Edge-sharing SiN_4 Tetrahedra in the Highly Condensed Nitridosilicate $BaSi_7N_{10}$

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Abstract: The novel nitridosilicate $BaSi_7N_{10}$ was obtained by the reaction of barium metal with $Si(NH)_2$ in a special high-frequency furnace at 1650 °C. The single-crystal structure determination ($a = 687.29(3)$, $b = 671.29(3)$, $c = 963.28(4)$ pm, $\beta = 106.269(3)°$, Pc, $Z = 2$, $R1 = 0.0497$, $wR2 = 0.0924$) reveals a network structure of connected SiN_4 tetrahedra. $BaSi_7N_{10}$ is the first nitridosilicate with both corner and edge-sharing SiN_4 tetrahedra. Unlike the situation in normal oxosilicates, vertex-sharing of SiN_4 tetrahedra is not exclusively favored over edge-sharing. With a Si:N molar ratio of 7:10, $BaSi_7N_{10}$ is the most highly condensed multinary nitridosilicate known and has almost the same degree of condensation as binary Si_3N_4.

Keywords
high-temperature synthesis · network structures · nitridosilicates · silicon · structure elucidation

Introduction

Recent investigations[1] have demonstrated that nitridosilicates contribute to the spectrum of structural types seen in the well-known oxosilicates.[2] "Normal" silicates contain SiO_4 tetrahedra, which are linked through common vertices. Oxygen is bound either terminally ($O^{[1]}$) or as a bridging atom ($O^{[2]}$) to one or two neighboring Si atoms, respectively.[3] Nearly all of the numerous oxosilicates known are based on variations of these structural motifs. In contrast, the nitridosilicates contain SiN_4 tetrahedra, which can be linked through common vertices to give $N^{[2]}$, $N^{[3]}$, or even $N^{[4]}$ connectivities to two, three, or four silicon atoms, respectively.[1, 4] Accordingly, a larger variety of structural features are possible for nitridosilicates than for oxosilicates.

Vertex-sharing of SiO_4 tetrahedra is exclusively favored over edge-sharing. In fact, the latter has only been postulated for the so-called fibrous polymorph of *silica* SiO_2.[5] However, the structure and existence of this polymorph have not yet been unambiguously confirmed.

Recently, DiSalvo described a novel barium nitridosilicate $Ba_5Si_2N_6$, which contains discrete $[Si_2N_6]^{10-}$ anions formed by two edge-sharing SiN_4 tetrahedra.[6] In addition, we have obtained $Ba_2Si_5N_8$ in the quasi-binary $Ba_3N_2-Si_3N_4$ system,[4c] whose network structure is built up of corner-sharing SiN_4 tetrahedra corresponding to the formula $^3_\infty[(Si_5^{[4]}N_4^{[2]}N_4^{[3]})^{4-}]$.

In this contribution we report on a novel barium nitridosilicate $BaSi_7N_{10}$, which is the first highly condensed network nitridosilicate with edge-sharing SiN_4 tetrahedra. It demonstrates for the first time that, in combination with a given metal, nitridosilicates exhibit a much more varied degree of condensation ($Ba_5Si_2N_6$, $Ba_2Si_5N_8$, $BaSi_7N_{10}$) than is possible for oxosilicates. Within the group of the hitherto known nitridosilicates, $BaSi_7N_{10}$ is the most highly condensed example. The Si:N molar ratio of 7:10 nearly reaches the value for binary Si_3N_4.

Experimental Procedure

Silicon diimide: In a three-necked bottle, CH_2Cl_2 (50 mL, p.a. Merck) was saturated with dried NH_3 (99.9%, BASF, dried by condensation on sodium and potassium) at −78 °C under a purified argon atmosphere. A precooled solution of $SiCl_4$ (20 mL, 0.17 mol; Merck) in CH_2Cl_2 (30 mL) was slowly added with stirring. The suspension was then warmed to room temperature under an NH_3 atmosphere [Eq. (1)]. The finely powdered residue was heated to 300 °C and finally to 600 °C [7].

