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# The silicon lanthanide oxynitrides

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A new group of materials called the silicon lanthanide oxynitrides has been prepared by the reaction between $Si_3N_4$ and several oxides of the lanthanide series ($La_2O_3$, $Sm_2O_3$, $Dy_2O_3$, $Er_2O_3$, and $Yb_2O_3$). These oxides formed compounds of the type $Si_3N_4 \cdot R_2O_3$ and $R_4Si_2O_7N_2$ (R being lanthanide). In addition $La_2O_3$ and $Yb_2O_3$ formed the compounds $2Si_3N_4 \cdot La_2O_3$ and $Yb_2Si_3O_5N_2$, respectively. Certain similarities in the unit cells of these compounds have been noted, and their structures are discussed in terms of similarity to known minerals. It is suggested that this group of materials contains a large number of compounds.

## 1. Introduction

The fundamental structural unit in all silicates is the $SiO_4$ group in which the silicon atom occupies the central position of a tetrahedron. Similarly $\beta$-$Si_3N_4$ consists of $SiN_4$ tetrahedra joined by sharing corners in a three-dimensional network [1]. The existence of a new group of ceramics in which the fundamental unit is the $Si(O, N)_4$ group has been suggested by Jack [2]. Except in the case of $Si_2N_2O$, partial replacement of the silicon atoms is required to maintain electrical neutrality. Thus, in the sialons, which have a unit cell similar to $\beta$-$Si_3N_4$ [3], the structural unit is $(Si, Al)(O, N)_4$, electrical neutrality being maintained by partial replacement of silicon by aluminum. The silicon can also be replaced by a combination of Ga and Al [4], Mg and Al [2], or Be and Al [2]. Furthermore, additional silicon–metal oxynitrides based upon $Si_2N_2O$ and cristobalite can be prepared [2].

If the metal ion is much larger than the $Si^{4+}$ ion (0.42 Å) and exhibits little tendency to be tetrahedrally co-ordinated, formation of a substitutional silicon–metal oxynitride solid solution is not possible. This would appear to be the case with $Y^{3+}$ (0.92 Å). The formation of three silicon yttrium oxynitrides has been reported [5, 6]. Ions having comparable properties might be expected to behave similarly.

This paper is concerned with the reaction of $Si_3N_4$ with $La_2O_3$, $Sm_2O_3$, $Dy_2O_3$, $Er_2O_3$, and $Yb_2O_3$. Here La has been considered as a lanthanide, although strictly speaking it is not.

## 2. Experimental

The $Si_3N_4$ powder (~ 85% $\alpha$, 15% $\beta$) was obtained from Advanced Materials Engineering Ltd, Gateshead, England. The $Dy_2O_3$, $Sm_2O_3$, $Er_2O_3$, $La_2O_3$, and $Yb_2O_3$ were all high-purity powders having mean particle sizes of 3 to 7 μm. The $La_2O_3$ and $Sm_2O_3$ powders hydrolysed slowly in air and, consequently, were calcined at 1000° C prior to use.

Compositions ranging from 10 to 90 mol% $Si_3N_4$ were prepared from each rare earth oxide,

TABLE I Compositions of the silicon lanthanide oxynitrides

| | | |
|---|---|---|
| $2Si_3N_4 \cdot La_2O_3$ | $Si_3N_4 \cdot La_2O_3$ | $La_4Si_2O_7N_2$ |
| | $Si_3N_4 \cdot Sm_2O_3$ | $Sm_4Si_2O_7N_2$ |
| | $Si_3N_4 \cdot Dy_2O_3$ | $Dy_4Si_2O_7N_2$ |
| | $Si_3N_4 \cdot Y_2O_3$ | $Y_4Si_2O_7N_2$ |
| | $Si_3N_4 \cdot Er_2O_3$ | $Er_4Si_2O_7N_2$ |
| $Yb_2Si_3O_5N_2$ | $Si_3N_4 \cdot Yb_2O_3$ | $Yb_4Si_2O_7N_2$ |

TABLE II Ionic radii (Ahren's scale) of the lanthanides

| | | | |
|---|---|---|---|
| $La^{3+}$ | 1.14 Å | $Y^{3+}$ | 0.92 Å |
| $Sm^{3+}$ | 1.00 Å | $Er^{3+}$ | 0.89 Å |
| $Dy^{3+}$ | 0.92 Å | $Yb^{3+}$ | 0.86 Å |

TABLE III X-ray diffraction spectra and unit cell dimensions of $2Si_3N_4 \cdot La_2O_3$

| $hkl$ | $d$ (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|
| 200 | 8.230 | 8 | 0.0148 | 0.0148 |
| 020 | 7.262 | 8 | 0.0190 | 0.0190 |
| 002 | 4.812 | 17 | 0.0432 | 0.0432 |
| 130, 221 | 4.698 | 36 | 0.0453 | 0.0464, 0.0445 |
| 112 | 4.450 | 24 | 0.0505 | 0.0516 |
| 230, 202 | 4.169 | 7 | 0.0576 | 0.0574, 0.0579 |
| 410 | 3.962 | 22 | 0.0637 | 0.0638 |
| 411 | 3.674 | 42 | 0.0741 | 0.0746 |
| 032 | 3.427 | 6 | 0.0852 | 0.0858 |
| 113, 412 | 3.065 | 65 | 0.1064 | 0.1056, 0.1070 |
| 340, 511 | 3.033 | 78 | 0.1087 | 0.1091, 0.1078 |
| 520 | 3.014 | 57 | 0.1101 | 0.1112 |
| 023, 213 | 2.937 | 85 | 0.1159 | 0.1161, 0.1167 |
| 332, 042 | 2.899 | 100 | 0.1190 | 0.1191, 0.1190 |
| 440, 530 | 2.724 | 16 | 0.1348 | 0.1349 |
| 512 | 2.655 | 20 | 0.1419 | 0.1402 |
| 531, 441 | 2.618 | 8 | 0.1459 | 0.1457, 0.1456 |
| 611 | 2.595 | 7 | 0.1485 | 0.1484 |
| 620, 350 | 2.572 | 3 | 0.1512 | 0.1517, 0.1518 |
| 540 | 2.442 | 41 | 0.1677 | 0.1681 |
| 160, 423 | 2.394 | 7 | 0.1745 | 0.1744, 0.1752 |
| 114 | 2.349 | 22 | 0.1812 | 0.1812 |
| 503, 053 | 2.302 | 9 | 0.1887 | 0.1894 |
| 360 | 2.217 | 10 | 0.2035 | 0.2039 |
| 134, 153, 641 | 2.136 | 15 | 0.2192 | 0.2191, 0.2194, 0.2195 |
| 702 | 2.112 | 20 | 0.2242 | 0.2240 |
| 404, 443, 533 | 2.078 | 21 | 0.2316 | 0.2318, 0.2320, 0.2321 |
| 461 | 2.045 | 16 | 0.2391 | 0.2405 |
| 171 | 2.020 | 10 | 0.2451 | 0.2468 |
| 424 | 1.999 | 23 | 0.2502 | 0.2508 |
| 740 | 1.974 | 5 | 0.2566 | 0.2567 |
| 741 | 1.933 | 21 | 0.2676 | 0.2675 |
| 015, 072 | 1.907 | 24 | 0.2750 | 0.2747, 0.2756 |
| 802, 172 | 1.890 | 8 | 0.2800 | 0.2794, 0.2792 |
| 154, 652 | 1.841 | 12 | 0.2950 | 0.295 , 0.2946 |
| 363, 742 | 1.824 | 15 | 0.3006 | 0.3010, 0.2999 |
| 901, 372 | 1.798 | 16 | 0.3093 | 0.3098, 0.3087 |
| 840, 035 | 1.789 | 14 | 0.3124 | 0.3121, 0.3126 |
| 273, 752 | 1.706 | 20 | 0.3436 | 0.3442, 0.3426 |
| 145, 182 | 1.691 | 14 | 0.3497 | 0.3495, 0.3503 |
| 345 | 1.627 | 4 | 0.3778 | 0.3790 |
| 290, 10.21 | 1.582 | 28 | 0.3996 | 0.3987, 0.3989 |
| 680, 564 | 1.514 | 8 | 0.4363 | 0.4363, 0.4357 |
| 10.40, 635 | 1.499 | 11 | 0.4450 | 0.4450, 0.4454 |
| 10.41, 715, 772 | 1.481 | 14 | 0.4559 | 0.4558, 0.4555, 0.4563 |
| 11.11, 952 | 1.472 | 14 | 0.4615 | 0.4621, 0.4607 |
| 474 | 1.469 | 13 | 0.4634 | 0.4641 |
| 1.100 | 1.447 | 14 | 0.4776 | 0.4777 |
| 735, 583 | 1.424 | 7 | 0.4932 | 0.4934, 0.4938 |

