Nitridosilicates—A Significant Extension of Silicate Chemistry

Wolfgang Schnick* and Hubert Huppertz

Abstract: Because of its low chemical reactivity Si_3N_4 has hardly been used as a starting material for the preparation of multinary silicon nitrides or nitridosilicates, but has gained increasing importance as a nonoxidic material for high-performance applications. A novel synthetic approach is presented, which starts from silicon diimide ($Si(NH)_2$) and makes available a large variety of novel nitridosilicates. The structures of these nitridosilicates represent a significant extension from those found in the family of oxosilicates. Because of their outstanding chemical and physical stability, nitridosilicates might be of particular interest for the development of novel inorganic nitridic materials.

Keywords
high-temperature synthesis · materials science · nitridosilicates · nitrogen · silicon

Introduction

The polymeric binary compounds BN and Si_3N_4 are of particular interest for the development of novel inorganic materials for high-performance applications. The structures of these nonmetal nitrides are based on networks of corner-sharing BN_4 and SiN_4 tetrahedra, respectively. Their outstanding chemical, thermal, and mechanical stabilities are a direct consequence of the high degree of crosslinking in the structures and of the high stability of the chemical bonding between the constituent elements.

Another polymeric nonmetal nitride is P_3N_5. Similar to BN and Si_3N_4 it is built up from connected PN_4 tetrahedra into a network structure.[1] In the last few years we have studied the chemistry, structures, and properties of phosphorus nitrides and further multinary compounds incorporating electropositive elements. The P–N substructures of these compounds exhibit structural similarities to oxosilicates and oxophosphates.[2]

Unlike the situation with P_3N_5, only a few ternary or multinary compounds based on Si_3N_4 have been synthesized and characterized in the past.[2a] Examples are $MSiN_2$ (M = Be, Mg, Mn, Zn),[3] the structurally analogous compounds $LiSi_2N_3$,[4] Si_2N_2NH,[5] Si_2N_2O,[6] and $SiPN_3$,[2b] or $K_3Si_6N_5(NH)_6$[7] and $LnSi_3N_5$ (Ln = La, Ce, Pr, Nd).[8] However, no general synthetic approach was available leading to pure and defined multinary silicon nitrides.

Considering the diverse structural chemistry of oxosilicates,[9] a detailed investigation of nitridosilicates promised to yield compounds with interesting structures and properties, and also tailor-made ceramic materials based on the elements Si and N.

Synthetic Approach

No general synthetic approach is available for the synthesis of the above-mentioned nitridosilicates. These were mostly obtained by rather different synthetic procedures. For example, $MgSiN_2$ was obtained by reaction of the binary nitrides [Eq. (1)], $MnSiN_2$ from metallic Mn [Eq. (2)], and $LnSi_3N_5$ by nitriding the two-phase alloys with the composition "$LnSi_3$" [Eq. (3)].

$$Mg_3N_2 + Si_3N_4 \xrightarrow[N_2]{1200\,^{\circ}C} 3\,MgSiN_2 \qquad (1)$$

$$3\,Mn + Si_3N_4 + 2\,NH_3 \xrightarrow{1050\,^{\circ}C} 3\,MnSiN_2 + 3\,H_2 \qquad (2)$$

$$2\,\text{"}LnSi_3\text{"} + 5\,N_2 \xrightarrow{1500\,^{\circ}C} 2\,LnSi_3N_5 \qquad (3)$$

Ln = Ce, Pr, Nd

Even at higher temperatures silicon nitride (Si_3N_4) exhibits only low chemical reactivity.[2a, 10] This property is an important precondition for the application of Si_3N_4 in high-temperature and high-performance devices (e.g. turbochargers, valve tappets). Owing to its inertness, Si_3N_4 can only be used as a starting material for the synthesis of ternary nitridosilicates [e.g., Eq. (1)] when it is treated with highly reactive metal nitrides (e.g. Li_3N, Mg_3N_2) which show a sufficient thermal stability.

