

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

The compound Be_4SiN_4 , which also exists in the binary system $\text{Si}_3\text{N}_4\text{-}\beta\text{-Be}_3\text{N}_2$, has an extended solubility in the ternary along a sequence of compositions with constant metal-to-nonmetal ratio. The homogeneity range is described by $\text{Be}_{4-x}\text{Si}_{1-x}\text{Al}_{2x}\text{N}_4$ for $x=0$ to $x=0.1$, as shown by a single-phase sample with compositions of 17.25 mol% Si_3N_4 , 9.02 AlN, and 73.73 Be_3N_2 . In this case Si^{4+} and Be^{2+} are substituted simultaneously by 2Al^{3+} . The other members of the homologous series previously reported^{2,4} have no substantial solubility in the ternary.

Phase analysis of multiphase samples with compositions in the ternary revealed equilibrium between the solid solution $\text{Be}_{1-x}\text{Si}_{1-x}\text{Al}_{2x}\text{N}_2$ and Si_3N_4 . Also, a two-phase equilibrium was established between $\beta\text{-Be}_3\text{N}_2$ and the Al-rich part of the solid solution. The Be- and Si-rich part is in equilibrium with $\text{Be}_{4-x}\text{Si}_{1-x}\text{Al}_{2x}\text{N}_4$ ($x=0$ to $x=0.1$) (Fig. 1). The equilibrium condi-

tions for the homologous series between Be_4SiN_4 and $\text{Be}_{1-x}\text{Si}_{1-x}\text{Al}_{2x}\text{N}_2$ solid solution were not investigated further.

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References

- ¹ A. Rabenau and P. Eckerlin; pp. 136-43 in *Special Ceramics 1*. Edited by P. Popper. Academic Press, New York, 1960.
- ² I. C. Huseby, H. L. Lukas, and G. Petzow, "Phase Equilibria in the System $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-BeO-Be}_3\text{N}_2$," *J. Am. Ceram. Soc.*, **58** [9-10] 377-80 (1975).
- ³ D. P. Thompson, "New Polytypes in the Be-Si-O-N System," *J. Mater. Sci.*, **11** [7] 1377-80 (1976).
- ⁴ D. P. Thompson and L. J. Gauckler, "Further Study of the Be-Si-O-N Polytypes," *J. Am. Ceram. Soc.*, **60** [9-10] 470-71 (1977).
- ⁵ L. J. Gauckler, H. L. Lukas, and G. Petzow, "Contribution to the Phase Diagram $\text{Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3\text{-SiO}_2$," *ibid.*, **58** [7-8] 346-47 (1975).
- ⁶ L. J. Gauckler, "Equilibrium in the Systems Si, Al/N, O and Si, Al, Be/N, O," Ph. D. Thesis, University of Stuttgart, Federal Republic of Germany, 1975.
- ⁷ P. Eckerlin, "System $\text{Be}_3\text{N}_2\text{-Si}_3\text{N}_4$: 1V," *Z. Anorg. Allg. Chem.*, **353** [5-6] 225-35 (1967).

The System $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Y}_2\text{O}_3$

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Subsolidus phase relations were established in the system $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Y}_2\text{O}_3$. Four ternary compounds were confirmed, with compositions of $\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$, $\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$, YSiO_2N , and $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$. The eutectic in the triangle $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7\text{-Y}_{10}(\text{SiO}_4)_6\text{N}_2$ melts at 1500°C and that in the triangle $\text{Si}_2\text{N}_2\text{O-SiO}_2\text{-Y}_2\text{Si}_2\text{O}_7$ at 1550°C. The eutectic temperature of the $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ join was $\approx 1520^\circ\text{C}$.

I. Introduction

FOUR versions of the subsolidus phase equilibria in the system $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Y}_2\text{O}_3$ have been published in the past few years.¹⁻⁵ However, they do not agree.

