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The crystal structure of $Y_3Si_5N_9O$ and revision of the compositions of some high nitrogen-containing M–Si–O–N (M = Y, La) phases

Katharine Liddell* and Derek P. Thompson

Materials Division, Department of Mechanical, Materials & Manufacturing Engineering, University of Newcastle, UK. E-mail: Kath.Liddell@ncl.ac.uk

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Phase relationships in M_2O_3–SiO_2–Si_3N_4–MN systems (M = Y, Ln (Ln = La–Sm)) are discussed in relation to the compositions and stability of the high nitrogen-containing phases. Application of the carbothermal reduction and nitridation preparative technique and single crystal structure determination have revealed the presence of minor amounts of carbon or oxygen in compounds previously believed to be pure nitrides. Thus, the phases originally reported as $Y_6Si_3N_{10}$, YSi_3N_5 and $Y_2Si_3N_6$ are now found to be $Y_2Si_4N_6C$, $Y_6Si_{11}N_{20}O$ and $Y_3Si_5N_9O$ respectively. The crystal structure of $Y_3Si_5N_9O$ is described and compared with other M–Si–O–N structures; this phase has orthorhombic symmetry with $a = 4.9697(6)$, $b = 16.1192(11)$, $c = 10.6277(17)$ Å; $Z = 4$; S.G. *Pbcm* (no. 57); $R1 = 0.0307$, $wR2 = 0.0748$.

Introduction

In the early 1970s the oxides of yttrium and the rare earths began to be investigated as additives in the densification of silicon nitride and sialon ceramics; as a result of heat treatment of these samples, phase relationships in the M–Si–O–N systems were mapped out for M = Y, Ln (where Ln = La, Ce, Nd). Along with Si_2N_2O and the various polymorphs of the metal silicates,[1] the quaternary phases common to each of these systems are N-apatite ($M_5Si_3O_{12}N$), N-YAM ($M_4Si_2O_7N_2$) and N-wollastonite ($MSiO_2N$);[2–6] the apatite phase has a range of solid solubility in the Ln systems, extending to the oxide edge of the phase diagram, but in the Y system any range is either very limited or non-existent. A fourth oxynitride is the N-melilite phase ($M_2Si_3O_3N_4$), which is unstable in the La system and is substituted by a phase whose original composition was assumed to be $La_2Si_6O_3N_8$,[7] but which is presently believed[8] to be $La_3Si_8N_{11}O_4$ (monoclinic: $a = 18.372$, $b = 4.8645$, $c = 7.8911$ Å, $\beta = 117.03°$). The Ce system contains both $Ce_2Si_3O_3N_4$ and $Ce_3Si_8N_{11}O_4$.[6]

These products represent those observed in only half of the square M_2O_3–SiO_2–Si_3N_4–MN plane in the Jänecke prism, since it is not possible to prepare higher nitrogen-containing phases without the use of the metal nitrides; these are invariably subject to hydrolysis during use and so have been avoided as starting constituents in experimental practice. Nevertheless, commercially supplied yttrium nitride was used, together with Y_2O_3 and Si_3N_4 at 1800–1900 °C, to investigate the uncharacterised region,[9] and for compositions along the YN–Si_3N_4 join, every attempt was made to avoid the introduction of oxygen into the sample during processing. The resulting phase diagram is shown in Fig. 1 and includes the phases YSi_3N_5 (hexagonal: $a = 9.814$, $c = 10.621$ Å), $Y_6Si_3N_{10}$ (orthorhombic: $a = 9.854$, $b = 10.288$, $c = 5.978$ Å), and $Y_2Si_3N_6$ and Y_3O_3N (both unindexed). It can be seen from these results that no tie line is observed between $Y_2Si_3O_3N_4$ and Y_2O_3, but instead, lines exist across the system from $Y_4Si_2O_7N_2$ to $Y_6Si_3N_{10}$ and $Y_2Si_3N_6$; this is in agreement with observations previously made, in which additional uncharacterised phase(s) in this region were reported.[10]

Additional work relating to the Y–Si–Al–O–N system[11] has confirmed the presence of $Y_2Si_3N_6$ as the only Y–Si–N phase, attributing the other products to a mixture of melilite and other oxygen-containing phases. In this case the YN constituent was pre-prepared by carbothermal reduction and nitridation (CRN) of Y_2O_3 at 1900–1920 °C and stored in a dry environment. Subsequent use of the CRN process[12] has confirmed the existence of all three Y–Si–N phases; in this work, both SiO_2–Y_2O_3 and Si–Y_2O_3 mixtures were used in combination with added carbon at 1400–1450 °C. These authors indexed the $Y_2Si_3N_6$ phase on an orthorhombic unit cell: $a = 16.1492$, $b = 10.6465$, $c = 4.9758$ Å, and concluded that the composition of the $Y_6Si_3N_{10}$ phase was much less Y-rich than suggested, quoting a revised composition of $Y_3Si_6N_{11}$.

