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$(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ ($x \approx 0.24$, $y \approx 0.18$, $z \approx 0.19$) – A Novel Sialon with a Highly Condensed Silicate Framework

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$(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ ($x \approx 0.24$, $y \approx 0.18$, $z \approx 0.19$) was obtained by high-temperature synthesis (1650 °C – 1700 °C) using $CaSiAlN_3$, Si_3N_4, AlN, SiO_2, and Sr_2N as starting materials. The crystal structure [*Imm*2 (no. 44), a = 20.6973(6), b = 10.7292(4), c = 4.8881(2) Å, Z = 2, $R1$ = 0.0326, $wR2$ = 0.0735] was determined from single-crystal X-ray data using dual space methods and confirmed for the bulk material by Rietveld refinement on X-ray powder diffraction data. The structural results are corroborated by lattice energy calculations (MAPLE). The compound is the first representative of a novel silicate framework. The anionic part of the structure is built up from highly-condensed *dreier* ring layers extending parallel (100), which are interconnected by common N and O atoms. In the resulting voids of this framework, there are three different cation sites, which are coordinated by six, eight, and twelve nitrogen and oxygen atoms, respectively. The largest one is fully occupied by Sr atoms, whereas the other two sites host Sr and Ca atoms or vacancies, respectively.

Introduction

In the last years, a number of (oxo)nitridosilicates [e.g. $M_2Si_5N_8$, $MSi_2O_2N_2$ (M = Ca, Sr, Ba)] have emerged as host lattices for highly efficient rare-earth doped luminescent materials (so-called phosphors) applied in phosphor-converted (pc)LEDs. These materials stand out due to their remarkable thermal stability, quantum efficiency, chemical inertness, and environmental compatibility.[1–10]

Coupled substitution N/O and Si/Al in (oxo)nitridosilicates leads to oxonitridoaluminosilicates (so-called sialons). Upon doping with rare-earth ions (e.g. Eu^{2+}) sialons have been discussed as phosphors for white-light (pc)LEDs as well. In this context, investigations on the luminescence properties of $MAlSi_5O_2N_7$:Eu^{2+} (M = Sr, Ba), $SrSiAl_2O_3N_2$:Eu^{2+} and $Sr_5Al_{5+x}Si_{21-x}N_{35-x}O_{2+x}$:$Eu^{2+}$ ($x \approx 0$), as well as of Eu^{2+}-doped α- and β-sialons and related materials have been carried out.[11–16] The flexible charge of the anionic substructure allows for fine-tuning of the optical properties of sialon host lattices due to the considerable variety of possible cation substitutions in these compounds. Sialons thus exhibit a very broad and versatile structural chemistry.

There is a number of sialons deriving from the respective (oxo)nitridosilicates by coupled substitution: e.g. SrEr[$SiAl_3O_3N_4$][17] (isotypic to MYb[Si_4N_7]; M = Sr, Ba),[18,19] $Nd_3[Si_5AlON_{10}]$[20] (isotypic to $Ln_3Si_6N_{11}$; Ln = La, Ce, Pr, Nd, Sm),[21–23] $Y_2Si_{3-x}Al_xO_{3+x}N_{4-x}$[24] (isotypic to $Y_2Si_3O_3N_4$),[25–28] and $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$)[29] (isotypic to $BaSi_6N_8O$).[30] Whereas other sialons are isostructural to oxosilicates, as AlN can replace SiO without changing the charge balance, several representatives of this class of compounds exhibit unique structure types (e.g. $Sr_{10}Sm_6Si_{30}Al_6O_7N_{54}$, $Sr_3Ln_{10}[Si_{18}Al_{12}O_{18}N_{36}]$; Ln = Ce, Pr, Nd).[31,32] The Si and Al atoms in these compounds are frequently disordered [e.g., $MLn(Si_{4-x}Al_xO_xN_{7-x})$ (M = Eu, Sr, Ba; Ln = Ho–Yb)],[33] however, ordered anionic structures have been observed as well (e.g. $Sr_{10}Sm_6Si_{30}Al_6O_7N_{54}$).[31] The same is true concerning the O/N ordering.

