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Synthesis and Crystal Structure of Cubic $Ca_{16}Si_{17}N_{34}$

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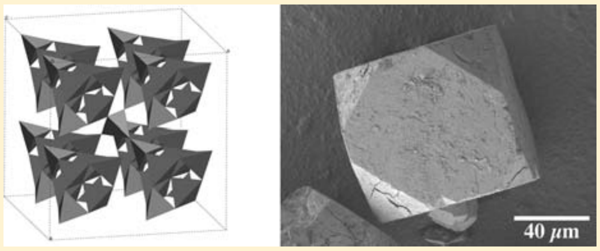
Ⓢ *Supporting Information*

ABSTRACT: Since the late 1960s, the exact structure of cubic calcium silicon nitride has been a source of debate. This paper offers evidence that the cubic phase $CaSiN_2$ described in the literature is actually $Ca_{16}Si_{17}N_{34}$. Presented here is a method for synthesizing single crystals of cubic-calcium silicon nitride from calcium nitride and elemental silicon under flowing nitrogen at 1500 °C. The colorless millimeter-sized crystals of $Ca_{16}Si_{17}N_{34}$ with a refractive index (n_{25}) = 1.590 were found to be cubic (a = 14.8882 Å) and belong to the space group $F\bar{4}3m$ (216). The synthesis of bulk, powdered cubic-$Ca_{16}Si_{17}N_{34}$ from calcium cyanamide and silicon is also discussed. $Ca_{16}Si_{17}N_{34}$ is a relatively air-stable refractory ceramic. In contrast to the orthorhombic phase of $CaSiN_2$, in which Ca^{2+} sits in octahedral sites, this cubic phase has Ca^{2+} in cubic sites that makes it an interesting host for new phosphors and gives rise to unique crystal field splitting.



INTRODUCTION

Nitrides and oxynitrides have attracted great interest due to their potential as host lattices for fluorescent species.[1−3] The structure and crystal field splitting accessible in ternary silicon nitrides offers the promise of new colors from emitting species.[4−8] Unfortunately, nitrides are notoriously difficult to crystallize. A variety of methods[9] have been attempted to obtain single crystals of nitride materials. These include flux growth,[10,11] vapor transport,[12,13] growth under pressure,[14] and melt growth.[15] However, ternary silicon nitrides do not readily lend themselves to any of these methods since they are not soluble in most of the fluxes used for crystal growth, do not crystallize by vapor transport, and decompose before melting.

Two different phases of calcium silicon nitride ($CaSiN_2$) have been reported in the literature. Early work indicated a cubic unit cell with an a parameter of 14.8642 Å.[16−18] However, this structure has been disputed and it has been suggested that the cubic phase is, in fact, an oxynitride. Work by Ottinger et al. produced an orange, orthorhombic phase ($Pbca$) with a = 5.129(3) Å, b = 10.224(1) Å, and c = 14.821(4) Å by heating Ca, $CaSi_2$, and Ca_3N_2 in a sealed niobium tube at 1400 °C.[19] The same structure was later obtained by heating Ca, NaN_3, and Si in a sealed tantalum tube at 1000 °C.[20]

Until now, single crystals of the initially reported cubic phase have not yet been synthesized. Previously, the cubic phase was synthesized by the reaction (eq 1):

$$Si_3N_4 + Ca_3N_2 \rightarrow 3CaSiN_2 \qquad (1)$$

We have been able to obtain near-millimeter sized crystals of a calcium deficient nitride ($Ca_{16}Si_{17}N_{34}$) using a reaction (eq 2) analogous to that used to prepare a germanium antiperovskite lattice with the formula Ca_3GeN.[21]

$$51Si + 16Ca_3N_2 + N_2 \rightarrow 3Ca_{16}Si_{17}N_{34} \qquad (2)$$

The structure of this compound exhibits similar characteristics to other nitridosilicates.[22]

EXPERIMENTAL SECTION

Reagents. The following reagents were used as received: Ca_3N_2 (Cerac; 99%, 200 mesh) and $CaCN_2$ (Alfa Aesar, technical grade). Silicon powder was prepared from virgin polyfine Sipolyfines (99.999% Alfa Aesar), by grinding under argon for 30 min in a SPEX mixer mill using a tungsten carbide vial and three 0.5 in. tungsten carbide balls and then sieving to −270 mesh in an argon-filled glovebox. The reagents were stored in an argon-filled glovebox.

