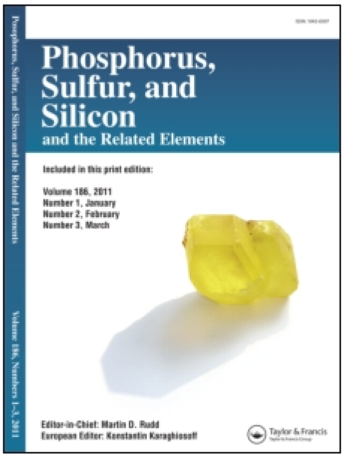

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NITRIDOSILICATES - A SIGNIFICANT EXTENSION OF SILICATE CHEMISTRY

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A novel synthetic approach is presented which starts from silicon diimide $Si(NH)_2$ and makes available a manifold variety of novel nitridosilicates. Structurally these nitridosilicates represent a significant extension of the family of oxosilicates. With respect to their outstanding chemical and physical stability nitridosilicates might be of particular interest for the development of novel inorganic nitridic materials.

Keywords: nitridosilicates; nitrides; high-temperature synthesis; nitridozeolites; materials science

INTRODUCTION

The most abundant elements on the surface and in the crust of our planet are silicon and oxygen. Both elements exhibit a high affinity to each other and this is the reason for the omnipresence of silica SiO_2

and silicious minerals. Nitrogen plays a minor role and one of the very few nitridic minerals is Si_2N_2O which is found in meteorites and in cosmic dust. However, synthetic silicon nitride Si_3N_4 is well known and represents the most important non-oxidic ceramic which is used for high-performance applications[1]. The formal exchange of oxygen in oxosilicates against nitrogen leads to novel nitridosilicates. Especially highly condensed networks as well as open frameworks constructed out of SiN_4 tetrahedra are accesible which show remarkable properties.

SYNTHESIS AND PROPERTIES OF NITRIDOSILICATES

In the past only very few nitridosilicates have been synthesized. Now, a generalized and broad synthetic approach for this class of compounds has been achieved. Therefore we have developed a novel procedure leading to ternary and multinary nitridosilicates. We found that the reaction of the pure metals with silicon diimide $Si(NH)_2$ in a high-frequency furnace leads to the formation of pure and single phase multinary nitridosilicates[2]. The reaction between a metal and $Si(NH)_2$ may be interpreted as the dissolution of an electropositive metal in a nitrido analogous polymeric acid $Si(NH)_2$ accompanied by the evolution of hydrogen [Eq. (1)].

$$2\,M + 5\,Si(NH)_2 \xrightarrow[\text{HF furnace}]{1500\text{-}1650°C} M_2Si_5N_8 + N_2 + 5\,H_2 \qquad (1)$$

$M = Ca, Sr, Ba, Eu$

A specific advantage of this method is the possibility for the variation of the metals and the matter of fact that preparative amounts of the products are accessible as coarse crystalline and single phase products in short reaction times. The highly condensed nitridosilicates obtained so far show a remarkable chemical, thermal, and mechanical stability (up to ~ 1600 °C) which is comparable to the outstanding properties of Si_3N_4 being one of the most important non-oxidic materials for high-performance applications[1].

RESULTS

Oxosilicates as well as nitridosilicates contain SiX_4 tetrahedra ($X = O, N$) as 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 stoichiometry Si_nX_m is the molar ratio n : m of tetrahedral centers Si 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. Nitridosilicates may have a degree of condensation in the extended range $0.25 \leq Si : N \leq 0.75$. This is due to the fact that the structural possibilities of oxosilicates are limited to terminal oxygen atoms and simple bridging $O^{[2]}$ atoms while the nitridosilicates show terminal nitrogen atoms $N^{[2]}$ and even $N^{[3]}$ connections.

For example in $Ca_2Si_5N_8$ a three-dimensional network structure of corner sharing SiN_4 tetrahedra $^{3}_{\infty}[(Si^{[4]}_{5}N^{[2]}_{4}N^{[3]}_{4})^{4-}]$ occurs (Fig. 1)[3]. Half of the nitrogen atoms each are connecting two silicon atoms (denoted as $N^{[2]}$) and the rest of the N atoms are bridging three silicon ($N^{[3]}$). These $N^{[3]}$ are arranged nearly coplanar in sheets vertical to [100] resulting in layers of highly condensed Si_3N_3 dreier rings (Fig. 1). As expected the bonds Si-$N^{[2]}$ are markedly shorter (167 to 171 pm) as compared to the bonds Si-$N^{[3]}$ (173 to 180 pm). According to lattice-energy and point-potential calculations only the simply bridging $N^{[2]}$ atoms have a negative charge coordinating the Ca^{2+}

ions. The distances Ca^{2+}-$N^{[2]}$ (232 to 284 pm) correspond to the sum of the ionic radii.

