Inorganic Chemistry
Article
pubs.acs.org/IC

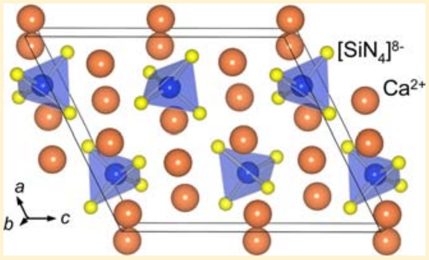
Synthesis and Crystal Structures of Ca_4SiN_4 and New Polymorph of $Ca_5Si_2N_6$

Hisanori Yamane* and Haruhiko Morito

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Aoba-ku, Sendai 980-8577, Japan

Ⓢ *Supporting Information*

ABSTRACT: Single crystals of Ca_4SiN_4 were found in the product prepared by heating Ba, Ca, Si, NaN_3, and Na at 900 °C. Ca_4SiN_4 [space group $P2_1/c$ (No. 14), $Z = 4$, $a = 9.1905(4)$ Å, $b = 5.9775(3)$ Å, $c = 11.0138(7)$ Å, $\beta = 116.4054(17)°$] is isotypic with Ca_4GeN_4 and K_4SiO_4. Isolated $[SiN_4]^{8-}$ tetrahedra were identified in the structure by single-crystal X-ray diffraction. After reheating the product at 900 °C, a new polymorph of $Ca_5Si_2N_6$ crystallized. The space group of the polymorph [$C2/m$ (No. 12), $Z = 4$, $a = 6.2712(5)$ Å, $b = 10.0175(8)$ Å, $c = 12.0287(8)$ Å, $\beta = 99.303(2)°$] is different from $C2/c$ previously reported for $Ca_5Si_2N_6$, while both polymorphs are composed of Ca^{2+} and edge-sharing double tetrahedra $[Si_2N_6]^{10-}$.



■ INTRODUCTION

Many compounds based on silicon nitrides and oxy-nitrides have been synthesized and used for structural ceramic materials and host crystals of phosphor materials.[1] The crystal structures of nitridosilicates have been classified as SiN_4 tetrahedra linkages similar to oxosilicates composed of the SiO_4 tetrahedral unit.[1−3] Nesosilicates (orthosilicates), such as K_4SiO_4 and Ca_2SiO_4,[4,5] consist of cations and noncondensed tetrahedral anion groups of $[SiO_4]^{4-}$. However, structures composed of isolated $[SiN_4]^{8-}$ tetrahedra have not been elucidated in spite of their assumed presence in Li_8SiN_4[6,7] and Ca_4SiN_4.[8,9] Structures containing isolated $[SiN_3O]^{7-}$ tetrahedra have been reported for oxynitrides, $Gd_3[SiON_3]O$[10] and $La_{16}[Si_8N_{22}][SiON_3]_2$.[11]

In the Ca−Si−N system, $CaSiN_2$, $Ca_5Si_2N_6$, and Ca_4SiN_4 were reported by Laurent and Lang.[8,9] The single crystals of $CaSiN_2$ and $Ca_5Si_2N_6$ were synthesized using a Na flux, and a Ca_2N flux, respectively, and their structures were determined by X-ray diffraction (XRD).[12,13] $CaSiN_2$ has a three-dimensional network structure composed of corner-sharing SiN_4 tetrahedra,[12] and edge-sharing double tetrahedra of $[Si_2N_6]^{10-}$ were found in $Ca_5Si_2N_6$.[13] Three dimensional network structures were clarified for $Ca_2Si_5N_8$ prepared by high-temperature heating and for its high-pressure phase.[14,15] A cluster of eight SiN_4 tetrahedra was revealed in the structure of $Ca_{16}Si_{17}N_{34}$.[16]