Single Crystal Synthesis. Single crystals of $Ca_{16}Si_{17}N_{34}$ were synthesized by preparing a reaction mixture consisting of Si and Ca_3N_2 in a molar ratio of 1:1. The reagents were ground together in a synthetic sapphire mortar and pestle; the powder was transferred to a 12 mm diameter die and pressed into a pellet under a load of 10 000 lbs while in the glovebox. The pellet was placed in a hexagonal boron nitride (binderless grade AX05 Saint-Gobain Ceramic Materials) boat or powdered graphite-lined graphite boat. The boat was loaded into a 2 in. diameter alumina tube in a high temperature furnace utilizing silicon carbide heating elements. Initial syntheses were performed by removing the boat from the glovebox in a plastic bag and quickly transferring to the furnace tube in air. Later syntheses were loaded through a specially constructed glovebox antechamber directly connected to the furnace tube. Using this method, the reactant mass

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was never in contact with air. The system was sealed and a flow of high purity nitrogen (ultrahigh purity nitrogen further purified using a Cr^{2+} column) gas was maintained. The system was heated to 1500 °C at a heating rate of 100 °C/h and held at temperature for 2 h then cooled to room temperature at a rate of 100 °C/h. Upon removal from the furnace, the product was washed with distilled water and characterized.

Powder Synthesis. A slight excess of calcium cyanamide, $CaCN_2$ (5 g, 62 mmol), was mixed with silicon powder (1.578 g, 56 mmol). The reagents were ground together in an artificial sapphire mortar and pestle; the powder was transferred to a 12 mm diameter die and pressed into a pellet under a load of 10 000 lbs while under an inert atmosphere. The pellet was placed in a powdered graphite-lined graphite boat. Initial syntheses were performed by removing the boat from the glovebox in a plastic bag and quickly transferring to the furnace tube in air. Later syntheses were loaded through a specially constructed glovebox antechamber directly connected to the furnace tube. Using this method, the reactant mass was never in contact with air. The system was sealed and a flow of high purity nitrogen (ultrahigh purity nitrogen further purified using a Cr^{2+} column) gas was maintained. The system was heated to 1500 °C at a heating rate of 100 °C/h and held at temperature for two hours then cooled to room temperature at a rate of 100 °C/h. Upon removal from the furnace, the product was washed with distilled water and characterized.

Refractive Index. The refractive index of the crystalline material was determined using an optical microscope and Cargille Refractive Index Liquids.

Characterization. A cubic crystal of approximately 0.2 mm in each dimension was obtained from the synthesis using Ca_3N_2 and mounted on a glass fiber for X-ray analysis. Single crystal X-ray intensity data were measured at 293 K on a Bruker SMART 1000 CCD-based X-ray diffractometer equipped with a Mo-target X-ray tube (λ = 0.71703 Å) operated at 2.25 kW. The detector was placed at a distance of 4.986 cm from the crystal.

The structure was refined using Bruker SHELXTL software (version 5.3) package.[23] The final anisotropic, full-matrix, least-squares refinement on F2 converged at R1 = 3.97%. The final cell constants are listed in Table 2 together with other relevant crystallographic data.

The powders were characterized by X-ray diffraction (XRD) using a PANalytical X'pert Pro powder X-ray diffractometer with a copper source (Cu Kα λ = 1.5418 Å). Spectra were collected from 5 to 100 degrees 2θ using 0.03 degree intervals and a 1 s dwell time. The patterns obtained were then analyzed and interpreted using the PANalytical X'pert Highscore Plus software and the Joint Committee on Powder Diffraction Standards (JCPDS) database.

■ RESULTS

Colorless, transparent crystals of $Ca_{16}Si_{17}N_{34}$ (Figure 1) with a refractive index n_{25} of 1.590 were synthesized by the reaction of Si with Ca_3N_2 in a 1:1 ratio under flowing nitrogen in a graphite boat. The product was rinsed with water to remove any water reactive byproducts, such as Ca_2Si, and dried for 1 h at 180 °C. Upon washing, the distinct odor of acetylene was noted, indicating that some of the excess Ca_3N_2 reacted with the graphite boat. Crystals were isolated by density using a mixture of CH_2I_2 (density = 3.3254 g/mL) and $CHBr_3$ (density = 2.8859 g/mL) and/or physical separation. Figure 2 illustrates the material separated by a 170 (90 μm opening) mesh screen.