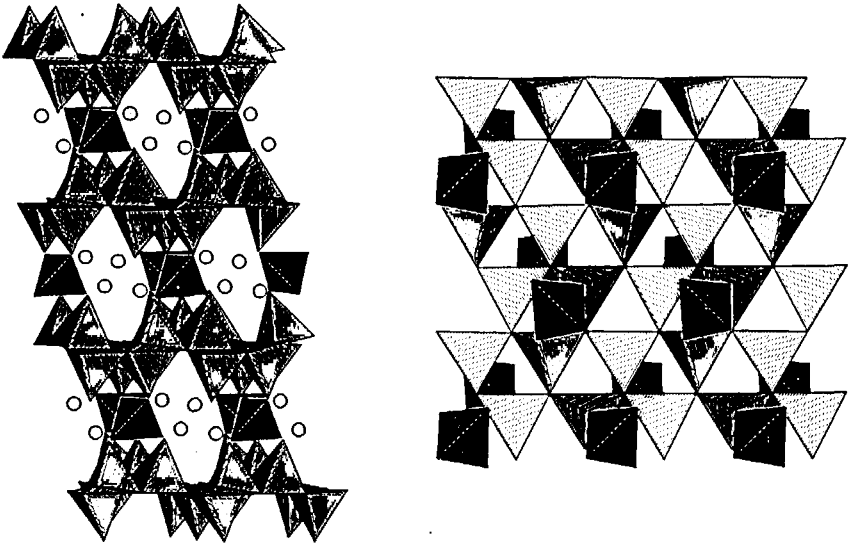

FIGURE 1 Crystal structure of $Ca_2Si_5N_8$. Left: view along [021]; right: sheets of highly condensed dreier rings perpendicular to [100].

$Sr_2Si_5N_8$, $Ba_2Si_5N_8$, and $Eu_2Si_5N_8$ are isotypic[4,5] and have a network structure of corner sharing SiN_4 tetrahedra similar to $Ca_2Si_5N_8$. However both structure types are topologically different as the distribution of (Si_nN_n) ring sizes differ markedly (see below). According to $^{3}_{\infty}[(Si^{[4]}_{5}N^{[2]}_{4}N^{[3]}_{4})^{4-}]$ half of the nitrogen atoms each are connecting two or three silicon, respectively. And again the $N^{[3]}$ are arranged in sheets vertical to [100], however in contrast to $Ca_2Si_5N_8$, these sheets are significantly corrugated. The metal cations Sr^{2+}, Ba^{2+}, and Eu^{2+} are situated in channels along [100] formed by Si_6N_6 sechser rings. Analogously to $Ca_2Si_5N_8$ the metal ions are mainly coordinated by $N^{[2]}$ atoms.

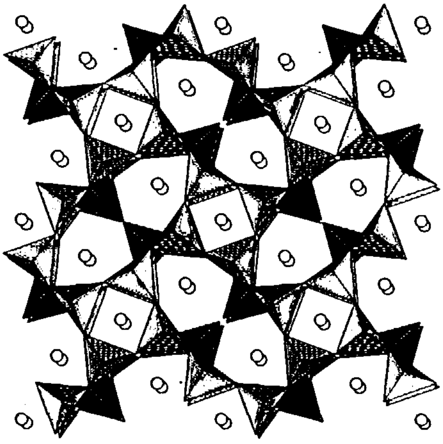

FIGURE 2
Crystal structure of $Ln_3Si_6N_{11}$ (Ln=La, Ce, Pr, Nd, Sm); view along [001].

With the rare-earth metals Ce and Pr we obtained yellow $Ce_3Si_6N_{11}$ and greenish $Pr_3Si_6N_{11}$.[6,7] According to $^{3}_{\infty}[(Si^{[4]}_{6}N^{[2]}_{9}N^{[3]}_{2})^{9-}]$ a three-dimensional network structure of corner sharing SiN_4 tetrahedra occurs besides Ce^{3+} and Pr^{3+}, respectively. In these two compounds only a minor portion of the nitrogen atoms each connect three silicon ($N^{[3]}$) while most of them form simple Si-$N^{[2]}$-Si bridges. The SiN_4 tetrahedra form layers which are built up by Si_4N_4 vierer and Si_8N_8 achter rings. These layers are stacked along [001] and are connected by double tetrahedra bridging the achter rings (Fig. 2). The nitridosilicates $Ln_3Si_6N_{11}$ (Ln = La, Ce, Pr, Nd, Sm) have also been synthesized by the reaction of the silicides $LnSi_2$ with N_2. However, a problem of this procedure is the avoidance of metallic impurities of the products.[8]