Recently, we synthesized new quaternary silicon nitrides, $Ba_4MgSi_2N_6$, $Ba_3Ca_2Si_2N_6$, and $Ba_{1.6}Sr_{3.4}Si_2N_6$, using a Na flux, and analyzed their structures.[17] All of these quaternary alkaline-earth silicon nitrides are composed of edge-sharing double tetrahedra $[Si_2N_6]^{10-}$. $Ba_3Ca_2Si_2N_6$ and $Ba_{1.6}Sr_{3.4}Si_2N_6$ are isostructural with $Ca_5Si_2N_6$ (space group, $C2/c$), and $Ba_4MgSi_2N_6$ crystallizes in a new orthorhombic structure (space group $Fddd$) in which Mg^{2+} ions are planar-rectangularly coordinated by two N−N edges of $[Si_2N_6]^{10-}$. In the sample from which $Ba_3Ca_2Si_2N_6$ single crystals were obtained, we found some tiny single crystals of Ca_4SiN_4. After a secondary heating and cooling step, we obtained a new polymorph of $Ca_5Si_2N_6$ (hereafter the original and new polymorphs are described as α- and β-$Ca_5Si_2N_6$, respectively). This paper reports the synthesis and crystal structures of Ca_4SiN_4 and β-$Ca_5Si_2N_6$.

■ EXPERIMENTAL SECTION

Reagents. Barium (Sigma-Aldrich, 99.99%), calcium (Alfa Aesar, 99.98%), silicon (Kojundo Chemical Laboratory, 99.999%), sodium azide (Toyo Kasei Kogyo Co. Ltd., 99.9%), and sodium (Nippon Soda Co., Ltd., 99.95%) were used as received. Reagents were handled in an Ar gas-filled glovebox (O_2 and H_2O < 1 ppm).

Single Crystal Synthesis. Pieces of Ba (1 mmol, 137 mg), Ca (0.5 mmol, 20 mg), and Na (2.4 mmol, 55 mg), and powders of Si (0.5 mmol, 14 mg) and NaN_3 (1.2 mmol, 78 mg), were weighed and placed in a crucible (inside diameter, 6.5 mm; depth, 18 mm) of polycrystalline sintered BN (99.5%, Showa Denko). The crucible was sealed in a one-end welded stainless-steel tube (inside diameter, 10.6 mm; length, 70 mm) with a stainless steel cap, prior to heating in an electric furnace. The temperature was raised to 900 °C (rate 200 °C/h), and this temperature was maintained for 2 h, before cooling to 650 °C (rate −4 °C/h). Subsequently, the sample was cooled to room temperature by shutting off the electric power to the furnace (sample A). Sample B was prepared by reheating and cooling sample A under the conditions described above. The stainless steel tube was opened in the glovebox, and the product contained in the crucible was washed with liquid NH_3 (>99.999%, Japan Fine Products) to dissolve away the Na flux. The details of the Na extraction procedure have been described previously.[18]

Characterization. Single-crystal samples were analyzed using an energy-dispersive X-ray detector (EDX, EDAX, Genesis) attached to a scanning electron microscope (SEM, Hitachi, S-4800). The crystals were fixed on a stage with carbon adhesive tape under an optical microscope in the glovebox. Due to the instability of Ca_4SiN_4 and β-$Ca_5Si_2N_6$ crystals in air, a transfer cell was used to carry the samples from the glovebox into the SEM, thereby maintaining a reduced

Received: February 28, 2013
Published: April 16, 2013

atmosphere around the stage. The molar ratios of Ca and Si were obtained by semiquantitative analysis of EDX spectra using the software installed to the detector system without standard samples. After picking up some single crystals, sample A was powdered in an agate mortar with a pestle and set in a sample cell with a window of mylar plastic film for powder XRD using Cu Kα radiation (Rigaku, RINT2500).

Single crystals for XRD were sealed in glass capillaries in the glovebox. XRD data were collected using Mo Kα radiation with a graphite monochromator and an imaging plate on a single-crystal X-ray diffractometer (Rigaku, R-AXIS RAPID-II). Diffraction-data collection and unit-cell refinement were performed by the PROCESS-AUTO program.[19] Numerical absorption correction was performed by the NUMABS program.[20] The crystal structure of β-$Ca_5Si_2N_6$ was solved by the direct method using the SIR2004 program.[21] The structure parameters were refined by the full-matrix least-squares method on F^2 using the SHELXL-97 program.[22] All calculations were carried out on a personal computer using the WinGX software package.[23] Crystal structures were illustrated with the VESTA program.[24] Bond valence sums (BVS),[25] Madelung potentials (MP), and Madelung energies per formula unit (ME)[26] were calculated with the software program EUTAX.[27]

■ RESULTS AND DISCUSSION

Synthesis of Single Crystals. In sample A, formation of BaSi, $BaSiN_2$, and $Ba_3Ca_2Si_2N_6$ were confirmed by powder and single-crystal XRD. Reddish-brown granular single crystals, approximately 50 μm in size, were found in the sample in small quantities. The elements detected by the EDX analyzer were C, N, O, Ca, and Si. C and O contaminants were probably introduced from the carbon tape utilized to fix the samples and from the atmosphere in the transfer cell. The Ca:Si molar ratio measured by EDX analysis was 77:23, close to the ideal ratio (80:20) derived from the chemical formula of Ca_4SiN_4.