$$SiCl_4 + 6\,NH_3 \xrightarrow{CH_2Cl_2} Si(NH)_2 + 4\,NH_4Cl \qquad (1)$$

$BaSi_7N_{10}$: A mixture of Ba (68.7 mg, 0.5 mmol, ABCR, >99.99%) and silicon diimide (116.2 mg, 2 mmol) was mixed thoroughly under argon in a glove box and transferred to a tungsten crucible positioned in a water-cooled quartz-reactor [4b–d]. The crucible was heated under a pure nitrogen atmosphere by inductive coupling through a water-cooled induction coil, which was connected to a high-frequency generator (Fa. Hüttinger, Freiburg, Type IG 10/200 Hy, frequency: 200 kHz, electrical output: 0–12 kW). The experimental setup of the high-frequency furnace is shown in Figure 1. The nitrogen had previously been purified over silica gel, potassium hydroxide, molecular sieve, P_4O_{10}, and a BTS catalyst. The reaction mixture was heated to 650 °C within 1 h and to 1650 °C within another 24 h, maintained at that temperature for 2 h, and then slowly cooled to 1400 °C within 65 h. Finally, the product was quenched to room temperature [Eq. (2)]. This process led to the formation of $BaSi_7N_{10}$ as a single-phase, coarsly crystalline, colorless

$$Ba + 7\,Si(NH)_2 \xrightarrow[\text{HF furnace}]{1650 \rightarrow 1400\,°C,\ 65\,h} BaSi_7N_{10} + 2\,N_2 + 7\,H_2 \qquad (2)$$

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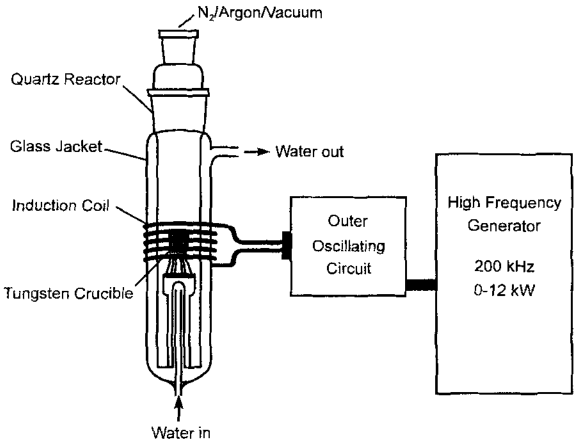

Figure 1. Experimental set-up of the high-frequency furnace.

solid. During the reaction, excess barium evaporated out of the tungsten crucible and condensed on the inner wall of the water-cooled quartz-reactor. Energy dispersive X-ray microanalysis (JEOL, JSM-6400) showed that the Ba:Si atomic ratio in the transparent, colorless crystals is 1:6.9–7.0. This is close to the ideal ratio of 1:7 in $BaSi_7N_{10}$. The absence of hydrogen (NH) was checked by IR spectroscopy. Similar to all nitridosilicates we have synthesized so far, $BaSi_7N_{10}$ is stable up to 1600 °C and resistant to hot acid and alkaline solutions.

Crystal-Structure Analysis: X-ray diffraction data were collected on a four-circle diffractometer (Siemens P4). Relevant crystallographic data and details of the data collection are listed in Table 1. According to the observed systematic absences ($h0l$ with $l = 2n$ and $00l$ with $l = 2n$), the space groups $P2/c$ (no.13) and Pc (no.7) were considered. The crystal structure of $BaSi_7N_{10}$ was solved by direct methods using SHELXTL-Plus [8] in the noncentrosymmetric space group Pc (no. 7) and refined with anisotropic displacement parameters for all atoms. Table 2 shows the positional and displacement parameters. Table 3 gives selected interatomic distances and angles [9]. Powder diffraction investigations (Siemens D5000) revealed a single-phase product. All reflections have been indexed (Table 1) and their observed intensities correspond to a calculated diffraction pattern based on the single-crystal structural data.

Table 1. Crystallographic data for $BaSi_7N_{10}$.