Tsuge *et al.*¹ reported two ternary compounds, $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$ and $\text{Si}_3\text{N}_4\text{-2Y}_2\text{O}_3$, along the join $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3$. Wills *et al.*² reported a 1700°C isotherm of the system and three ternary phases were suggested. Jack³ indicated the existence of seven ternary compounds. However, only five were characterized by chemical compositions. Later, Jack⁴ reported that only four of these seven ternary phases existed at 1600°C. Lange *et al.*⁵ showed similar results for most of the phases; however, the composition of N-apatite and the compatibility triangles in the oxygen-rich region of the diagram differ from those reported by Jack.

The present paper reports the results obtained for the subsolidus phase relations in the system $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Y}_2\text{O}_3$ and the melting behavior of some of the oxygen-rich compositions.

II. Experimental Procedure

Specimens were prepared by milling $\alpha\text{-Si}_3\text{N}_4$,[†] SiO_2 ,[‡] and Y_2O_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 regrinding 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 $\text{CuK}\alpha$ 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_2SO_4 . Silicon and yttrium were analyzed using an electron microprobe. Chemical compositions of heat-treated specimens did not differ within ± 2 eq.% 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-W25Re thermocouples. The heating rate was 5°C/min. Melting points were determined using at least two heating and two cooling curves.

III. Results and Discussion

(I) 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 I, along with data from the literature for comparison.

Three of the four ternary compounds reported³⁻⁵ in the system Si, Y/N, O have the same compositions. They are: $\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$ (the YAM or wohlerite), YSiO_2N (wollastonite), and $\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$ (melilitite). The reported compositions with an apatite structure are different. Jack⁴ reported that the apatite has a wide single-phase region

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‡Controlled phase 85, Kawecki Beryllco Industries, Inc., Boyertown, Pa.

§Flint No. 25, Rovin Ceramics, Detroit, Mich.

§No. 5600 (Y_2O_3 99.99%), Molycorp Inc., White Plains, N.Y.

Table I. Ternary Compounds in the System Si, Y/N, O

Structure	Chemical composition				
	Ref. 1	Ref. 2	Ref. 4	Ref. 5	Present study
Apatite		$10\text{Y}_2\text{O}_3 \cdot 9\text{SiO}_2 \cdot \text{Si}_3\text{N}_4$	$(\text{Y}_4\text{Si})(\text{Si}_3\text{O}_{11}\text{N})_3\text{N}$	$\text{Y}_{10}\text{Si}_7\text{O}_{23}\text{N}_4$	$\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$
Wollastonite			YSiO_2N	YSiO_2N	YSiO_2N
Wohlerite (YAM)		$\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$	$\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$	$\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$	$\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$
Melilite	$\text{Si}_3\text{N}_4 \cdot \text{Y}_2\text{O}_3$ $\text{Si}_3\text{N}_4 \cdot 2\text{Y}_2\text{O}_3$	$\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$	$\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$	$\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$	$\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$

based on the formula $(\text{Y}_4\text{Si})(\text{Si}_3\text{O}_{11}\text{N})\text{N}$. Lange *et al.*⁵ reported that the apatite has a formula $\text{Y}_{10}\text{Si}_7\text{O}_{23}\text{N}_4$. Wills *et al.*² reported a formula of $10\text{Y}_2\text{O}_3 \cdot 9\text{SiO}_2 \cdot \text{Si}_3\text{N}_4$. 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 $\text{A}_{10}(\text{XO}_4)_6\text{Z}_2$. The most common member of this compound is $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. Nitrogen-containing apatites have been reported⁶; their general formula is $(\text{RE})_{10}(\text{SiO}_4)_6\text{N}_2$ (where RE is rare-earth ions). Rare-earth silicate apatites have also been reported.^{7,8} These apatites contain A and Z site vacancies, with a formula of $(\text{RE})_8\Box_2(\text{SiO}_4)_6\Box_2$. 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 SiO_4 position has not been reported.

A site vacancies and substitutions have been reported⁸ for $\text{A} = \text{Ce}, \text{Nd}, \text{Sm}, \text{and Eu}$. 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 $< 1 \text{ \AA}$ was reported to be possible but probably not in high concentrations.⁸ Thus, it is questionable whether Si^{4+} can be accommodated in the A position, since Si^{4+} is $\ll 1 \text{ \AA}$.