Sample B prepared by reheating and cooling at the same condition of preparation for sample A was more homogeneous. The size of $Ba_3Ca_2Si_2N_6$ platelet single crystals increased from about 200 μm in sample A to 400 μm in sample B. Colorless or pale-brownish prismatic single crystals smaller than 100 μm in size were observed in sample B. Ba, Na and other metal elements were not detected from the crystals by EDX, with exception of Ca and Si. A Ca:Si molar ratio of around 67:33 was measured for the crystals, which was close to the ratio of 71:29 from the chemical formula $Ca_5Si_2N_6$.

Ca_4SiN_4 included in sample A could not be found in sample B. Polycrystalline samples of CaSi and Ca_3N_2 were formed, and neither Ca_4SiN_4 nor $Ca_5Si_2N_6$ were obtained by heating of Ca, Si, NaN_3, and Na according to the heating−cooling condition utilized for the preparation of sample A. Formation and single-crystal growth of Ca_4SiN_4 or $Ca_5Si_2N_6$ were possible using a starting mixture containing Ba, accompanying the growth of $Ba_3Ca_2Si_2N_6$ crystals. Two cycles of heating and cooling accomplished growth of larger platelet crystals of $Ba_3Ca_2Si_2N_6$, which subsequently yielded $Ca_5Si_2N_6$ as the crystalline product of a more homogeneous melt.

Crystal Structure of Ca_4SiN_4. The data collection and refinement results for the single crystal of Ca_4SiN_4 are listed in Table 1. The XRD reflections were indexed with monoclinic cell parameters [a = 9.1905(4) Å, b = 5.9775(3) Å, c = 11.0138(7) Å, β = 116.4054(17)°]. The space group was determined by systematic absences to be $P2_1/c$. Due to similarities of cell parameters and the same space group, the crystal structure of Ca_4SiN_4 was analyzed using the structure model of Ca_4GeN_4 [$P2_1/c$, a = 9.2823(8) Å, b = 6.0429(5) Å, c = 11.1612(9) Å, β = 116.498(6)°].[28]

Table 1. Crystal Data and Refinement Results for Ca_4SiN_4 and β-$Ca_5Si_2N_6$

chemical formula	Ca_4SiN_4	β-$Ca_5Si_2N_6$
fw, g mol^{-1}	244.45	340.64
T, K	293(2)	293(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$C2/m$ (No. 12)
cell dimensions, a, Å	9.1905(4)	6.2712(5)
b, Å	5.9775(3)	10.0175(8)
c, Å	11.0138(7)	12.0287(8)
β, deg	116.4054(17)	99.303(2)
cell volume, V, $Å^3$	541.93(5)	745.72(10)
Z	4	4
D_{calcd}, Mg m^{-3}	2.996	3.034
radiation, Å	0.710 75	0.710 75
crystal form	granule	prism
color	reddish brown	colorless
μ, mm^{-1}	4.095	3.855
crystal size, mm^3	0.06 × 0.04 × 0.04	0.09 × 0.07 × 0.03
F_{000}	488	680
θ range, deg	3.75−27.48	3.87−27.47
reflns collected	5029	3630
R_{int}	0.0713	0.0504
data/restraints/params	1225/0/82	895/0/68
weight parameters, A, B[c]	0.021, 0.7352	0.0457, 14.009
GOF on F^2, S[d]	1.121	1.055
R1, wR2 ($I > 2\sigma(I)$)[a,b]	0.0361, 0.0663	0.0456, 0.1093
R1, wR2 (all data)[a,b]	0.0642, 0.0821	0.0553, 0.1170
largest diff peak, hole, $\Delta\rho$, e $Å^{-3}$	0.877, −0.802	1.503, −0.808

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/[\sum w(F_o{}^2)^2]\}^{1/2}$. [c] $w = [\sigma^2(F_0)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$. [d] $S = \{\sum w[(F_o)^2 - (F_c)^2]^2/[(n - p)^2]\}^{1/2}$.

