so that the metal-to-nonmetal ratio and the valence electron concentration remain constant.

The compound Be$_4$Si$_4$, which also exists in the binary system Si$_3$N$_4$-Be$_2$N$_2$, has an extended solubility in the ternary along a sequence of compositions with constant metal-to-nonmetal ratio. The homogeneity range is described by Be$_4$Si$_x$Al$_{2-x}$N$_4$ for $x = 0$ to $x = 1$, as shown by a single-phase sample with compositions of 17.25 mol% Si$_3$N$_4$, 9.02 AlN, and 73.73 Be$_2$N$_2$. In this case Si$^{1+}$ and Be$^{2+}$ are substituted simultaneously by 2A$^{1+}$. The other members of the homologous series previously reported have no substantial solubility in the ternary.

Phase analysis of multiphase samples with compositions in the ternary revealed equilibrium between the solid solution Be$_4$Si$_1$Al$_{2-x}$N$_4$ and Si$_3$N$_4$. Also, a two-phase equilibrium was established between Be$_2$N$_2$ and the Al-rich part of the solid solution. The Be- and Si-rich part is in equilibrium with Be$_4$Si$_x$Al$_{2-x}$N$_4$ ($x = 0$ to $x = 1$) (Fig. 1). The equilibrium conditions for the homologous series between Be$_4$Si$_4$ and Be$_4$Si$_x$Al$_{2-x}$N$_4$ solid solution were not investigated further.

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References

The System Si$_3$N$_4$-SiO$_2$-Y$_2$O$_3$

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Subsolidus phase relations were established in the system Si$_3$N$_4$-SiO$_2$-Y$_2$O$_3$. Four ternary compounds were confirmed, with compositions of Y$_2$Si$_3$O$_4$N, $Y$$_2$Si$_3$O$_4$N, $Y$SiO$_2$N, and $Y$$_4$Si$_2$O$_7$N$_2$. The eutectic in the triangle Si$_3$N$_4$-Y$_2$Si$_3$O$_4$N-$Y$$_4$Si$_2$O$_7$N$_2$ melts at 1500°C and that in the triangle Si$_3$N$_4$-SiO$_2$-Y$_2$O$_3$ at 1550°C. The eutectic temperature of the Si$_3$N$_4$-$Y$SiO$_2$N$_2$ join was $\approx 1520°C$.

II. Experimental Procedure

Specimens were prepared by milling $\alpha$-Si$_3$N$_4$, SiO$_2$, and Y$_2$O$_3$ powders in a hard metal mill under acetone for 1 h. The powder mixtures were dried, compacted under a uniaxial pressure of 110 MPa, and heat-treated in BN-coated graphite crucibles in a graphite resistance furnace under static nitrogen until equilibrium was reached. Equilibrium was assumed when no further phase change was observed after regliding and reheating. Only compositions with $<2$% weight loss were used to construct the phase diagram.

Phase compositions after heat treatment were identified using X-ray diffraction (XRD) (monochromated CuK$\alpha$ radiation). Some of the specimens showing partial melting were polished and examined by optical microscopy in reflected light for identification of minor, mainly noncrystalline, phases.

Some of the compositions were analyzed chemically after heat treatment. Nitrogen contents were analyzed by dissolving the nitrides in lithium hydroxide. The amount of NH$_3$ liberated was determined volumetrically using standard H$_2$SO$_4$. Silicon and yttrium were analyzed using an electron microprobe. Chemical compositions of heat-treated specimens did not differ within $\pm 2$% from the starting compositions.

Liquid formation was studied by light-microscopy examination of quenched specimens. Differential thermal analysis was also used to determine the melting behavior of some compositions in this system. Equilibrated specimens were placed in a Ta crucible in DTA equipment using W-$W$25Re thermocouples. The heating rate was 5°C/min. Melting points were determined using at least two heating and two cooling cycles.

III. Results and Discussion

1. Ternary Compounds

The ternary compounds were synthesized in the solid state at 1550°C. Chemical compositions were analyzed after heat treatment. Nitrogen contents were analyzed by hot gas extraction and Si and Y were analyzed using an electron microprobe. The results are given in Table 1, along with data from the literature for comparison.

Three of the four ternary compounds reported in the system Si, $Y$, N, O have the same compositions. They are: $Y$$_2$Si$_3$O$_4$N (the YAM- or wohlerite), Y$_2$Si$_3$O$_4$N (wollastonite), and $Y$Si$_3$O$_2$N$_2$ (melilite). The reported compositions with an apatite structure are different. Jack reported that the apatite has a wide single-phase region
Table I. Ternary Compounds in the System Si, Y/N, O