Compared to the oxosilicates, the formal replacement of O by N, yields more or less condensed network structures made up of $Si(O,N)_4$ tetrahedra and gives rise to manifold structural possibilities of (oxo)nitrido(alumino)silicates. While oxygen in classical oxosilicates occurs mostly as terminal $O^{[1]}$ atoms or is simply bridging two neighboring Si atoms ($O^{[2]}$), nitrogen can also bridge three ($N^{[3]}$) or even four ($N^{[4]}$) tetrahedra centers, so that new building blocks become possible. For example, various highly-condensed *dreier* ring[34] layers with $N^{[3]}$ atoms are characteristic structural elements in (oxo)nitrido(alumino)silicates. Such layers have been observed both in layered structures like $MSi_2O_2N_2$ (M = Ca, Sr, Ba, Eu)[35–38] or as part of frameworks [e.g., $M_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ (M = Sr, Ba),[29,39,40] $Ba_2AlSi_5N_9$,[41] $Sr_5Al_{5+x}Si_{21-x}N_{35-x}O_{2+x}$ ($x \approx 0$)[16]]. This il-

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lustrates that (oxo)nitrido(alumino)silicates exhibit a significantly broader spectrum for the degree of condensation κ [i.e., the molar ratio (Si,Al):(O,N)] that can vary in the range $1:4 \leq \kappa \leq 3:4$. Contrary, classical oxosilicates are restricted to $1:4 \leq \kappa \leq 1:2$,[42,43] because larger values of κ would result in cationic silicate substructures which has been never observed so far.[44]

In this contribution, we report on synthesis and crystal structure of the sialon $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ ($x \approx 0.24$, $y \approx 0.18$, $z \approx 0.19$), which exhibits a novel silicate framework.

Results and Discussion

Synthesis and Sample Characterization

The novel sialon $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ ($x \approx 0.24$, $y \approx 0.18$, $z \approx 0.19$) was synthesized according to equation (1) at temperatures between 1650 and 1700 °C in a radio-frequency furnace under nitrogen atmosphere. The product was obtained as colorless, air- and water resistant crystals. The synthesis was not optimized with respect to the yield or purity of the samples. By-products include compounds like $SrAlSi_4N_7$[45,46] or $SrSiAl_2N_2O_3$.[47]

$$1.72\ Sr_2N + 1.07\ CaAlSiN_3 + 1.81\ AlN + 2.43\ SiO_2 + 3.21\ Si_3N_4 + 0.28\ N_2 \rightarrow Sr_{3.44}Ca_{1.07}Si_{13.12}Al_{2.88}N_{20.14}O_{4.87} \quad (1)$$

As the crystals of the title compound exhibit a characteristical lamina shape, they can easily be distinguished from the by-products. Thereby, it was possible to mechanically separate crystals of the novel sialon in order to yield small single-phase amounts of the product. The purity of these samples was confirmed by Rietveld refinement of X-ray powder diffraction data (cf. Figure 1).

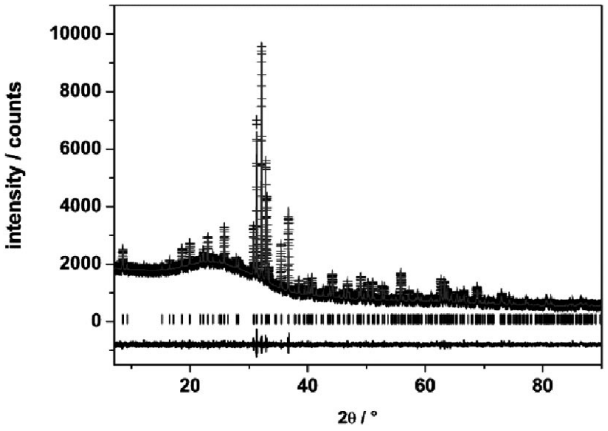

Figure 1. Observed (crosses) and calculated (line) X-ray powder diffraction pattern as well as difference profile for the Rietveld refinement of $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ ($x \approx 0.24$, $y \approx 0.18$, $z \approx 0.19$). The vertical bars indicate possible peak position.

