Ca[$Si_2O_2N_2$]—A Novel Layer Silicate**

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Dedicated to Professor Martin Jansen
on the occasion of his 60th birthday

Silicates are one of the largest classes of compounds in inorganic chemistry.[1] Most of them are pure oxidic compounds (oxosilicates). SiX_4 tetrahedrons ($X = O$, N) are a typical feature of almost all previously described oxo- and nitridosilicates.[2] They are connected through common corners ($X = O$, N) or edges ($X = N$) and form condensed anionic structures with a wide range of degree of condensation.[1,3]

The degree of condensation κ (i.e. the molar ratio Si/X) of oxosilicates, which can easily be derived from the empirical formula, usually allows a conclusion to be drawn about the dimensionality of the framework of simple oxosilicates: Nesosilicates such as almandine ($Fe_3Al_2[SiO_4]_3$) or zircon ($ZrSiO_4$) contain only non-condensed (isolated) $[SiO_4]^{4-}$ tetrahedrons. Hence, they exhibit the lowest degree of condensation ($\kappa = {}^1/_4$) possible in ordinary silicates. With increasing connectivity of the SiO_4 tetrahedrons the degree of condensation is raised to $\kappa = {}^2/_7$ in disilicates (e.g. in thortveitite ($Sc_2[Si_2O_7]$)), to $\kappa = {}^1/_3$ in ring silicates (e.g. in benitoite ($BaTi[Si_3O_9]$) or in beryl ($Al_2Be_3[Si_6O_{18}]$)) and to $\kappa = {}^2/_5$ in single-layer silicates such as pyrophyllite ($Al_2[Si_4O_{10}(OH)_2]$) or serpentine ($Mg_3[Si_2O_5(OH)_4]$).[1] The highest degree of condensation possible in all known oxosilicates is $\kappa = {}^1/_2$. It can be found in frames of SiO_2 in which all SiO_4 tetrahedrons are connected to each other through their four O vertices. Because of the higher charge of nitridic nitrogen (N^{3-}) in highly condensed nitridosilicates (e.g. $BaYb[Si_4N_7]$, $Ba[Si_7N_{10}]$)[3] and silicon nitride Si_3N_4 itself, degrees of condensation have been observed even within the range ${}^1/_2 < \kappa < {}^3/_4$, which are not accessible in oxosilicates.

During the last few years we have conducted a systematic investigation of new oxonitridosilicates (sions) and oxonitridoaluminosilicates (sialons).[9] Both classes are of considerable significance in materials science due to their extraordinary chemical and thermal stability, and they are of special interest to us as host lattices for rare-earth-doped phosphors.[10]

In the system CaO-SiO_2-Si_3N_4 we recently discovered $Ca[Si_2O_2N_2]$, which was obtained by facile reaction of $CaCO_3$ with Si_3N_4 at 1580 °C in a radio frequency (r. f.) furnace as colorless lath-shaped single crystals (see Experimental Section). The single-crystal X-ray structure analysis[11] of the oxonitridosilicate $Ca[Si_2O_2N_2]$ revealed an unexpected structure: According to the empirical formula and the respective degree of condensation of $\kappa = {}^1/_2$ one would expect a three-dimensional framework structure of corner-sharing SiX_4 entities (i.e. $SiO_{4/2} = SiO_2$) for a silicate such as $Ca[Si_2O_2N_2]$ formed by SiX_4 tetrahedrons ($X = O$, N). However, $Ca[Si_2O_2N_2]$ is a layer silicate composed of $SiON_3$ tetrahedrons of the type Q^3 (Figure 1). The unusual composition of this corrugated layer anion $[Si_2O_2N_2]^{2-}$ originates from the fact that in this compound every N atom—unlike the O atoms in oxosilicates[1]—links three neighboring Si tetrahedron centers ($N^{[3]}$), whereas the O atoms in $Ca[Si_2O_2N_2]$ are exclusively bonded terminally to Si atoms ($O^{[1]}$). In structures of oxosilicates that consist of SiO_4 tetrahedrons, oxygen is either bonded terminally to a single Si atom ($O^{[1]}$) or bridges two Si atoms ($O^{[2]}$). In contrast, in nitridosilicates $N^{[3]}$ connections are observed frequently[3] and, moreover, even ammonium-like $N^{[4]}$ bridges have been found.[12]

Owing to their very similar scattering factors the direct experimental differentiation between O and N in the $[Si_2O_2N_2]^{2-}$ framework is impossible with X-ray methods.