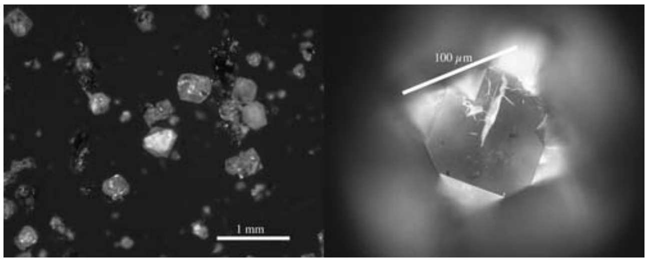

Figure 1. Optical microscope images of the transparent $Ca_{16}Si_{17}N_{34}$ crystals produced in this study. The left image is under 50× magnification, and the right is under 500×.

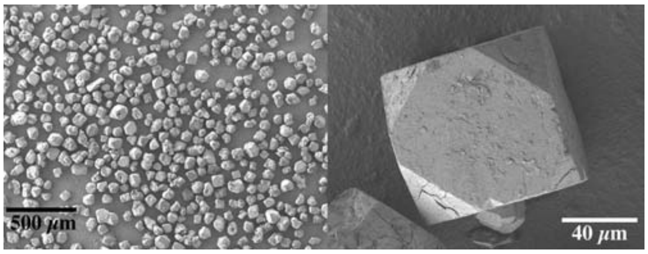

Figure 2. Scanning electron microscope images of $Ca_{16}Si_{17}N_{34}$ separated from the reaction mass using a 170-mesh screen. This nitride exhibits cubic crystals often in the form of cuboctahedra (right).

The role of the boat material, oxygen level, and calcium source were examined by using an inert boat (binderless boron nitride), adding oxygen in the form of CaO, and substituting $CaCN_2$ for Ca_3N_2 (Table 1). In most reactions, the $Ca_{16}Si_{17}N_{34}$ phase formed. The reaction 17$CaCN_2$ + 17Si + CaO produced a crystalline material that could not be matched to a known compound in the JCPDS filecard.

Table 1. $Ca_{16}Si_{17}N_{34}$ Forming Reactions[a]

reaction	boat material	phases present
Si + Ca_3N_2	boron nitride	$Ca_{16}Si_{17}N_{34}$ + *o*-$CaSiN_2$
*Si + Ca_3N_2	graphite	$Ca_{16}Si_{17}N_{34}$
$CaCN_2$ + Si	graphite	$Ca_{16}Si_{17}N_{34}$
6$CaCN_2$ + 12Si + Ca_3N_2	graphite	$Ca_{16}Si_{17}N_{34}$ + $Ca_3N_2Si_2O_4$
17$CaCN_2$ + 17Si + CaO	graphite	unknown phase
102$CaCN_2$ + 204Si + 17Ca_3N_2 + 6CaO	graphite	$Ca_{16}Si_{17}N_{34}$ and CaO
17Si + 17Ca_3N_2 + CaO	graphite	$Ca_{16}Si_{17}N_{34}$ and CaO

[a] The reaction marked with a (*) produced the most crystalline product.

The product generally consists of crystals that exhibit octahedral and cuboctahedral morphologies (Figures 1 and 2). Single crystals large enough for X-ray analysis were produced by this method. The unit cell was determined to be cubic (a = 14.8882 Å) with the space group $F\bar{4}3m$ (216). The atomic positions are summarized in Table 3. Figure 3 shows the difference in connectivity between the cubic phase and orthorhombic $CaSiN_2$.

■ DISCUSSION

The structure of the $Ca_{16}Si_{17}N_{34}$ unit cell is better understood by viewing it without the calcium atoms (Figure 3 left). The unit cell consists of eight clusters of SiN_4 tetrahedra arranged around a central SiN_4 tetrahedron. Each cluster, in turn, consists of eight SiN_4 tetrahedra. There are three distinct Ca sites (Figure 4). Ca1 and Ca3 are distorted octahedral sites, while Ca2 is an elongated cubic site. This structure has been observed previously in other calcium nitridosilicates.[22] Le

Table 2. Crystal Data and Structural Refinement Parameters for Cubic $Ca_{16}Si_{17}N_{34}$

empirical formula	$Ca_{16}Si_{17}N_{34}$
radiation	MoKα, λ = 0.71073 Å
instrument	Bruker SMART 1000
temperature	293(2) K
space group	$F\bar{4}3m$ (216)
fw	93.79
a/Å	14.8882(3)
V/Å^3	3300.10(12)
Z	48
ρ_{calc} (mg m^{-3})	3.211 g cm^{-3}
crystal size	0.20 mm × 0.20 mm × 0.18 mm
independent reflections	453 [R(int) = 0.0224]
R1	0.0397
wR2	0.1078