The composition of crystals obtained in several experiments differs slightly. Such variations have frequently been observed for sialons (e.g. in $MLn[Si_{4-x}Al_xO_xN_{7-x}]$)[33] due to the interchangeability of Si/O and Al/N, which does not affect charge neutrality. Thus, the compound can be assumed to exhibit a certain range of homogeneity. Therefore, the composition of the title compound was analyzed via EDX on selected, similar crystals from the same reaction batch as the crystal chosen for crystal structure determination. These analyses yielded a composition that agrees well with that obtained from the structure refinement which, however, is based on the experimentally determined Si/Al and Sr/Ca atomic ratios [calcd. for $x = 0.24$, $y = 0.18$ and $z = 0.19$, i.e., $Sr_{3.44}Ca_{1.07}Si_{13.12}Al_{2.88}N_{20.14}O_{4.87}$ (atom-%): Sr 7.6, Ca 2.4, Al 6.3, Si 28.8, N 44.2, O 10.7; found (atom-%): Sr 7.9(8), Ca 2.4(3), Al 6.4(6), Si 30(3), N 41(5), O 12(2)].

Crystal Structure Determination

The orthorhombic Laue symmetry of the diffraction pattern corresponds to the metrics of a body centered lattice. As no systematic absences indicating glide planes or screw axes were observed, all symmorphic orthorhombic space groups with *I* lattices were taken into account. However, the structure could not be solved by conventional direct methods or simple Patterson techniques. A solution in space group *I*1 (assuming pseudomerohedral twinning) was achieved by means of the dual space approach.[48] After an approximate refinement, additional symmetry was found using PLATON.[49] The true space group turned out to be *Imm*2. The non-centrosymmetric crystals occur as balanced inversion twins, which were taken into account in the refinement (full-matrix least-squares calculations on F^2).[50]

The structure of the sialon shows a framework consisting of vertex-sharing tetrahedra. As Si and Al cannot be distinguished by X-ray diffraction and Si/Al disorder is quite common in sialons, the atomic ratio Si/Al was fixed at a value of 82/18 according to the chemical analysis. The Si/Al disorder can also be expected due to the similar surrounding and connectivity of the tetrahedral centers. The framework contains three sites that are suitable for alkaline earth ions. Although these positions are not very close to each other and can, in principle, be simultaneously occupied, the scattering density yields Ca concentrations far beyond the error limits of the chemical analysis on these sites if full occupancy by either Sr or Ca is assumed. Thus, the atomic ratio Sr/Ca, which could be reliably determined by EDX spectroscopy, was fixed according to the analysis and additional vacancies were allowed in the refinement. Thereby also the atomic ratio of alkaline earth ions and tetrahedral centers (Si+Al) refined to a quite reasonable value. It turned out that one site is exclusively occupied by Sr and the other two exhibit Ca, Sr, and vacancies. As the compound is transparent, charge neutrality is required. The three-bridging light atom sites were assumed to be exclusively occupied with N atoms according to Pauling's rules and concluding from our experience during structure determination of many sions and sialons. The charge neutrality was provided by accordingly constraining the atomic ratio

O/N on all other light atom sites. All atom sites could be refined anisotropically.

In order to corroborate the assumed O/N distribution, calculations of the Madelung part of lattice energy (MAPLE)[52,53] were performed. The total MAPLE value (276735 kJ mol^{-1}) for the structure model described above is in excellent agreement with the sum of the total MAPLE values of 3.44 $SrSiN_2$ + 1.07 $CaSiN_2$ + 2.88 AlN + 2.06 Si_3N_4 + 2.435 SiO_2 (278108 kJ mol^{-1}) [cf. Equation (1)], the difference Δ = 0.49% is within the typical error range of MAPLE calculations. The partial MAPLE values are also within the typical ranges. However, the assumption that terminal light atom positions are exclusively occupied by O yields equally satisfactory results.

