[d]	8
0	2	4	2.2278	
2	2	3	2.0314	7
0	4	3	2.0253	10
2	4	0	1.9456[d]	3
0	1	5	1.9425[d]	
1	5	0	1.9416[d]	
3	1	1	1.9154[d]	3
2	4	1	1.9090[d]	
2	0	4	1.9037[d]	5
1	3	4	1.9000[d]	
0	5	2	1.8964[d]	
1	1	5	1.8471	7
3	0	2	1.8451	
2	4	2	1.8105[d]	3
1	5	2	1.8073[d]	
2	2	4	1.7849[d]	3
0	4	4	1.7808[d]	
3	3	0	1.7194[d]	8
0	6	0	1.7111[d]	6
3	1	3	1.6799	23
2	4	3	1.6756	
1	5	3	1.6730	
2	0	5	1.6486[d]	3
2	1	5	1.6278[d]	3
0	1	6	1.6277[d]	
3	3	2	1.6241[d]	9
1	6	1	1.6225[d]	
0	6	2	1.6171[d]	5
3	2	3	1.6163[d]	
1	1	6	1.5703[d]	17
2	2	5	1.5697[d]	
0	2	6	1.5696[d]	
0	4	5	1.5668[d]	2

$F_{24} = 20(0.013,94)$

[a] YSi_3N_5 indexed on a hexagonal cell with $a = 9.8126(3)$ Å, $c = 10.6373(5)$ Å, $V = 887.0$ Å^3. [b] $Y_2Si_3N_6$ indexed on an orthorhombic cell with $a = 16.1492(9)$ Å, $b = 10.6465(6)$ Å, $c = 4.9758(3)$ Å, $V = 855.5$ Å^3. [c] $Y_3Si_6N_{11}$ indexed on an orthorhombic cell with $a = 5.965(1)$ Å, $b = 10.267(2)$ Å, $c = 9.892(2)$ Å, $V = 605.8$ Å^3. Intensities based on peak heights of the α_1 reflections. [d] These reflections were not resolved by Guinier–Hagg camera but are calculated from the cell parameters and demonstrated by pattern-fitting techniques.

identification of the XRD pattern of this phase[1] with $Y_6Si_3N_{10}$ was not accompanied by supporting analytical data, and that the pattern has been identified by subsequent authors[5] with $Y_2Si_3N_6$; the present results suggest it contains even less Y than this.

The phase YSi_3N_5 could not be prepared totally free of the compound we now identify as $Y_3Si_6N_{11}$, possibly owing to a slow reaction rate and the loss of SiO, which is particularly significant in high Si compositions. Although YSi_3N_5 forms more efficiently at higher temperatures, the loss of SiO is also greater under these conditions, leading to the additional appearance of $Y_3Si_6N_{11}$ or even small amounts of YN. The EDX analyses of these samples are fairly variable, with a typical mean bulk Y : Si ratio of 0.45, approximating to a 1 : 1 mixture of the two phases.

Portions of typical X-ray powder diffractograms of the three phases prepared from SiO_2 starting materials are shown in Fig. 2.

The XRD data obtained from the Guinier camera for the three Y–Si nitrides were used to determine the cell parameters, from which the X-ray powder diffractometer data presented in Table 1 were indexed. The data of Table 1 are presented in the accepted ICDD format, and include the associated Smith–Snyder figure of merit value F_{30} for the mono- and di-yttrium phases, expressed in the form $F_{30}=F(\Delta 2\theta, N)$, where F is the figure of merit, $\Delta 2\theta$ is the mean deviation between the calculated and observed 2θ values and N is the number of calculated lines up to the 30th observed line. The figure of merit value quoted for $Y_3Si_6N_{11}$ is F_{24}, calculated from the first 24 observed lines free of overlap. The quoted relative intensity values were derived from the diffractometer data for the α_1 reflections; the values for overlapping peaks were derived by pattern-fitting procedures.

