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Articles

Preparation and Crystal Structure of the Nitridosilicates $Ln_3Si_6N_{11}$ (Ln = La, Ce, Pr, Nd, Sm) and $LnSi_3N_5$ (Ln = Ce, Pr, Nd)

Michael Woike and Wolfgang Jeitschko*

Anorganisch-Chemisches Institut, Universität Münster, Wilhelm-Klemm-Strasse 8,
D-48149 Münster, Germany

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The title compounds were prepared by reaction of the binary rare earth silicides $LnSi_2$ and the two-phase alloys "$LnSi_3$" with nitrogen at high temperatures. The crystal structure of the compounds $Ln_3Si_6N_{11}$ was determined from single-crystal X-ray data of $Sm_3Si_6N_{11}$: $P4bm$, $a = 999.7(1)$ pm, $c = 483.6(1)$ pm, $Z = 2$, $R = 0.010$ for 757 structure factors and 38 variable parameters. The tetrahedral SiN_4 groups are linked via corners, forming a three-dimensional network. The samarium atoms occupy two different cavities of that network both with eight nitrogen neighbors. The new compounds $LnSi_3N_5$ (Ln = Ce, Pr, Nd) were found to be isotypic with the previously reported nitridosilicate $LaSi_3N_5$.

Introduction

While the binary rare earth silicides and nitrides are well-known, little information is available about ternary compounds of the rare earth elements with silicon and nitrogen. The preparation and the primitive tetragonal cell of $Sm_3Si_6N_{11}$ was reported by Gaudé, Lang, and Louër.[1] Here we report the crystal structure of this compound and the preparation of several isotypic nitridosilicates. We also communicate the preparation of the compounds $CeSi_3N_5$, $PrSi_3N_5$, and $NdSi_3N_5$, which we found to be isotypic with the previously reported compound $LaSi_3N_5$.[2] A preliminary account of this work was briefly presented at a conference.[3]

Sample Preparation, Properties, and Lattice Constants

Starting materials were the elemental components, all with purities >99.9%. Filings of the rare earth metals were prepared from ingots under paraffin oil. The oil was washed away with *n*-hexane, and the filings were dried and stored under vacuum. Cold-pressed pellets of the compositions Ln:Si = 1:2 and 1:3 were arc-melted under argon, reduced to powders in a steel mortar, and reacted in molybdenum boats with nitrogen under normal pressure at 1500 °C within 1 week. To prevent the contamination with oxygen, the samples were placed between additional molybdenum boats filled with cerium filings.[4]

The compounds were identified by their Guinier powder patterns using Cu $K\alpha_1$ radiation and α-quartz as a standard ($a = 491.30$ pm, $c = 540.46$ pm). The lattice constants (Table 1) were obtained by least-squares fits. The plot of the cell volumes (Figure 1) indicates cerium to be trivalent in both series of compounds.

Table 1. Cell Dimensions of Nitrides with $Sm_3Si_6N_{11}$ and $LaSi_3N_5$ Type Structures[a]

compound	*a*, pm	*c*, pm	*c*/*a*	*V*, nm^3
$La_3Si_6N_{11}$	1018.9(1)	483.7(2)	0.4747(3)	0.5022(3)
$Ce_3Si_6N_{11}$	1013.1(2)	484.7(3)	0.4784(5)	0.4975(5)
$Pr_3Si_6N_{11}$	1008.6(1)	484.2(2)	0.4801(3)	0.4926(3)
$Nd_3Si_6N_{11}$	1006.3(2)	483.8(2)	0.4808(4)	0.4899(4)
$Sm_3Si_6N_{11}$	999.7(1)	483.6(1)	0.4837(2)	0.4833(2)
$Sm_3Si_6N_{11}$[b]	999.31(5)	483.61(4)	0.48394(9)	0.48294(9)

compound	*a*, pm	*b*, pm	*c*, pm	*V*, nm^3
$LaSi_3N_5$	785.3(1)	1126.4(2)	481.72(8)	0.4261(2)
$LaSi_3N_5$[c]	783.8	1123.6	480.7	0.4233
$CeSi_3N_5$	783.7(2)	1123.3(3)	479.9(2)	0.4225(4)
$PrSi_3N_5$	782.6(2)	1121.5(2)	478.3(1)	0.4198(3)
$NdSi_3N_5$	780.8(3)	1118.2(3)	477.6(2)	0.4170(4)

[a] Standard deviations in the least significant digits are given in parentheses throughout the paper. [b] From ref 1. [c] From ref 2.