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref. 1</th>
<th>Ref. 2</th>
<th>Ref. 4</th>
<th>Ref. 5</th>
<th>Present study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apatite</td>
<td>10Y₂O₃·9SiO₂·Si₃N₄</td>
<td>(Y, Si)(SiO₁₃)N₂</td>
<td>Y₅Si₃O₁₂N₂</td>
<td>Y₅(SiO₄)₆N₂</td>
<td>Y₅Si₃O₁₂N₂</td>
</tr>
<tr>
<td>Wollastonite</td>
<td></td>
<td></td>
<td>YSiO₂N</td>
<td>YSiO₂N</td>
<td>YSiO₂N</td>
</tr>
<tr>
<td>Wohlerite (YAM)</td>
<td></td>
<td></td>
<td>Y₂Si₃O₁₂N₂</td>
<td>Y₂Si₃O₁₂N₂</td>
<td>Y₂Si₃O₁₂N₂</td>
</tr>
<tr>
<td>Melilite</td>
<td>Si₄N₃·Y₂O₃</td>
<td>Y₂Si₃O₁₂N₂</td>
<td>Y₂Si₃O₁₂N₂</td>
<td>Y₂Si₃O₁₂N₂</td>
<td>Y₂Si₃O₁₂N₂</td>
</tr>
</tbody>
</table>

Based on the formula (Y₅Si)(Si₃O₁₁N). Lange et al. ² reported that the apatite has a formula Y₅Si₃O₁₂N₂. Wills et al. ² reported a formula of 10Y₂O₃·9SiO₂·Si₃N₄. However, they claimed that this composition is the same as the H phase reported by Jack (apatite). The apatite compositions suggested by these writers are compared in Table I.

The compound apatite has a formula A₅₀(XO₄)₆Z₂. The most common member of this compound is Ca₅₀(PO₄)₆F₂. Nitrogen-containing apatites have been reported; their general formula is (RE)ₓ(SiO₄)₆Nₓ (where RE is rare-earth ions). Rare-earth silicate apatites have also been reported.² These apatites contain A and Z site vacancies, with a formula of (RE)ₓ(SiO₄)₆Nₓ. It was reported that only rare-earth ions with larger radii can form this type of compound. Yttrium is too small to form apatite. Fluorine reportedly replaces oxygen in the lattice; however, the replacement of oxygen with nitrogen in the SiO₂ position has not been reported.

A site vacancies and substitutions have been reported for A = Ce, Nd, Sm, and Eu. A site interstitials have also been reported, but not confirmed. Therefore, it is still questionable if such interstitials exist.

Substitution in the A site with ions <1 Å was reported to be possible but probably not in high concentrations.⁸ Thus, it is questionable whether Si⁴⁺ can be accommodated in the A position, since Si³⁻ is ≈1 Å.

The apatite found in this investigation has the formula Y₅Si₃O₁₂N₂. The X-ray pattern of this compound was indexed on the basis of a hexagonal cell, with calculated lattice parameters of a = 9.368 ± 0.002 Å and c = 6.355 ± 0.002 Å. The homogeneity range is less than 5 ± 2 eq. %.

The data were analyzed and used to construct the phase diagram shown in Fig. 2.

(2) Subsolidus Equilibria

Two-phase joins and three-phase compatibility triangles were established by studying compositions lying on the joins and inside the triangles. At least two composition points were used to establish each of the compatibility relations. Samples were prepared at 1550°C and heat-treated at lower temperatures when there was apparent liquid in the sample. The results are tabulated in Table II.* The data were analyzed and used to construct the phase diagram shown in Fig. 2.

Two versions of the quadrangle Si₃N₄·Y₁₀(SiO₄)₁₀N₈ (apatite)–Y₂Si₃O₉·Si₅N₈·O and the Y₂O₃-rich region of the diagram were reported in the literature. Lange et al. ² reported a two-phase field

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* For Table II, order ACSDE-160 from Data Depository Service. The American Ceramic Society, 65 Ceramic Drive, Columbus, Ohio 43214.
An endothermic peak was observed at 1550°C on heating DTA unit under He atmosphere at normal pressure, and heated at eutectic temperature on the join Si₃N₄-Y₂Si₂O₇ is thermocouples were W-W₂5Re. These results indicate that the they can be used to construct a 1550°C isothermal section of this triangle in specimens with compositions of 10 eq. % Si and 80 eq. % O at 1550°C. No liquid formation was found at 1450°C. The 1550°C-annealed specimens showed bloating and weight losses up to 8 wt% after 20-min heat treatment in N₂ atmosphere at normal pressure and 1550°C, due to loss of SiO₂. Therefore, this area of the diagram was not studied further.

A specimen containing 50.0 eq. % Y and 92.5 eq. % O, lying in the apatite solid-solution composition suggested by Jack⁴, was prepared by annealing the powder compact at 1550°C for 15 min in N₂. The sample was ground, recompacted, and reannealed three times to ensure homogenization. All preparation steps were performed in glove boxes in an Ar atmosphere to avoid oxygen contamination. After the third annealing, a polished section was prepared. Microprobe analysis showed the same Si/Y ratio as in the starting powder. Nitrogen analysis also indicated that there was no shift in chemical composition. The optical micrograph is given in Fig. 4. The XRD showed two crystalline phases, i.e. the Y₆(SiO₄)₂N₂ apatite (very strong) and the high-temperature modification (α) of Y₂Si₂O₇ (weak). These two phases can clearly be correlated with the medium-gray and light-gray grains in Fig. 4. The dark-gray phase with a volume fraction of ≈10 to 15% is amorphous material, i.e. glass.

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References