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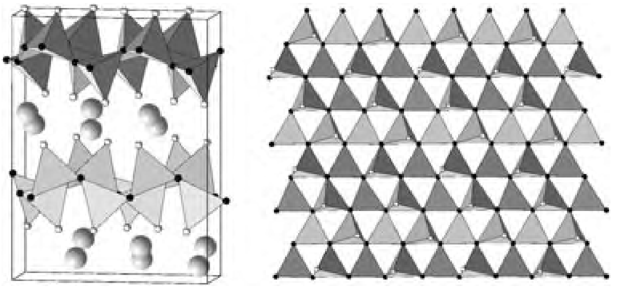

Figure 1. Crystal structure of Ca[$Si_2O_2N_2$]; left: view along [100]; right: view perpendicular to a layer of tetrahedrons along [010] (Ca^{2+} light gray, O^{2-} white, N^{3-} black).

^{29}Si solid-state NMR investigations on Ca[$Si_2O_2N_2$] revealed a group of closely adjoining signals in the range from $\delta = -50$ to -54 ppm, which is typical for chemical shifts of Q^3-type $SiON_3$ tetrahedrons.[9,13] According to the calculations of the Madelung part of the lattice energy (MAPLE)[14] in Ca[$Si_2O_2N_2$] a complete O/N-ordering seems to be very likely. Accordingly, the O atoms are bonded terminally to the Si atoms ($O^{[1]}$), and each N atom links three Si atoms within the layers ($N^{[3]}$). This result agrees well with Pauling's rules and reflects our experiences with sions and sialons, in which nitrogen more so than oxygen prefers to adopt those sites that offer higher connectivities with respect to the tetrahedron centers.[9] Assuming this ordering, we calculated the following partial MAPLE values for Ca[$Si_2O_2N_2$]: O^{2-}: 2272–2404, N^{3-}: 6125–6353, Ca^{2+}: 2115–2214, and Si^{4+}: 9281–9555 kJ mol^{-1}. The values fit well into the typical ranges for these ions.[9] The analysis of the interatomic distances Si–O (159–162 pm) and Si–N (168–178 pm) as well as the exclusive presence of $SiON_3$ tetrahedrons confirm the described O/N ordering, since a clear difference in bond lengths Si–N > Si–O was found for all $SiON_3$ entities.[15]

The Ca^{2+} ions are surrounded by six O atoms to form a distorted trigonal prism, which is capped by a single N atom. The shortest distances in the coordination spheres of Ca^{2+} are those to the O atoms (229–241 pm); these distances agree well with the sum of the ionic radii.

The structure of Sr[$Si_2O_2N_2$] is closely related, and exhibits an analogous O/N ordering. This has been confirmed experimentally by the luminescence of the doped compound Sr[$Si_2O_2N_2$]:Eu^{2+} in which the emission wavelength and the width of the emission band allow the unequivocal conclusion that the Eu^{2+} ions (and thus the Sr^{2+} ions) are predominantly coordinated by O atoms that are terminally bonded to the Si atoms inside the $SiON_3$ tetrahedrons.[16]

The [$Si_2O_2N_2$]$^{2-}$ layers in Ca[$Si_2O_2N_2$] are assembled from condensed "dreier" rings (Figure 1), a building unit which is unknown in purely oxidic layer silicates and very rare in higher condensed oxosilicates.[1] Similar layers built up of condensed dreier rings have also been found in other nitridosilicates (e.g. M^{II}_2[Si_5N_8] with M = Ca,[17] Sr and Ba[18] or Ba[Si_7N_{10}][19]). However, in these compounds the layers are connected by further SiN_4 tetrahedrons to form highly condensed framework structures and, moreover, these layers differ topologically by the specific sequence of their vertices pointing upwards (U) and downwards (D) with respect to the layer plane.[1] Within the horizontal rows of tetrahedrons shown in Figure 1 the strictly alternating sequence UDUD… is found in Ca[$Si_2O_2N_2$], whereas, for instance, the layers in M^{II}_2[Si_5N_8] and Ba[Si_7N_{10}] exhibit more complex patterns.[17–19] Although in principle there is an arbitrary number of completely different sequences to form such layers from condensed dreier rings, topologically very similar layers with the same sequence UDUD… were found in the crystal structure of the mineral sinoite (Si_2N_2O) (Figure 2).[20] In Sr[$Si_2O_2N_2$] topologically identical layers are present. The structural relationship between Si_2N_2O and Sr[$Si_2O_2N_2$] can therefore be illustrated by an imaginary topochemical intercalation of SrO into sinoite. The feasibility of performing this intercalation experimentally is currently being investigated. Furthermore, it will be interesting to see whether the M^{2+} ions in Ca[$Si_2O_2N_2$] and Sr[$Si_2O_2N_2$] can undergo ion exchange.