formula	$BaSi_7N_{10}$
formula weight [$g mol^{-1}$]	474.07
crystal system	monoclinic
space group	Pc (no. 7)
powder diffractometer	Siemens D 5000
radiation	$Cu_{K\alpha 1}$ ($\lambda = 154.06$ pm, germanium monochromator)
unit cell dimensions	$a = 686.82(6)$ pm
	$b = 671.00(6)$ pm
	$c = 962.73(7)$ pm
	$\beta = 106.249(6)°$
four-circle diffractometer	Siemens P4
radiation	Mo-K_α ($\lambda = 71.073$ pm, graphite monochromator)
unit cell dimensions	$a = 687.29(3)$ pm
	$b = 671.29(3)$ pm
	$c = 963.28(4)$ pm
	$\beta = 106.269(3)°$
cell volume [10^6 pm^3]	426.63(3)
Z	2
X-ray density [$g cm^{-3}$]	3.690
$F(000)$	448
absorption coefficient [mm^{-1}]	5.633
temperature [K]	292(2)
crystal size [mm^3]	0.12 × 0.12 × 0.12
range	$2 \leq 2\theta \leq 90°$
h, k, l	$-13 \leq h \leq 13$
	$-13 \leq k \leq 13$
	$-19 \leq l \leq 18$
scan type	ω
total no. reflections	14083
independent reflections	7050 ($R_{int} = 0.0412$)
observed reflections	7050 ($F_o^2 \geq 0\sigma(F_o^2)$)
refined parameters	164
corrections	Lorentz, polarization, absorption, extinction
absorption correction	empirical (ψ scans)
min./max. transmission ratio	0.2763/0.3760
flack parameter x	0.168(11)
min./max. residual electron density [$e Å^{-3}$]	$-1.650/3.528$
extinction coefficient	0.0303(13)
GOF	1.031
R indices (all data)	$R1 = 0.0497$
	$wR2 = 0.0924$

Results and Discussion

In the solid-state $BaSi_7N_{10}$ is built up of Ba^{2+} ions in a three-dimensional Si–N network structure. $BaSi_7N_{10}$ is the first nitridosilicate with both corner and edge-sharing SiN_4 tetrahedra. As seen in the formula $^3_\infty[(Si_7^{[4]}N_2^{[2]}N_8^{[3]})^{2-}]$, every fifth nitrogen connects two Si centers ($N^{[2]}$) and the remaining nitrogen atoms bridge three Si atoms ($N^{[3]}$). This is consistent with the observation that nitridosilicates with a molar ratio of tetrahedral centers to bridging atoms (Si:N) larger than 1:2 form topologically closed networks of alternating Si and N atoms according to the formula $^3_\infty[(Si_x^{[4]}N_y^{[2]}N_z^{[3]})^{(4x-3(y+z))}]$, where $Si:N = x/(y+z)$ and $4x = 2y + 3z$. Remarkable exceptions to this rule are the nitridosilicates $SrYbSi_4N_7$ and $BaYbSi_4N_7$, in which $N^{[4]}$ centers connecting four Si atoms were found for the first time.[1]

Abstract in German: *Das neuartige Nitridosilicat* $BaSi_7N_{10}$ *wurde durch Umsetzung von Barium mit* $Si(NH)_2$ *in einem speziellen Hochfrequenzofen bei 1650 °C erhalten. Nach der Einkristall-Röntgenstrukturanalyse* ($a = 687.29(3)$, $b = 671.29(3)$, $c = 963.28(4)$ pm, $\beta = 106.269(3)°$, Pc, $Z = 2$, $R1 = 0.0497$, $wR2 = 0.0924$) *liegt eine Raumnetzstruktur aus verknüpften* SiN_4*-Tetraedern vor.* $BaSi_7N_{10}$ *ist das erste Nitridosilicat, in dem sowohl Ecken- als auch Kantenverknüpfung von* SiN_4*-Tetraedern auftritt. Anders als bei den Oxosilicaten ist hier die Eckenverknüpfung gegenüber der Kantenverknüpfung nicht bevorzugt. Mit einem Verhältnis von* $Si:N = 7:10$ *ist* $BaSi_7N_{10}$ *das bislang am höchsten kondensierte multinäre Nitridosilicat, in dem der Kondensationsgrad annähernd den von* Si_3N_4 *erreicht.*

In $BaSi_7N_{10}$ the corner-sharing SiN_4 tetrahedra are arranged in nearly coplanar, corrugated sheets vertical to [010]. This results in layers of highly condensed dreier rings (Figure 2).[10] Similar planar and corrugated layers of dreier rings also exist in Si_2N_2NH[11] and $M_2Si_5N_8$ (M = Ca, Sr, Ba)[4b, 4c] although the configuration pattern of the SiN_4 tetrahedra within the layers is different in each compound. Cross-linking of these layers is accomplished by further corner-sharing SiN_4 tetrahedra. However, in $BaSi_7N_{10}$ vierer single chains occur in which every second connection between neighboring SiN_4 tetrahedra is through common edges. These chains run along [0 0 1] bridging the layers (Figure 3). The Ba^{2+} ions are thus positioned in the linear channels formed.