$a = 16.460$ Å, $b = 14.524$ Å, $c = 9.624$ Å: orthorhombic.

the powders being dry mixed in a Spex mixer/mill (Spex Industries, Inc, Metuchen, N.J.). Disc specimens (3 to 5 g), prepared by cold compaction of the mixed powders, were fired in an $N_2$ atmosphere in the temperature range 1500 to 1750° C. Firing was interrupted at various times and temperatures in order to observe the degree of completion of the reaction. Samples generally exhibited a 1 to 2% weight loss during firing. The sintered discs were examined by powder X-ray diffraction (Cu$K\alpha$, 35 kV, 15 mA) using a diffractometer. The number of phases present in each sample was confirmed with the aid of optical and SEM micrographs.

## 3. Results and discussion

### 3.1 Compound formation

The compositions of the silicon lanthanide oxynitrides are shown in Table I. In all instances the compounds $Si_3N_4 \cdot R_2O_3$ and $R_4Si_2O_7N_2$ (R = La, Dy, Sm, Er, Yb) were formed. $Y_2O_3$ also forms analogous oxynitrides [5], and thus the behaviour of Y is similar to that of the other lanthanide oxides studied. In addition, $La_2O_3$ and $Yb_2O_3$ formed the compounds $2Si_3N_4 \cdot La_2O_3$ and $Yb_2Si_3O_5N_2$ respectively. The composition of the additional ytterbium oxynitride was initially considered to be $3Si_3N_4 \cdot 2Yb_2O_3$ but was modified after indexing its X-ray diffraction spectra, and noting its similarity with the pattern of $Si_3N_4 \cdot Y_2O_3$. A similar problem arose with the formula $R_4Si_2O_7N_2$. The formula proposed initially was $Si_3N_4 \cdot 3R_2O_3$, before it was determined that the structure was analogous to that of cuspidine. In the case of Y this has been discussed elsewhere [5]. Until the structure of the silicon lanthanium oxynitride $2Si_3N_4 \cdot La_2O_3$ is known, a similar uncertainty must exist with its formula.

TABLE IV X-ray diffraction spectra and unit cell dimensions of $Si_3N_4 \cdot La_2O_3$

| $hkl$ | $d$ (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|
| 002 | 6.741 | 31 | 0.0220 | 0.0220 |
| 330, 401 | 4.590 | 3 | 0.0475 | 0.0474, 0.0476 |
| 411 | 4.436 | 5 | 0.0508 | 0.0503 |
| 203 | 4.070 | 3 | 0.0604 | 0.0600 |
| 412 | 3.850 | 6 | 0.0675 | 0.0668 |
| 422 | 3.650 | 84 | 0.0751 | 0.0746 |
| 004 | 3.410 | 14 | 0.0860 | 0.0879 |
| 104, 512 | 3.320 | 3 | 0.0907 | 0.0906, 0.0904 |
| 600, 531 | 3.250 | 3 | 0.0947 | 0.0948, 0.0950 |
| 204, 522 | 3.180 | 5 | 0.0989 | 0.0985, 0.0983 |
| 540 | 3.040 | 5 | 0.1082 | 0.108 |
| 630, 612 | 2.900 | 100 | 0.1189 | 0.1185, 0.1194 |
| 523 | 2.811 | 5 | 0.1266 | 0.1258 |
| 542, 404 | 2.771 | 25 | 0.1302 | 0.1299, 0.1301 |
| 105 | 2.673 | 9 | 0.1400 | 0.1400 |
| 641 | 2.652 | 9 | 0.1422 | 0.1424 |
| 623 | 2.545 | 3 | 0.1544 | 0.1548 |
| 325 | 2.414 | 9 | 0.1716 | 0.1716 |
| 811 | 2.381 | 18 | 0.1764 | 0.1767 |
| 901, 226, 714 | 2.136 | 13 | 0.2192 | 0.2188, 0.2189, 0.2196 |
| 316, 724 | 2.110 | 43 | 0.2246 | 0.2242, 0.2249 |
| 850, 615 | 2.065 | 3 | 0.2345 | 0.2344, 0.2348 |
| 851, 406, 734 | 2.039 | 7 | 0.2405 | 0.2399, 0.2400, 0.2399 |
| 426 | 1.996 | 31 | 0.2510 | 0.2505 |
| 941 | 1.959 | 5 | 0.2606 | 0.2609 |
| 007, 10.01, 715 | 1.928 | 30 | 0.2690 | 0.2693, 0.2688, 0.2691 |
| 952 | 1.826 | 15 | 0.2999 | 0.3011 |
| 10.13 | 1.781 | 7 | 0.3153 | 0.3154 |
| 11.30, 881, 11.12, 944 | 1.708 | 15 | 0.3428 | 0.3423, 0.3426,<br>0.3432, 0.3434 |
| 10.71, 707, 338 | 1.584 | 8 | 0.3986 | 0.3979, 0.3983, 0.3991 |

$a$ = 19.487 Å, $c$ = 13.489 Å: tetragonal.