The crystal structure refinement of Ca_4SiN_4 was performed with R1 of 3.61% and wR2 of 8.21% for all data. The atomic coordinates and equivalent isotropic displacement parameters, and ranges of Ca−N and Si−N bond lengths and bond angles of N−Si−N are listed in Tables 2 and 3, respectively. The anisotropic displacement parameters are listed in Supporting Information Table S1.

Figure 1a shows the arrangement of N atoms around Ca and Si atoms. Si atom is coordinated by four N atoms at the independent N1, N2, N3, and N4 sites. The Si−N bond distances range from 1.767(4) to 1.833(4) Å, and are consistent with those reported for other silicon nitrides.[1] N−Si−N bond angles of 102.88(19)−117.08(18)° are deviated from the ideal angle of tetrahedral coordination (109.47°).

As shown in Figure 1b, isolated $[SiN_4]^{8-}$ tetrahedra are surrounded by Ca atoms in the crystal structure. There are four Ca sites which are coordinated by six N atoms for Ca1 site with Ca−N interatomic distances of 2.399(4)−3.078(4) Å, and five N atoms coordinate to Ca atoms in Ca2, Ca3, and Ca4 sites with the Ca−N distances 2.361(4)−2.749(4) Å.

The BVS, shown in Table 4, were calculated with the EUTAX program using interatomic distances of Ca_4SiN_4. BVS values for Ca_4GeN_4 and K_4SiO_4, which crystallize in the same space group $P2_1/c$, are also listed for comparison. The BVS of Si (3.79) in Ca_4SiN_4 is smaller than the valence expected for Si^{IV}. Comparatively, BVS values smaller than four were also obtained for Ca_4GeN_4 and K_4SiO_4. BVS values calculated for Ca sites were scattered between 1.74 and 2.20, deviating from

Table 2. Atomic Coordinates and Isotropic Equivalent Displacement Parameters for Ca_4SiN_4 and β-$Ca_5Si_2N_6$

atom	x	y	z	$U_{eq}{}^{a}$ (Å^2)
Ca_4SiN_4				
Ca1	0.648 24(11)	0.421 94(15)	0.154 78(10)	0.0137(2)
Ca2	0.546 38(11)	0.418 55(15)	0.379 66(10)	0.0112(2)
Ca3	0.145 26(11)	0.350 69(15)	0.269 26(10)	0.0127(2)
Ca4	0.080 46(11)	0.756 17(15)	0.042 96(11)	0.0119(2)
Si1	0.266 73(14)	0.3526(2)	0.047 75(14)	0.0094(3)
N1	0.4043(4)	0.2465(6)	0.4880(4)	0.0120(8)
N2	0.3382(4)	0.5675(6)	0.1745(4)	0.0131(9)
N3	0.2002(4)	0.1204(6)	0.1098(4)	0.0122(9)
N4	0.1012(4)	0.0311(6)	0.3946(4)	0.0128(9)
β-$Ca_5Si_2N_6$				
Ca1	0.054 38(18)	0.324 79(10)	0.260 70(9)	0.0168(3)
Ca2	0.0887(2)	0	0.206 94(13)	0.0156(4)
Ca3	0	0.185 78(13)	1/2	0.0091(3)
Ca4	0	0.241 39(15)	0	0.0153(4)
Si1	0.3512(3)	0	0.424 22(17)	0.0129(4)
Si2	0.6756(3)	0	0.068 23(17)	0.0128(4)
N1	0.2437(7)	0.1459(4)	0.3609(4)	0.0160(9)
N2	0.3015(7)	0.3559(4)	0.1262(4)	0.0153(9)
N3	0.3922(11)	0	0.0847(5)	0.0162(13)
N4	0.3550(11)	0	0.5736(6)	0.0187(14)

[a] The equivalent isotropic atomic displacement parameter U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Ranges of Ca–N and Si–N Bond Lengths (Å^2) and Angles (deg) of N–Si–N in Ca_4SiN_4 and β-$Ca_5Si_2N_6$, and Si–Si Distances of $[Si_2N_6]$ in β-$Ca_5Si_2N_6$