Crystal Structure Description

$(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ is a novel framework sialon. The anionic part of the structure is built up from highly condensed *dreier* ring[34] layers extending parallel (100), which are interconnected via common (N,O) atoms (cf. Figure 2). These layers consist exclusively of vertex-sharing $(Si,Al)(N,O)_4$ tetrahedra. The vertices that interconnect the layers exhibit an unique up-down-sequence with respect to the layer plane. Tetrahedra with vertices pointing into the same direction form rings that are condensed along [001] and separated by chains of tetrahedra along [010] with vertices in the opposite direction (cf. Figure 2, b). Although highly condensed *dreier* ring layers occur frequently in (oxo)nitridosilicates, the configuration in $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ has not been observed so far. It can be interpreted in terms of chemical twinning. If the layer of the title compound would be exclusively built up of sections 1 or 2 (cf. Figure 2, b), the layer would be identical with the ones in $MSi_2O_2N_2$ (M = Sr, Ba, Eu),[36–38] which consists of 2–2-zig-zag lines.

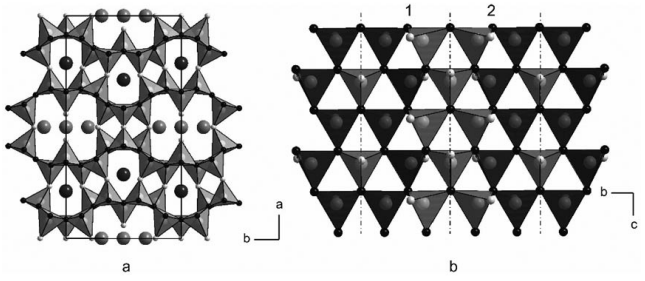

Figure 2. a) Structure of $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$, projection along [001]; the $(Si,Al)(N,O)_4$ tetrahedra are shown as well as the unit cell. (Sr dark gray, Sr/Ca gray, N black, N/O light gray). b) Highly condensed silicate layer (projection along [100]). For clarity, tetrahedra with vertices up are depicted light gray, those with vertices down dark gray. (N black, N/O light gray, Si/Al gray).

A projection of the structure of $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ along [010] (cf. Figure 3, a) illustrates clearly that the framework is non-centrosymmetric. It can be formally separated into a sequence of identical silicate layers extending parallel (001), and the vertices ($N^{[3]}$ atoms) interconnecting the layers all point into the same direction (cf. Figure 3, b). These layers are built up of *vierer*, *fünfer*, *siebener*, *achter* and *zehner* rings.[34] There are two layers per unit cell which are shifted against each other by (0.5 0.5 0.5).

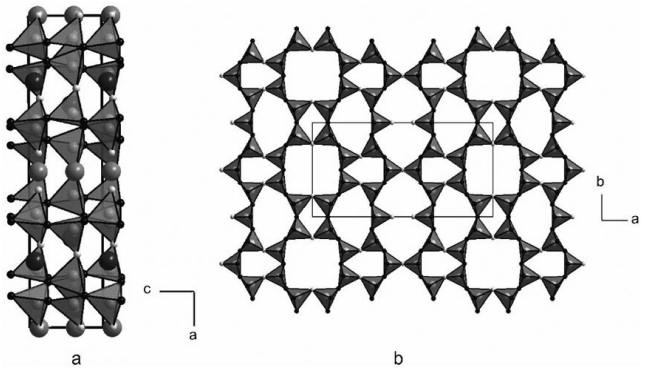

Figure 3. a) Structure of $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$, projection along [010]; the $(Si,Al)(N,O)_4$ tetrahedra are shown as well as the unit cell (Sr dark gray, Sr/Ca gray, N black, N/O light gray). b) Silicate layer built up from different kinds of rings (projection along [001]; N black, N/O light gray, Si/Al gray).

For an overview of the frequency of different ring sizes in the framework, the cycle-class sequence of $(Si,Al)_n(N,O)_n$ rings was calculated using the method given by Klee.[54–57] The result of the calculation is summarized in Table 1.

In the cavities of the silicate framework, there are three crystallographically independent cation sites with coordination numbers six, ten, and twelve, respectively (cf. Figure 4). The largest one is exclusively occupied by Sr^{2+} ions, whereas the both other sites exhibit Sr^{2+} and Ca^{2+} ions, as well as vacancies. The coordination numbers were derived by ECON calculations.[58] The distance between these both mixed occupied sites (3.177 Å) is not the reason for the vacancies, as even shorter distances could be observed in other well characterized calcium-containing nitridosilicates with fully occupied cation sites (e.g.$CaSiN_2$[59]: > 3.05 Å; $Ca_5Si_2N_6$:[60] > 3.17 Å).