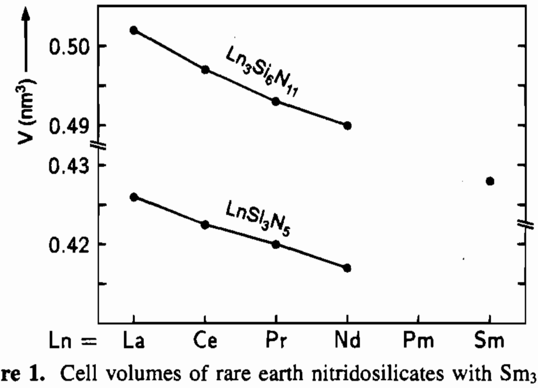

Figure 1. Cell volumes of rare earth nitridosilicates with $Sm_3Si_6N_{11}$ and $LaSi_3N_5$ type structure.

The crystals of $Sm_3Si_6N_{11}$ had a metallic luster similar to that of elemental silicon. However, we have obtained $CeSi_3N_5$ in the form of a yellow powder, and it seems that the gray color, observed by us for the powders of the other nitridosilicates, is not intrinsic. They are stable in air for long periods of time. A sample of $Sm_3Si_6N_{11}$ was boiled for 1 h in slightly diluted solutions of HCl, H_2SO_4, HNO_3, and KOH. This treatment did not visibly attack the samples, and their X-ray powder patterns were unchanged. Similarly, a sample of $LaSi_3N_5$ was resistant to aqua regia, and similar resistivities can be assumed for the other compounds.

[®] Abstract published in *Advance ACS Abstracts,* September 1, 1995.

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(2) Inoue, Z.; Mitomo, M.; Ii, N. *J. Mater. Sci.* **1980**, *15*, 2915.

(3) Woike, M.; Jeitschko, W. Preparation and Crystal Structure of the Nitridosilicates $Ln_3Si_6N_{11}$ (Ln = La, Ce, Pr, Nd, and Sm) and $LnSi_3N_5$ (Ln = Ce, Pr, and Nd). In *Abstracts of the 11th International Conference on Solid Compounds of Transition Elements*; Suski, W., Ed.; W. Trzebiatowski Institute of Low Temperature and Structure Research: Wrocław, Poland, 1994.

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Table 2. Crystallographic Data for $Sm_3Si_6N_{11}$[a]

chem formula: $Sm_3Si_6N_{11}$
$a = 999.7(1)$ pm
$c = 483.6(1)$ pm
$V = 0.4833(2)$ nm^3
$Z = 2$
fw: 773.8
space group: *P4bm* (No. 100)

$T = 21$ °C
$\lambda = 71.07$ pm
$\varrho_{calcd} = 5.32$ g·cm^{-3}
$\mu = 94.0$ cm^{-1}
$R(F_o) = 0.010$
$R_w(F_o) = 0.012$

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$; $R_w = ((\sum(\sigma(F))^{-2}||F_o| - |F_c||^2)/(\sum(\sigma(F))^{-2}|F_o|^2)^{1/2}$.

Table 3. Atomic Parameters of $Sm_3Si_6N_{11}$[a]

atom	*P4bm*	occupancy	*x*	*y*	*z*	*B*
Sm1	4c	1.0005(7)	0.68157(1)	$^1/_2 + x$	0	0.364(1)
Sm2	2a	0.9995(5)	0	0	0.98454(7)	0.229(2)
Si1	8d	0.991(2)	0.20913(7)	0.07867(6)	0.5322(1)	0.218(9)
Si2	4c	0.999(3)	0.11791(7)	$^1/_2 + x$	0.0432(2)	0.209(9)
N1	8d	1.021(7)	0.0802(2)	0.1801(2)	0.6478(4)	0.39(2)
N2	8d	1.033(7)	0.2271(2)	0.0763(2)	0.1778(4)	0.39(2)
N3	4c	1.020(9)	0.1521(2)	$^1/_2 + x$	0.6947(6)	0.32(3)
N4	2b	1.03(1)	$^1/_2$	0	0.0770(9)	0.50(5)

[a] The last column contains the isotropic *B* values ($\times 10^2$, in units of nm^2) of the nitrogen atoms and the equivalent isotropic *B* values of the anisotropic displacement parameters of the metal and silicon atoms. The occupancy parameters were obtained in a separate refinement cycle. In the final cycle the ideal occupancy parameters were used. The *z* parameter of the Sm1 position was set to zero to fix the origin of the cell.