We therefore developed a novel synthetic approach leading to ternary and multinary nitridosilicates, abandoning the use of the metal nitrides and treating the pure metals with silicon diimide ($Si(NH)_2$) instead. This strategy proved to be successful

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[*] Prof. Dr. W. Schnick, Dipl.-Chem. H. Huppertz
Laboratorium für Anorganische Chemie der Universität
D-95440 Bayreuth (Germany)
Fax: Int. code +(921)55-2788
e-mail: wolfgang.schnick@uni-bayreuth.de

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for the synthesis of nitridosilicates [Eq. (4) and (5)].

$$2\,M + 5\,Si(NH)_2 \xrightarrow[\text{HF furnace}]{1500-1650\,^{\circ}C} M_2Si_5N_8 + N_2 + 5\,H_2 \qquad (4)$$

M = Ca, Sr, Ba

$$3\,M' + 6\,Si(NH)_2 \xrightarrow[\text{HF furnace}]{1650\,^{\circ}C} M'_3Si_6N_{11} + {}^1/_2\,N_2 + 6\,H_2 \qquad (5)$$

M′ = Ce, Pr, Sm, Nd

Silicon diimide ($Si(NH)_2$) is an amorphous and relatively undefined but reactive compound, which is converted to amorphous Si_3N_4 at temperatures above 900 °C. It is an important precursor for the technical production of Si_3N_4 ceramics.[10] In the laboratory $Si(NH)_2$ is obtained by ammonolysis of $SiCl_4$ in CH_2Cl_2 followed by thermal treatment below 600 °C [Eq. (6)].[10]

$$SiCl_4 + 6\,NH_3 \xrightarrow[2)\,600\,^{\circ}C]{1)\,CH_2Cl_2} Si(NH)_2 + 4\,NH_4Cl \qquad (6)$$

The reactions between a metal and $Si(NH)_2$ [Eq. (4) and (5)] may be interpreted as the dissolution of the electropositive metal in the nitrido-analogous, polymeric acid $Si(NH)_2$, accompanied by the evolution of hydrogen. The advantages of this method include the fact that the metal can be varied and that preparative amounts of the products are accessible as coarse-crystalline, single-phase products in short reaction times. A specially developed high-frequency furnace, used for the inductive heating of the crucibles containing the reaction mixture (Figure 1), is essential for obtaining high yield in these reactions. This technique allows very fast heating of reaction mixtures as well as fast quenching of the high-temperature products.[11]

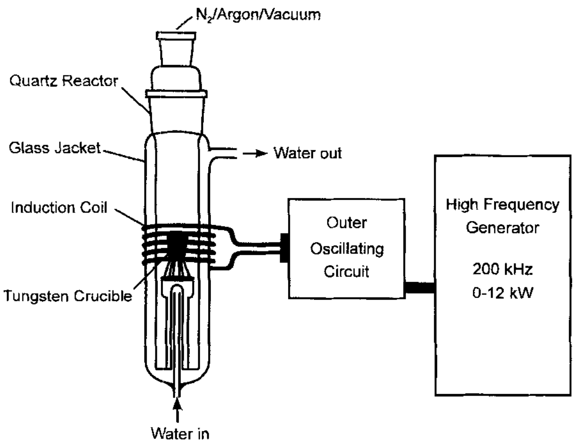

Figure 1. Experimental set-up of the high-frequency furnace for the synthesis of nitridosilicates.

Abstract in German: *Wegen seiner geringen chemischen Reaktivität ist Siliciumnitrid Si_3N_4 in der Vergangenheit selten als Ausgangsverbindung für die Synthese multinärer Siliciumnitride oder Nitridosilicate eingesetzt worden. Stattdessen erlangte Si_3N_4 in den letzten Jahren zunehmende Bedeutung als nichtoxidisches Material für Hochleistungsanwendungen. In dieser Arbeit wird ein neues synthetisches Verfahren präsentiert, das – ausgehend von Siliciumdiimid $Si(NH)_2$ – einen Zugang zu neuartigen Nitridosilicaten eröffnet. Wie an verschiedenen Beispielen demonstriert wird, erweitern die Nitridosilicate signifikant die strukturellen Möglichkeiten der konventionellen Oxosilicate. Im Hinblick auf ihre bemerkenswerte chemische und physikalische Stabilität sind die Nitridosilicate von besonderem Interesse für die Entwicklung neuartiger anorganischer Materialien.*