Corresponding phase diagrams have not been reported for the nitrogen-rich regions of rare earth systems, although the quaternary oxynitride phases are observed in the Ce[6] and Nd[5] systems. However, the crystal structures of $LaSi_3N_5$[13] (orthorhombic: $a = 7.838$, $b = 11.236$, $c = 4.807$ Å) and $Sm_3Si_6N_{11}$[14] (tetragonal: $a = 9.9931$, $c = 4.8361$ Å) were reported in the 1980s, the $LaSi_3N_5$ phase being made by reacting together the binary nitrides at 2000 °C and under 50 bar N_2. More recently, a series of $LnSi_3N_5$ (Ln = La–Nd) and $Ln_3Si_6N_{11}$ (Ln = La–Sm)

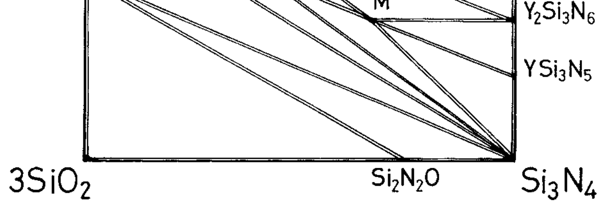

Fig. 1 Phase relationships in the Y_2O_3–SiO_2–Si_3N_4–YN system; after Thompson[9] (A = $Y_5Si_3O_{12}N$, J = $Y_4Si_2O_7N_2$, W = $YSiO_2N$, M = $Y_2Si_3O_3N_4$).

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phases have been prepared[15] by reacting the lanthanide silicides with nitrogen at 1500 °C. Also, lanthanide metals can be reacted with $Si(NH)_2$ to give single crystals of $Ln_3Si_6N_{11}$ (Ln = Ce,Pr).[16,17] Crystals of two other cerium silicon oxynitrides, $Ce_{16}Si_{15}O_6N_{32}$ (cubic: $a = 15.4$ Å) and $Ce_4Si_4O_5N_6$ have been reported,[18] but it is not known whether these have analogues in any of the other rare earth systems. By standardising on the main phases known to exist in these Ln–Si–O–N systems, a revised phase diagram for low atomic number rare earths has been constructed and is shown in Fig. 2, in order to compare with the Y system. Note that the phase N is plotted as the composition $La_3Si_8N_{11}O_4$, rather than $La_2Si_6N_8O_3$, since this gave a better fit in the powder structure refinement of the phase.[8]

Experimental

The primary aim of the investigation was to prepare single crystals of pure nitrides and high nitrogen containing phases for crystal structure determination. Starting powders for CRN experiments comprised SiO_2 (BDH; silica gel precipitated), Si_3N_4 (Starck; B7 grade), Y_2O_3 and La_2O_3 (Sigma Chemicals) and carbon black (Cabot Carbon; Monarch 1000 grade). These were fired in various combinations in a molybdenum-wound furnace or a carbon element resistance furnace in flowing N_2 at 1400–1450 °C. For higher temperature work, metallic Si, along with Y and La metal powders (Aldrich Chemicals; 99.9%) were used, since the melting points (Si = 1410, Y = 1522, La = 921 °C) were thought to provide liquid to assist in complete reaction. Although Si is a stable product, both the Y and La require special care to prevent undue hydrolysis during sample preparation, so in all cases the powder mixtures were dry mixed using a pestle and mortar. The Y powder was, in fact, YH_2 as received, although this was not thought to affect the results to any extent, since hydrogen would be lost during the reaction process. The La, however, is stored in oil, and so was "dried" with laboratory tissue before mixing. Powder mixtures were fired in the reducing atmosphere of a carbon resistance furnace at 1700 or 1900 °C in swiftly flowing N_2.

Resulting samples were analysed by powder X-ray diffraction using the Hägg-Guinier focusing camera technique; $CuK\alpha_1$ radiation was used and an internal standard of KCl added. Powder photographs were measured using an automatic line scanner (LS-20) and accompanying SCANPI and PIRUM software. EDX analysis was performed by means of a Hitachi 2400 electron microscope and analyser (Oxford Instruments Microanalysis ISIS-II). Single crystal diffraction data were collected using the synchrotron X-ray source at the EPSRC Daresbury Laboratory (Station 9.8) and structure refinement was carried out by means of the Bruker SMART and SHELXTL systems. Structures are plotted using ATOMS 4.1.