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (× 10^3) for Cubic $Ca_{16}Si_{17}N_{34}$[a]

	site	x	y	z	U(eq)
Ca(1)	24f	1/2	0.7920(1)	0	9(1)
Ca(2)	24g	0.5009(2)	3/4	3/4	10(1)
Ca(3)	16e	0.5799(2)	0.4201(2)	0.9201(2)	39(1)
Si(1)	4b	1/2	0	0	5(1)
Si(2)	16e	0.3657(1)	0.8657(1)	0.8657(1)	6(1)
Si(3)	16e	0.3194(2)	0.8194(2)	0.6806(2)	19(1)
Si(4)	16e	0.6372(1)	0.6372(1)	0.8628(1)	8(1)
Si(5)	16e	0.6769(1)	0.6769(1)	0.6769(1)	9(1)
N(1)	16e	0.4319(3)	0.9319(3)	0.9319(3)	6(2)
N(2)	48h	0.3861(3)	0.8861(3)	0.7532(4)	9(1)
N(3)	4c	1/4	3/4	3/4	4(4)
N(4)	4d	3/4	3/4	3/4	10(5)
N(5)	48h	0.6146(3)	0.6146(3)	0.7521(4)	9(1)
N(6)	16e	0.5733(4)	0.5733(4)	0.9267(4)	10(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

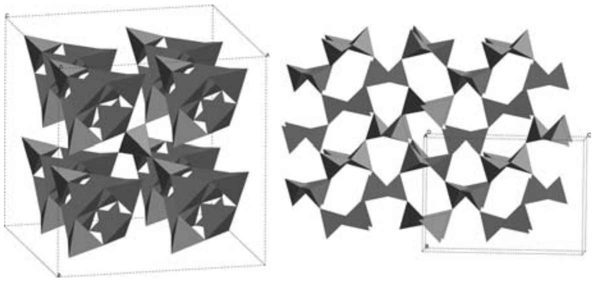

Figure 3. The unit cell for cubic $Ca_{16}Si_{17}N_{34}$ (left) consisting of clusters of SiN_4 units (gray tetrahedra) and that of orthorhombic $CaSiN_2$ (right) consisting of SiN_4 units in rings. The calcium atoms have been removed to highlight the connectivity of the SiN_4 units.

Toquin and Cheetham's cerium substituted structure[4] gave a red luminescence which would be consistent with a spectral shift associated with cerium in a cubic site.[24] The open framework of SiN_4 tetrahedra may also help to explain the unusually low thermal conductivity measured for the cubic phase (2.4 versus 17 W m^{-1} K^{-1} for $MgSiN_2$)[16] as well as the low refractive index for a nitride (n_{25} = 1.590). This structure is markedly different from orthorhombic $CaSiN_2$ (Figure 3 right) that has a structure analogous to other alkaline earth silicon nitrides like $MgSiN_2$. Previous attempts to synthesize $CaSiN_2$ have produced the orthorhombic phase. These syntheses were carried out at 1400[19] and 1000 °C.[20]

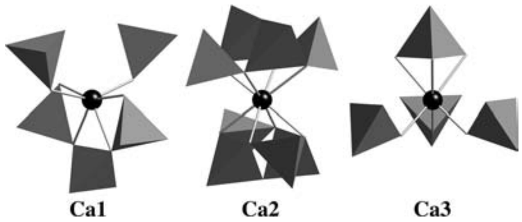

Figure 4. Ca1 and Ca3 positions 6-coordinate with the Ca1 position in a severely distorted octahedron. The Ca2 position is 8-coordinate in an elongated cubic site.

The simulated powder pattern matches the experimental data well (Figure 5) and matches the previously deleted JC-PDS pattern for $CaSiN_2$ (40-1151).

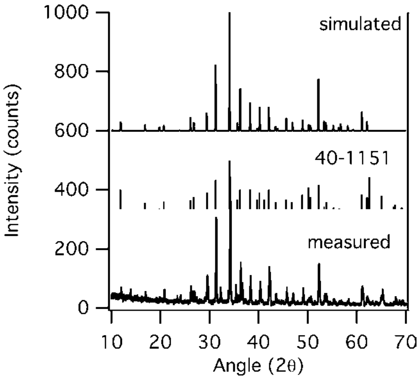

Figure 5. Powder X-ray diffraction pattern simulated from the structural data (top) matches the measured pattern (bottom) and the deleted JC-PDS file 40-1151 (middle).