Results

Oxosilicates and nitridosilicates both contain SiX_4 tetrahedra (X = O, N) as the basic structural building blocks. By condensation of these tetrahedra more complex Si–O and Si–N structures are possible. A simple general measure for the degree of condensation within a network of SiX_4 tetrahedra with the stoichiometry Si_nX_m is the molar ratio $n:m$, that is, of tetrahedral Si centers and bridging atoms X. In oxosilicates a maximum value for the degree of condensation of 1:2 = 0.5 is reached in SiO_2. No multinary oxosilicate is known exceeding this limit. According to Table 1 nitridosilicates may have a degree of condensation of $0.25 \leq Si:N \leq 0.75$. This is due to the fact that the structural possibilities in oxosilicates are limited to terminal oxygen atoms and simple bridging $O^{[2]}$ atoms, while the nitridosilicates contain terminal nitrogen atoms, $N^{[2]}$, and even $N^{[3]}$ connections.[*]

Table 1. Degree of condensation (molar ratio Si:X) in oxo- and nitridosilicates.

Si:X	Formula	Structure of Si_nX_m
1:4	Na_4SiO_4	$[Si\ X_4^{[1]}]^{4-}$
2:6	$Ba_5Si_2N_6$	$[Si_2\ X_4^{[1]}\ X_2^{[2]}]^{10-}$
1:3	$CaSiO_3$	${}^1_\infty[(Si\ X_2^{[1]}\ X_{2/2}^{[2]})^{2-}]$
2:5	$Li_2[Si_2O_5]$	${}^2_\infty[(Si\ X^{[1]}\ X_{3/2}^{[2]})^{2-}]$
1:2	SiO_2	${}^3_\infty[(Si_1\ X_2^{[2]})]$
	$MgSiN_2$	${}^3_\infty[(Si_1\ X_2^{[2]})^{2-}]$
6:11	$M_3Si_6N_{11}$ [a]	${}^3_\infty[(Si_6\ X_9^{[2]}\ X_2^{[3]})^{9-}]$
4:7	$MYbSi_4N_7$ [b]	${}^3_\infty[(Si_4\ X_6^{[2]}\ X_1^{[4]})^{5-}]$
5:8	$M_2Si_5N_8$ [c]	${}^3_\infty[(Si_5\ X_4^{[2]}\ X_4^{[3]})^{4-}]$
7:10	$BaSi_7N_{10}$	${}^3_\infty[(Si_7\ X_2^{[2]}\ X_8^{[3]})^{2-}]$
3:4	Si_3N_4	${}^3_\infty[(Si_3\ X_4^{[3]})]$

[a] M^{III} = La, Ce, Pr, Nd, Sm. [b] M^{II} = Sr, Ba. [c] M^{II} = Ca, Sr, Ba.

For example, in $Ca_2Si_5N_8$ the three-dimensional network structure is made up of corner-sharing SiN_4 tetrahedra ${}^3_\infty[(Si_5^{[4]}N_4^{[2]}N_4^{[3]})^{4-}]$ (Figure 2).[11] Half of the nitrogen atoms connect two silicon atoms ($N^{[2]}$) and half bridge three silicon atoms ($N^{[3]}$). These $N^{[3]}$ atoms are arranged nearly coplanar in sheets perpendicular to [100], resulting in layers of highly condensed dreier rings (Figure 2).[12] As expected, the $Si-N^{[2]}$ bonds are much shorter (167–171 pm) than the $Si-N^{[3]}$ bonds (173–180 pm). According to lattice-energy and point-potential calculations only the simple bridging $N^{[2]}$ atoms have a negative charge when coordinating the Ca^{2+} ions. The $Ca^{2+}-N^{[2]}$ distances (232–284 pm) correspond to the sum of the ionic radii.

$Sr_2Si_5N_8$ and $Ba_2Si_5N_8$ are isotypic and have a network structure of corner-sharing SiN_4 tetrahedra similar to that found in $Ca_2Si_5N_8$. However, the two structure types are topologically different, as the distribution of (Si_nN_n) ring sizes differ markedly.[13] According to the formula ${}^3_\infty[(Si_5^{[4]}N_4^{[2]}N_4^{[3]})^{4-}]$,

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[*] The superscripted numbers in square brackets following element symbols define their coordination numbers.