The distances Sr–(N,O) are between 2.627(3) and 3.171(4) Å for 12-fold coordination. Thereby, some distances are slightly shorter than the sum of the ionic radii (Sr–O: 2.82 Å, Sr–N: 2.90 Å).[61] However, even shorter dis-

Table 1. Cycle-class sequences for the crystal structure of $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$.

	Frequency of cycle classes											
$(Si,Al)_n(N,O)_n$	n = 1	2	3	4	5	6	7	8	9	10	11	12
$Sr_{3.44}Ca_{1.07}Si_{13.12}Al_{2.88}N_{20.14}O_{4.87}$	–	0	16	9	68	117	474	1369	4734	16109	57412	207366

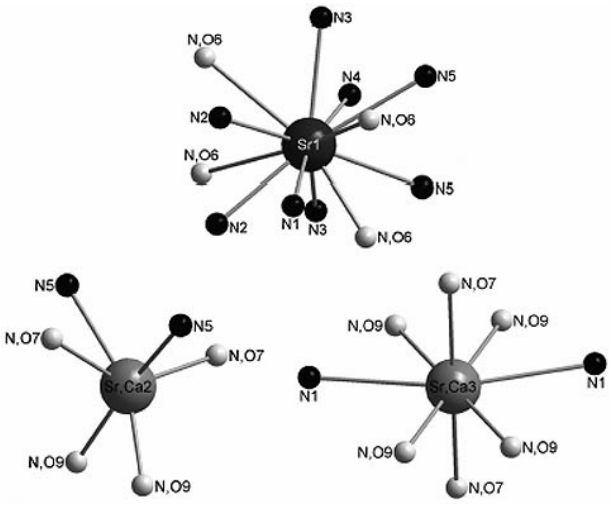

Figure 4. Coordination spheres of the three crystallographically independent cation sites in $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ (Sr dark gray, Sr/Ca gray, N black, N/O light gray).

tances have been reported for other oxonitridoaluminosilicates [e.g., $Sr_5Al_{5+x}Si_{21-x}N_{35-x}O_{2+x}$ ($x \approx 0$):[16] 2.45–3.44 Å; $SrSiAl_2O_3N_2$:[47] 2.50–3.18 Å; $Sr_{10}Sm_6Si_{30}Al_6O_7N_{54}$:[31] 2.45–3.33 Å]. As expected, some distances (Sr,Ca)–(N,O) [2.388(2)–3.349(5) Å] are shorter than the respective values for Sr–(N,O). Compared with the sums of the ionic radii (Ca–O: 2.36 Å, Ca–N: 2.46 Å, Sr–O: 2.54 Å, Sr–N: 2.64 Å),[61] the values are in excellent agreement with the values for Ca^{2+} ions and slightly shorter than the values for Sr^{2+}. For other oxonitridoaluminosilicates the distances Ca–(O,N) are in the same range [$Ca_7Si_{4-x}Al_xN_{10-x}O_x$ ($x \approx 0.5$):[62] 2.345(2)–2.869(2); $Ca_x(Si,Al)_{12}(N,O)_6$:[63] 2.36(1)–2.694(4) Å] and the distances Sr–(O,N) are slightly longer.

The disorder on the mixed occupied cation sites lead to some rather oblate displacement ellipsoids, e.g. for the (Sr,Ca)(3) site, which probably exhibits a varying local offset from its special position. This disorder also influences the averaged distance (Si,Al)–(O,N),[1] which is slightly shorter than similar bond lengths (Si,Al)–(N,O)[1] in other oxonitridosilicates [$La_{16}(Si_8N_{22})(SiON_3)_2$:[64] 1.689(5)–1.743(8) Å; $Ln_{10}(Si_{10}O_9N_{17})X$:[65] 1.664(4)–1.709(7) Å (Ln = Ce, X = Br), 1.666(3)–1.713(5) Å (Ln = Nd, X = Br), 1.665(3)–1.718(5) Å (Ln = Nd, X = Cl)]. As expected, the bond lengths (Si,Al)–(O,N)[2] [1.609(2)–1.765(2) Å] and (Si,Al)–N[3] [1.708(5)–1.817(2) Å] depend on the connectivity of the N and O atoms, respectively. These distances are in the typical range for such kinds of bonds as comparable values have been observed for other (oxo)nitridosilicates [e.g., $BaSi_6N_8$:[66] Si–N[2] 1.6255(3) Å, Si–N[3] 1.7058(3)–1.7640(3) Å; $BaSi_6N_8O$:[30] Si–O[2] 1.591(2) Å, Si–N[2] 1.674(2) Å, Si–N[3] 1.716(3)–1.780(2) Å; $Sr_2Si_5N_8$:[67] Si–N[2] 1.65–1.69 Å, Si–N[3] 1.74–1.79 Å; $Ba_2Nd_7Si_{11}N_{23}$:[68] Si–N[2] 1.67(1)–1.754(12) Å].