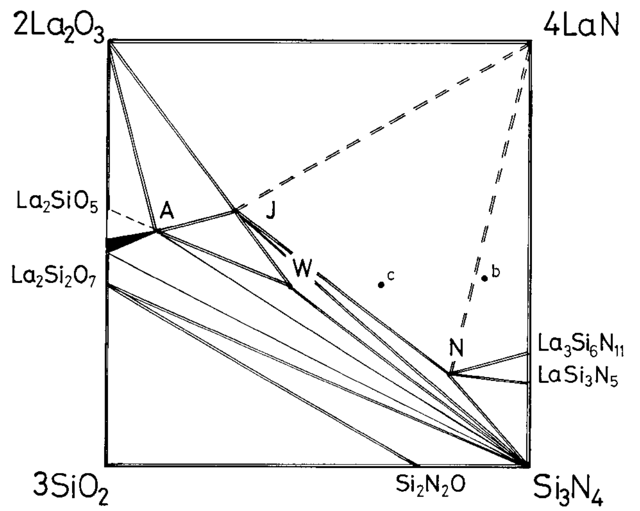

Fig. 2 Phase relationships in the La_2O_3–SiO_2–Si_3N_4–LaN system; after Thompson *et al.*[8] (A = $La_5Si_3O_{12}N$, J = $La_4Si_2O_7N_2$, W = $LaSiO_2N$, N = $La_2Si_8N_{11}O_4$). Points b and c show the positions of $Ce_{16}Si_{15}O_6N_{32}$ and $Ce_4Si_4O_5N_6$ respectively; it is not known whether these phases exist in the La system.

Results

CRN results obtained from the low temperature work using Y_2O_3–SiO_2 or Y_2O_3–Si_3N_4 as the starting constituents invariably showed a substantial amount of N-YAM, particularly after only a short firing time, which suggested that this phase formed readily from the starting powders before the nitriding process had been completed. All three Y–Si–N phases were observed in varying proportions; in particular, the "$Y_6Si_3N_{10}$" and "YSi_3N_5" phases always appeared together, with YN and/or Y_2O_3 observed in Y : Si = 2 : 1 samples and Si_3N_4 remaining in samples of Y : Si = 1 : 3. At the higher temperatures, the yttrium and silicon reacted together partially to give minor amounts of YSi or YSi_2, but in general the fired pellets showed an outside sintered layer, high in the "$Y_6Si_3N_{10}$" phase and an inner, less dense layer more rich in the "YSi_3N_5" phase. Compositions of Y : Si = 2 : 3 gave a high proportion of the "$Y_2Si_3N_6$" phase, particularly at lower temperatures. The pink colour of these samples is attributed to the presence of this phase and the X-ray powder diffraction pattern indexes on an orthorhombic unit cell, with $a = 4.9762(4)$, $b = 16.1517(10)$, $c = 10.6489(8)$ Å, in agreement with that previously reported.[12]

Crystal structure determination

Experimental. The crystal selected for structure determination was from a sample of starting composition Y : Si 2 : 3 fired at 1900 °C; the high temperature allowed the growth of a crystal, size 25 × 15 × 10 μm, large enough for data collection at the Daresbury Laboratory.

Crystal data. $Y_3Si_5N_9O$, $M = 549.27$, orthorhombic, $a = 4.9697(6)$, $b = 16.1192(11)$, $c = 10.6277(17)$ Å, $V = 851.36(18)$ Å^3, $T = 150(2)$ K, space group *Pbcm* (no. 57), $Z = 4$, $\mu(\lambda = 0.69290\ \text{Å}) = 20.982\ \text{mm}^{-1}$, 5481 reflections measured, 1240 unique ($R_{\text{int}} = 0.0221$) which were used in all calculations. Final $R1 = 0.0331$, $wR2 = 0.0748$.

CCDC 1145/253. See http://www.rsc.org/suppdata/jm/b0/b006053o/ for crystallographic files in .cif format

Discussion

The centrosymmetric space group *Pbcm* (no. 57) was unequivocally selected, being of higher symmetry than the corresponding non-centrosymmetric space group $Pca2_1$ (no. 29), for which there was no improvement in the final parameters. During the refinement process, 12 yttrium and 20 silicon atoms were immediately located, indicating a Y : Si atomic ratio of 3 : 5 instead of 2 : 3 hitherto assumed. A total of 10 non-metal atoms were also located, although if all sites were fully occupied, the composition $Y_3Si_5N_{10}$ would be electrically unstable. One of the non-metal sites, when occupied by N, always gave a negative temperature factor, but when this site was replaced by O, a B_{iso} value was obtained consistent with the other non-metals; this substitution restored electrical neutrality of the molecular constituents and the final unit cell contents totalled $Y_{12}Si_{20}N_{36}O_4$ ($Z = 4$). This change in the atomic constituents is consistent with two other phases reported, having similar unit cell parameters and intensity data,[19,20] *i.e.* $Ca_3MgAl_4O_{10}$ ($a = 16.77$, $b = 10.72$, $c = 5.13$ Å, S.G. *Pb*a* (no. 57)) and $Ca_3ZnAl_4O_{10}$ ($a = 5.142$, $b = 16.756$, $c = 10.710$ Å, S.G. $Pbc2_1$ (no. 29)). The space group quoted for these may actually be *Pbcm*, as observed in the present work,