In the family of oxosilicates vertex sharing of SiO_4 tetrahedra exclusively is favored above edge sharing. The latter case only has been postulated for one representative which is the so-called fibrous polymorph of silica SiO_2 [9]. However, the structure and existence of this polymorph has not as yet unambiguously been confirmed. In the system Ba_3N_2 - Si_3N_4 a further ternary nitridosilicate $BaSi_7N_{10}$ occurs with both corner sharing and edge sharing of SiN_4 tetrahedra[10].

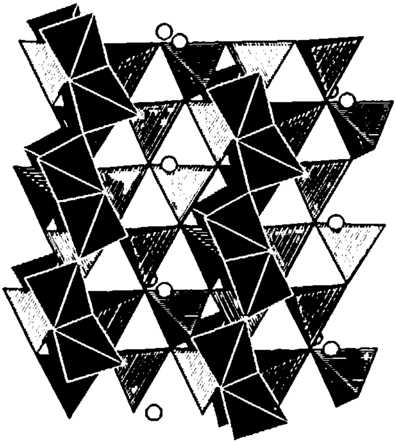

FIGURE 3
Crystal structure of $BaSi_7N_{10}$, view along [010].

The corner sharing SiN_4 tetrahedra are arranged nearly coplanar in corrugated sheets vertical to [010] resulting in layers of highly condensed dreier rings (Fig. 3). In $BaSi_7N_{10}$ vierer single chains occur in which every second connection between neighboring SiN_4 tetrahedra is realized via 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. 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 from the degree of condensation in the Si-N substructure (e.g. $Ba_5Si_2N_6$[11], $BaSi_7N_{10}$). 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 interpreted by the fact that in contrast to the more ionic Si-O bonds the nitridosilicates exhibit more covalency. With a molar ratio Si : N = 7 : 10 $BaSi_7N_{10}$ is the highest condensed multinary nitridosilicate known so far and it nearly reaches the degree of condensation of binary Si_3N_4.

All nitridosilicates discussed so far with a molar ratio of tetrahedral centers (Si) to bridging atoms (N) of Si : N $\geq$ 1 : 2 build up topologically closed networks of alternating Si and N atoms according to

$^{3}_{\infty}[(Si^{[4]}_{x}N^{[2]}_{y}N^{[3]}_{z})^{(4x-3(y+z))}]$, where Si : N = x /(y+z) and 4x = 2y + 3z. Remarkable and surprising exceptions from this rule are the nitridosilicates $MYbSi_4N_7$ (M=Sr, Ba, Eu)[5,12,13] where for the first time $N^{[4]}$ have been found which are each connecting four Si atoms. Both compounds contain a network structure of corner-sharing SiN_4 tetrahedra $^{3}_{\infty}[(Si^{[4]}_{4}N^{[2]}_{6}N^{[4]})^{5-}]$. Although a stoichiometric ratio of Si : N = 4 : 7 is expected to give $^{3}_{\infty}[(Si^{[4]}_{4}N^{[2]}_{5}N^{[3]}_{2})^{5-}]$, no $N^{[3]}$ atoms were found. 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 $N^{[2]}$. The Si-N network structure is built up from starlike $[N(SiN_3)_4]$ building blocks (Fig. 4). Systematic elimination of tetrahedra from this arrangement along [100] leads to the formation of sechser ring channels, in which the M^{2+} and Yb^{3+} are positioned.

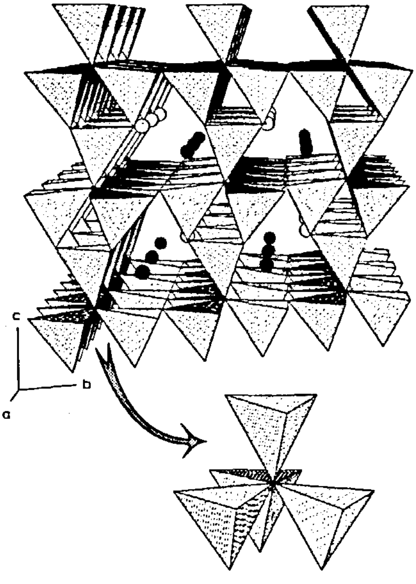

FIGURE 4
Crystal structure of $MYbSi_4N_7$ (M=Sr, Ba, Eu)

While the structural chemistry of oxosilicates is limited to terminal oxygen atoms and simple bridging $O^{[2]}$, the nitridosilicates show extended structural possibilities with $N^{[2]}$, $N^{[3]}$, and $N^{[4]}$ connections of Si tetrahedral centers. These variations have not as yet been found in oxosilicates and may not be possible with silicon and oxygen.