The Si–N bond lengths in $BaSi_7N_{10}$ are in the typical range for $N^{[2]}$ (N3, N4: 164–169 pm) and $N^{[3]}$ (N1, N2, N5–N10:

Table 2. Atomic coordinates and anisotropic displacement parameters [Å^2] for $BaSi_7N_{10}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent is of the form $-2\pi^2[(ha^*)^2U_{11} + \ldots 2hka^*b^*U_{12}]$.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ba	0.28706(4)	0.59904(3)	0.71225(3)	0.01474(7)	0.01164(6)	0.01687(7)	0.00175(9)	0.00801(5)	0.00196(9)	0.01369(4)
Si1	0.6846(2)	0.4721(2)	0.55534(8)	0.0033(3)	0.0049(4)	0.0038(4)	−0.0001(2)	0.0013(3)	−0.0003(2)	0.0039(2)
Si2	−0.1323(2)	0.4732(2)	0.86723(9)	0.0047(3)	0.0039(4)	0.0039(4)	0.0001(2)	0.0017(3)	0.0003(2)	0.0041(2)
Si3	0.1784(2)	0.1241(2)	0.8469(2)	0.0074(3)	0.0056(3)	0.0058(3)	0.0006(2)	0.0038(2)	0.0006(2)	0.0059(2)
Si4	0.4382(2)	0.1061(2)	0.6123(2)	0.0063(3)	0.0055(3)	0.0058(3)	−0.0011(3)	0.0025(2)	−0.0014(2)	0.0057(2)
Si5	0.6250(2)	0.1186(2)	0.9227(2)	0.0074(3)	0.0048(3)	0.0057(3)	−0.0006(2)	0.0029(2)	−0.0013(3)	0.0057(2)
Si6	0.8122(2)	0.8712(2)	0.7265(2)	0.0082(4)	0.0050(2)	0.0059(3)	0.0000(2)	0.0032(3)	0.0000(2)	0.0061(2)
Si7	−0.0048(2)	0.8652(2)	0.0316(2)	0.0072(3)	0.0055(3)	0.0060(3)	−0.0005(2)	0.0029(2)	−0.0009(3)	0.0060(2)
N1	−0.1024(4)	0.6321(5)	0.0154(3)	0.0070(8)	0.0053(8)	0.0049(8)	−0.0023(7)	0.0036(6)	−0.0011(7)	0.0053(3)
N2	0.6503(4)	0.3692(5)	0.9044(3)	0.0056(8)	0.0044(8)	0.0057(8)	0.0011(7)	0.0021(6)	−0.0010(6)	0.0051(3)
N3	0.4874(5)	0.3339(5)	0.5561(4)	0.0086(10)	0.0051(10)	0.0093(11)	0.0011(8)	0.0016(9)	−0.0004(7)	0.0078(4)
N4	0.0744(5)	0.3384(5)	0.8687(4)	0.0081(10)	0.0075(11)	0.0116(11)	−0.0011(9)	0.0047(9)	0.0019(8)	0.0087(5)
N5	−0.2264(5)	0.6176(3)	0.7113(4)	0.0072(8)	0.0043(6)	0.0048(6)	0.0003(8)	0.0011(5)	−0.0016(8)	0.0055(3)
N6	0.8284(3)	0.0369(4)	0.0633(2)	0.0064(7)	0.0065(7)	0.0050(7)	−0.0005(6)	0.0016(6)	0.0016(6)	0.0060(3)
N7	0.6147(3)	0.9990(4)	0.7633(2)	0.0045(7)	0.0074(7)	0.0054(7)	0.0004(6)	0.0005(6)	0.0018(6)	0.0059(3)
N8	0.4083(3)	0.9220(3)	0.4768(2)	0.0043(6)	0.0070(8)	0.0057(7)	−0.0012(6)	0.0000(5)	0.0002(6)	0.0060(3)
N9	0.2172(3)	0.8897(4)	0.1711(2)	0.0046(7)	0.0103(8)	0.0047(7)	−0.0003(7)	0.0009(5)	−0.0015(6)	0.0066(3)
N10	0.0341(3)	0.9150(3)	0.8629(2)	0.0045(6)	0.0069(7)	0.0051(7)	0.0004(6)	0.0008(5)	−0.0007(6)	0.0056(3)

Table 3. Interatomic distances [pm] and angles [°] in the structure of $BaSi_7N_{10}$.