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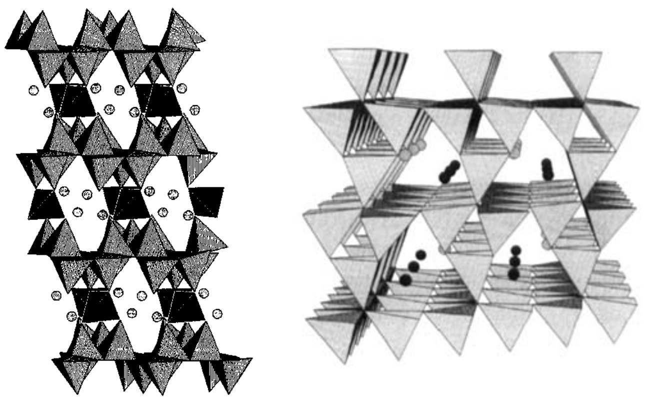

Figure 2. Crystal structure of $Ca_2Si_5N_8$. Left: view along [021]; right: sheets of highly condensed dreier rings perpendicular to [100].

half of the nitrogen atoms connect two and half three silicon atoms. Again the $N^{[3]}$ are arranged in sheets perpendicular to [100]; however, in contrast to the arrangement in $Ca_2Si_5N_8$, these sheets are significantly corrugated (Figure 3). The metal ions Sr^{2+} and Ba^{2+} are situated in channels along [100] formed by sechser rings. Analogously to $Ca_2Si_5N_8$, the metal ions Sr^{2+} and Ba^{2+} are mainly coordinated by $N^{[2]}$ atoms.

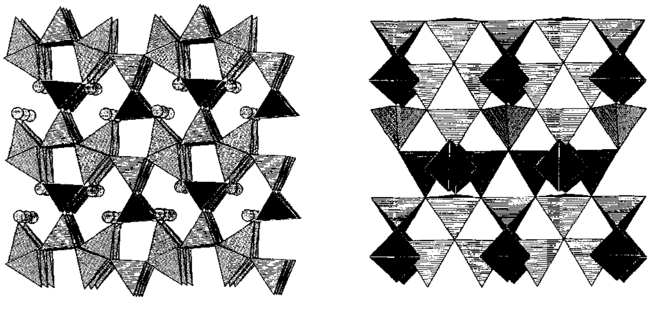

Figure 3. Crystal structure of $Sr_2Si_5N_8$ and $Ba_2Si_5N_8$. Left: view along [100]; right: corrugated sheets of highly condensed dreier rings perpendicular to [010].

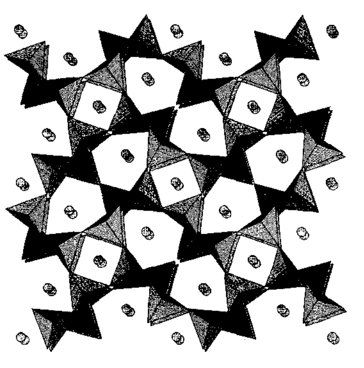

Figure 4. Crystal structure of $Ln_3Si_6N_{11}$ (Ln = La, Ce, Pr, Nd, Sm); view along [001].

The general procedure for the synthesis of nitridosilicates by reaction of pure metal with silicon diimide ($Si(NH)_2$) can also be applied to the rare-earth metals. We obtained yellow $Ce_3Si_6N_{11}$ and greenish $Pr_3Si_6N_{11}$.[14, 15] According to the formula $^3_\infty[(Si_6^{[4]}N_9^{[2]}N_2^{[3]})^{9-}]$, a three-dimensional network structure of corner-sharing SiN_4 tetrahedra is observed, in addition to the Ce^{3+} or Pr^{3+} ions. In these two compounds only a minor portion of the nitrogen atoms connect three silicon atoms ($N^{[3]}$), while most form simple Si-$N^{[2]}$-Si bridges. The SiN_4 tetrahedra form layers, which are built up from vierer and achter rings. These layers are stacked along [001] and are connected by double tetrahedra bridging the achter rings (Figure 4). The nitridosilicates $Ln_3Si_6N_{11}$ (Ln = La, Ce, Pr, Nd) have also been synthesized by the reaction of the silicides $LnSi_2$ with N_2. However, with this procedure, it is a problem avoiding metallic impurities in the products.[8b]