Structure Determination of $Sm_3Si_6N_{11}$

A single crystal of $Sm_3Si_6N_{11}$ (40 × 20 × 20 μm^3) was isolated from a nitrided sample with the initial composition Sm:Si = 1:3, prepared as described above. Intensity data were recorded in a four-circle diffractometer with $\theta/2\theta$ scans using graphite-monochromated Mo Kα radiation with a scintillation counter and a pulse-height discriminator. Background counts were taken at both ends of each scan. A total of 6472 reflections were recorded in half of the reciprocal sphere up to $2\theta = 80°$, and an absorption correction was made from ψ-scan data. The crystallographic data are summarized in Table 2 and in a more detailed table of the Supporting Information.

The structure was solved using the SHELXS program.[5] The positions of the samarium atoms were determined by direct methods, and the lighter atoms were found by difference Fourier syntheses. The structure was refined by full-matrix least-squares cycles in the tetragonal space group *P4bm*, a *translationengleiche* subgroup of *P4/mbm*. The centrosymmetric higher symmetry space group could definitely be ruled out on the basis of the refined structure. Atomic scattering factors[6] were used, corrected for anomalous dispersion,[7] and a parameter accounting for isotropic secondary extinction was refined and applied to the calculated structure factors. The samarium and the silicon atoms were refined with anisotropic displacement parameters; the nitrogen atoms, with isotropic ones. As a check for the ideal composition, we fixed the scale factor and varied the occupancy parameters of all atoms. All occupancy parameters were within five standard deviations at the ideal values, and in the final cycles, the ideal occupancy parameters were used. The final conventional and weighted residuals are $R = 0.010$ and $R_w = 0.012$ for 38 variable parameters and 757 independent structure factors. As *P4bm* is noncentrosymmetric, we also refined the structure in the enantiomorphic setting, which resulted in the somewhat higher residuals $R = 0.014$ and $R_w = 0.018$. The atomic parameters were standardized using the program STRUCTURE TIDY.[8] The crystallographic data are summarized in Tables 2–4. The anisotropic displacement parameters are available as Supporting Information.