The X-ray data are in general agreement with Thompson[1] (re-defining his $Y_6Si_3N_{10}$ as $Y_3Si_6N_{11}$), but are reported here for a wider range of *d*-values, which has permitted the identification of the major peak for each phase. The compound $Y_2Si_3N_6$ has been indexed on the basis of a primitive orthorhombic unit cell.

Typical ^{29}Si and ^{89}Y MAS NMR spectra are shown in Fig. 3. Although the samples of Fig. 3 are predominantly of one phase, they are known from XRD measurements to contain various amounts of a second phase which can, however, be allowed for, as follows. The sample of $Y_3Si_6N_{11}$ (Fig. 3C,F) contains a small amount of J-phase ($Y_4Si_2O_7N_2$), of which the ^{29}Si spectrum contains a resonance at δ −71 to −73,[16,17] and the ^{89}Y spectrum contains a peak at δ 214.5.[16] The absence of these resonances from the present ^{29}Si and ^{89}Y spectra suggests that the J-phase is not detected in the spectra shown in Fig. 3C,F, which are therefore assumed to arise solely from $Y_3Si_6N_{11}$. On this basis, the peaks at δ −37.3 and −35 in the ^{29}Si spectrum of YSi_3N_5 (Fig. 3A) are assigned to the $Y_3Si_6N_{11}$ impurity known to be present in this sample; by a process of elimination, the peaks at δ −44.7 and −41.5 are due to YSi_3N_5. On the basis of relative intensities, the resonance at δ −47.9 (Fig. 3A) must contain contributions from both YSi_3N_5 and $Y_3Si_6N_{11}$. By similar reasoning, the ^{89}Y resonances at δ 391 and 131 in this sample are assigned to YSi_3N_5, although the possibility cannot be ruled out that the resonance intensity at δ 506 contains a contribution from this phase as well as from the impurity phase $Y_3Si_6N_{11}$.

On this basis, the ^{29}Si resonances of YSi_3N_5 can be eliminated from the spectrum of $Y_2Si_3N_6$ which contains the former as an impurity phase (Fig. 3B); the group of peaks at δ −64.4, −59.7 and −57 are therefore associated with $Y_2Si_3N_6$. The ^{89}Y spectrum of this phase (Fig. 3E) consists predominantly of the resonance at δ 394 (which will, however, also contain a component from the YSi_3N_5 impurity). The origin of the smaller peak at δ 510 in this spectrum is less clear; it could arise solely from the YSi_3N_5 impurity, but the possibility that it contains a contribution from $Y_2Si_3N_6$ cannot be ruled out. These spectral assignments are summarised in Table 2, which includes the NMR data of related compounds for comparison.