Table 1 X-Ray diffraction data for $Y_3Si_5N_9O$

$h\ k\ l$	d_{obs}/Å	I_{obs}	$h\ k\ l$	d_{obs}/Å	I_{obs}	$h\ k\ l$	d_{obs}/Å	I_{obs}
0 2 1	6.4389	1	2 2 3	1.9755	18	1 5 6	1.4849	4
1 0 0	4.9774	9	2 4 2	1.9675	1	0 6 6	1.4823	4
1 1 0	4.7577	26	1 7 2	1.9482	6	3 2 3	1.4772	27
0 2 2	4.4460	15	2 5 1	1.9384	14	0 10 3	1.4702	6
0 4 0	4.0384	7	1 2 5	1.9036	15	2 9 0	1.4555	2
1 2 1	3.9372	10	1 5 4	1.8988	6	2 5 5	1.4469	18
1 3 0	3.6547	18	0 6 4	1.8927	11	2 1 6	1.4393	7
1 0 2	3.6361	2	0 8 2	1.8872	9	2 8 3	1.4344	9
1 1 2	3.5470	5	0 4 5	1.8840	14	1 9 4	1.4263	4
1 3 1	3.4569	11	1 8 1	1.8427	5	3 6 1	1.3994	3
1 2 2	3.3133	<1	1 7 3	1.8029	16	2 3 6	1.3951	10
0 2 3	3.2497	15	0 0 6	1.7742	25	2 6 5	1.3866	5
0 4 2	3.2173	10	2 2 4			3 3 4	1.3621	7
1 4 0	3.1355	3	1 4 5	1.7618	4	1 7 6	1.3531	7
1 3 2	3.0131	69	0 8 3	1.7547	13	0 12 0	1.3458	6
1 1 3	2.8448	100	2 6 2	1.7279	12	0 0 8	1.3318	2
1 2 3	2.7212	43	2 3 4	1.7222	18	1 5 7	1.3260	7
1 4 2	2.7015	17	2 7 0	1.6917	4	1 9 5	1.3231	2
0 6 0	2.6924	14	1 9 0	1.6883	2	3 6 3	1.3118	3
0 0 4	2.6617	7	1 5 5	1.6740	40	1 11 3	1.3084	9
1 5 1	2.6261	68	0 6 5	1.6698	4	0 12 2	1.3049	4
0 6 1	2.6099	47	1 1 6	1.6623	14	2 1 7	1.2930	1
1 3 3	2.5458	21	3 0 0	1.6587	9	3 8 1	1.2720	1
0 2 4	2.5281	7	1 8 3	1.6543	1	3 3 5	1.2708	1
2 0 0	2.4895	1	1 7 4	1.6455	5	0 4 8	1.2638	5
2 1 0	2.4589	13	1 2 6	1.6360	3	0 12 3	1.2576	6
1 5 2	2.4148	8	3 2 0	1.6243	18	1 3 8	1.2499	3
0 6 2	2.4024	13	0 4 6			3 4 5	1.2446	7
2 2 0	2.3785	6	2 6 3			1 11 4		
1 6 0	2.3683	4	3 0 2	1.5834	3	4 1 0	1.2401	4
1 1 4	2.3221	4	1 6 5			2 4 7	1.2350	1
1 6 1	2.3118	2	3 3 1	1.5682	10	1 7 7	1.2304	1
2 3 0	2.2586	14	2 8 0			2 7 6	1.2235	2
2 2 2	2.1712	5	3 2 2	1.5539	3	1 9 6		
1 6 2	2.1636	3	3 4 0	1.5349	6	3 9 0	1.2188	2
1 5 3	2.1537	8	1 9 3	1.5244	4	4 0 2	1.2108	9
1 7 0	2.0929	2	3 3 2	1.5189	6	1 13 0	1.2044	15
2 3 2	2.0788	21	3 4 1			0 12 4	1.2008	1
2 4 1			2 8 2	1.5032	4	0 6 8	1.1933	6
0 2 5	2.0593	6	3 1 3	1.4957	4	2 11 3	1.1906	3
1 4 4	2.0305	1	0 2 7					
2 1 3	2.0214	20						

[a]Orthorhombic: $a = 4.9762(4)$ Å, $b = 16.1517(10)$ Å, $c = 10.6489(8)$ Å.

since the 2_1 absence rule of $00l$ for l odd is implicit in the c glide plane absence rule of $h0l$ for l odd. No crystal structure was reported.

Table 1 shows powder diffraction data for the present sample with revised composition. Fig. 3(a) and (b) represent the $Y_3Si_5N_9O$ crystal structure viewed perpendicular to [100] and show a 3D lattice of Si-centred SiN_4 and SiN_3O tetrahedra, with yttrium atoms in [6]-coordinated holes. Final atomic coordinates are shown in Table 2. The Si : (O,N) ratio of 1 : 2 in this compound is consistent with the framework silicates, which would imply a distribution of tetrahedra in which every corner would be joined to one other tetrahedron. Fig. 3(a) and (b) show that this is the case except for the N_3O tetrahedron centred around Si2, for which the oxygen atom is bonded to only one silicon atom. This is compensated for by the nitrogen atom N5 being three-planar coordinated by three silicon atoms