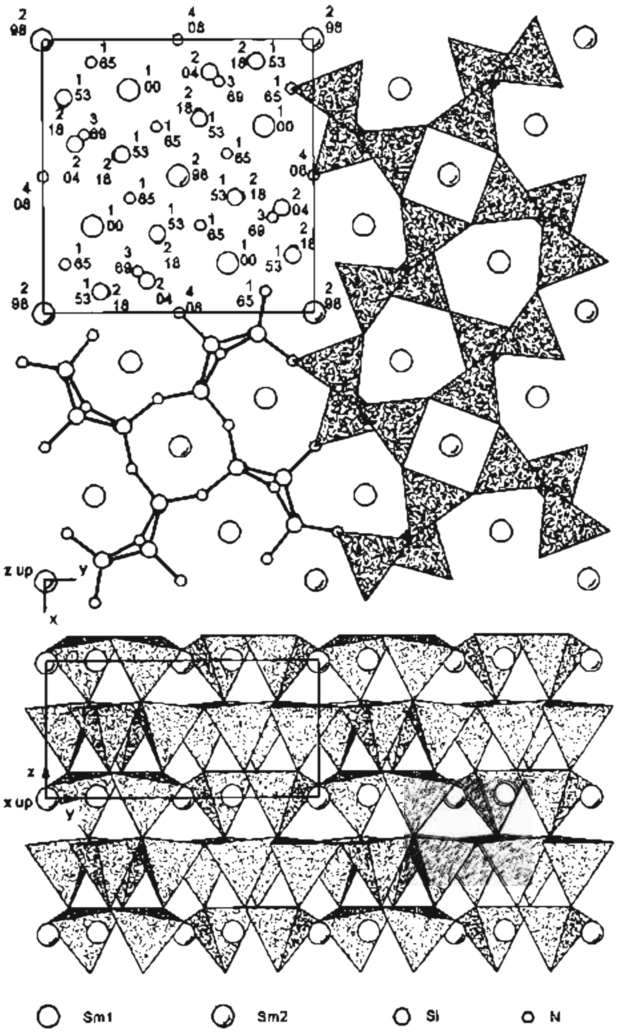

Figure 2. Crystal structure of $Sm_3Si_6N_{11}$. A projection along the tetragonal axis is shown in the upper part. The heights of the atoms are given in hundredths. Single-digit numbers correspond to the atom designations. The network of the corner-sharing SiN_4 tetrahedra is emphasized in views along the tetragonal axis and perpendicular to it (below).

Discussion

$Sm_3Si_6N_{11}$ crystallizes with a new polar, pyroelectric tetragonal structure in the uncommon space group *P4bm*. The absence of the mirror plane perpendicular to the 4-fold axis can easily be seen from the lower part of Figure 2. Only 26 of the 5180 tetragonal solid state compounds known up to 1994 crystallize in that noncentrosymmetric space group.[9] The new compounds $LnSi_3N_5$ (Ln = Ce, Pr, Nd) crystallize with a structure that was determined for $LaSi_3N_5$.[2] The structure of $LaSi_3N_5$ was presented only in the form of a drawing, and positional parameters as well as interatomic distances have not been published. Nevertheless, the isotypism of the new nitridosilicates $LnSi_3N_5$ (Ln = Ce, Pr, Nd) with $LaSi_3N_5$ could be ascertained by a comparison of our Guinier powder patterns with the one published[2] for $LaSi_3N_5$.

Both structure types consist of SiN_4 tetrahedra which share corners, thus forming three-dimensional networks with large voids containing the rare earth elements. In the structure of $Sm_3Si_6N_{11}$ the SiN_4 tetrahedra are arranged in two planes extending perpendicularly to the *z* axis. The SiN_4 tetrahedra of the Si1 atoms are all at $z \sim {}^1/_2$. They may be considered to form the main layer of condensed SiN_4 tetrahedra. Within that

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(9) Inorganic Crystal Structure Database, Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen 2, 1991, update 1994.

Table 4. Interatomic Distances in the Structure of $Sm_3Si_6N_{11}$[a]

Sm1:	2 N1	241.7	Sm2:	4 N1	255.7	Si1:	1 N1	170.9	Si2:	1 N4	167.5
	1 N4	259.4		4 N2	257.1		1 N2	172.4		2 N2	173.1
	2 N2	260.9		4 Si1	312.6		1 N1	173.2		1 N3	175.3
	1 N3	277.7		4 Si1	346.5		1 N3	175.5		1 Sm1	284.3
	2 N2	286.6					1 Sm2	312.6		2 Sm1	306.8
	1 Si2	284.3					1 Sm1	330.7			
	2 Si2	306.8					1 Sm2	346.5			
	2 Si1	330.7									
N1:	1 Si1	170.9	N2:	1 Si1	172.4	N3:	1 Si2	175.3	N4:	2 Si2	167.5
	1 Si1	173.2		1 Si2	173.1		2 Si1	175.5		2 Sm1	259.4
	1 Sm1	241.7		1 Sm2	257.1		1 Sm1	277.7			
	1 Sm2	255.7		1 Sm1	260.9						
				1 Sm1	286.6						

[a] All distances shorter than 350 pm (Sm−Sm, Sm−Si, Sm−N), 290 pm (Si−Si), and 270 pm (Si−N, N−N) are listed. Standard deviations, computed from those of the lattice constants and the positional parameters, are all equal to or smaller than 0.3 pm.