In the family of oxosilicates vertex-sharing of SiO_4 tetrahedra is favored exclusively over edge-sharing. The latter arrangement has only been postulated for one example, the so-called fibrous polymorph of silica SiO_2.[16] However, the structure and existence of this polymorph has not as yet been unambiguously confirmed.

DiSalvo obtained $Ba_5Si_2N_6$, which contains discrete $[Si_2N_6]^{10-}$ anions, formed by two edge-sharing SiN_4 tetrahedra.[17] In the quasi-binary system $Ba_3N_2-Si_3N_4$, we also obtained $Ba_2Si_5N_8$,[13] which is built up exclusively from corner-sharing of SiN_4 tetrahedra in a network structure (see above).

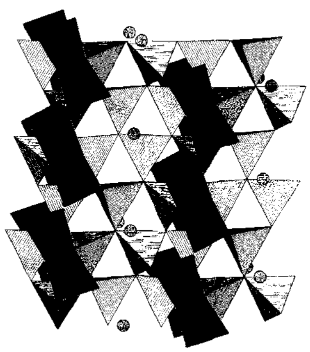

Figure 5. Crystal structure of $BaSi_7N_{10}$, view along [010]. Vierer single chains (black) occur in which every second connection between neighboring SiN_4 tetrahedra occurs through common edges.

In the system $Ba_3N_2-Si_3N_4$ a further ternary nitridosilicate $BaSi_7N_{10}$ occurs with both corner-sharing and edge-sharing SiN_4 tetrahedra.[18] The corner-sharing SiN_4 tetrahedra are arranged nearly coplanar in corrugated sheets perpendicular to [010]; this results in layers of highly condensed dreier rings (Figure 5). Similar planar and corrugated layers of dreier rings also exist in Si_2N_2NH[5] and $M_2Si_5N_8$ (M = Ca, Sr, Ba), but the configuration patterns of the SiN_4 tetrahedra within the layers are different in each compound. The layers in these compounds are cross-linked by further corner-sharing of SiN_4 tetrahedra. However, in $BaSi_7N_{10}$ vierer single chains occur in which every second connection between neighboring SiN_4 tetrahedra occurs through common edges. These chains run along [001], bridging the layers. In contrast to the situation in the above-mentioned nitridosilicates, the $N^{[3]}$ atoms show a remarkable coordinative contribution towards the Ba^{2+} ions as well.

The layers of highly condensed dreier rings in Si_2N_2NH, $M_2Si_5N_8$ (M = Ca, Sr, Ba), and $BaSi_7N_{10}$ differ substantially from the topologies observed in oxosilicates, since $N^{[3]}$ atoms occur exclusively in the layers, each bridging three neighboring Si tetrahedral centers. In contrast, $O^{[2]}$ oxygen atoms in oxosilicates can only bridge two neighboring Si atoms.[19] Unlike the situation in oxosilicates where edge-sharing of SiO_4 tetrahedra does not occur, this phenomenon is more favored in the nitridosilicates. Apparently, edge-sharing of SiN_4 tetrahedra occurs independently of the degree of condensation in the Si–N substructure (e.g. $Ba_5Si_2N_6$, $BaSi_7N_{10}$). Furthermore, edge-sharing does not seem to compete with corner-sharing, as both phenomena occur side by side in $BaSi_7N_{10}$. This might be explained in terms of the fact that, in contrast to the more ionic Si–O bonds, the bonds in nitridosilicates are more covalent. The electrostatic repulsion between neighboring Si atoms, which gives Si···Si distances of around 306 pm in oxosilicates,[9] is significantly smaller in the nitridosilicates. Here, the Si···Si distances fall between 251 and 337 pm. Similarly, the

Si-N-Si bond angles (113–172°) indicate a greater flexibility in the structures of nitridosilicates compared to those of oxosilicates.