The apatite found in this investigation has the formula $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$. The X-ray pattern of this compound was indexed on the base of a hexagonal cell, with calculated lattice parameters of $a = 9.368 \pm 0.002$ and $c = 6.355 \pm 0.002 \text{ \AA}$. The homogeneity range is less than $\pm 2 \text{ eq.}\%$. The directions for forming possible solid solutions have been explored. They are:

(1) $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2 \rightarrow \text{Y}_8\Box_2(\text{SiO}_4)_6\Box_2$ defect model with vacancies on the yttrium and nitrogen sites.

(2) $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2 \rightarrow \text{Y}_{10+2x}(\text{SiO}_{4-x}\text{N}_x)_6\text{N}_2$ with A site interstitials and nitrogen in oxygen sites.

(3) $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2 \rightarrow \text{Y}_{10}(\text{SiO}_{4-x}\text{N}_x)_6\Box_2$ with Z site vacancies and nitrogen in the oxygen sites.

(4) $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2 \rightarrow \text{Y}_{9.33}\text{Si}_{0.5}\Box_{0.16}(\text{SiO}_4)_6\text{N}_2$ with substitutions and vacancies in the A sites and nitrogen in the Z sites.

Compositions were prepared in 2 eq. % intervals along all of the proposed possible solid-solution directions; no single-phase material was found. Jack's formula,⁴ $(\text{Y}_4\text{Si})(\text{Si}_3\text{O}_{11}\text{N})\text{N}$, requires Si^{4+} ions in the yttrium sites. Compositions of this type, as well as those of the homogeneity range (Fig. 1), were prepared; no single-phase material was found.

(2) Subsidiary 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 $\text{Si}_3\text{N}_4\text{-Y}_{10}(\text{SiO}_4)_6\text{N}_2$ (apatite)- $\text{Y}_2\text{Si}_2\text{O}_7\text{-Si}_2\text{N}_2\text{O}$ and the Y_2O_3 -rich region of the diagram were reported in the literature. Lange *et al.*⁵ reported a two-phase field

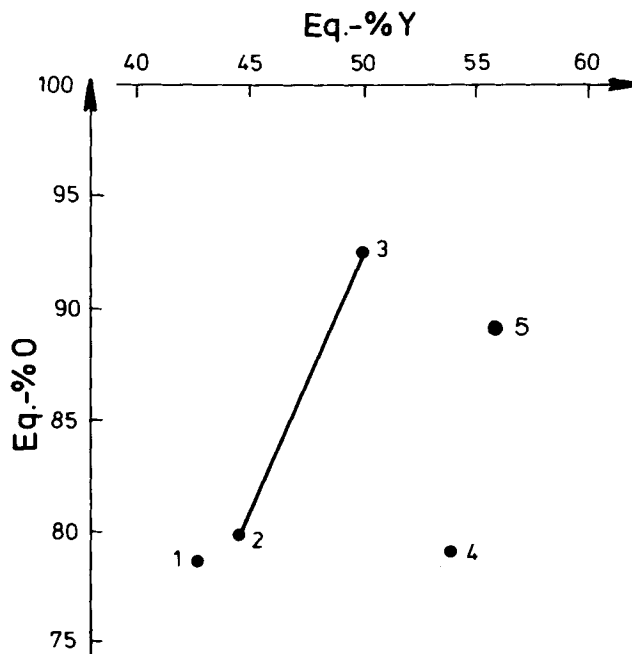


Fig. 1. Compositions of the apatite structure proposed in the literature. Point 1, Ref. 4 (text); points 2 and 3, Ref. 4 (diagram); point 4, Ref. 5; and point 5, present study.

