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$Ce_{16}Si_{15}O_6N_{32}$—An Oxonitridosilicate with Silicon Octahedrally Coordinated by Nitrogen**

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Octahedrally coordinated silicon is a peculiarity in silicate chemistry because the vast majority of natural and synthetic oxosilicates contain SiO_4 tetrahedra as typical structural building units.[1] However, there are only a small number of silicates, in which the coordination number of silicon is larger than four.[1–3] Most of the known examples are high-pressure phases like the rutile-type SiO_2 modification stishovite, the perovskite-analogous (Mg,Fe)SiO_3, which is found in the deeper crust of the earth, or hollandite-analogous $CaAl_2Si_2O_8$.[2] At lower pressure several silicates are accessible that contain SiO_6 octahedra and SiO_4 tetrahedra (e.g. $K_2Si_4O_9$,[4] $BaSi_4O_9$,[5] and $Na_{1.8}Ca_{1.1}Si_6O_{14}$[6]). Furthermore there are a small number of silicon phosphates that have been obtained at ambient pressure and these contain polymeric network structures of SiO_6 octahedra and PO_4 tetrahedra (e.g. SiP_2O_7 (form I),[7] $Rb_2SiP_4O_{13}$,[8] $(NH_4)_2SiP_4O_{13}$[9]). Owing to its enhanced basicity Si rather than P prefers the octahedral coordination in these compounds.[8]

A formal exchange of oxygen by nitrogen leads from the oxosilicates to the nitridosilicates. Yet all known representatives are constructed from SiN_4 tetrahedra. Unlike their oxidic analogues, more varied possibilities for the linkage of the SiX_4 building units (X = N, O) occur in the nitridosilicates.[10]

The compounds in the Si-Al-O-N and Si-O-N systems ("sialons" and "sions", respectively) have gained significant importance in materials science because of their outstanding thermal, chemical, and mechanical stability.[11] These compounds may be viewed as a link between oxidic silicates and aluminosilicates on one hand and the nitridosilicates and nitridoaluminosilicates on the other.[12, 13] Among the hitherto known crystalline nitridosilicates,[10] oxonitridosilicates, and oxonitridoaluminosilicates[11–13] as well as all the glassy phases that have been investigated in the systems Si-O-N and Si-Al-O-N[11, 14] no experimental evidence for the occurence of octahedrally coordinated silicon has yet been found.

With $Ce_{16}Si_{15}O_6N_{32}$ we have now synthesized the first oxonitridosilicate containing SiN_6 octahedra.[15] This new sion has been obtained by the reaction of stoichiometric amounts of cerium metal with silicon diimide and silicon dioxide in a radio frequency (rf) furnace under nitrogen atmosphere (ambient pressure) [Eq. (a)].

$$30\,Ce + 8\,SiO_2 + 27\,Si(NH)_2 + 6\,N_2 \xrightarrow[\text{rf furnace}]{1000-1540\,^{\circ}C,\ N_2} Ce_{16}Si_{15}O_6N_{32} + 2\,Ce_3Si_6N_{11} + 2\,Ce_4Si_4O_5N_6 + 27\,H_2 \qquad (a)$$

Despite varying all experimental parameters (stoichiometry, reaction temperature, reaction time) we have not yet succeeded in synthesizing single-phase $Ce_{16}Si_{15}O_6N_{32}$. Under optimized conditions (see Experimental Section) coarsely crystalline $Ce_{16}Si_{15}O_6N_{32}$ was obtained as ruby-red single crystals in a yield of approximately 20% among yellow $Ce_3Si_6N_{11}$[16] and yellow-orange $Ce_4Si_4O_5N_6$.[17] All three phases are easily distinguishable in the reaction product due to their crystal habitus and their color, and they are obtained in the ratio given in Equation (a). Similar to all other highly condensed nitridosilicates, $Ce_{16}Si_{15}O_6N_{32}$ is stable up to 1600 °C and insensitive to hot acids and alkalis.

The X-ray structural analysis using diffraction data obtained on a four-circle diffractometer initially yielded a simple perovskite-type structure with a cubic lattice constant $a = 385.1$ pm. However neither a plausible composition of the compound nor a sufficient anisotropic refinement of the crystal structure could be performed based on this unit cell. A complete set of precession photographs revealed a $4\times4\times4$ superstructure with a cubic lattice constant $a' = 1540.36(9)$ pm. Accordingly the volume of the unit cell is 64 times as large as that of the simple perovskite structure type. In order to record even the weak superstructure reflections the data collection was performed by using the Stoe-IPDS image plate diffraction system.

According to the single-crystal X-ray structure determination,[18] the solid contains a three-dimensional network of corner-sharing SiN_6 octahedra and $Si(O,N)_4$ tetrahedra[15] (Figure 1). The structure may be viewed as a distorted defect variant $Ce_{16}(Si_{15}\square_1)O_6N_{32}\square_{10}$ of a $4\times4\times4$ superstructure derived from the perovskite type (ABX_3). From a total of 64 octahedra per unit cell only four remain unchanged, four have been eliminated, and 56 have been replaced by tetrahedra (Figure 2).