With a molar ratio Si:N of 7:10, $BaSi_7N_{10}$ is the most highly condensed multinary nitridosilicate, which nearly reaches the degree of condensation of binary Si_3N_4. Thus, with one and the same metal (Ba) the nitridosilicates exhibit a much wider spectrum in the degree of condensation (e.g. $Ba_5Si_2N_6$, $Ba_2Si_5N_8$, $BaSi_7N_{10}$) than is possible for the oxosilicates.

All nitridosilicates discussed so far with a molar ratio of tetrahedral centers (Si) to bridging atoms (N) of $Si:N \geq 1:2$ form topologically closed networks of alternating Si and N atoms according to the formula ${}^3_\infty[(Si^{[4]}_x N^{[2]}_y N^{[3]}_z)^{(4x-3(y+z))}]$, where $Si:N = x/(y+z)$ and $4x = 2y+3z$. Remarkable and surprising exceptions to this rule are the nitridosilicates $SrYbSi_4N_7$ and $BaYbSi_4N_7$, in which, for the first time, $N^{[4]}$ atoms have been found, each connecting four Si atoms.[20, 21]

$SrYbSi_4N_7$ and $BaYbSi_4N_7$ both contain a network structure of corner-sharing SiN_4 tetrahedra ${}^3_\infty[(Si^{[4]}_4 N^{[2]}_6 N^{[4]})^{5-}]$. Although a stoichiometric Si:N ratio of 4:7 is expected to give ${}^3_\infty[(Si^{[4]}_4 N^{[2]}_5 N^{[3]}_2)^{5-}]$, no $N^{[3]}$ atoms are present. Instead, there is a corresponding number of $N^{[4]}$ bridges, which connect four Si tetrahedral centers. The bond lengths to the $N^{[4]}$ atoms are significantly longer than those to the $N^{[2]}$ atoms (Figure 6). The Si–N network structure in $BaYbSi_4N_7$ is built up from star-shaped $[N(SiN_3)_4]$ building blocks (Figure 7). By connecting these groups through common $N^{[2]}$ atoms a stacking variant of the wurtzite-analogous aluminum nitride structure type is formed (Figure 8). Systematic elimination of tetrahedra from this arrangement along [100] leads to the formation of sechser-ring channels, containing Ba^{2+} and Yb^{3+} ions. No other example of a compound containing $N^{[4]}$ atoms covalently connected to four neighboring Si atoms has yet been reported from the areas of solid-state chemistry or molecular chemistry.

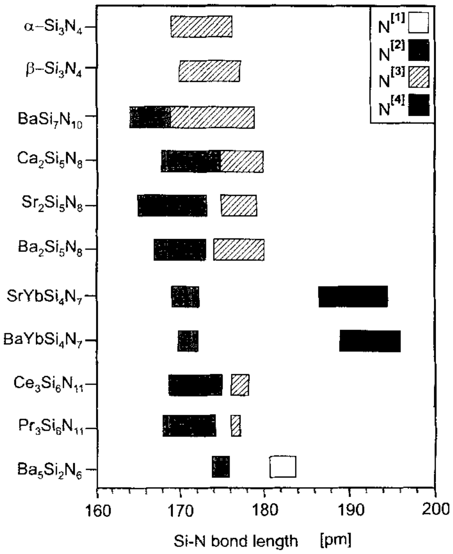

Figure 6. Si–N bond lengths in nitridosilicates. The distances Si–$N^{[4]}$ are significantly longer than Si–$N^{[3]}$, Si–$N^{[2]}$, and Si–$N^{[1]}$.

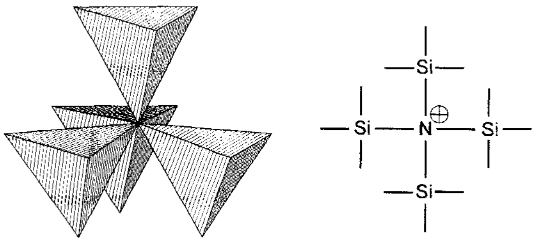

Figure 7. Four SiN_4 tetrahedra are connected through a common nitrogen atom to give star-shaped $[N(SiN_3)_4]$ building blocks.

