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High-temperature synthesis, single-crystal X-ray and neutron powder diffraction, and materials properties of $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd)—novel sialons with an ordered distribution of Si, Al, O, and N

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The novel oxonitridoaluminosilicates (sialons) $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) were obtained by the reaction of the respective lanthanide metals with $Si(NH)_2$, $SrCO_3$, and AlN using a radiofrequency furnace at temperatures between 1550–1650 °C. The crystal structures of the isotypic sialons were determined by single-crystal X-ray investigations ($Sr_3Ce_{10}Si_{18}Al_{12}O_{18}N_{36}$: $I\bar{4}3m$, $Z = 2$, $a = 1338.2(2)$ pm, $R1 = 0.0333$; $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$: $a = 1334.54(6)$ pm, $R1 = 0.0296$; $Sr_3Nd_{10}Si_{18}Al_{12}O_{18}N_{36}$: $a = 1332.85(6)$ pm, $R1 = 0.0271$) and in the case of $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$ with powder neutron diffraction as well. The three-dimensional sialon network is built up by $SiON_3$, SiN_4, and $AlON_3$ tetrahedra. Besides the bridging O and N atoms of the sialon network there are isolated O^{2-} which are tetrahedrally coordinated by Sr and Ln. The crystallographic differentiation of Si/Al and O/N seemed to be possible by a careful evaluation of the single-crystal X-ray diffraction data combined with lattice energy calculations using the MAPLE concept (Madelung Part of Lattice Energy). In the case of $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$ the differentiation of O and N and the proposed ordering was completely confirmed by powder neutron diffraction.

1 Introduction

Oxonitridoaluminosilicates (sialons) are excellent materials due to their high mechanical hardness and strength, and their exceptional thermal and chemical stability.[1–3] The first members of this class of compound have been synthesised by the reaction of Si_3N_4 and Al_2O_3.[4–6] The crystallographic structures of these sialons derive from those of α- and β-Si_3N_4. Therefore, these sialons have been called α- or β-sialons, respectively. In the meantime sialons have been synthesised which are structurally related to oxygen containing compounds like melilite (M-phase), apatite (H-Phase), or wollastonite (K-phase).[7] Concerning their solid-state chemistry most of these compounds have been only insufficiently characterised. Detailed structural information was missing as single-crystal data only for one compound, the so called Nd-U-phase, has been obtained.[8–13]

Our synthetic approach using a radiofrequency (rf) furnace and silicon diimide and metals as starting compounds led to a considerable number of novel nitridosilicates.[14,15] This synthetic strategy has now been successfully transferred to the synthesis of new oxonitridoaluminosilicates (sialons) and oxonitridosilicates (sions), namely $SrSiAl_2O_3N_2$,[16] $SrErSiAl_3O_3N_4$,[17] $Sm_2Si_3O_3N_4$ and $Ln_2Si_{2.5}Al_{0.5}O_{3.5}N_{3.5}$ (Ln = Ce, Pr, Nd, Sm, Gd),[18] $Nd_3Si_5AlON_{10}$,[19] and most recently $Ce_{16}Si_{15}O_6N_{32}$.[20,21]

A specific problem during the structural characterisation of the sialons and sions arises from the question, whether the Si/Al and O/N atoms, respectively, are crystallographically ordered. And if they are ordered, how this ordering can be exactly proved. Si^{4+}/Al^{3+} and O^{2-}/N^{3-}, respectively, have very similar atomic form factors. Therefore X-ray diffraction methods are not reliable for their differentiation and neutron diffraction experiments have to be performed.

In this paper we present the new sialons $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd). These compounds are the first representatives of a new structure type. The ordering of the Si/Al and O/N atoms, respectively, was determined by X-ray single-crystal investigations, lattice energy calculations using the MAPLE concept and in the case of $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$ by neutron powder diffraction.

2 Experimental procedure

The synthetic procedure using a radiofrequency furnace for the high-temperature syntheses has been developed primarily in our laboratory for the preparation of nitridosilicates. We now have adopted this method for the synthesis of several new sialons and sions. Details of the experimental setup are given in ref. 17. As starting materials for the preparation of $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) we used silicon diimide ($Si(NH)_2$), AlN, $SrCO_3$ (Merck, p.a.), and the powdered metals Ce, Pr, or Nd (ABCR, purity 99.9%), respectively.

2.1 Synthesis of silicon diimide ($Si(NH)_2$)

Using $Si(NH)_2$ instead of the relatively unreactive Si_3N_4 as the starting material proved to be advantageous for the synthesis of the nitridosilicates and this also holds for the sialons.[14,15] $Si(NH)_2$ was obtained by ammonolysis of $SiCl_4$ in CH_2Cl_2 followed by a thermal treatment at 600 °C under an atmosphere of pure NH_3 [eqn. (1)].