This pattern was replaced by $CaSi(O,N)_2$ (45-1215) and illustrates a particular problem when dealing with ternary nitrides—determination of the oxygen content. Every effort was made in this work to ensure low levels of oxygen contamination. However, commercially obtainable Ca_3N_2 can contain oxide impurities.[21] If site occupancies of 100% are assumed, then the unit cell, which has 268 atoms, will have a charge imbalance of −8. This could be remedied by 1.9 at % nitrogen vacancies or random substitution of 8 of the 136 nitrogens with oxygen, which would represent an oxygen level in the lattice of 2 mass %. These values are difficult to determine with the current methods available, especially in the highly symmetric space group $F\bar{4}3m$. The Si−N bond lengths range from 1.653 to 1.885 Å. Oxygen substitution should result in reduced bond lengths suggesting that oxygen replacement is most likely on the N6 site. Substitution of half the N6 sites with oxygen would produce a charge-balanced lattice. This would also explain the high U(eq) for Ca3, which sits in a distorted octahedral site with vertices occupied by N3 and N6 nitrogens. The Ca1 and Ca2 sites do not directly interact with the N6 site. Alternatively, 12.5 at % 3+ ion substitution (such as in Le Toquin and Cheetham's Ce^{3+}-doped nitride)[4] for Ca would also provide unit cell neutrality.

Previous efforts to prepare $CaSiN_2$ have used oxide precursors,[18] nitride precursors,[16,25] or silicides.[19] Although Gal, et al. utilized silicon, their syntheses were performed at a much lower temperature (1000 °C). We have been able to obtain single crystals of the cubic ternary nitride, $Ca_{16}Si_{17}N_{34}$, by heating a mixture of Ca_3N_2 and Si to 1500 °C for a relatively short period of time (2 h). A ratio of 1.0 to 1.0 was found to produce the largest crystals. This may be due to the fact that some of the Ca_3N_2 evaporates from the reaction zone and that molten Ca_3N_2 acts as a flux.

The reactions summarized in Table 1 show that the nitride phase forms with or without carbon, and from calcium cyanamide as well. More crystalline products were formed from reactions utilizing Ca_3N_2, suggesting that the nitride acts as a flux. Calcium nitride melts at 1195 °C, and silicon melts at 1414 °C. At 1500 °C, calcium nitride is molten and evaporation is a major concern.[16] Performing the reaction in a nitrogen atmosphere and using an excess of Ca_3N_2 reduces the impact of Ca_3N_2 evaporation. Some of the calcium present reacted with the graphite in the boat to produce CaC_2; this was confirmed by the production of acetylene upon washing the reaction product with water. The reaction of CaC_2 with nitrogen forms calcium cyanamide, $CaCN_2$. Calcium cyanamide has a melting point of 1340 °C. A calcium nitride/calcium cyanamide mixture may be the flux in which the $CaSiN_2$ crystals actually grow. In fact, $Ca_{16}Si_{17}N_{34}$ powders can be realized by heating a mixture of $CaCN_2$ and Si in stoichiometric quantities (Figure 6).

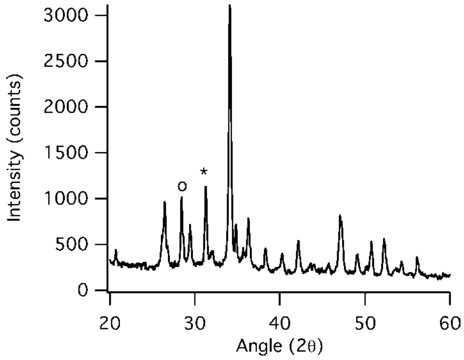

Figure 6. Powder X-ray diffractogram of the product produced from the reaction $16CaCN_2 + 17Si + N_2 \rightarrow Ca_{16}Si_{17}N_{34} + 16C$ shows that the sample contains silicon (*) and graphite (○) impurities with the remaining peaks matching the pattern expected for $Ca_{16}Si_{17}N_{34}$.

These nitrides are not indefinitely stable in air. Samples kept in air for longer than 3 months lose much of their crystallinity.

■ CONCLUSIONS

Single crystals of cubic $Ca_{16}Si_{17}N_{34}$ were readily grown from a mixture of Ca_3N_2 and Si heated in a furnace to 1500 °C. The lattice consists of an open framework of SiN_4 tetrahedra with Ca ions in the voids; the structure has some uncertainty due to potential oxygen substitutions. Powders of cubic $Ca_{16}Si_{17}N_{34}$ were synthesized from calcium cyanamide and silicon. The compound's most highly oxidized formula may actually be $Ca_{16}Si_{17}N_{32}O_2$, but current methods cannot readily determine this subtle compositional discrepancy. One of the calcium sites in this nitride is cubic. Partial substitution with other metals could produce interesting new phosphors.

■ ASSOCIATED CONTENT

Supporting Information

Crystal structure file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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