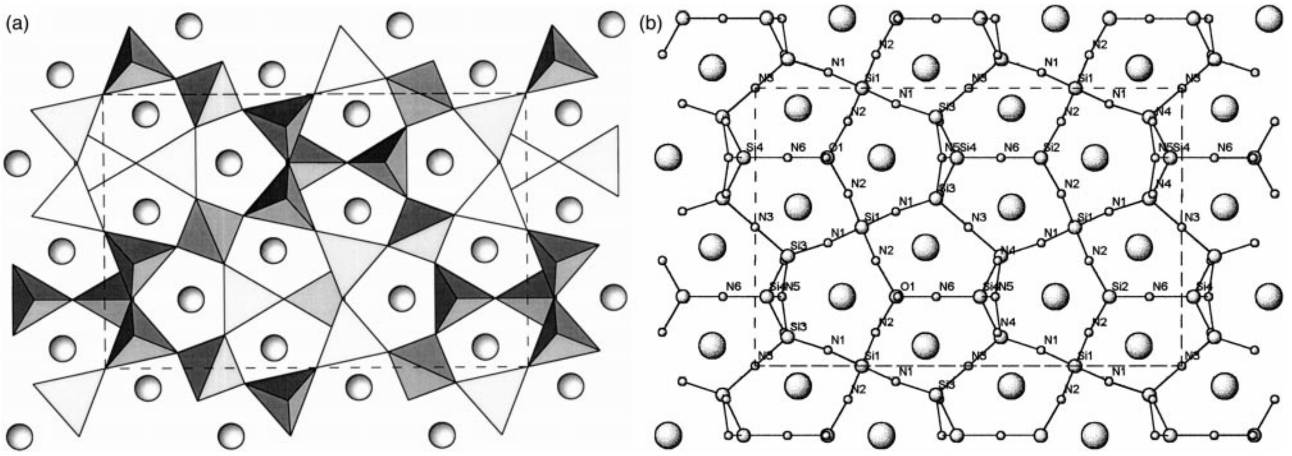

Fig. 3 Crystal structure of $Y_3Si_5N_9O$ perpendicular to [100].

Table 2 Final atomic coordinates for $Y_3Si_5N_9O$

Atom	Site	x	y	z	sof	U_{iso}
Y1	8(e)	0.1656(1)	0.6003(1)	0.5726(1)	1.0	0.0034(2)
Y2	4(d)	0.2029(1)	0.7038(1)	0.2500(0)	0.5	0.0038(2)
Si1	4(c)	0.6824(3)	0.7500(0)	0.5000(0)	0.5	0.0041(3)
Si2	4(d)	−0.2524(4)	0.6695(1)	0.7500(0)	0.5	0.0042(3)
Si3	8(e)	0.3944(2)	0.4235(1)	0.6037(1)	1.0	0.0040(2)
Si4	4(d)	−0.1112(3)	0.4728(1)	0.7500(0)	0.5	0.0078(7)
O1	4(d)	0.4152(8)	0.6662(3)	0.7500(0)	0.5	0.0078(7)
N1	8(e)	0.4763(7)	0.6707(2)	0.4434(3)	1.0	0.0050(6)
N2	8(e)	−0.1111(7)	0.7173(2)	0.6204(3)	1.0	0.0055(6)
N3	4(b)	0.5000(0)	0.5000(0)	0.5000(0)	0.5	0.0043(8)
N4	8(e)	−0.0515(7)	0.5682(2)	0.3798(3)	1.0	0.0073(6)
N5	4(d)	0.4416(9)	0.5625(3)	0.2500(0)	0.5	0.0037(8)
N6	4(d)	−0.0961(10)	0.5759(3)	0.7500(0)	0.5	0.0050(8)

(and no other cations) exactly as in silicon nitride itself. Whereas in oxide silicates it is rare to find such variations in non-metal coordination, this has been observed in several oxynitride compounds, and corresponds to regions of more ionic bonding (associated with oxygen atoms) and more covalent bonding (associated with Si–N-rich regions). Thus, for example, the atomic arrangement proposed for $La_3Si_8N_{11}O_4$[8] has oxygen atoms in a coordination identical to that observed here, and also has pairs of nitrogen atoms three-planar coordinated by silicon. Further confirmation of the assignment of oxygen to the O1 site is provided by the bond with the adjoining Si2 atom, in that it is shorter than any other Si–non-metal bond length in the structure (Table 3). Another characteristic structural feature, which is common to other oxynitride features, is the five-membered rings of tetrahedra. A comparison of Fig. 3(a) with an (001) projection of the nitrogen melilite structure (Fig. 4) shows an identical distribution of both tetrahedra and cations in the square region outlined. An alternative way of describing the $Y_3Si_5N_9O$ structure is, therefore, of these square features linked together by the tri-tetrahedral silicon nitride units centred about the N5 atoms.