Ca_4SiN_4		β-$Ca_5Si_2N_6$	
Ca1–N	2.399(4)–3.078(4)	Ca1–N	2.368(5)–2.811(5)
Ca2–N	2.361(4)–2.579(4)	Ca2–N	2.389(5)–2.586(7)
Ca3–N	2.432(4)–2.749(4)	Ca3–N	2.474(5)–2.927(5)
Ca4–N	2.402(4)–2.484(4)	Ca4–N	2.327(4)–2.904(3)
Si1–N	1.767(4)–1.833(4)	Si1–N	1.734(5)–1.838(7)
		Si1–Si1	2.389(4)
		Si2–N	1.736(5)–1.820(7)
		Si2–Si2	2.525(4)
N–Si1–N	102.88(19)–117.08(18)	N–Si1–N	97.7(3)–114.9(3)
		N–Si2–N	92.2(3)–114.99(18)

the expected valence of 2. The BVS values of N similarly deviated from a valence of 3, lying between 2.68 and 3.33. Similar disagreements were reported not only for Ca_4SiN_4 and other ternary and quaternary nitrides containing Ca.[29]

MP values calculated with EUTAX are similarly listed in Table 4. The MP values of Ca^{2+} and N^{3-} sites in Ca_4SiN_4 and Ca_4GeN_4 are almost constant around ∼−21 V and ∼+32 V, respectively. The MP values for Si^{4+} in Ca_4SiN_4 (−50.4 V) and K_4SiO_4 (−48.9 V) are also close to each other.

The *d*-spacings and relative intensities of powder XRD reflections of Ca_4SiN_4, reported by Laurent and Lang,[8,9] did not agree with those calculated from the crystallographic data for Ca_4SiN_4 presented in the current study (Tables 1 and 2). Laurent suggested a reversible phase transition between 360 and 420 °C, corresponding to an observed color change and the temperature dependence of dielectric properties. The density of Ca_4SiN_4 measured by Laurent was 3.18 Mg m^{-3},[9] which was higher than the density of 2.996 Mg m^{-3} obtained from the single-crystal XRD structure analysis. Thus, Ca_4SiN_4 crystallized in the present study might be a high-temperature or metastable phase.

Crystal Structure of β-$Ca_5[Si_2N_6]$. The monoclinic lattice parameters of β-$Ca_5Si_2N_6$ [a = 6.2712(5) Å, b = 10.0175(8) Å, c = 12.0287(8) Å, β = 99.303(2)°] differ from that of α-$Ca_5Si_2N_6$ [a = 9.836(2) Å, b = 6.052(1) Å, c = 12.757(3) Å, β = 100.20(3)°] with the space group $C2/c$.[13] $Ca_5Ge_2N_6$ reported in the Ca–Ge–N system crystallizes in an orthorhombic cell (*Pbca*).[28] The structure model of β-$Ca_5Si_2N_6$ was obtained by the direct method with the space group $C2/m$ that has the highest-symmetry among the possible space groups indicated by systematic extinction of the single-crystal XRD reflections. The final R1 and S parameters were 4.56% and 1.055, respectively, for the data of $I > 2\sigma(I)$ (Table 1).

There are four Ca sites and two Si sites in the structure of β-$Ca_5Si_2N_6$ (Table 2). Figure 2 shows the N atom coordination to Si and Ca atoms. Nitrogen tetrahedra containing Si1 and Si2 sites share N4–N4 and N3–N3 edges to form the double tetrahedra of $[(Si1)_2N_6]^{10-}$ and $[(Si2)_2N_6]^{10-}$, respectively. The Si–N distances of 1.736(5)–1.820(7) Å observed in β-$Ca_5Si_2N_6$ are similar to those in Ca_4SiN_4, and Si–Si distances of 2.389(4) and 2.525(4) Å are similarly consistent with the distances (2.379(2)–2.556(7) Å) observed in the ternary and