A partial replacement of octahedra by tetrahedra in the perovskite structure type under formation of a superstructure has been reported, for example, for $Sr_3Al_2O_6$,[19] in which every fourth octahedron remains unchanged. A nearly complete substitution of 15 from 16 octahedra, as occurs in $Ce_{16}Si_{15}O_6N_{32}$, is to our knowledge unprecedented. However the few remaining SiN_6 octahedra in $Ce_{16}Si_{15}O_6N_{32}$ are nearly regular and they are only slightly tilted from their ideal

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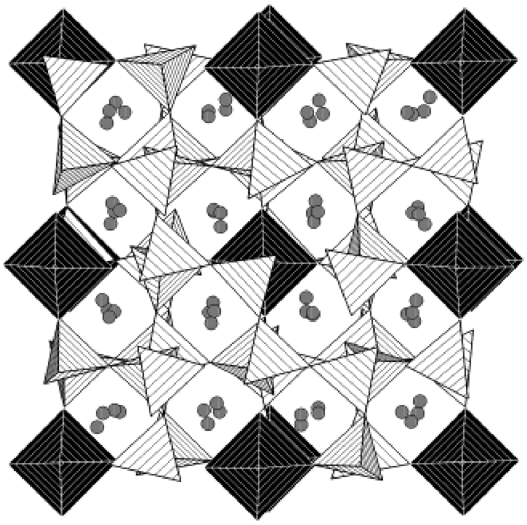

Figure 1. Crystal structure of $Ce_{16}Si_{15}O_6N_{32}$ (view along [100]), which is a defect variant of a 4 × 4 × 4 superstructure of the perovskite type.

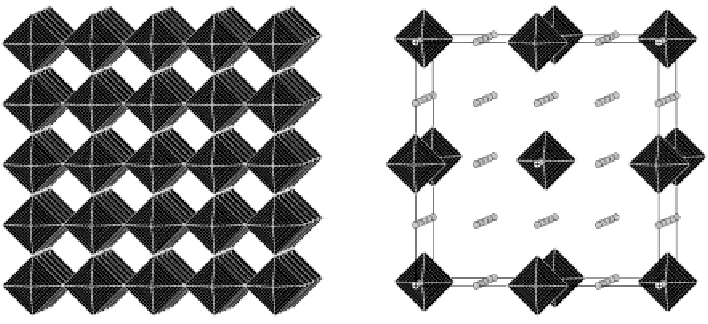

Figure 2. Idealized representation of the Si-O-N network in $Ce_{16}Si_{15}O_6N_{32}$ (right) and the relation to a 4 × 4 × 4 superstructure of the cubic perovskite type (left). The octahedra (four per unit cell) are depicted as closed polyhedra, the tetrahedral centers (56 per unit cell) as grey spheres, and the omitted octahedra (four per unit cell) as spheres marked with a cross.

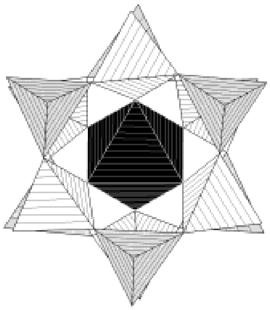

Figure 3. Environment of the SiN_6 octahedra in $Ce_{16}Si_{15}O_6N_{32}$ (view along [111]). Each SiN_6 octahedron is connected to two parallel rings formed from six $Si(O,N)_4$ tetrahedra.

position corresponding to the perovskite structure type (Figure 1).

The SiN_6 octahedra in $Ce_{16}Si_{15}O_6N_{32}$ are connected through corners with two parallel rings each formed from six $Si(O,N)_4$ tetrahedra (Figure 3). Together with further $Si(O,N)_4$ tetrahedra these units form a network structure $^3_\infty[(Si^{[4]}_{14}Si^{[6]}O_6N_{32})^{48-}]$ (Figure 4). According to Pauling's rules[20] in Si-O-N and Si-Al-O-N compounds nitrogen prefers those sites in which the N atoms in comparison with the O atoms are directly bound to the same[29] or a higher number [12, 13, 29] of neighboring Si atoms. Therefore the $Si(O,N)_4$ tetrahedra of the network presumably are Q^3 units, and each of them contains one $O^{[1]}$ atom terminally bound to Si.[*]

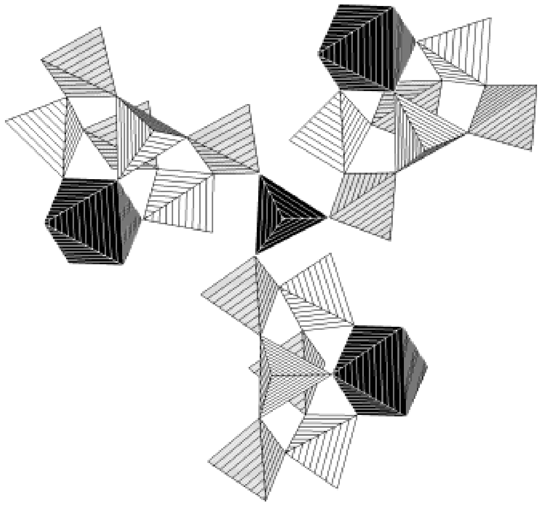

Figure 4. Connection of octahedra and tetrahedra in $Ce_{16}Si_{15}O_6N_{32}$ (view along [$\bar{1}$11]). The octahedron ring units are further connected by $Si(O,N)_4$ tetrahedra (black). Here only one ring per octahedron is depicted.