If a comparison is made with the related Ca compounds listed above, it should be possible to identify which silicon atom in $Y_3Si_5N_9O$ provides the site occupied by the Mg,Zn atoms. Each Mg,Zn is in four coordination, and since there are 4 atoms per unit cell, each of the sites Si1, Si2 and Si4 would be suitable. It is most likely that the more ionic (*i.e.* N_3O rather than N_4) environment provided by the Si1 site would be favoured by these cations.

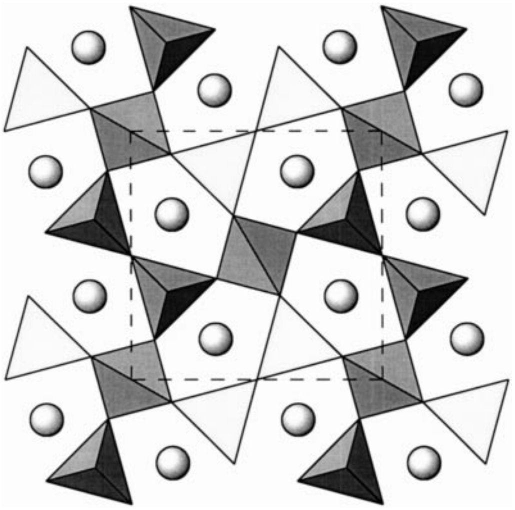

Fig. 4 Crystal structure of $Y_2Si_3O_3N_4$ perpendicular to [001].

Phase relationships

This revision of the composition of the "$Y_2Si_3N_6$" phase to $Y_3Si_5N_9O$ has meant a change in the Y : Si ratio from that originally assumed, and also the inclusion of a small amount of oxygen. Since YN is very easily hydrolysed, it is possible that oxygen could be introduced to some extent during processing. If the metal nitride is pre-prepared and stored before use, as reported in one case,[11] it is likely that the powder is not oxygen-free at the point of use; this may explain why these authors observed only the $Y_3Si_5N_9O$ phase and not other pure nitrides in their results. However, if either of the other two Y–Si–N phases were also actually oxynitrides, these would have been

Table 3 Bond lengths and angles for $Y_3Si_5N_9O$ (Å,°)

Y1–N6	2.324(3)	Y2–O1	2.347(4)	N1–Si3	1.723(3)	N2–Si1	1.723(3)
Y1–N1	2.357(3)	Y2–N2	2.439(3)	N1–Si1	1.745(3)	N2–Si2	1.727(3)
Y1–N4	2.372(3)	Y2–N2	2.439(3)	N1–Y1	2.357(3)	N2–Y1	2.389 (3)
Y1–N2	2.389(3)	Y2–N1	2.521(3)	N1–Y2	2.521(3)	N2–Y2	2.439(3)
Y1–N3	2.443(1)	Y2–N1	2.521(3)				
Y1–O1	2.494 (3)	Y2–N5	2.56 (4)7	N3–Si3	1.735(1)	N4–Si3	1.718(3)
				N3–Si3	1.735(3)	N4–Si4	1.731(3)
Si1–N2	1.723(3)	Si2–O1	1.653(4)	N3–Y1	2.443(1)	N4–Y1	2.372(3)
Si1–N2	1.723(3)	Si2–N6	1.698(5)	N3–Y1	2.443(1)		
Si1–N1	1.745(3)	Si2–N2	1.727(3)				
Si1–N1	1.745(3)	Si2–N2	1.727(3)	N5–Si4	1.738(5)	N6–Si4	1.663(5)
				N5–Si3	1.769(2)	N6–Si2	1.698(5)
Si3–N4	1.718(3)	Si4–N6	1.663(5)	N5–Si3	1.769(2)	N6–Y1	2.324(3)
Si3–N1	1.723(3)	Si4–N4	1.731(3)	N5–Y2	2.567(5)	N6–Y1	2.324(3)
Si3–N3	1.735(1)	Si4–N4	1.731(3)	O1–Si2	1.653(4)		
Si3–N5	1.769(2)	Si4–N5	1.738(5)	O1–Y2	2.347(4)		
				O1–Y1	2.494(3)		
				O1–Y1	2.494(3)		
N2–Si1–N2	106.9(2)			N4–Si3–N1	117.9(2)		
N2–Si1–N1	112.4(2)			N4–Si3–N3	108.0(2)		
N2–Si1–N1	108.5(2)			N1–Si3–N3	109.2(2)		
N2–Si1–N1	108.5(2)			N4–Si3–N5	111.0(2)		
N2–Si1–N1	112.4(2)			N1–Si3–N5	101.3(2)		
N2–Si1–N1	108.1(2)			N3–Si3–N5	109.2(2)		
O1–Si2–N6	115.3(2)			N6–Si4–N4	111.2(2)		
O1–Si2–N2	114.9(2)			N6–Si4–N4	111.2(2)		
N6–Si2–N2	102.1(2)			N4–Si4–N4	105.7(2)		
O1–Si2–N2	114.9(2)			N6–Si4–N5	111.7(2)		
N6–Si2–N2	102.1(2)			N4–Si4–N5	108.4(2)		
N2–Si2–N2	105.8(2)			N4–Si4–N5	108.4(2)		

observed alongside. A probable change in Y : Si ratio has already been reported[12] for one of the other Y–Si–N phases, *i.e.* the original "$Y_6Si_3N_{10}$" phase is reckoned to have a Y : Si ratio nearer 1 : 2. Since, in the present work, an excess of YN invariably occurs in samples of starting ratio 2 : 1 or 1 : 1, all three of the observed phases must guarantee $Y/Si < 1$.