The bond angles (N,O)–(Si,Al)–(N,O) are between 100.92(16) and 116.49(18) °, which is reasonably close to the regular tetrahedral angle. Concerning the angles (Si,Al)–(N,O)[2]–(Si,Al) [128.2(3)–146.2(5) °] and (Si,Al)–N[3]–(Si,Al) [111.30(17)–126.22(19)°], the reported values for other nitridosilicates are approximately in the same range [$BaSi_6N_8O$:[30] Si–N[3]–Si 112.0(2)–127.3(2)°, $Ba_2Nd_7Si_{11}N_{23}$:[68] Si–N[2]–Si 117.9(4)–180°].

Comparison with $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$)

The so-called S-phase $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$) is a well-known sialon, which also crystallizes in the same orthorhombic space group *Imm*2.[29] Its unit cell contains two highly condensed *dreier* ring[34] silicate layers parallel (010) (cf. Figure 5), in contrast to the title compound, which exhibits four layers extending parallel (100). In both compounds, the layers are interconnected via common N and O atoms. The configuration of these layers is similar in both compounds as it contains the same chains of tetrahedra, however, in $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$) these are not separated by other structural elements but directly connected to similar chains with vertices in the opposite direction (cf. Figure 5, b).

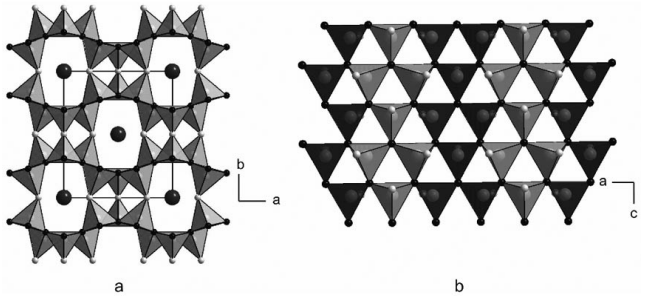

Figure 5. a) Structure of $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$), projection along [001]; the $(Si,Al)(N,O)_4$ tetrahedra are shown as well as the unit cell. (Sr dark gray, N black, N/O light gray). b) Highly condensed silicate layer (projection along [010]). For clarity, tetrahedra with vertices up are depicted light gray, those with vertices down dark gray (N black, N/O light gray, Si/Al gray).

Due to the similarity of the highly condensed silicate layers, the latter show related interconnection schemes for both compounds. Pairs of condensed *dreier* rings form characteristic units of six tetrahedra, which are interconnected via common vertices to catenae. The crystal structure of $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$) is built up exclusively from these units, whereas further building blocks (four interconnected tetrahedra also interconnected to catenae) are included in $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$.

Viewing along [100], the framework of $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$) is built up of two equivalent silicate layers per unit cell, which are interconnected via common N atoms (cf. Figure 6, a). A similar constitution of the framework could also be observed for $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$, viewing along [010]. In both structures, the layers are shifted against each other as imposed by the *I* centering. However, the rings of these less condensed layers differ in the occurring ring sizes. The corresponding layer of $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ (cf. Figure 3,

b) is built up of *vierer*, *fünfer*, *siebener*, *achter*, and *zehner* rings, whereas the layer of $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$) contains *vierer*, *sechser*, and *achter* rings (cf. Figure 6, b).