TABLE V X-ray diffraction spectra and unit cell dimensions of $La_4Si_2O_7N_2$

| *hkl* | *d* (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|
| 210, 211 | 7.563 | 10 | 0.0175 | 0.0175, 0.0174 |
| 400 | 5.488 | 6 | 0.0332 | 0.0331 |
| 220 | 4.701 | 27 | 0.0452 | 0.0450 |
| 510 | 4.077 | 8 | 0.0602 | 0.0609 |
| 204, 304, 513 | 3.875 | 5 | 0.0667 | 0.0667, 0.0668, 0.0670 |
| 420, 104 | 3.774 | 10 | 0.0702 | 0.0698, 0.0707 |
| 61, $40\bar{2}$, 223 | 3.689 | 15 | 0.0735 | 0.0735, 0.0732, 0.0740 |
| 130 | 3.443 | 8 | 0.0844 | 0.0847 |
| $10\bar{4}$, 230 | 3.308 | 34 | 0.0914 | 0.0911, 0.0909 |
| 722, $60\bar{1}$, 523 | 3.249 | 100 | 0.0947 | 0.0946, 0.0948, 0.0945 |
| 331, 132 | 3.181 | 13 | 0.0988 | 0.0985, 0.0993 |
| $22\bar{3}$, $61\bar{1}$ | 3.094 | 27 | 0.1044 | 0.1047, 0.1040 |
| $52\bar{1}$, $51\bar{2}$, $20\bar{4}$, 124 | 3.058 | 34 | 0.1069 | 0.1062, 0.1076, 0.1074 |
| 802, 620, 505 | 2.991 | 42 | 0.1118 | 0.1113, 0.1112, 0.1111 |
| 524, 430, 024, 803 | 2.936 | 52 | 0.1160 | 0.1163, 0.1157, 0.1156, 0.1156 |
| 515, 812, 233 | 2.885 | 45 | 0.1202 | 0.1203, 0.1205, 0.1199 |
| 800, 015, 115 | 2.745 | 6 | 0.1328 | 0.1325, 0.1324, 0.1332 |
| 902, 810, 425 | 2.659 | 14 | 0.1414 | 0.1414, 0.1417, 0.1420 |
| $42\bar{3}$, 724 | 2.625 | 19 | 0.1451 | 0.1448, 0.1455 |
| $40\bar{4}$, 134 | 2.556 | 9 | 0.1530 | 0.1528, 0.1533 |
| 606, 025, 125 | 2.498 | 4 | 0.1602 | 0.1600, 0.1599, 0.1607 |
| $71\bar{2}$, 340, $21\bar{5}$, 824 | 2.455 | 4 | 0.1659 | 0.1661, 0.1655, 0.1662, 0.1664 |
| 116, $13\bar{4}$, $14\bar{2}$ | 2.401 | 8 | 0.1734 | o.1733, 0.1738 |
| 006, $63\bar{1}$ | 2.374 | 4 | 0.1774 | 0.1774 |
| 716, $30\bar{5}$, 440 | 2.353 | 4 | 0.1806 | 0.1808, 0.1801, 0.1800 |
| 832, $82\bar{1}$ | 2.269 | 10 | 0.1942 | 0.1940, 0.1946 |
| 643, 11.13, $44\bar{2}$ | 2.134 | 21 | 0.2196 | 0.2198, 0.2201 |
| 150, 126, 436, 10.06 | 2.078 | 11 | 0.2316 | 0.2316, 0.2315, 0.2319, 0.2312 |
| 817, $83\bar{1}$, 527, 427 | 2.040 | 20 | 0.2402 | 0.2402, 0.2404, 0.2406, 0.2398 |
| $63\bar{3}$, $81\bar{3}$, 11.23, 252 | 2.010 | 22 | 0.2475 | 0.2474, 0.2473, 0.2472 |
| $45\bar{1}$, 1002, $93\bar{1}$, 027, $13\bar{6}$ | 1.897 | 26 | 0.2778 | 0.2778, 0.2782, 0.2774 |
| 11.11, 12.06 | 1.850 | 7 | 0.2922 | 0.2927, 0.2917 |
| 944, 256, 814, 653 | 1.821 | 13 | 0.3017 | 0.3015, 0.3019, 0.3022, 0.3024 |
| $50\bar{6}$, 12.25, $84\bar{1}$ | 1.809 | 16 | 0.3056 | 0.3058, 0.3048, 0.3047 |

$a = 23.948$ Å, $b = 10.437$ Å, $c = 15.538$ Å, $\beta = 113.53°$ : monoclinic.

TABLE VI X-ray diffraction spectra and unit cell dimensions of $Sm_2O_3 \cdot Si_3N_4$

| *hkl* | *d* (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ | *hkl* | *d* (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|---|---|---|---|---|
| 110 | 5.406 | 27 | 0.0342 | 0.0340 | 311 | 2.182 | 11 | 0.2100 | 0.2104 |
| 001 | 4.952 | 19 | 0.0408 | 0.0405 | 202 | 2.094 | 6 | 0.2280 | 0.2301 |
| 200 | 3.834 | 9 | 0.0680 | 0.0679 | 212 | 2.020 | 27 | 0.2451 | 0.2471 |
| 111 | 3.663 | 12 | 0.0745 | 0.0745 | 400 | 1.916 | 9 | 0.2724 | 0.2717 |
| 210 | 3.421 | 20 | 0.0854 | 0.0849 | 410 | 1.861 | 9 | 0.2887 | 0.2887 |
| 201 | 3.044 | 27 | 0.1079 | 0.1085 | 222 | 1.829 | 4 | 0.2989 | 0.2981 |
| 211 | 2.830 | 100 | 0.1249 | 0.1255 | 330 | 1.811 | 12 | 0.3049 | 0.3057 |
| 220 | 2.711 | 49 | 0.1361 | 0.1359 | 401 | 1.792 | 4 | 0.3114 | 0.3123 |
| 002 | 2.488 | 9 | 0.1615 | 0.1622 | 411 | 1.742 | 25 | 0.3295 | 0.3293 |
| 310 | 2.424 | 17 | 0.1702 | 0.1698 | 420 | 1.717 | 4 | 0.3392 | 0.3397 |
| 221 | 2.386 | 4 | 0.1756 | 0.1764 | 331 | 1.700 | 11 | 0.3460 | 0.3462 |
| 102 | 2.377 | 4 | 0.1770 | 0.1792 | | | | | |
| 301 | 2.274 | 4 | 0.1937 | 0.1934 | | | | | |
| 112 | 2.267 | 4 | 0.1946 | 0.1962 | | | | | |

$a = 7.673$ Å, $c = 4.966$ Å: tetragonal.