Ba –N3	291.3(3)	Si3 –N4	164.6(3)
–N4	295.0(4)	–N8	174.6(2)
–N2	307.4(3)	–N10	175.0(2)
–N1	321.3(3)	–N9	178.9(2)
–N3	324.3(3)		
–N4	324.9(4)	Si4 –N3	168.8(3)
–N10	332.3(2)	–N9	176.4(2)
–N9	332.3(2)	–N7	176.5(2)
–N5	334.9(3)	–N8	176.7(2)
–N8	340.6(2)		
–N7	345.0(2)	Si5 –N2	170.6(3)
–N9	347.3(2)	–N7	171.6(3)
–N5	352.9(3)	–N8	173.1(2)
		–N6	174.0(2)
Si1 –N3	164.4(3)		
–N5	175.3(3)	Si6 –N6	172.2(2)
–N1	176.0(3)	–N5	172.2(2)
–N2	176.4(3)	–N7	172.5(2)
–Si2	250.6(1)	–N10	173.7(2)
Si2 –N4	168.1(3)	Si7 –N1	169.2(3)
–N1	174.7(3)	–N6	171.3(2)
–N5	175.2(3)	–N9	173.5(2)
–N2	177.4(3)	–N10	175.2(2)
N1–Si1–N2	89.3(2)	N1–Si2–N2	89.3(2)
N2–Si1–N5	107.7(2)	N4–Si2–N1	114.6(2)
N5–Si1–N3	113.6(2)	N4–Si2–N5	114.4(2)
N3–Si1–N1	120.9(2)	N1–Si2–N5	107.0(2)
N5–Si1–N1	107.3(2)	N4–Si2–N2	122.9(2)
N3–Si1–N2	115.1(2)	N5–Si2–N2	105.1(2)
Si1–N3–Si4	138.8(2)	Si3–N4–Si2	150.0(2)

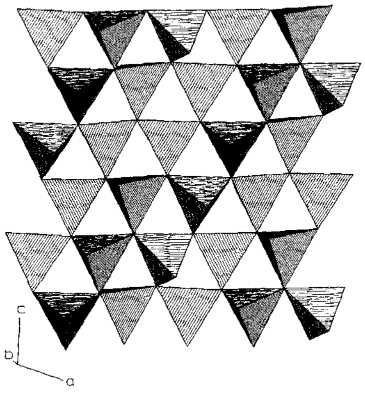

Figure 2. Layers of highly condensed dreier rings occur vertical to [010] in the crystal structure of $BaSi_7N_{10}$.

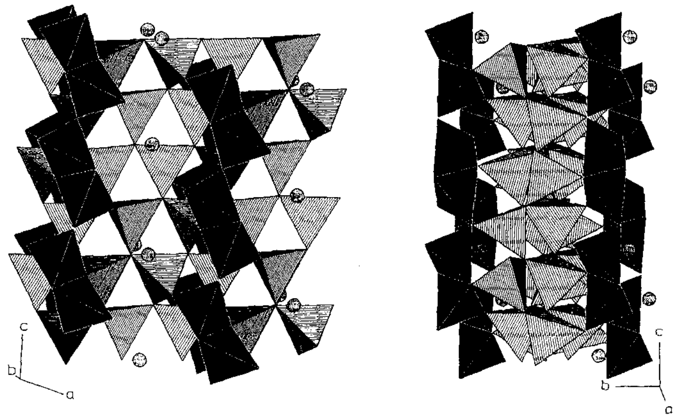

Figure 3. Crystal structure of $BaSi_7N_{10}$: view along [010] (left) and view along [100] (right). Vierer single chains (black) appear in which every second connection between neighboring SiN_4 tetrahedra is realized through common edges.

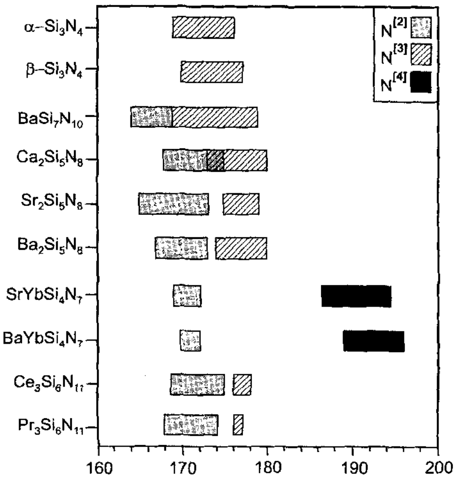

Figure 4. Si–N bond lengths in nitridosilicates. The degree of condensation (molar ratio Si:N) increases from bottom to top.