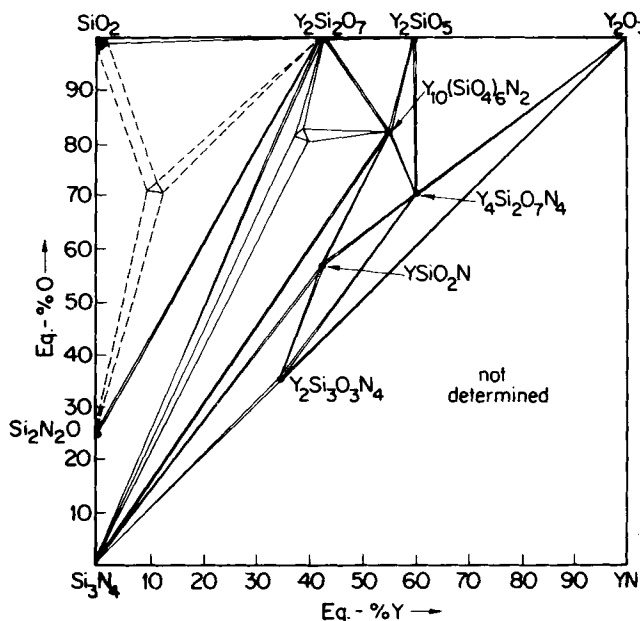


Fig. 2. Isothermal section of the system $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Y}_2\text{O}_3$ at 1500°C .

*For Table II, order ACSD-160 from Data Depository Service, The American Ceramic Society, 65 Ceramic Drive, Columbus, Ohio 43214.

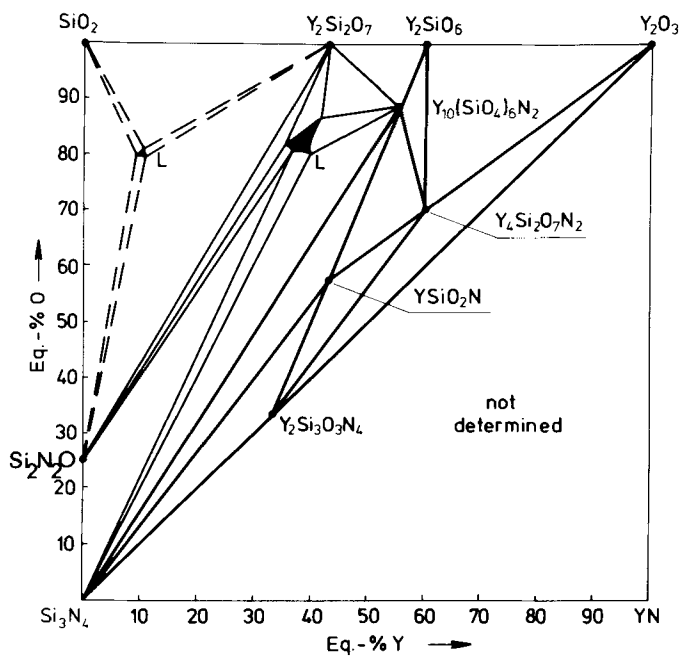


Fig. 3. Isothermal section of the system $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Y}_2\text{O}_3$ at 1550°C .

between Si_3N_4 and $\text{Y}_2\text{Si}_2\text{O}_7$, based on the analysis of at least 10 specimens, whereas Jack⁴ reported the join $\text{Si}_2\text{N}_2\text{O}$ -apatite. The results of the present study indicate a two-phase field between Si_3N_4 and $\text{Y}_2\text{Si}_2\text{O}_7$, in agreement with Lange *et al.*⁵ However, in the Y_2O_3 -rich region there was no indication of a new ternary compound with a possible composition in the $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-YN}$ triangle. However, a binary join between $\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$ and Y_2O_3 was confirmed.

(3) Liquid Formation

Liquid formation in the system was observed from the appearance of microstructures of specimens after heat treatment and by DTA experiments. Two liquid-forming regions were found at 1550°C . These liquids became glass when cooled. The glass formation in this system may be the reason for misinterpretation of phase analysis based on XRD only.

In the triangle $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7\text{-Y}_{10}(\text{SiO}_4)_6\text{N}_2$, specimens near the $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ join were completely molten at 1550°C . The lowest melting composition was near 60 eq.% Si and 85 eq.% O_2 . This liquid contains 19.8 at.% Si, 17.6 Y, 56 O, and 6.6 N. Specimens of this composition annealed at 1520°C showed liquid remaining. None was observed after heat treatment at 1480°C , indicating that the solidus temperature is between 1520° and 1480°C .