The bond lengths to the bridging atoms $(Si-(O,N)^{[2]}$ 170.1(8) – 176.8(9) pm) are in a typical range.[1, 2, 10, 12, 13] As expected[21] the respective distances to the terminal atoms in the $Si(O,N)_4$ tetrahedra are shorter (165.2(8) – 171.1(9) pm). Due to the higher coordination number of silicon in the SiN_6 octahedra ($Si^{[6]}$-N: 210.5(8) pm) the Si – N bond lengths are longer than those in SiN_4 tetrahedra ($Si^{[4]}$ – N 164 – 197 pm).[10] Because of the larger ionic radius[22] of N^{3-} these distances are longer than those in SiO_6 octahedra (typical values for $Si^{[6]}$ – O 170 – 184 pm).[1]

In this defect variant the Ce^{3+} ions occupy positions that are comparable to the respective sites in the regular perovskite structure type (Figure 1). The Ce^{3+} ions are octahedrally, eightfold, or tenfold coordinated (Ce ··· (N,O) 232.0(8) – 300.7(8) pm).

Most oxosilicates are constructed from SiO_4 tetrahedra.[1, 23] Accordingly oxygen may be terminally bound to Si ($O^{[1]}$) or it may function as a simple bridge between two Si ($O^{[2]}$, e.g. in quartz SiO_2).[24] In nitridosilicates nitrogen can either be bound to one ($N^{[1]}$), two ($N^{[2]}$), three ($N^{[3]}$), or even four ($N^{[4]}$) neighboring Si.[10] As in oxosilicates, the SiX_4 tetrahedra (X = O, N) in nitridosilicates may be linked through corners but additionally they may also be connected through edges.[10] $Ce_{16}Si_{15}O_6N_{32}$ is the first nitridosilicate with silicon in an octahedral coordination. In analogy to oxosilicates, SiX_6 octahedra (X = O, N) are predominantly expected in high-pressure phases.[1–3] However investigations (e.g. high-pressure sintering, hot-pressing) on Si_3N_4, which is currently the most important nitridic material, gave no indication of a possible increase of the coordination number of silicon from four to six.[11]

On the basis of the results of this work, the occurrence of silicon in an octahedral coordination is anticipated in nitridosilicates, oxonitridosilicates, and oxonitridoaluminosilicates as well as in the glassy phases of the systems Si-O-N and Si-Al-O-N. Furthermore, high-pressure investigations in these systems might reveal several interesting and new compounds.

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

1433-7851/99/3803-0358 $ 17.50+.50/0

Experimental Section

In a typical batch $Si(NH)_2$ (0.69 mmol), Ce (0.76 mmol), and SiO_2 (0.20 mmol) were thoroughly mixed in a glove box under a purified argon atmosphere. The reaction batch then was transferred into a tungsten crucible, and placed into the reactor of a radio frequency (rf) furnace which was inductively heated[25] under a purified N_2 atmosphere (1 bar). During the reaction the crucible was heated to 850 °C within 5 min. After 10 min at this temperature, it was heated to 1540 °C over 3 h and held at this temperature for 1 h. Afterwards the crucible was allowed to cool down to 1200 °C over 53 h and to 900 °C over 15 h. Finally the reaction product was quenched to room temperature. In accordance with the X-ray structure determination, the analytical composition of $Ce_{16}Si_{15}O_6N_{32}$ was confirmed by energy-dispersive X-ray microanalysis (Ce, Si). The absence of hydrogen (N–H) was checked by IR spectroscopy.

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A Paramagnetic Copper(III) Complex Containing an Octahedral $Cu^{III}S_6$ Coordination Polyhedron[**]

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Most inorganic chemistry textbooks[1] comment on the coordination chemistry of copper in the "unusual", that is rare, oxidation state +III with d^8 electron configuration that there is only one *paramagnetic* ($S = 1$) species containing an octahedral coordination polyhedron known, namely $K_3[Cu^{III}F_6]$.[2] On the other hand, a number of diamagnetic, square-planar Cu^{III} complexes have been described and have even been structurally characterized. We report here the synthesis, as well as the molecular and electronic structure of a new paramagnetic Cu^{III} species containing an octahedral $Cu^{III}S_6$ coordination polyhedron.

It is well established that thiolato ligands can lower the Cu^{III}/Cu^{II} redox potential.[3] In principle, they can stabilize high formal oxidation states of a given transition metal ion.

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