TABLE VII X-ray diffraction spectra and unit cell dimensions of $Sm_4Si_2O_7N_2$

| *h k l* | *d* (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|
| 1 1 0 (1 0 1) | 7.491 | 8 | 0.0178 | 0.0178 |
| 2 1 0 | 4.730 | 12 | 0.0447 | 0.0428 |
| 1 2 0 | 4.642 | 27 | 0.0464 | 0.0461 |
| 1 0 2, 2 0 2 | 3.806 | 7 | 0.0690 | 0.0669, 0.0712 |
| 3 1 1 | 3.695 | 7 | 0.0732 | 0.0733 |
| 2 1 | 3.487 | 8 | 0.0822 | 0.0832 |
| 0 1 2 | 3.364 | 9 | 0.0884 | 0.0884 |
| 1 3 0 | 3.276 | 32 | 0.0932 | 0.0933 |
| 3 2 1, 3 1 2 | 3.145 | 100 | 0.1011 | 0.1016, 0.1017 |
| 2 2 1, 4 0 1 | 2.991 | 32 | 0.1118 | 0.1118 |
| 0 2 2 | 2.924 | 41 | 0.1169 | 0.1169 |
| 2 3 0 | 2.887 | 61 | 0.1200 | 0.1183 |
| 1 3 1 | 2.851 | 13 | 0.1230 | 0.1234 |
| 3 0 1 | 2.820 | 13 | 0.1257 | 0.1257 |
| 4 1 2 | 2.671 | 27 | 0.1402 | 0.1394 |
| 0 4 0 | 2.576 | 27 | 0.1507 | 0.1510 |
| 1 4 0, 2 1 3 | 2.506 | 9 | 0.1592 | 0.1594, 0.1590 |
| 2 4 1 | 2.333 | 11 | 0.1837 | 0.1835 |
| 2 2 $\bar{2}$ | 2.285 | 7 | 0.1915 | 0.1915 |
| 5 0 0 | 2.194 | 7 | 0.2077 | 0.2082 |
| 0 4 2 | 2.083 | 18 | 0.2305 | 0.2302 |
| 1 5 0, 3 3 3 | 2.021 | 30 | 0.2448 | 0.2443, 0.2452 |
| 2 0 4 | 1.943 | 18 | 0.2649 | 0.2675 |
| 5 3 0, 1 1 4 | 1.850 | 23 | 0.2922 | 0.2933 |
| 4 0 $\bar{2}$ | 1.838 | 20 | 0.2960 | 0.2950 |
| 2 5 1 | 1.796 | 13 | 0.3100 | 0.3097 |
| 0 1 4 | 1.750 | 18 | 0.3250 | 0.3262 |
| 3 2 $\bar{3}$ | 1.614 | 27 | 0.3839 | 0.3838 |
| 3 5 3 | 1.589 | 7 | 0.3960 | 0.3963 |
| 1 6 2 | 1.568 | 7 | 0.4067 | 0.4067 |
| 0 6 2, 2 4 4, 3 4 4 | 1.545 | 7 | 0.4189 | 0.4190, 0.4186, 0.4190 |

$a = 11.965$ Å, $b = 10.292$ Å, $c = 7.761$ Å, $\beta = 113.69°$ : monoclinic.

TABLE VIII X-ray diffraction spectra and unit cell dimensions of $Dy_2O_3 \cdot Si_3N_4$

| *h k l* | *d* (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|
| 2 2 0 | 5.400 | 8 | 0.0343 | 0.0344 |
| 0 0 3 | 4.951 | 20 | 0.0408 | 0.0409 |
| 4 0 0 | 3.814 | 10 | 0.0687 | 0.0687 |
| 2 2 3 | 3.645 | 15 | 0.0753 | 0.0753 |
| 4 2 0 | 3.411 | 21 | 0.0859 | 0.0859 |
| 4 2 2 | 3.086 | 9 | 0.1050 | 0.1041 |
| 4 0 3 | 3.015 | 25 | 0.1100 | 0.1096 |
| 3 2 4 | 2.794 | 100 | 0.1281 | 0.1285 |
| 5 3 2 | 2.466 | 12 | 0.1644 | 0.1642 |
| 6 2 0, 1 1 6 | 2.414 | 17 | 0.1716 | 0.1718, 0.1721 |
| 6 2 3 | 2.169 | 4 | 0.2126 | 0.2127 |
| 6 3 3, 7 1 2 | 2.069 | 4 | 0.2336 | 0.2341, 0.2329 |
| 7 0 3, 4 4 5 | 1.995 | 25 | 0.2512 | 0.2513, 0.2510 |
| 5 1 6, 8 0 0 | 1.905 | 6 | 0.2756 | 0.2751, 0.2748 |
| 8 0 2, 8 2 0 | 1.846 | 6 | 0.2934 | 0.2930, 0.2920 |
| 6 6 0, 5 3 6, 4 2 7 | 1.799 | 6 | 0.3090 | 0.3092, 0.3095, 0.3085 |
| 7 5 0, 8 3 1, 6 0 6 | 1.776 | 2 | 0.3170 | 0.3178, 0.3180, 0.3181 |
| 2 2 8, 7 0 5 | 1.754 | 3 | 0.3250 | 0.3251, 0.3240 |
| 7 5 2, 6 2 6 | 1.726 | 22 | 0.3357 | 0.3360, 0.3353 |

$a = 15.260$ Å, $c = 14.838$ Å: tetragonal.

TABLE IX X-ray diffraction spectra and unit cell dimensions of $Dy_4Si_2O_7N_2$

| *h k l* | *d* (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|
| 1 1 0 | 7.300 | 9 | 0.0188 | 0.0190 |
| 1 1 $\bar{1}$ | 4.580 | 15 | 0.0477 | 0.0472 |
| 1 3 0 | 3.206 | 12 | 0.0973 | 0.0982 |
| 1 0 $\bar{2}$ | 3.076 | 100 | 0.1057 | 0.1048 |
| 3 2 1 | 2.931 | 21 | 0.1164 | 0.1156 |
| 0 2 2 | 2.909 | 21 | 0.1182 | 0.1182 |
| 3 2 0 | 2.873 | 24 | 0.1212 | 0.1216 |
| 2 3 0 | 2.837 | 38 | 0.1242 | 0.1255 |
| 4 1 1 | 2.665 | 4 | 0.1408 | 0.1412 |
| 4 0 0 | 2.619 | 7 | 0.1458 | 0.1458 |
| 4 1 0, 4 0 2 | 2.533 | 11 | 0.1558 | 0.1557, 0.1561 |
| 0 4 0, 2 1 $\bar{2}$ | 2.513 | 10 | 0.1583 | 0.1584, 0.1591 |
| 3 3 1, 4 1 2 | 2.459 | 3 | 0.1654 | 0.1651, 0.1660 |
| 1 4 0, 0 3 2 | 2.440 | 4 | 0.1680 | 0.1675, 0.1677 |
| 3 1 3 | 2.290 | 4 | 0.1907 | 0.1919 |
| 5 1 1 | 2.159 | 2 | 0.2145 | 0.2147 |
| 2 3 $\bar{2}$ | 2.047 | 4 | 0.2386 | 0.2382 |
| 3 2 $\bar{2}$ | 1.987 | 11 | 0.2533 | 0.2513 |
| 5 0 3 | 1.897 | 7 | 0.2779 | 0.2766 |
| 2 0 4 | 1.886 | 5 | 0.2811 | 0.2825 |
| 1 3 $\bar{3}$, 3 3 $\bar{2}$ | 1.822 | 10 | 0.3012 | 0.3006, 0.3009 |
| 4 4 0, 2 2 $\bar{3}$, 3 1 4 | 1.813 | 11 | 0.3042 | 0.3041, 0.3040, 0.3039 |
| 2 2 4 | 1.763 | 5 | 0.3217 | 0.3221 |
| 6 2 1 | 1.723 | 8 | 0.3368 | 0.3361 |
| 2 6 0, 4 5 0 | 1.596 | 6 | 0.3926 | 0.3927, 0.0392 |
| 2 6 1, 6 0 $\bar{1}$ | 1.583 | 9 | 0.3991 | 0.3987, 0.3989 |
| 7 0 2 | 1.571 | 5 | 0.4052 | 0.4056 |

$a = 11.053$ Å, $b = 10.052$ Å, $c = 7.527$ Å, $\beta = 108.59°$: monoclinic.