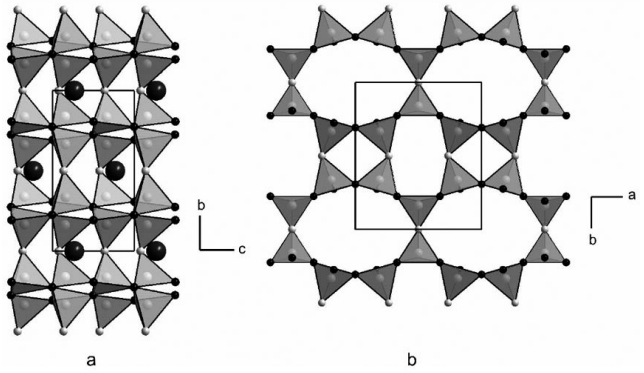

Figure 6. a) Structure of $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$), projection along [100]; the $(Si,Al)(N,O)_4$ tetrahedra are shown as well as the unit cell. (Sr dark gray, N black, N/O light gray). b) Silicate layer built up of different kinds of rings (projection along [001]; N black, N/O light gray, Si/Al gray).

In contrast to the crystal structure of the title compound, which contains three crystallographically independent cation sites, the framework of $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$) hosts only one Sr^{2+} site, which is surrounded by eight light atoms with distances between 2.660(5) and 3.219(7) Å. This range approximately corresponds to the bond length Sr(1)–(N,O) in the title compound.

Conclusions

With the synthesis of $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ ($x \approx 0.24$, $y \approx 0.18$, $z \approx 0.19$) a further sialon could be obtained, which representes a novel silicate framework type. The latter is built up of highly condensed silicate layers interconnected via common (N,O) atoms. Moreover, this contribution demonstrates with the comparison of the crystal structure with $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ ($x \approx 2$) that only a small difference in the up-down-sequence of a layer leads to a novel silicate framework. Thereby, numerous further novel frameworks in (oxo)nitrido(alumino)silicates are supposable.

Experimental Section

Syntheses

Synthesis of Sr_2N: For the synthesis of Sr_2N,[69–71] Sr (A.B.C.R., Karlsruhe, 99.95%, small pieces) was filled in a silica tube lined with a tungsten foil (0.1 mm thickness). Under a continuous stream of pure nitrogen, the tube was heated to 800 °C with a rate of 5 °C min^{-1}, and this temperature was kept for 4 h. Finally, the furnace was switched off and the tube cooled down to room temperature. Thereby, Sr_2N was obtained next to Sr_4N_3[72] as by-product, which was confirmed by X-ray powder diffraction measurements.

Synthesis of $CaSiAlN_3$: $CaSiAlN_3$[73] was synthesized using Ca_3N_2 (Alfa Aesar, Karlsruhe, 99%), Si_3N_4 (UBE Industries Ltd, Tokyo, SN-E10, 98%), and AlN (Tokuyama, Tokyo, 99%) in stoichiometric ratio as starting materials. After grinding the reactants in a ball mill under cyclohexane, the mixture was heated to 1500 °C under a H_2/N_2 (5%/95%) atmosphere with a rate of about 150 °C/h. This maximum temperature was kept for 6 h. The samples contain $CaSiAlN_3$ and small amounts of by-products like the unreacted starting material AlN, for example, which was confirmed by X-ray powder diffraction measurements.

Synthesis of $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ ($x \approx 0.24$, $y \approx 0.18$, $z \approx 0.19$): For the synthesis of $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ ($x \approx 0.24$, $y \approx 0.18$, $z \approx 0.19$), 0.25 mmol (47.3 mg) of Sr_2N, 0.17 mol (23.6 mg) of $CaSiAlN_3$, 1.00 mmol (40.8 mg) of AlN (Tokuyama, Tokyo, 99%), 0.42 mmol (25.1 mg) of SiO_2 (Degussa, Frankfurt, ≥99.8%), and 0.56 mmol (78.6 mg) α-Si_3N_4 (Aldrich Chemical Co., Milwaukee, > 99.9%) were mixed in an agate motar and filled in a tungsten crucible under argon atmosphere in a glove box (Unilab, MBraun; $O_2 < 1$ ppm, $H_2O < 1$ ppm).