With regard to the material properties and the high stability of nitridosilicates it seemed to be a challenge to built up zeolite analogous, microporous network structures from SiN_4 tetrahedra. With the synthesis of $Ba_2Nd_7Si_{11}N_{23}$ we obtained the first nitridosilicate with a zeolite analogous Si-N network structure (Fig. 5)[14].

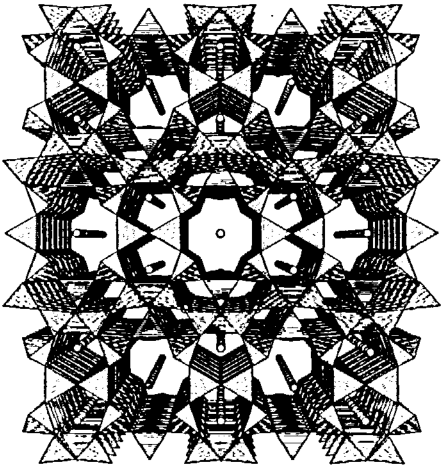

FIGURE 5 Crystal structure of $Ba_2Nd_7Si_{11}N_{23}$; view along [001].

Characteristic for the structure of $Ba_2Nd_7Si_{11}N_{23}$ are channels along [001]. The Ba^{2+}-ions are centered in the achter ring channels and in the sechser ring channels along [100]. The Nd^{3+}-ions are positioned in the smaller hollows. A measure for the microporous character of a zeolite analogous structure is the framework density (FD), which counts the number of tetrahedral centers (T) in a volume of 1000 Å^3. With a FD of 18.5 T/(1000 Å^3) $Ba_2Nd_7Si_{11}N_{23}$ is similar to typical zeolites (framework densities of some zeolites in T/(1000 Å^3): 17.5 ($AlPO_4$-5), 17.9 (ZSM-5), 19.3 (Nonasil))[15].

For the classification and differentiation of the complex Si-N network structures in the nitridosilicates we calculated the cycle-class sequences using an algorithm presented by *Klee* et al.[16]. Substantially, this algorithm counts the number of (Si_nN_n) rings per unit cell. As summarized in Table 1 the highly condensed nitridosilicates in contrast to the modifications of SiO_2 show a tendency to form odd ring sizes, while in the SiO_2 modifications only even ring sizes (Si_nN_n) with n = 4, 6, 8 ... occur.

TABLE 1 Ring size distribution in oxo- and nitridosilicates

Si_nN_n rings	n = 2	3	4	5	6	7	8
α-Si_3N_4	-	6	15	33	137	540	1911
β-Si_3N_4	-	3	6	21	67	264	972
$BaSi_7N_{10}$	1	7	10	40	101	334	1101
$Ca_2Si_5N_8$	-	6	2	16	20	83	219
$M_2Si_5N_8$ (M=Sr, Ba, Eu)	-	5	3	16	25	90	239
MSi_3N_5 (M=La, Ce)	-	2	1	6	10	32	97
$MYbSi_4N_7$ (M=Sr, Ba, Eu)	-	8	-	-	8	48	156
$M_3Si_6N_{11}$ (M=Ce, Pr)	-	2	1	-	12	20	55
$MSiN_2$ (M=Be, Mg, Mn)	-	-	-	-	2	-	3
$Ba_2Nd_7Si_{11}N_{23}$	-	6	1	-	12	24	30
Zeolite RHO	-	-	18	-	28	-	78
Coesite	-	-	4	-	6	-	18
Cristobalite	-	-	-	-	4	-	6
Quartz	-	-	-	-	3	-	21

MOLECULAR PREORGANIZATION

For the multinary nitridosilicates which are not accessible through conventional solid state reactions we used molecular preorganization as a synthetic tool. For instance $SiPN_3$ was obtained by ammonolysis and condensation starting from a molecular precursor Cl_3Si-N=PCl_3. In this compound the required structural elements of two vertex sharing tetrahedra centered by P and Si and connected via a common nitrogen atom is preorganized on a molecular level[17].

Acknowledgements

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