A comparison can be made with related phases occurring in the La–Si–O–N system. For La-containing samples, $LaSi_3N_5$ formed very easily, and three other uncharacterised phases were also observed. The X-ray diffraction pattern of one, a yellow phase from a starting composition of La : Si = 1 : 2, appeared similar to the yttrium "$Y_6Si_3N_{10}$" phase and indexed on an orthorhombic unit cell with $a = 10.1276(10)$, $b = 10.5667(16)$, $c = 6.0321(6)$ Å. The second, from a La : Si = 2 : 3 composition, was orthorhombic with $a = 12.0966(17)$, $b = 9.5537(14)$, $c = 9.4741(9)$ Å, while the third, from La : Si = 2 : 1, remains unindexed. The yellow phase was found to produce small crystals suitable for single crystal structure determination, and diffraction data were collected at the Daresbury Laboratory. The resulting structure is analogous to a series of phases $MYbSi_4N_7$ (M = Ba, Sr, Eu)[21,22] and will be reported in detail elsewhere.[23] These are hexagonal structures with $a \sim 6.0$, $c \sim 10.0$ Å, in which nitrogen atoms in one particular site lie in four-coordination with silicon. It was noticed that the yellow phase gave appreciably larger bond lengths (typically 1.9 Å) for this site. Whereas the EDX La : Si cation ratio of 1 : 2 is consistent with the 2 : 4 : 7 stoichiometry of the $MYbSi_4N_7$ series, an overall composition of $La_2Si_4N_7$ would not preserve valency balance. However, all observations can be satisfied if the [4]-coordinated nitrogen site is occupied by carbon. This would account for the long bond lengths and the formula would then be $La_2Si_4N_6C$, consistent with the 2 : 4 : 7 stoichiometry expected for this phase. The presence of carbon has been confirmed by NMR and is not unrealistic since the La metal is stored in oil, containing carbon which must, to some extent, remain in the mixture. The corresponding yttrium composition ("$Y_6Si_3N_{10}$") would then become $Y_2Si_4N_6C$; even though Y metal is not stored in oil, this again might not be unexpected, since carbon is readily available from the sintering furnace environment. The Y : Si ratio is thus confirmed as 1 : 2. Also, in both the La and Y cases, this phase forms in the outer layer of the pellets, particularly at the highest temperatures, which suggests that carbon is absorbed into the structure from the reducing atmosphere of the carbon element furnace.

In order further to verify the compositions of these Y–Si–N phases, control experiments were carried out using a Y : Si ratio of 1 : 2, (a) with and (b) without added carbon and fired at 1700 °C; X-ray diffraction patterns gave (a) ~88% $Y_2Si_4N_6C$, ~10% "YSi_3N_5", ~2% $Y_3Si_5N_9O$ and (b) ~96% "YSi_3N_5", ~4% $Y_3Si_5N_9O$, respectively. These results strongly suggest that both $Y_2Si_4N_6C$ and "YSi_3N_5" own the same Y : Si ratio of 1 : 2. In addition, EDX analyses on these and other selected samples result in a Y : Si ratio of 1 : 2 for both these samples and 3 : 5 for the "$Y_2Si_3N_6$" phase. Table 4 shows that analyses can be interpolated to such values if an atomic ratio of 5 : 3 is assumed for the apatite present with the "2 : 3" phase; a scale factor of 0.8 is applied to the heavier yttrium atom measurement. The 3 : 5 Y : Si ratio for the $Y_3Si_5N_9O$ phase proved correct on determination of the crystal structure, as described.

Table 4 EDX analyses (atomic %)

Sample Y : Si	EDX Y : Si	Corr. Y : Si	Result Y : Si
5 : 3	68 : 32	63 : 37	5 : 3
2 : 3	43 : 57	38 : 62	3 : 5
1 : 2(a)	38 : 62	33 : 67	1 : 2
1 : 2(b)	37 : 63	32 : 68	1 : 2