TABLE X X-ray diffraction spectra and unit cell dimensions of $Y_2O_3 \cdot Si_3N_4$

| *h k l* | *d* (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ | *h k l* | *d* (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 1 0 | 5.400 | 8 | 0.0343 | 0.0346 | 2 0 2 | 2.065 | 3 | 0.2345 | 0.2353 |
| 0 0 1 | 4.951 | 11 | 0.0408 | 0.0415 | 1 2 2 | 1.991 | 19 | 0.2523 | 0.2526 |
| 2 0 0 | 3.830 | 7 | 0.0682 | 0.0693 | 4 0 0 | 1.897 | 8 | 0.2779 | 0.2772 |
| 1 1 1 | 3.644 | 15 | 0.0753 | 0.0762 | 4 1 0 | 1.843 | 7 | 0.2944 | 0.2945 |
| 1 2 0 | 3.411 | 9 | 0.0859 | 0.0866 | 2 2 2 | 1.812 | 12 | 0.3046 | 0.3046 |
| 2 0 1 | 3.015 | 25 | 0.1100 | 0.1108 | 3 3 0 | 1.792 | 10 | 0.3114 | 0.3118 |
| 1 2 1 | 2.794 | 100 | 0.1281 | 0.1281 | 4 1 1 | 1.726 | 12 | 0.3357 | 0.3359 |
| 2 2 0 | 2.696 | 5 | 0.1376 | 0.1386 | 3 1 2 | 1.717 | 17 | 0.3392 | 0.3392 |
| 0 0 2 | 2.459 | 9 | 0.1654 | 0.1660 | 4 2 0 | 1.699 | 5 | 0.3464 | 0.3464 |
| 1 3 0 | 2.408 | 17 | 0.1724 | 0.1732 | 3 3 1 | 1.682 | 9 | 0.3535 | 0.3533 |
| 2 2 1 | 2.359 | 4 | 0.1797 | 0.1801 | 2 1 3 | 1.474 | 12 | 0.4603 | 0.4602 |
| 1 0 2 | 2.336 | 3 | 0.1832 | 0.1833 | 3 3 2 | 1.449 | 5 | 0.4763 | 0.4778 |
| 3 0 1 | 2.252 | 3 | 0.1978 | 0.1974 | 5 2 1 | 1.359 | 9 | 0.5414 | 0.5438 |
| 1 1 2 | 2.230 | 3 | 0.2011 | 0.2006 | | | | | |
| 1 3 1 | 2.159 | 4 | 0.2145 | 0.2147 | | | | | |

$a = 7.598$ Å, $c = 4.908$ Å: tetragonal.

TABLE XI X-ray diffraction spectra and unit cell dimensions of $Y_4Si_2O_7N_2$

| *hkl* | *d* (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|
| 1 1 0 | 7.248 | 12 | 0.0190 | 0.0190 |
| 0 2 0 | 5.034 | 2 | 0.0395 | 0.0394 |
| 1 2 0 | 4.525 | 15 | 0.0488 | 0.0485 |
| 2 2 0 | 3.644 | 5 | 0.0753 | 0.0759 |
| 1 3 0 | 3.195 | 22 | 0.0980 | 0.0978 |
| 1 3 1 | 3.055 | 100 | 0.1071 | 0.1088 |
| 0 2 2 | 2.919 | 15 | 0.1174 | 0.1174 |
| 3 2 0 | 2.864 | 31 | 0.1219 | 0.1215 |
| 2 3 0 | 2.828 | 54 | 0.1250 | 0.1251 |
| 4 0 1 | 2.736 | 7 | 0.1336 | 0.1317 |
| $\bar{3}$ 1 1 | 2.712 | 7 | 0.1360 | 0.1368 |
| 4 0 0 | 2.619 | 8 | 0.1458 | 0.1459 |
| 0 4 0 | 2.519 | 16 | 0.1576 | 0.1576 |
| 2 0 3, $\bar{2}$ 3 1 | 2.499 | 11 | 0.1601 | 0.1612, 0.1615 |
| $\bar{3}$ 2 1, 4 1 2 | 2.453 | 6 | 0.1662 | 0.1662 |
| 3 1 3 | 2.284 | 6 | 0.1917 | 0.1913 |
| 2 4 0 | 2.273 | 5 | 0.1936 | 0.1941 |
| $\bar{3}$ 3 1 | 2.149 | 4 | 0.2165 | 0.2156 |
| 3 4 0 | 2.042 | 10 | 0.2398 | 0.2397 |
| 5 2 1 | 2.029 | 7 | 0.2429 | 0.2447 |
| $\bar{3}$ 2 2 | 1.979 | 15 | 0.2553 | 0.2501 |
| 2 5 0 | 1.890 | 15 | 0.2799 | 0.2827 |
| $\bar{3}$ 4 1 | 1.875 | 7 | 0.2844 | 0.2845 |
| $\bar{2}$ 4 2, 6 0 2 | 1.815 | 14 | 0.3056 | 0.3058, 0.5050 |
| 6 1 1 | 1.805 | 14 | 0.3069 | 0.3071 |
| $\bar{2}$ 5 1 | 1.773 | 5 | 0.3181 | 0.3191 |
| 3 5 1 | 1.760 | 6 | 0.3228 | 0.3225 |
| 6 0 0, 3 5 0 | 1.749 | 6 | 0.3269 | 0.3284 |
| 6 1 0 | 1.717 | 14 | 0.3392 | 0.3382 |
| $\bar{6}$ 0 1 | 1.588 | 5 | 0.3966 | 0.3985 |
| 0 3 4 | 1.576 | 11 | 0.4026 | 0.4004 |
| $\bar{6}$ 1 1 | 1.564 | 8 | 0.4088 | 0.4084 |
| $\bar{2}$ 6 1 | 1.531 | 6 | 0.4266 | 0.4275 |
| 3 6 1 | 1.526 | 6 | 0.4294 | 0.4308 |
| 3 6 0 | 1.517 | 5 | 0.4345 | 0.4337 |

$a = 11.038$ Å, $b = 10.076$ Å, $c = 7.552$ Å, $\beta = 108.46°$: monoclinic.

In the course of identifying these compounds and determining the conditions required to achieve equilibrium, it was observed that in the initial stages of the reactions, a compound of composition $R_4Si_2O_7N_2$ was always formed, even from mixtures containing high concentrations of $Si_3N_4$. Samples containing $Sm_2O_3$ or $La_2O_3$ exhibited melting at low $Si_3N_4$ concentrations; the observed melting points were 1550° C for $Si_3N_4$–$La_2O_3$ and 1600° C for $Si_3N_4$–$Sm_2O_3$.