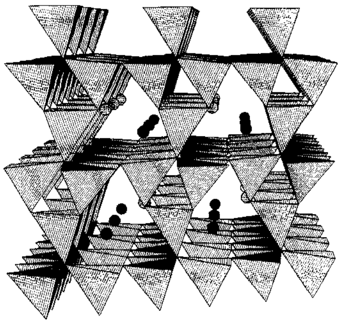

Figure 8. Crystal structure of $SrYbSi_4N_7$ and $BaYbSi_4N_7$; view along [100].

We also attempted to synthesize ternary nitridosilicates containing transition metals. During our experiments using cobalt metal and silicon diimide, we did not obtain the desired ternary cobalt nitridosilicate, but observed the formation of hollow hexagonal Si_3N_4 microtubes, which might be useful in the microtechnology of ceramic Si_3N_4 components.[22] These tubes are partially filled with Co_2Si and have a well-defined shape, exhibiting hexagonal symmetry. The tubes have a diameter of approximately 6 μm and are up to 1 mm in length. The wall thickness of the Si_3N_4 microtubes is approximately 1 μm (Figure 9). Liquid alkaline-earth or rare-earth metals might possibly play an important role during the formation of crystalline multinary nitridosilicates. Melts of transition metals like cobalt seem to behave completely differently, as the reduction of $Si(NH)_2$ not only yields H_2 but also Co_2Si, which acts as a filler in the resulting hexagonal Si_3N_4 microtubes and might be important for the formation of these unique hollow tubes.

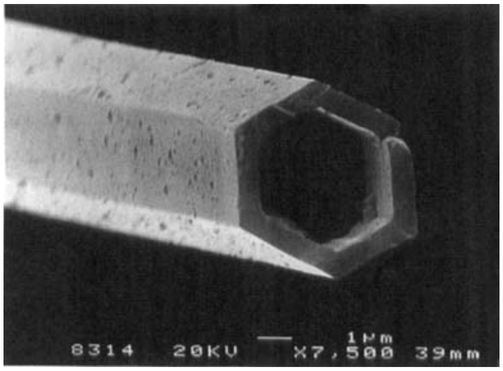

Figure 9. Crystalline hexagonal Si_3N_4 microtubes (SEM micrograph) formed by reaction of Co metal and $Si(NH)_2$. The diameter of the hollow tubes (length up to 1 mm) is approximately 6 μm.

Conclusions

The reaction of pure metals with silicon diimide ($Si(NH)_2$) provides a straightforward preparative route to novel nitridosilicates. Within short reaction times of only a few hours coarse-crystalline, single-phase products are formed. While the structural chemistry of oxosilicates is limited to terminal oxygen atoms and simple bridging $O^{[2]}$ atoms, the nitridosilicates show a greater range of structural arrangements, namely, terminal $N^{[1]}$ and $N^{[2]}$, $N^{[3]}$, and $N^{[4]}$ atoms, connected to two, three, and even four neighboring Si tetrahedral centers. Unlike the situation in the normal oxosilicates, vertex-sharing of SiN_4 tetrahedra is not exclusively favored over edge-sharing, and both modes may coexist. The degree of condensation (molar ratio Si:N) shows a much wider spectrum ($0.25 \leq Si:N \leq 0.75$) than is possible for oxosilicates ($0.25 \leq Si:O \leq 0.5$), and thus particularly highly condensed network structures of SiN_4 tetrahedra are formed, which have no structural analogues in the manifold family of oxosilicates. Especially the highly condensed nitridosilicates show remarkable chemical, thermal, and mechanical stabilities (up to ca. 1600 °C), comparable to the outstanding properties of Si_3N_4, which is one of the most important nonoxidic materials for high-performance applications. The nitridosilicates thus not only extend the structural possibilities of the well-known oxosilicates, but they also might be of particular interest for the development of novel inorganic materials.

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[12] The term "dreier" ring was coined by Liebau [9] and is derived from the German word drei, which means three. However, a dreier ring is not a three-membered ring, but a six-membered ring comprising *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.
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