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

A detailed description of the synthesis of $Si(NH)_2$ is given in ref. 22. $Si(NH)_2$ was yielded as an X-ray amorphous and relatively undefined but reactive product 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.[22]

2.2 Synthesis of aluminium nitride

Single-phase and crystalline AlN was obtained by the reaction of Al (purity > 99%, Fluka) in a continuous stream of nitrogen (purity 5.0, Linde). Five reaction cycles of 2 h each at 900 °C (heating rate 1 °C min^{-1}, cooling rate 20 °C min^{-1}) with subsequent grinding of the sintered product were performed. IR-spectroscopic investigations excluded the presence of N–H groups in the product. Furthermore the purity was checked by X-ray powder diffraction.

2.3 Synthesis of the sialons $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd)

The sialons $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) were obtained by high-temperature reaction of $SrCO_3$, $Si(NH)_2$, AlN, and the respective powdered lanthanide metals Ce, Pr, and Nd using an rf furnace. Under an atmosphere of pure argon the respective starting compounds were placed in a tungsten crucible which was positioned in the centre of the induction coil of an rf furnace. The reaction was then performed under a pure atmosphere of nitrogen (purified by silica gel, potassium hydroxide, molecular sieve, P_4O_{10}, and a BTS catalyst). The compositions of the starting compounds and the respective reaction conditions are summarised in Tables 1 and 2.

The sialons $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) were yielded as coarsely crystalline materials. In the case of the Pr compound the average yield was nearly 75%. For the Ce and the Nd compounds the yields range between 30–40%. As by-products the individually coloured N-containing melilites[18] were obtained. Furthermore X-ray amorphous strontium-rich sialons were observed. The title compounds can easily be separated from their by-products due to their differing colour and the crystal habit (Fig. 1). Each of the sialons $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) shows a specific colour: Ce: orange, Pr: dark green, Nd: blue violet. The materials are very hard (see hardness investigations later), scratching agate while grinding.

The compositions of the products were analysed by energy-dispersive X-ray microanalysis (JEOL, JSM 6400, Institute of Materials Research, University of Bayreuth, Germany). The analyses revealed the molar ratios of Sr, Ln, Si, Al, O, and N (Ln = Ce, Pr, Nd) as theoretically expected. Additionally, the amount of nitrogen was checked by photometric determination after digestion of the compounds by microwave treatment using a matrix of conc. H_2SO_4, aqueous conc. HF, and aqueous conc. H_2O_2 in a volume proportion of 5 : 1 : 1. The absence of hydrogen (N–H) in the reaction products was proved by IR spectroscopy. The title compounds exhibit great chemical and thermal stability. They are stable up to more than 1700 °C and they are resistant against hot acid and alkaline solutions.

3 Crystal structure analysis and lattice energy calculations

X-Ray diffraction data of the title compounds were collected on a four-circle diffractometer (Siemens P4). According to the observed extinction conditions of the cubic lattice (only reflections hkl with $h+k+l=2n$ and $h00$ with $h=2n$) the space groups $I23$, $I2_13$, $Im\bar{3}$, $I432$, $I\bar{4}3m$, and $Im\bar{3}m$ were considered. The structure solution and refinement was only possible choosing space group $I\bar{4}3m$ (no. 217). The crystal structures of $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) were solved by direct methods using SHELXTL[23] and refined with anisotropic displacement parameters for all atoms. Furthermore all reflections detected by X-ray powder diffraction (Siemens D5000) of single-phase $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) have been indexed and their observed intensities are in good agreement with the calculated diffraction patterns based on the single-crystal data. The relevant crystallographic data and further details of the X-ray data collection are summarised in Tables 3–5. Table 6 shows the positional and displacement parameters for all atoms. In Table 7 selected interatomic distances and angles are listed.

Due to their identical electronic configuration and their very similar atomic form factors the unequivocal differentiation of N^{3-}/O^{2-} and Al^{3+}/Si^{4+}, respectively, by X-ray diffraction methods is not reliable. We therefore refined an approach leading to the differentiation of N/O and Al/Si, respectively, by a careful examination of the single-crystal X-ray diffraction data combined with lattice energy calculations using the MAPLE concept (MAPLE = Madelung Part of Lattice Energy).[24–26]