The lanthanide ions have similar electronic structures and ionic radii (Table II), the $R^{3+}$ ion being the usual oxidation state. The chemistry of the group is thus frequently very uniform. For example, the lanthanide oxides form silicates having general formulae $R_2O_3 \cdot SiO_2$ and $R_2O_3 \cdot 2SiO_2$ [7], and borates having general formulae $R_2O_3 \cdot B_2O_3$ and $3R_2O_3 \cdot B_2O_3$ [8]. The formation of silicon lanthanide oxynitride appears to be consistent with this behaviour.

## 3.2 X-ray diffraction spectra and crystal structures

The diffraction spectra, observed and calculated $Q$ values ($Q = 4\sin^2\theta/\lambda^2$), and lattice parameters of the compounds are given in Tables III to XVI. The data for $Si_3N_4 \cdot Y_2O_3$ and $Y_4Si_2O_7N_2$ [5] have been included for completeness. Comparison of these spectra indicates certain similarities. The spectra of the $R_4Si_2O_7N_2$ compounds of Sm, Dy, Y, Er and Yb are similar, and each can be indexed on the basis of a similar monoclinic unit cell (e.g. $Er_4Si_2O_7N_2$, $a = 10.987$ Å, $b = 10.100$ Å, $c = 7.528$ Å, $\beta = 108.72°$). The spectra of $Si_3N_4 \cdot$

TABLE XII X-ray diffraction spectra and unit cell dimensions of $Er_2O_3 \cdot Si_3N_4$

| $hkl$ | $d$ (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|
| 0 0 2 | 7.252 | 4 | 0.0190 | 0.0190 |
| 2 2 0 | 5.374 | 7 | 0.0346 | 0.0346 |
| 2 1 2 | 4.906 | 20 | 0.0416 | 0.0406 |
| 1 0 3 | 4.635 | 7 | 0.0466 | 0.0471 |
| 3 1 1 | 4.557 | 7 | 0.0482 | 0.0480 |
| 3 2 0 | 4.246 | 5 | 0.0555 | 0.0563 |
| 3 2 1 | 4.036 | 4 | 0.0614 | 0.0610 |
| 2 1 3 | 3.931 | 6 | 0.0647 | 0.0644 |
| 4 0 0 | 3.794 | 13 | 0.0695 | 0.0693 |
| 0 0 4 | 3.627 | 15 | 0.0760 | 0.0760 |
| 3 1 3 | 3.409 | 21 | 0.0860 | 0.0861 |
| 2 0 4 | 3.264 | 10 | 0.0939 | 0.0934 |
| 2 1 4 | 3.202 | 9 | 0.0975 | 0.0977 |
| 5 0 0 | 3.054 | 37 | 0.1072 | 0.1082 |
| 2 2 4 | 3.002 | 35 | 0.1110 | 0.1107 |
| 0 0 5 | 2.908 | 10 | 0.1182 | 0.1188 |
| 3 3 3, 3 1 4 | 2.887 | 10 | 0.1200 | 0.1207, 0.1193 |
| 5 2 0 | 2.832 | 39 | 0.1247 | 0.1255 |
| 5 0 2 | 2.794 | 100 | 0.1281 | 0.1272 |
| 3 2 4 | 2.736 | 30 | 0.1336 | 0.1323 |
| 2 0 5 | 2.720 | 30 | 0.1352 | 0.1362 |
| 4 1 4 | 2.597 | 10 | 0.1483 | 0.1496 |
| 4 4 2, 3 0 5 | 2.520 | 9 | 0.1575 | 0.1575, 0.1578 |
| 6 0 1 | 2.493 | 19 | 0.1609 | 0.1606 |
| 5 3 2 | 2.450 | 19 | 0.1666 | 0.1662 |
| 6 2 0 | 2.399 | 20 | 0.1738 | 0.1732 |
| 4 4 4 | 2.157 | 10 | 0.2149 | 0.2146 |
| 6 1 4 | 2.058 | 5 | 0.2361 | 0.2362 |
| 1 1 7 | 2.039 | 7 | 0.2405 | 0.2416 |
| 5 5 4 | 1.986 | 15 | 0.2535 | 0.2535 |
| 6 1 5 | 1.896 | 7 | 0.2782 | 0.2790 |
| 6 5 2 | 1.881 | 7 | 0.2826 | 0.2831 |
| 5 4 5, 8 2 0 | 1.840 | 7 | 0.2954 | 0.2963, 0.2944 |

$a = 15.199$ Å, $c = 14.504$ Å: tetragonal.

$Er_2O_3$, $Si_3N_4 \cdot Yb_2O_3$, and $Si_3N_4 \cdot Dy_2O_3$ form a second group, and those of $Si_3N_4 \cdot Y_2O_3$, $Si_3N_4 \cdot Sm_2O_3$ and $Yb_2Si_3O_5N_2$ form a third group. The spectra of the last two groups were indexed as tetragonal unit cells, the first group having a larger cell size (e.g., $Si_3N_4 \cdot Er_2O_3$, $a = 15.199$ Å, $c = 14.504$ Å; $Si_3N_4 \cdot Sm_2O_3$, $a = 7.673$ Å, $c = 4.966$ Å). Rae *et al.* [6] and Tsuge *et al.* [9] have also indexed the spectra of $Si_3N_4 \cdot Y_2O_3$, and their values for the lattice parameters are in close agreement with those given in Table X. The spectra of the silicon lanthanum oxynitrides were indexed on larger unit cells: $2Si_3N_4 \cdot La_2O_3$ orthorhombic $a = 16.460$ Å, $b = 14.524$ Å, $c = 9.624$ Å; $Si_3N_4 \cdot La_2O_3$ tetragonal $a = 19.487$ Å, $c = 13.489$ Å; $La_4Si_2O_7N_2$ monoclinic $a = 23.948$ Å, $b = 10.437$ Å, $c = 15.538$ Å, $\beta = 113.53°$.

Warshaw and Roy [7] have reviewed the oxides, aluminates and silicates of the lanthanides and have concluded that they can be classified into three groups based upon the size of the lanthanide ionic radii. A similar classification may be made in the present instance, but it should be considered tentative since only six lanthanides have been studied. The similarities in crystal structures noted above suggest that the $Si_3N_4 \cdot R_2O_3$ compounds can be divided into three groups; the smallest rare earths Yb, Er, and Dy form one group, the rare earths of intermediate size Y and Sm form a second, and the largest rare earth La forms a third group. Dy may represent a transitional stage between the first two groups since its spectra, except for one line at $d = 3.086$ Å, can be indexed on the smaller tetragonal unit cell. In the $R_4Si_2O_7N_2$ compounds only two groups are suggested – La forming one group and the other five elements forming the other.