On the join $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$, a composition with 62.5 eq.% Si and 87.5 eq.% O was equilibrated at 1520°C for 30 min. The specimen was ground, cold-compacted, reannealed in a Ta crucible inside a DTA unit under He atmosphere at normal pressure, and heated at $5^\circ/\text{min}$. An endothermic peak was observed at 1550°C on heating and an exothermic peak at 1520°C on cooling. The differential thermocouples were W-W25Re. These results indicate that the eutectic temperature on the join $\text{Si}_3\text{N}_4\text{-Y}_2\text{Si}_2\text{O}_7$ is $\approx 1520 \pm 15^\circ\text{C}$; they can be used to construct a 1550°C isothermal section of this system (Fig. 3).

Liquid formation was also observed in the $\text{Si}_2\text{N}_2\text{O-Y}_2\text{Si}_2\text{O}_7\text{-SiO}_2$ triangle in specimens with compositions of 10 eq.% Y and 80 eq.%

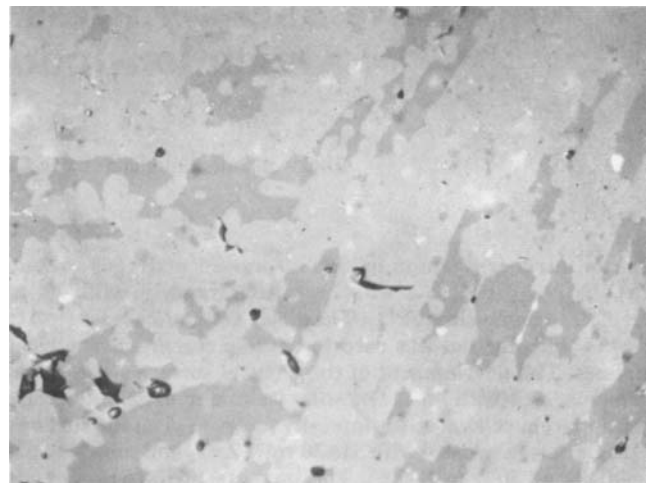


Fig. 4. Microstructure of the composition containing 50.0 eq.% Y and 92.5 eq.% O, sintered at 1550°C ($\times 770$).

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 N_2 atmosphere at normal pressure and 1550°C , due to loss of SiO_2 . 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 Jack,⁴ was prepared by annealing the powder compact at 1550°C for 15 min in N_2 . The sample was ground, recompact, 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 $\text{Y}_{10}(\text{SiO}_4)_6\text{N}_2$ apatite (very strong) and the high-temperature modification (α) of $\text{Y}_2\text{Si}_2\text{O}_7$ (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

- 1 A. Tsuge, H. Kudo, and K. Komeya, "Reaction of Si_3N_4 and Y_2O_3 in Hot-Pressing," *J. Am. Ceram. Soc.*, **57** [6] 269-70 (1974).
- 2 R. R. Wills, S. Holmquist, J. M. Wimmer, and J. A. Cunningham, "Phase Relations in the System $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-SiO}_2$," *J. Mater. Sci.*, **11** [7] 1305-1309 (1976).
- 3 K. H. Jack, "Review: Sialons and Related Nitrogen Ceramics," *ibid.*, [6] 1135-58.
- 4 K. H. Jack; pp. 109-28 in *Nitrogen Ceramics*, Edited by F. L. Riley. Noordhoff International, Reading, Mass., 1977.
- 5 F. F. Lange, S. C. Singhal, and R. C. Kuznicki, "Phase Relations and Stability Studies of the $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Y}_2\text{O}_3$ Pseudoternary System," Westinghouse Res. Rept., No. 76-9D4-POWDR-R1, 1976.
- 6 C. Hamon, R. Marchand, M. Maunaye, J. Gaude, and J. Guyader, "Compounds Having an Apatite Structure: IV," *Rev. Chim. Miner.*, **12** [3] 259-67 (1975).
- 7 J. Felsche, "A New Cerium(IV) Orthosilicate with One Apatite Structure," *Naturwissenschaften*, **56** [6] 325-26 (1969).
- 8 E. R. Kreidler and F. A. Hummel, "Crystal Chemistry of Apatite: Structure Fields of Fluor- and Chlorapatite," *Am. Mineral.*, **55** [1-2] 170-84 (1970).