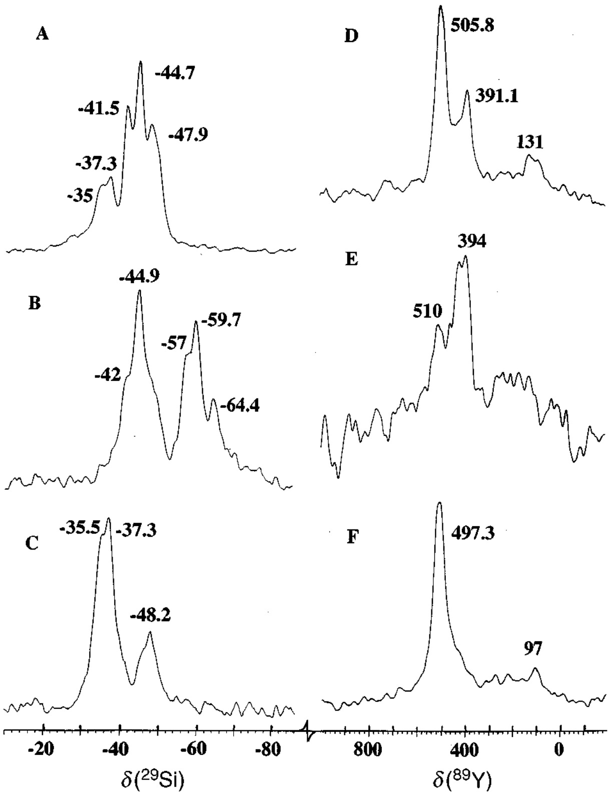

Fig. 3 Representative 11.7 T ^{29}Si (A–C) and ^{89}Y (D–F) MAS NMR spectra of Y–Si–N phases. A,D, predominantly YSi_3N_5 with $Y_3Si_6N_{11}$ impurity; B,E, predominantly $Y_2Si_3N_6$ with YSi_3N_5 impurity; C,F, predominantly $Y_3Si_6N_{11}$ with a trace of J-phase.

Table 2 ^{29}Si and ^{89}Y NMR assignments for the present Y–Si–N phases and related compounds (resonances listed in order of decreasing intensity)

phase	$\delta(^{29}Si)$	$\delta(^{89}Y)$
YSi_3N_5	−44.7, −41.5, −47.9	391.1, 131, 505.8(?)
$Y_2Si_3N_6$	−59.7, −57, −64.4	394, 510(?)
$Y_3Si_6N_{11}$	−37.3, −35.5, −48.2	497.3, 97
$Y_4Si_2O_7N_2$	−71 to −73[a,b]	214.5[a]
$Y_2Si_3O_4N_3$	−56.7 to −57.5[a,d]	160.5[a]
$Y_5Si_3O_{12}N$	−73.7 to −74.9, −67.4[d]	—
$YSiO_2N$	−64.7 to −65.3[d]	—
$Y_{10}Al_2Si_3O_{18}N_4$	−76.1[c]	—
Y_2SiO_5	−79.8 to −80.0[d]	237, 148[b]
γ-$Y_2Si_2O_7$	−92.8[d]	198[b]
α-$Y_2Si_2O_7$	—	114[b]
β-$Y_2Si_2O_7$	—	208[b]
δ-$Y_2Si_2O_7$	—	122[b]
Y_2O_3	—	314, 272.5[b]

[a] Ref. 16. [b] Ref. 17. [c] Ref. 18. [d] Ref. 19.

The NMR results suggest the presence of at least three Si sites in each of these phases, those in YSi_3N_5 having shifts in the general region of those of Si_3N_4. The ^{89}Y spectra suggest at least two types of Y site in each phase, one of which (at δ 490–510) appears in all the spectra. In addition, YSi_3N_5 and $Y_2Si_3N_6$ have a similar Y site, resonating at δ *ca.* 390. All three Y spectra contain intensity at δ *ca.* 100–200, but peaks can be resolved in this region only in YSi_3N_5 and $Y_3Si_6N_{11}$. The shifts of the peaks at δ *ca.* 390 and 500 are distinctly different from those reported for oxygenated Y compounds including Y_2O_3, the various yttrium silicates[18] and J-phase and N-melilite,[16] which appear at δ 100–300. The present shifts may reflect the predominantly nitrogen environment of the yttrium, with the minor spectral features at δ 100–200 arising from small amounts of oxygenated phases.

In summary, this work shows CRN to be an excellent method for preparing complex silicon yttrium nitrides at considerably lower temperatures (1400–1450 °C) than reported previously. The usefulness of this technique for determining phase relationships in other Si_3N_4–LnN systems will be explored in future studies. The present work confirms the existence in the Si_3N_4–YN system of the phases YSi_3N_5 and $Y_2Si_3N_6$, but suggests that the phase identified previously as $Y_6Si_3N_{10}$ may be $Y_3Si_6N_{11}$. The X-ray powder diffraction data and ^{29}Si and ^{89}Y solid-state MAS NMR spectra of these three phases are reported.

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