TABLE XIII X-ray diffraction spectra and unit cell dimensions of $Er_4Si_2O_7N_2$

| $hkl$ | $d$ (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|
| 1 1 0 | 7.256 | 16 | 0.0190 | 0.0190 |
| 2 0 0 | 5.227 | 3 | 0.0366 | 0.0369 |
| 0 2 0 | 5.058 | 3 | 0.0391 | 0.0392 |
| 2 1 0, 1 0 $\bar{2}$ | 4.634 | 10 | 0.0466 | 0.0468, 0.0462 |
| 1 2 0 | 4.541 | 32 | 0.0485 | 0.0484 |
| 2 2 0 | 3.626 | 5 | 0.0760 | 0.0762 |
| 0 1 2 | 3.348 | 3 | 0.0892 | 0.0867 |
| 2 1 2 | 3.297 | 3 | 0.0920 | 0.0909 |
| 1 3 0 | 3.201 | 22 | 0.0976 | 0.0975 |
| 0 3 1 | 3.050 | 100 | 0.1075 | 0.1079 |
| 0 2 2, 3 2 1 | 2.911 | 24 | 0.1180 | 0.1180, 0.1161 |
| 2 2 2 | 2.882 | 23 | 0.1204 | 0.1203 |
| 3 2 0 | 2.862 | 45 | 0.1221 | 0.1223 |
| 2 3 0, 1 3 $\bar{1}$ | 2.825 | 77 | 0.1253 | 0.1252, 0.1258 |
| 2 3 1 | 2.798 | 5 | 0.1277 | 0.1276 |
| 4 0 0 | 2.607 | 10 | 0.1471 | 0.1478 |
| 0 4 0, 4 1 0 | 2.521 | 22 | 0.1573 | 0.1568, 0.1576 |
| 1 0 3 | 2.503 | 15 | 0.1596 | 0.1606 |
| 2 0 3, 2 3 $\bar{1}$ | 2.486 | 8 | 0.1618 | 0.1623, 0.1622 |
| 3 3 1 | 2.467 | 8 | 0.1643 | 0.1651 |
| 1 4 2 | 2.436 | 8 | 0.1685 | 0.1685 |
| 2 1 3 | 2.394 | 8 | 0.1745 | 0.1721 |
| 3 1 3 | 2.285 | 8 | 0.1915 | 0.1924 |
| 5 1 1 | 2.135 | 5 | 0.2194 | 0.2171 |
| 5 1 0, 3 4 0 | 2.039 | 10 | 0.2405 | 0.2407, 0.2400 |
| 0 5 0 | 2.025 | 6 | 0.2439 | 0.2451 |
| 1 5 0 | 1.983 | 15 | 0.2543 | 0.2543 |
| 1 5 $\bar{1}$, 2 5 0 | 1.880 | 15 | 0.2829 | 0.2827, 0.2820 |
| 2 2 $\bar{3}$, 4 4 0 | 1.810 | 15 | 0.3052 | 0.3054, 0.3036 |
| 2 4 $\bar{2}$, 4 1 $\bar{2}$ | 1.805 | 15 | 0.3069 | 0.3072, 0.3063 |
| 6 1 0, 3 4 3 | 1.713 | 15 | 0.3408 | 0.3423, 0.3394 |
| 1 6 0 | 1.665 | 5 | 0.3607 | 0.3622 |
| 2 5 $\bar{2}$ | 1.591 | 10 | 0.3951 | 0.3954 |
| 0 3 4 | 1.579 | 15 | 0.4011 | 0.4034 |
| 5 1 $\bar{2}$ | 1.562 | 10 | 0.4099 | 0.4060 |
| 4 0 $\bar{3}$, 3 6 1 | 1.527 | 10 | 0.4289 | 0.4289, 0.4298 |
| 5 5 0, 0 4 4 | 1.451 | 5 | 0.4750 | 0.4760, 0.4720 |
| 1 7 0, 6 4 0 | 1.430 | 5 | 0.4890 | 0.4896, 0.4893 |
| 0 2 5, 7 0 $\bar{1}$ | 1.372 | 5 | 0.5312 | 0.5317, 0.5328 |

$a = 10.987$ Å, $b = 10.100$ Å, $c = 7.528$ Å, $\beta = 108.72°$ : monoclinic.

## 3.3. Isomorphism

Rae *et al.* [10] have shown that the structure of $Si_3N_4 \cdot Y_2O_3$ is analogous to that of Akermanite ($Ca_2MgSi_2O_7$, $a = 7.846$ Å, $c = 5.020$ Å). In view of the similarity of the unit cells of $Si_3N_4 \cdot Y_2O_3$, $Si_3N_4 \cdot Sm_2O_3$, and $Yb_2Si_3O_5N_2$ it is likely that the last two compounds are also isostructural with Akermanite. On this basis the compositions may be represented by the formulae $Y_2Si_3(O, N)_7$, $Sm_2Si_3(O, N)_7$, and $Yb_2Si_3(O, N)_7$. The structures of $Si_3N_4 \cdot Dy_2O_3$, $Si_3N_4 \cdot Er_2O_3$, and $Si_3N_4 \cdot Yb_2O_3$ are probably also closely related to the Akermanite structure since their unit-cell dimensions are double (for the a lattice parameter) and triple (for the c lattice parameter) those of the $Y_2Si_3(O, N)_7$ cell.

Wills *et al.* [5] have suggested that $Y_4Si_2O_7N_2$ is isostructural with the silicates of the wohlerite-cuspidine series (cuspidine $Ca_4Si_2O_7F_2$ monoclinic $a = 10.35$ Å, $b = 10.43$ Å, $c = 7.55$ Å, $\beta = 110° 4'$). The similarity in cell structure and dimensions suggests that the $R_4Si_2O_7N_2$ compounds of Dy, Sm, Er and Yb are also isostructural with cuspidine. The *a* and *c* lattice parameters of $La_4Si_2O_7N_2$ are double those of the cuspidine unit cell; consequently, the structure is also likely to be closely related to that of cuspidine. Substitution of the cations in this structure can also occur. Thus, Y

TABLE XIV X-ray diffraction spectral and unit cell dimensions of $Yb_2Si_3O_5N_2$

| $h k l$ | $d$ (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|
| 1 1 0 | 5.335 | 11 | 0.0351 | 0.0350 |
| 0 0 1 | 4.870 | 30 | 0.422 | 0.0421 |
| 2 0 0 | 3.814 | 12 | 0.0687 | 0.0700 |
| 1 1 1 | 3.601 | 12 | 0.771 | 0.0771 |
| 2 1 0 | 3.373 | 28 | 0.0879 | 0.0876 |
| 2 0 1 | 2.985 | 24 | 0.1122 | 0.1121 |
| 2 1 1 | 2.777 | 100 | 0.1297 | 0.1296 |
| 0 0 2 | 2.440 | 11 | 0.1680 | 0.1683 |
| 3 1 0 | 2.390 | 17 | 0.1751 | 0.1751 |
| 3 1 1 | 2.144 | 9 | 0.2175 | 0.2172 |
| 2 0 2 | 2.047 | 4 | 0.2386 | 0.2383 |
| 2 1 2 | 1.975 | 21 | 0.2564 | 0.2559 |
| 4 0 0 | 1.890 | 8 | 0.2800 | 0.2802 |
| 4 1 0 | 1.826 | 10 | 0.2999 | 0.2977 |
| 3 3 0 | 1.787 | 10 | 0.3132 | 0.3152 |
| 4 1 1 | 1.717 | 11 | 0.3392 | 0.3398 |
| 3 1 2 | 1.708 | 12 | 0.3428 | 0.3434 |
| 3 3 1 | 1.674 | 10 | 0.3568 | 0.3573 |

$a = 7.557$ Å, $c = 4.875$ Å: tetragonal.

can be replaced by Ca [10] and Si by Al [12], in the latter case giving first $Y_4(Si, Al)O_8N$ which was originally thought to be $5Y_2O_3 \cdot Si_3N_4$: $Al_2O_3$ [11]. On further substitution $2Y_2O_3 \cdot Al_2O_3$ is formed. In each case electrical neutrality is maintained by substituting oxygen for nitrogen as in the Si–Al–O–N system. An additional example of isomorphism has been observed in the third silicon yttrium oxynitride $Y_5(SiO_4)_3N$ [5], its structure being analogous to that of fluoroapatite [12].