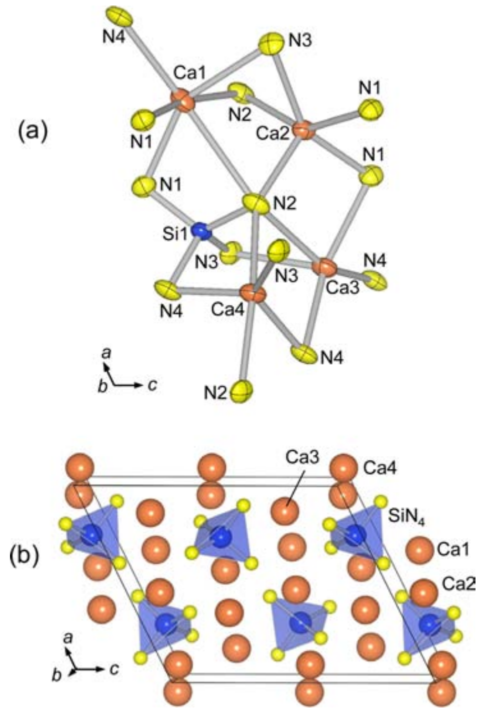


Figure 1. (a) Atomic arrangement around Ca and Si atoms in the structure of Ca_4SiN_4. Displacement ellipsoids are displayed at the 90% probability level. (b) The crystal structure of Ca_4SiN_4 represented with $[SiN_4]$ tetrahedra.

Table 4. Bond Valence Sums (BVS)[a] and Madelung Potentials (MP) in Ca_4SiN_4, Ca_4GeN_4,[28] and K_4SiO_4[4]

	Ca_4SiN_4		Ca_4GeN_4		K_4SiO_4	
atom	BVS	MP (V)	BVS	MP (V)	BVS	MP (V)
Si1/Ge1	3.79	−50.4	3.70	−45.8	3.87	−48.9
Ca1/K1	1.74	−19.9	1.73	−20.0	0.83	−9.4
Ca2/K2	2.20	−21.8	2.14	−20.7	1.10	−10.1
Ca3/K3	2.20	−20.6	2.17	−21.8	1.04	−10.5
Ca4/K4	1.75	−19.7	1.75	−20.2	0.94	−9.1
N1/O1	3.33	33.3	3.22	32.5	2.01	23.9
N2/O2	2.68	32.3	2.69	31.7	1.86	24.1
N3/O3	2.89	32.9	2.88	32.2	1.96	24.1
N4/O4	2.78	32.6	2.71	31.9	1.96	24.2

[a] BVS was calculated for the bond valence, $v > 0.03$.

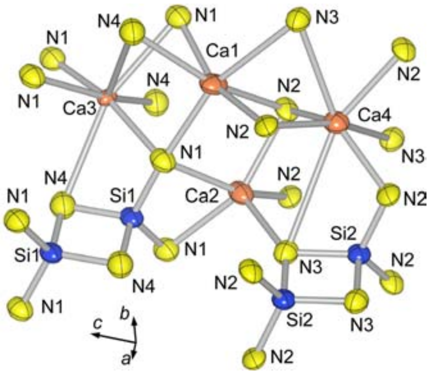


Figure 2. Atomic arrangement around Ca and Si atoms in the structure of β-$Ca_5Si_2N_6$. Displacement ellipsoids are drawn at the 90% probability level.

quaternary silicon nitrides containing isolated $[Si_2N_6]^{10-}$ double tetrahedra.[17]

As shown in Figure 3, $[Si_2N_6]^{10-}$ double tetrahedra align on the a−b plane for both α- and β-phases, forming a Ca_2−$[Si_2N_6]$ layer. In the α-phase structure, the Ca_2−$[(Si1)_2N_6]$ layer and Ca_3 layer stack along the c axis with a c-glide relation, alternating the direction of the $[(Si1)_2N_6]$ double tetrahedra. On the other hand, the Ca_2−$[(Si1)_2N_6]$ and Ca_2−$[(Si2)_2N_6]$ layers stack alternately on the Ca_3 layer in the β-phase.