Under purified N_2, the crucible was heated to 750 °C within 10 min in the reactor of a radio-frequency furnace[17] before the temperature was increased to 1650 or 1700 °C with a rate of about 8 °C/min, respectively. This maximum temperature was kept for 5 h. Subsequently, the crucible was cooled down to 750 °C with a rate of about 95 °C/h before quenching to room temperature by switching off the furnace. The samples contains $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ ($x \approx 0.24$, $y \approx 0.18$, $z \approx 0.19$) as colorless, air- and water resistant crystals in addition to by-products such as $SrAlSi_4N_7$[45,46] or $SrSiAl_2N_2O_3$.[47]

Chemical Analyses: Single crystals were examined by energy dispersive X-ray analysis using a Jeol JSM 6500F scanning electron microscope equipped with an EDX detector (Oxford Instruments, model 7418). As large flat faces of lamina-shaped crystals were accessible, the analyses showed excellent reproducibility. Results from 7 point analyses were averaged.

Single-Crystal X-ray Analysis: Single crystals were initially examined by Laue photographs recorded on a Buerger camera equipped with an image plate system (Fuji BAS-1800). Intensity data were collected using a Nonius Kappa-CCD diffractometer with graded multilayer X-ray optics. An absorption correction based on the intensities of equivalent reflections[51] was applied. The refinement is discussed above. Crystallographic data and details of the data collection are listed in Table 2. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-420495 as well as the names of the authors and citation of the paper (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de).

X-ray Powder Diffraction: X-ray powder diffraction data were collected on a STOE STADI P diffractometer [Cu-$K_{\alpha 1}$ radiation, Ge(111) monochromator] in Debye–Scherrer geometry. For the measurement, the sample was finely ground and enclosed in a glass capillary with 0.1 mm diameter. For pattern fitting (LeBail algorithm) and Rietveld refinement, the GSAS program package[74] was used. Thereby, the result of the single-crystal X-ray analysis was chosen as starting model. The isotropic displacement parameters for all atoms were constrained to be equal and the site occupancies for the mixed occupied positions (Ca, Sr), (Si,Al), and (N,O) were fixed to the values of the single-crystal analysis. The bond lengths agree with the values determined by the single-crystal analysis within on average 2.5 σ.

Table 2. Crystal data and refinement details of $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ ($x \approx 0.24$, $y \approx 0.18$, $z \approx 0.19$). Standard deviations are given in parentheses.

Formula	$Sr_{3.44}Ca_{1.07}Si_{13.12}Al_{2.88}N_{20.14}O_{4.87}$
Molar mass [g mol^{-1}]	1150.79
Crystal system	orthorhombic
Space group	*Imm*2 (no. 44)
Cell parameters [Å]	a = 20.6973(6)
	b = 10.7292(4)
	c = 4.8881(2)
Cell volume [Å^3]	1085.48(7)
Formula units per cell	2
X-ray density [g cm^{-3}]	3.521
Absorption coefficient [mm^{-1}]	9.605
F(000)	1106
Crystal size [mm^3]	0.13 × 0.03 × 0.01
Diffractometer	Kappa CCD
Radiation	Mo-K_α (λ = 0.71073 Å)
Temperature [K]	293(2)
θ Range [°]	3.5–32.5
Measured reflections	9548
Independent reflections	1971
Absorption correction	semi-empirical[51]
Refined parameters	128
GOF	1.051
R values [$I > 2\sigma(I)$]	R_1 = 0.0326, wR_2 = 0.0735
All data	R_1 = 0.0405, wR_2 = 0.0775
Max./min. residual electron density [e Å^{-3}]	1.315/–1.590

Supporting Information (see also the footnote on the first page of this article): The atomic coordinates, equivalent and anisotropic displacement parameters, and site occupancy factors of $(Sr_{1-x}Ca_x)_{(11+16y-25z)/2}(Si_{1-y}Al_y)_{16}(N_{1-z}O_z)_{25}$ ($x \approx 0.24$, $y \approx 0.18$, $z \approx 0.19$) as well as selected bond length and angles are available as supporting information. Furthermore, the crystallographic data and details of the Rietveld refinement are summarized there.

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