This work together with that of Rae *et al.* [6] suggests that an extensive range of compounds exists in this new group of silicon–metal oxynitrides and that they are related to known silicates, phosphates, nitrides, etc.

## Acknowledgements

The authors wish to thank R. Gray for technical assistance.

TABLE XV X-ray diffraction spectra and unit cell dimensions of $Si_3N_4 \cdot Yb_2O_3$

| $h k l$ | $d$ (Å) | Relative intensity | $Q_{obs}$ | $Q_{cal}$ |
|---|---|---|---|---|
| 0 0 2 | 7.248 | 18 | 0.0190 | 0.0190 |
| 2 2 0 | 5.368 | 11 | 0.0347 | 0.0347 |
| 2 1 2, 0 0 3 | 4.896 | 30 | 0.0417 | 0.0407, 0.0428 |
| 2 2 1 | 4.742 | 25 | 0.0445 | 0.0438 |
| 3 0 1 | 4.525 | 23 | 0.0488 | 0.0481 |
| 1 1 3 | 4.414 | 10 | 0.0513 | 0.0515 |
| 3 1 2 | 4.018 | 6 | 0.0619 | 0.0624 |
| 2 1 3 | 3.914 | 6 | 0.0653 | 0.0645 |
| 4 0 0 | 3.798 | 13 | 0.0693 | 0.0694 |
| 3 2 2 | 3.630 | 14 | 0.0759 | 0.0754 |
| 0 0 4 | 3.615 | 20 | 0.0765 | 0.0761 |
| 1 1 4 | 3.437 | 4 | 0.0846 | 0.0848 |
| 4 2 0 | 3.386 | 28 | 0.0872 | 0.0867 |
| 4 1 2 | 3.287 | 5 | 0.0926 | 0.0927 |
| 2 0 4 | 3.229 | 18 | 0.0959 | 0.0935 |
| 2 1 4, 3 3 2 | 3.197 | 21 | 0.0978 | 0.0978, 0.0971 |
| 5 0 0, 4 3 0 | 3.025 | 72 | 0.1093 | 0.1084 |
| 2 2 4 | 2.995 | 50 | 0.1115 | 0.1108 |
| 0 0 5 | 2.891 | 19 | 0.1197 | 0.1190 |
| 3 3 3 | 2.864 | 17 | 0.1219 | 0.1209 |
| 5 2 0 | 2.820 | 70 | 0.1258 | 0.1257 |
| 5 2 1 | 2.777 | 100 | 0.1297 | 0.1305 |
| 4 4 0, 205 | 2.696 | 27 | 0.1376 | 0.1387, 0.1363 |
| 5 3 0 | 2.612 | 30 | 0.1466 | 0.1474 |
| 5 3 1 | 2.575 | 12 | 0.1508 | 0.1522 |
| 6 0 0 | 2.536 | 10 | 0.1567 | 0.1561 |
| 6 1 0 | 2.506 | 18 | 0.1592 | 0.1604 |
| 4 2 4 | 2.479 | 15 | 0.1627 | 0.1628 |
| 5 2 3 | 2.440 | 22 | 0.1680 | 0.1686 |
| 6 0 2 | 2.390 | 25 | 0.1751 | 0.1751 |

$a = 15.188$ Å, $c = 14.506$ Å: tetragonal.

TABLE XVI X-ray diffraction spectra and unit cell dimensions of $Yb_4Si_2O_7N_2$

| *h k l* | *d* (Å) | Relative intensity | $Q_{\mathrm{obs}}$ | $Q_{\mathrm{cal}}$ |
|---|---|---|---|---|
| 1 1 0 | 7.248 | 15 | 0.0190 | 0.0190 |
| 0 2 0 | 5.034 | 2 | 0.0395 | 0.0396 |
| $1\,1\,\bar{1}$ | 4.766 | 6 | 0.0440 | 0.0477 |
| 2 1 1, 1 2 1 | 4.548 | 25 | 0.0483 | 0.0486, 0.0488 |
| 2 2 0 | 3.615 | 5 | 0.0765 | 0.0762 |
| 1 1 2, 2 0 2 | 3.517 | 2 | 0.0808 | 0.0807, 0.0805 |
| 2 1 2, 0 1 2 | 3.336 | 5 | 0.0899 | 0.0904, 0.0892 |
| 1 3 0 | 3.195 | 22 | 0.0980 | 0.0983 |
| 0 3 1 | 3.035 | 100 | 0.1086 | 0.1090 |
| 0 2 2 | 2.900 | 22 | 0.1189 | 0.1189 |
| 2 2 2 | 2.873 | 15 | 0.1212 | 0.1201 |
| 3 2 0 | 2.846 | 35 | 0.1235 | 0.1219 |
| 2 3 0 | 2.820 | 70 | 0.1258 | 0.1258 |
| $3\,1\,\bar{1}$ | 2.704 | 6 | 0.1368 | 0.1385 |
| 4 0 0 | 2.612 | 7 | 0.1466 | 0.1463 |
| $2\,0\,\bar{2}$ | 2.583 | 11 | 0.1499 | 0.1518 |
| 0 4 0 | 2.506 | 20 | 0.1592 | 0.1585 |
| $2\,1\,\bar{2}$ | 2.485 | 15 | 0.1619 | 0.1611 |
| 1 4 0 | 2.440 | 7 | 0.1680 | 0.1677 |
| 3 3 0 | 2.415 | 5 | 0.1715 | 0.1714 |
| $1\,3\,\bar{2}$, 2 4 0 | 2.263 | 6 | 0.1953 | 0.1952, 0.1951 |
| 4 3 1 | 2.125 | 3 | 0.2215 | 0.2199 |
| $2\,4\,\bar{1}$ | 2.074 | 2 | 0.2325 | 0.2326 |
| 5 2 1 | 2.026 | 9 | 0.2436 | 0.2438 |
| 0 5 0 | 2.012 | 9 | 0.2470 | 0.2477 |
| 1 5 0 | 1.975 | 16 | 0.2564 | 0.2569 |
| $3\,4\,\bar{1}$ | 1.864 | 16 | 0.2878 | 0.2871 |

$a = 11.071$ Å, $b = 10.046$ Å, $c = 7.519$ Å, $\beta = 109.15°$: monoclinic.

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