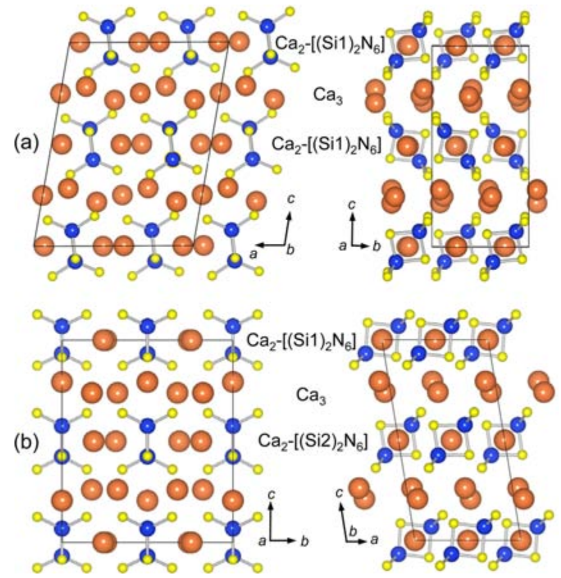


Figure 3. Crystal structures of (a) α-$Ca_5Si_2N_6$ ($C2/c$)[13] and (b) β-$Ca_5Si_2N_6$ ($C2/m$) in a representation using $[SiN_4]$ tetrahedra.

The BVS values calculated for the atoms of β-$Ca_5Si_2N_6$ are shown with those of α-$Ca_5Si_2N_6$ in Table 5. In the structures of these phases, the BVS of Si lie close to the Si^{IV} valence at 3.94−4.03, and those of Ca atoms are scattered in the 1.54−2.29 range. The MP values of Ca and Si atom sites are around −21 and −48 V, respectively, and are comparable with the values obtained for Ca_4SiN_4. The MP values of N at the sharing edge

Table 5. Bond Valence Sums (BVS)[a], Madelung Potentials (MP), and Madelung Energies per Formula Unit (ME) in α-$Ca_5Si_2N_6$[13] and β-$Ca_5Si_2N_6$

		α-$Ca_5Si_2N_6$		β-$Ca_5Si_2N_6$
space group		$C2/c$ (No.15)		$C2/m$ (No.12)
V, Å^3		747.4(3)		745.72(10)
D_{calcd}, Mg m^{-3}		3.027		3.034
ME, kJ mol^{-1}		−58 800		−58 700
atom	BVS	MP (V)	BVS	MP (V)
Si1	4.03 × 2	−48.6 × 2	3.98	−48.6
Si2			3.94	−47.8
Ca1	1.96	−21.5	2.01 × 2	−21.6 × 2
Ca2	1.65 × 2	−19.5 × 2	2.22	−21.0
Ca3	2.29 × 2	−21.4 × 2	1.54	−19.5
Ca4			2.21	−19.6
N1	2.96 × 2	33.5 × 2	3.12 × 2	33.5 × 2
N2	2.74 × 2	36.6 × 2	3.23 × 2	34.2 × 2
N3	3.25 × 2	33.9 × 2	2.63	37.0
N4			2.58	35.9

[a] BVS was calculated for the bond valence, $v > 0.03$.

of [Si_2N_6] double tetrahedra, N2 in α-$Ca_5Si_2N_6$, and N3 and N4 in β-$Ca_5Si_2N_6$ are 36−37 V and higher than those of other N sites of 34 V.

The *d*-spacings and relative intensities of $Ca_5Si_2N_6$ reported by Laurent and Lang[8,9] were compared with the data calculated from the crystal structure information for α-$Ca_5Si_2N_6$[13] and β-$Ca_5Si_2N_6$ (see Supporting Information Table S2). The reported XRD data could be explained with the data of α-$Ca_5Si_2N_6$ and β-$Ca_5Si_2N_6$, suggesting that the sample was a mixture of these two phases. The density of 3.01 Mg m^{-3} measured for $Ca_5Si_2N_6$ in the previous study is almost identical to the calculated values acquired from the single-crystal structure analyses (α-$Ca_5Si_2N_6$ 3.027 Mg m^{-3},[13] β-$Ca_5Si_2N_6$ 3.034 Mg m^{-3}).

Similar Madelung energies per formula unit (ME) were calculated for α-$Ca_5Si_2N_6$ (−58 800 kJ mol^{-1}) and β-$Ca_5Si_2N_6$ (−58 700 kJ mol^{-1}). The α-phase could not be prepared in the present study. α-$Ca_5Si_2N_6$ may be a high-temperature phase because $Ba_3Ca_2Si_2N_6$, formed as a major phase in samples A and B, has the same structure type of α-$Ca_5Si_2N_6$, wherein three Ca atoms in $Ca_5Si_2N_6$ are replaced with larger Ba atoms.