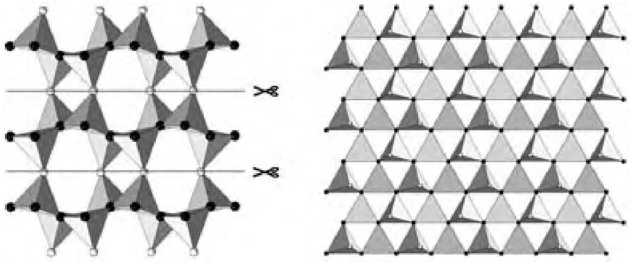

Figure 2. Crystal structure of the mineral sinoite Si_2N_2O; left: view along [001]. Cutting the structure in the indicated manner leads to layers topologically similar to those in Ca[$Si_2O_2N_2$]. Accordingly, the O atoms are bonded terminally to the Si atoms ($O^{[1]}$), and the N atoms are bridged threefold within the layers as $N^{[3]}$; right: view along [100]. The layers also show the sequence UDUD… with regard to the alignment of the tetrahedron vertices (O).

Experimental Section

In a typical experiment $CaCO_3$ (1.0 mmol; Merck, 99.95 %) was thoroughly mixed with amorphous Si_3N_4 (2.1 mmol; obtained by thermal decomposition of Si$(NH)_2$)[9b] in a glove box (Unilab, MBraun, $O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm) under an argon atmosphere using an agate mortar. The mixture was then heated in a tungsten crucible using a r.f. furnace[9b] under an N_2 atmosphere (dried over KOH/silica gel/molecular sieve (4 Å)/P_4O_{10} and activated BTS catalyst). The reaction mixture was heated to 1000 °C at a rate of 40 °C min^{-1} and subsequently to 1200 °C over 15 min. During this first reaction step reactive CaO was initially formed by gas loss, which was then allowed to react quantitatively with Si_3N_4 by further heating to 1580 °C (heating rate 1.1 °C min^{-1}) over 16 h to yield single-phase Ca[$Si_2O_2N_2$]. Elemental analysis (double determinations by the Mikroanalytisches Labor Pascher, Remagen) calcd (%) for Ca[$Si_2O_2N_2$] (156.28); Ca 25.6, Si 35.9, O 20.5, N 17.9; found: Ca 25.6, Si 36.1, O 21.8, N 17.1.

Large single crystals suitable for X-ray structure analysis were obtained by raising the temperature up to 1900 °C at which the thermal decomposition of the reaction product takes place. A theoretical powder diffraction pattern calculated on the basis of the single-crystal data shows excellent agreement with a measured powder diffraction pattern for Ca[Si$_2$O$_2$N$_2$] with respect to the position and intensity of all observed reflections.

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[2] In silicates, higher coordination numbers of Si (CN $>$ 4) are found only in a few cases, mostly high-pressure phases,[1,4,5] for example, the rutile-type SiO$_2$ high-pressure polymorph stishovite, the perowskite-type (Mg,Fe)SiO$_3$ that occurs in the deeper mantle of the earth or the hollandite-analogous CaAl$_2$Si$_2$O$_8$.[4] At lower pressures a few silicates can be obtained that contain both SiO$_6$ octahedrons and SiO$_4$ tetrahedrons (e.g. K$_2$Si$_4$O$_9$,[6] BaSi$_4$O$_9$,[7] and Na$_{1.8}$Ca$_{1.1}$Si$_6$O$_{14}$[8]).

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