169–179 pm) (Table 3 and Figure 4). The Si–N distances within the edge-sharing tetrahedra (Figure 5) are markedly shorter (164–177 pm) than in the isolated $(Si_2N_6)^{10-}$ group (174–

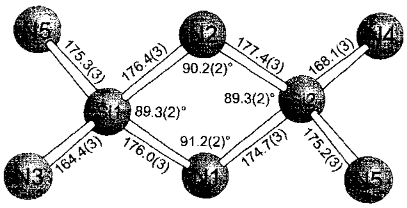

Figure 5. Interatomic distances [pm] and angles for the edge-sharing SiN_4 double tetrahedra in $BaSi_7N_{10}$.

184 pm) described by DiSalvo.[6] This may be due to the high degree of condensation in $BaSi_7N_{10}$, which nearly reaches the value for Si_3N_4.[12] A general trend observed in nitridosilicates is a decrease in the Si–N bond lengths with an increase in the degree of condensation (Figure 4).

The Ba^{2+} ion is coordinated by thirteen nitrogen atoms within a distance of 291–353 pm, of which the $N^{[2]}$ atoms are the closest (Figure 6). They therefore contribute most towards coordination of Ba^{2+} (Si–N3: 291 pm, Si–N4: 295 pm) and, in a simple valence bond approach, possess a formal negative charge. In contrast to $M_2Si_5N_8$ (M = Ca, Sr, Ba),[4b, 4c] the $N^{[3]}$ atoms in $BaSi_7N_{10}$ also show remarkable coordinative contributions.

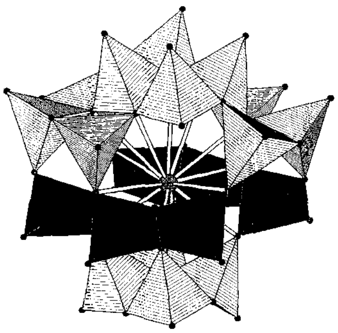

Figure 6. Coordination of Ba^{2+} in $BaSi_7N_{10}$.

Conclusions

Whereas edge-sharing of SiO_4 tetrahedra does not occur in oxosilicates, this phenomenon is favored in the nitridosilicates. Apparently, it occurs independently of the degree of condensation in the Si–N substructure (for example, $Ba_5Si_2N_6$ and $BaSi_7N_{10}$). Furthermore, edge-sharing does not seem to compete with corner-sharing, as both occur in $BaSi_7N_{10}$. This might be due to the covalency in the nitridosilicates, in contrast to the predominant ionic character of the Si–O bonds. An almost invariant Si···Si distance of 306 pm[2] is seen for oxosilicates as a result of the electrostatic repulsion between neighboring Si atoms. This is significantly lowered in nitridosilicates and the Si···Si distances vary from 251 to 337 pm. Similarily, the Si–N–Si bond angles (113 to 172°) indicate greater flexibility in the nitridosilicates than in the oxosilicates.

Edge-sharing of SiN_4 tetrahedra, along with $N^{[3]}$ and $N^{[4]}$ connectivities to Si tetrahedral centers, significantly extends the structural possibilities of nitridosilicates beyond the limits of oxosilicates.

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[9] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-405772.

[10] The term "dreier" ring was coined by Liebau [2] and is derived from the German word drei, which means three. However, a dreier ring is not a three-membered ring, but rather a six-membered ring with *three* tetrahedral centers (Si) and *three* electronegative atoms (N). Similar terms exist for rings made up of four, five, and six tetrahedral centers (and the corresponding number of electronegative atoms), namely "vierer", "fünfer", and "sechser" rings, respectively.

[11] D. Peters, H. Jacobs, *J. Less-Common Met.* **1989**, *146*, 241.

[12] A simple measure of the degree of condensation within a network of TX_4 tetrahedra with stoichiometry T_nX_m is the molar ratio $n:m$ (T = tetrahedral center, X = bridging atom). In nitridosilicates a maximum value of 0.75 (Si_3N_4) and in oxosilicates a maximum value of 0.5 (SiO_2) is observed.