CONCLUSIONS

Single crystals of Ca_4SiN_4 composed of Ca^{2+} and isolated tetrahedral nitridosilicate anions of $[SiN_4]^{8-}$ were obtained from the sample prepared by heating Ba, Ca, Si, NaN_3, and Na. Ca_4SiN_4 is isotypic with Ca_4GeN_4 and K_4SiO_4 (space group, $P2_1/c$). A new polymorph of $Ca_5Si_2N_6$ was obtained by twice heating and cooling the sample. The polymorph contains $Ca_2[Si_2N_6]$ layers stacked on the *ab* plane of *C*-centered monoclinic cells (space group, $C2/m$).

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format, tables of anisotropic displacement parameters of Ca_4GeN_4 and β-$Ca_5Si_2N_6$, and observed and calculated powder XRD data of $Ca_5Si_2N_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yamane@tagen.tohoku.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Takashi Kamaya for assistance with the EDX analysis. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports and Technology (MEXT), Japan.

REFERENCES

(1) Zeuner, M.; Pagano, S.; Schnick, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 7754−7775.

(2) Liebau, F. *Structural Chemistry of Silicates*; Springer: Berlin, 1985.

(3) Liebau, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1733−1737.

(4) Bernet, K.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1990**, *589*, 129−138.

(5) Jost, K. H.; Ziemer, B.; Seydel, R. *Acta Crystallogr.* **1977**, *B33*, 1696−1700.

(6) Lang, J.; Charlot, J.-P. *Rev. Chem. Miner.* **1970**, *7*, 121−131.

(7) Yamane, H.; Kikkawa, S.; Koizumi, M. *Solid State Ionics* **1987**, *25*, 183−191.

(8) Laurent, Y.; Lang, J. *C. R. Acad. Sci. Paris* **1966**, *262* (C), 103−106.

(9) Laurent, Y. *Rev. Chem. Miner.* **1968**, *5*, 1019−1050.

(10) Höppe, H. A.; Kotzyba, G.; Pöttgen, R.; Schnick, W. *J. Solid State Chem.* **2002**, *167*, 393−401.

(11) Schmolke, C.; Lupart, S.; Schnick, W. *Solid State Sci.* **2009**, *11*, 305−309.

(12) Gal, Z. A.; Mallison, P. M.; Orchard, H. J.; Clarke, S. J. *Inorg. Chem.* **2004**, *43*, 3998−4006.

(13) Ottinger, F.; Nesper, R. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1597−1602.

(14) Schlieper, T.; Schnick, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1037−1041.

(15) Römer, S. R.; Braun, C.; Oeckler, O.; Schmidt, P. J.; Kroll, P.; Schnick, W. *Chem.—Eur. J.* **2008**, *14*, 7892−7902.

(16) Hick, S. M.; Miller, M. I.; Kaner, R. B.; Blair, R. G. *Inorg. Chem.* **2012**, *51*, 12626−12629.

(17) Yamane, H.; Morito, H. *J. Alloys Compd.* **2013**, *555*, 320−324.

(18) Kowach, G. R.; Lin, H. Y.; DiSalvo, F. J. *J. Solid State Chem.* **1998**, *141*, 1−9.

(19) *PROCESS-AUTO*; Rigaku/MSC & Rigaku Corporation: The Woodlands, TX, and Akishima, Tokyo, 2005.

(20) Higashi, T. *NUMABS-Numerical Absorption Correction*; Rigaku Corporation: Tokyo, 1999.

(21) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Caro, L. D.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2005**, *38*, 381−388.

(22) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.

(23) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

(24) Momma, K.; Izumi, F. *J. Appl. Crystallogr.* **2008**, *41*, 653−658.

(25) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192−197.

(26) Ewald, P. P. *Ann. Phys.* **1921**, *64*, 253−287.

(27) O'Keeffe, M. *EUTAX, version 1.2*; Arizona State University: Tempe, AZ, 1992.

(28) Clarke, S. J.; DiSalvo, F. J. *Inorg. Chem.* **2000**, *39*, 2631−2364.

(29) Hunting, J. L.; Szymanski, M. M.; Johnson, P. E.; Kellar, C. B.; DiSalvo, F. J. *J. Solid State Chem.* **2007**, *180*, 31−40.