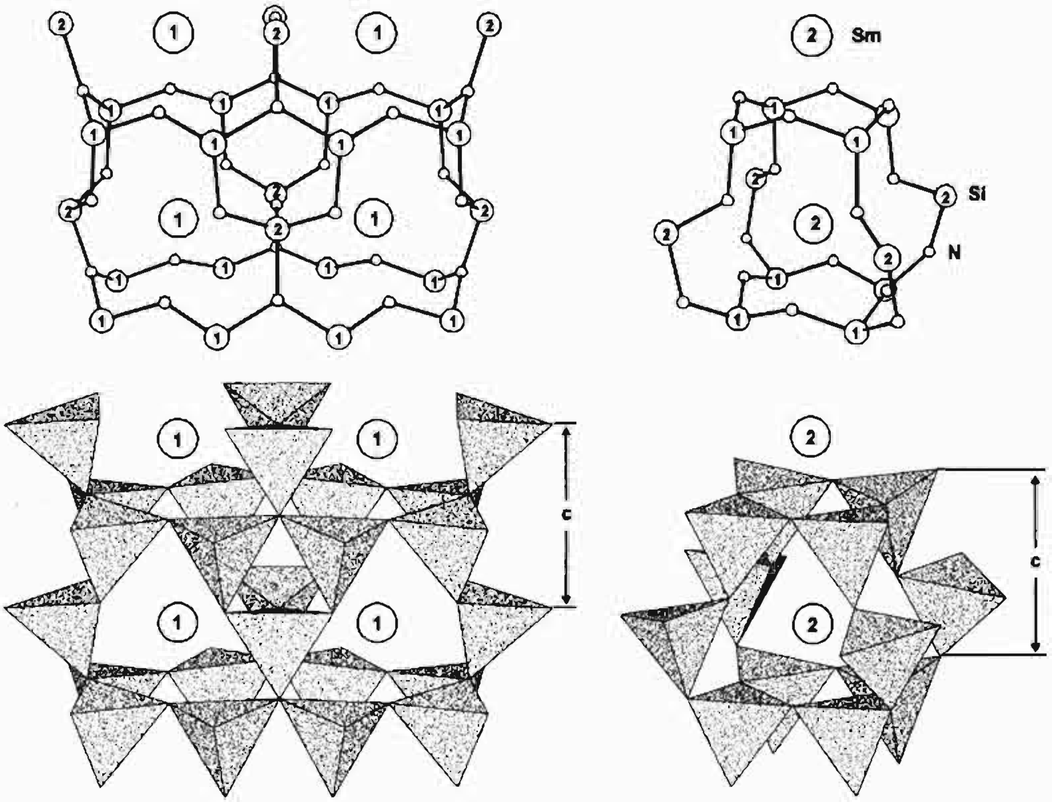

Figure 3. Frameworks of condensed SiN_4 tetrahedra surrounding the Sm1 and Sm2 atoms of $Sm_3Si_6N_{11}$ as viewed approximately perpendicular to the 4-fold axis. Single-digit numbers correspond to the atom designations. In the upper part of the figure, only the ring-forming atoms of the SiN_4 tetrahedra are shown for clarity.

layer, the SiN_4 tetrahedra form eight- and sixteen-membered Si_4N_4 and Si_8N_8 rings, as can be seen from the upper right-hand part of Figure 2. The SiN_4 tetrahedra of the Si2 atoms are situated at $z \sim 0$. In contrast to the Si1 atoms—which occupy an 8-fold position—the Si2 atoms are in a 4-fold position, and as a consequence they form only Si_2N_7 pairs within the plane at $z \sim 0$. The Si_2N_7 pairs of that minor layer are condensed with the two major layers, thus forming the three-dimensionally infinite network of SiN_4 tetrahedra. The two different samarium atoms occupy cavities of that network. The linking of the SiN_4 tetrahedra around the two samarium sites is shown in Figure 3. The cavities around the Sm1 and Sm2 atoms share common SiN_4 tetrahedra, and the smallest common silicon−nitrogen ring is formed by six silicon and six nitrogen atoms. In going from one Sm1 to the next Sm1 site above in the *z* direction, such twelve-membered Si_6N_6 rings have to be passed. The samarium atoms have a relatively high formal charge (+3), and therefore it can be assumed that they are firmly embedded in their cavities. Thus, an ion exchange can be expected to take place only at high temperatures. We have not pursued this idea.

The structures of $Sm_3Si_6N_{11}$ and $LaSi_3N_5$ have some similarity to the structures of framework silicates and zeolites, and for that reason we consider the term "nitridosilicates" appropriate for such compounds. However, there is a significant difference between the structures of the silicates and aluminosilicates on the one hand and the nitridosilicates on the other. In the usual silicate and aluminosilicate framework structures[10] the ratio of the Si (or Si + Al) atoms to oxygen atoms varies between 1:2 and 1:3, whereas in the nitridosilicates $Sm_3Si_6N_{11}$ and $LaSi_3N_5$ this ratio is greater than 1:2. This has to do with the fact that the oxygen atoms in silicates and aluminosilicates have two silicon or aluminum neighbors while the structures of $Sm_3Si_6N_{11}$ and $LaSi_3N_5$ contain some nitrogen atoms with three silicon neighbors.