In the case of the third Y–Si–N phase, since Si_3N_4 always occurs in Y : Si = 1 : 3 samples, it again seems likely that the cation ratio of "YSi_3N_5" is not 1 : 3 but nearer 1 : 2. The simplest electrically neutral pure nitride with this ratio is $Y_3Si_6N_{11}$. Although no such phase has been reported with precisely this composition, a series of rare earth silicon oxynitrides of the smaller rare earth atoms has been reported[24] with a small range of composition of the type $M_{6+x/3}Si_{11}N_{20+x}O_{1-x}$ (M = Y, Gd–Lu, $0 < x < 1$) and trigonal structures ($a \sim 9.8$, $c \sim 10.6$ Å), similar to "YSi_3N_5". The structures of two crystals, $Er_6Si_{11}N_{20}O$ and $Er_{6.245}Si_{11}N_{20.762}O_{0.238}$, were described, in which the range of Er content is attributed to excess electron density in the site (1/3, 2/3, 0.78), located too far from neighbouring N atoms to be tetrahedrally-coordinated Si. Oxygen is introduced into the formula to balance the valencies. Quoted compositions imply that the Si sites are well refined to give Si_{11} per formula unit; however, the table of atomic parameters shows that the distribution of Er, Si and (O,N) in (1/3, 2/3, z) sites parallel to the z axis is not beyond discussion. Since temperature and site occupation factors had to be fixed in order to stabilise the refinement, the possibility that the observed excess electron density is attributable to Si cannot be ruled out. Nevertheless, it is evident that the "YSi_3N_5" phase does have the same structure as $Er_6Si_{11}N_{20}O$ and therefore has a composition of the type $Y_6Si_{11}N_{20}O$, whilst a small variation in unit cell parameters observed in the present work would suggest that a range of composition is also possible.

On comparing the Y and La systems, it is clear that whilst $La_2Si_4N_6C$ and $Y_2Si_4N_6C$ are analogous, $La_3Si_6N_{11}$ and $Y_6Si_{11}N_{20}O$ are quite different in composition and structure, and there is now apparently no yttrium equivalent to $LaSi_3N_5$. However, it is quite common to find phases to be stable at one end of the rare earth atom series without extending throughout the complete range La–Lu. Yttrium is equivalent to Dy or Ho in ionic radius, *i.e.* near the middle of the series, so may form phases analogous to those at either end of the range. With reference to previous work on α-sialons in the system Si_3N_4–$YN{\cdot}3AlN$–$Al_2O_3{\cdot}AlN$[25] it is possible to validate the composition changes by comparing phase relationships in that system. Fig. 5 shows the phase diagram of the Y_2O_3–SiO_2–Si_3N_4–YN system, revised as a result of the present work.

Conclusions

Preparation of powder samples using the CRN technique at moderate temperature or solid state reaction at high tempera-

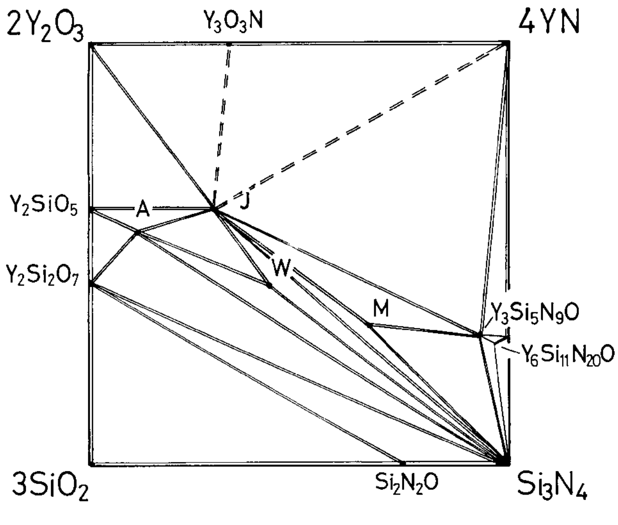

Fig. 5 Phase relationships in the Y_2O_3–SiO_2–Si_3N_4–YN system according to the present work ($A = Y_5Si_3O_{12}N$, $J = Y_4Si_2O_7N_2$, $W = YSiO_2N$, $M = Y_2Si_3O_3N_4$). The labelled $Y_6Si_{11}N_{20}O$ lies at one end of the range $Y_{6+x/3}Si_{11}N_{20+x}O_{1-x}$ ($0 < x < 1$).

ture, has enabled phase relationships in the high nitrogen-containing regions of the M_2O_3–SiO_2–Si_3N_4–MN systems (M = Y, La) to be more fully understood, particularly in relation to the ease with which a small amount of carbon or oxygen can be absorbed into a fired sample. The crystal structure reported in the present work, together with an EDX Y : Si ratio of 3 : 5, has proved the composition of the original "$Y_2Si_3N_6$" phase now to be $Y_3Si_5N_9O$, while the original phase "$Y_6Si_3N_{10}$", suggested by other authors[12] to be $Y_3Si_6N_{11}$, is now believed to be $Y_2Si_4N_6C$, by analogy with the $MYbSi_4N_7$ series[21,22] and with the structure of $La_2Si_4N_6C$, to be reported. For the original "YSi_3N_5" phase, an EDX Y : Si ratio of 1 : 2 implies a pure nitride composition of $Y_3Si_6N_{11}$ or the oxygen containing $Y_6Si_{11}N_{20}O$, analogous to the Er compound.[24] Structural confirmation remains to be carried out. A revised depiction of the Y_2O_3–SiO_2–Si_3N_4–YN phase diagram is given.

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