In the structure of $Sm_3Si_6N_{11}$ both samarium sites are

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

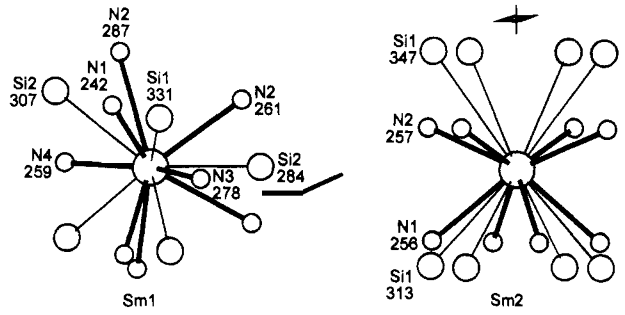

Figure 4. Coordination polyhedra of the samarium atoms in $Sm_3Si_6N_{11}$. Interatomic distances are indicated in units of pm. The Sm1 and Sm2 atoms have the site symmetries *m* and 4, respectively.

surrounded by eight nitrogen atoms (Figure 4) at average distances of 264.4 pm (Sm1) and 256.4 pm (Sm2). The relatively large difference between these two values can be rationalized by the large spread of the Sm1−N distances from 241.7 to 286.6 pm while the Sm2−N distances are all of comparable lengths, at 255.7 pm (4×) and 257.1 pm (4×). The average Si−N distances within the SiN_4 tetrahedra are very similar, at 173.0 and 172.3 pm for the Si1 and Si2 atoms, respectively. These distances are somewhat smaller than the Si−N distances in the compounds $MSiN_2$ (M = Be, Mg, Mn, Zn) with ordered wurtzite structures,[11−16] where they cover the range between 174 and 180 pm. The nitrogen atoms with two silicon neighbors have average N−Si distances of 172.0 (N1), 172.7 (N2), and 167.5 pm (N4), while the N3 atom has three silicon neighbors at the greatest average distance of 175.5 pm.

As already mentioned, the structural chemistry of the present nitridosilicates is similar to that of the oxosilicates. In both structures the silicon atoms obtain the oxidation number +4, i.e. $(Ln^{3+})_3(Si^{4+})_6(N^{3-})_{11}$ and $Ln^{3+}(Si^{4+})_3(N^{3-})_5$. This is not the case for the known transition metal, rare earth, and actinoid silicon carbon compounds, where the silicon atoms must be considered as anionic, and such compounds are better described as silicide carbides rather than "carbidosilicates". E.g., in Mo_5Si_3C,[17] Ti_3SiC_2,[18] $Mn_{23}Si_5C_4$[19] (formerly designated with the composition "$Mn_{17}Si_4C_3$"[20]), $DyFe_2SiC$,[21] and $ThFe_2SiC$,[22] the silicon and carbon atoms are isolated from each other. The structure of $U_{20}Si_{16}C_3$ contains Si_2 pairs as well as isolated silicon and carbon atoms.[23] Si−C dumbbells were found in $U_3Si_2C_2$.[23] Si_2 pairs and isolated carbon atoms occur in $Dy_2Fe_2Si_2C$[24] and in $Tm_2Fe_2Si_2C$.[25] And the structure of $Th_{17}Si_{16}C_2$ contains a four-membered C−Si−Si−C chain besides Si_4 and Si_6 groups, Si−C dumbbells, as well as isolated silicon and carbon atoms.[26] In all of these silicide carbides, the silicon atoms have metal neighbors. In contrast, $Sm_3Si_6N_{11}$ contains nearly perfect SiN_4 tetrahedra with N−Si−N angles varying between 101.5(1) and 115.1(1)°, and thus the samarium−silicon interactions seem to be weak.

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Supporting Information Available: Listings of the crystallographic data and the anisotropic displacement parameters for the samarium and the silicon atoms of $Sm_3Si_6N_{11}$ (2 pages). Ordering information is given on any current masthead page.

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