On the other hand neutron diffraction is an excellent tool for the differentiation of O and N because their scattering lengths differ significantly ($b(N) = 9.36 \times 10^{-15}$ m, $b(O) = 5.803 \times 10^{-15}$ m).[27] However, it is much more difficult to discriminate between Al^{3+} and Si^{4+} due to their more similar scattering lengths ($b(Al) = 3.449 \times 10^{-15}$ m, $b(Si) = 4.149 \times 10^{-15}$ m).[27] In the case of $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$ we were able to synthesise a sufficient amount to perform neutron powder diffraction. For the diffraction experiments the time-of-flight method (TOF) was used. About 250 mg of the pure sample were enclosed into a vanadium cylinder. The investigation was performed both at the POLARIS instrument of the ISIS/Rutherford Appleton Laboratory, Chilton, UK, and the D2B beamline at the Institute Laue Langevin (ILL), Grenoble, France, which permits the measurement of relatively small samples due to high flux. The Rietveld refinement was performed with the program GSAS[28] using the single-crystal X-ray data of $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$ as a starting model. The results of the Rietveld refinement of the neutron diffraction data are shown in Fig. 2, the details of the final refinement are listed in Table 8. Both structure refinements gave similar atomic coordinates and displacement parameters. Initially Si/Al and O/N were located on the same crystallographic positions, respectively, and their occupation factors were dependently refined. An unequivocal discrimination between

Table 1 Composition of reaction batches for the synthesis of $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd)

	Ln	$Si(NH)_2$	AlN	$SrCO_3$
$Sr_3Ce_{10}Si_{18}Al_{12}O_{18}N_{36}$	Ce; 170.8 mg (1.22 mmol)	78.6 mg (0.89 mmol)	55.6 mg (1.36 mmol)	91.2 mg (0.62 mmol)
$Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$	Pr; 120.1 mg (0.85 mmol)	85.0 mg (1.46 mmol)	70.1 mg (1.71 mmol)	120.3 mg (0.82 mmol)
$Sr_3Nd_{10}Si_{18}Al_{12}O_{18}N_{36}$	Nd; 120.0 mg (0.83 mmol)	75.4 mg (1.30 mmol)	60.1 mg (1.46 mmol)	106.6 mg (0.72 mmol)

Table 2 Reaction steps with final temperatures [°C] and heating/cooling rates [°C min^{-1}] for the high-temperature syntheses of $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd)

	Ln = Ce		Ln = Pr		Ln = Nd	
Reaction step	*T*/°C	Rate/°C min^{-1}	*T*/°C	Rate/°C min^{-1}	*T*/°C	Rate/°C min^{-1}
1	1200	20	1200	20	1200	20
2	1550	5.8	1650	7.5	1650	7.5
3	constant	30 min	constant	30 min	constant	30 min
4	900	−0.2	1400	−0.3	900	−0.3
5	23	−100	23	−100	23	−100

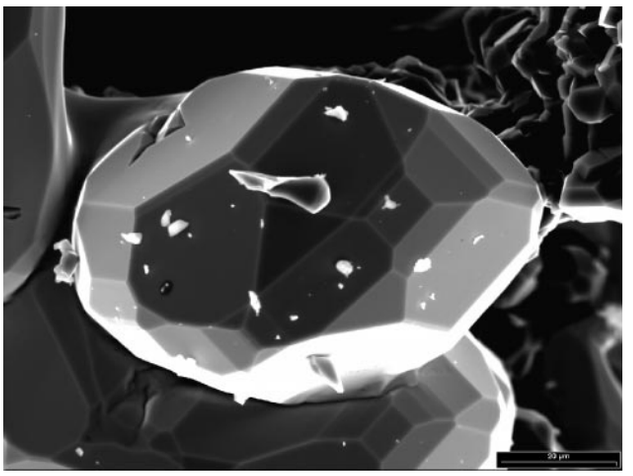

Fig. 1 Single crystal of $Sr_3Nd_{10}Si_{18}Al_{12}O_{18}N_{36}$ (diameter about 120 μm); SEM photograph.

O and N was possible and the results match exactly the O/N distribution obtained by the single-crystal X-ray structure determination and the MAPLE calculations. According to the refined occupancy factors (Table 8) which are unity within twice the standard deviations full crystallographic ordering of O and N sites was proved. Due to their similar scattering lengths of Al^{3+} and Si^{4+} (see above) the free refinement of their occupancy factors was not possible on the basis of the obtained neutron diffraction data. However an iterative MAPLE calculation on the basis of the O/N sites determined by neutron diffraction yielded strong evidence for the crystallographic ordering of Al and Si (Table 9).

For the exact differentiation of Si/Al and O/N, respectively, we performed lattice energy calculations using the MAPLE concept. As a result of these calculations each atom in a crystal structure has a particular range of partial MAPLE values (Si^{4+}: 9100–10200 kJ mol^{-1}, Al^{3+}: 5500–6000 kJ mol^{-1}, O^{2-}: 1870–3300 kJ mol^{-1}, N^{3-}: 5000–6200 kJ mol^{-1}) assigned. The ranges are characteristic for the concerned elements. Atoms on a specific site which have been assigned to a wrong atom type (*e.g.* Si instead of Al or O instead of N) normally exhibit a partial MAPLE value, which significantly differs from the characteristic range. These effects indicate a wrong occupation of the concerned crystallographic site (Table 9).

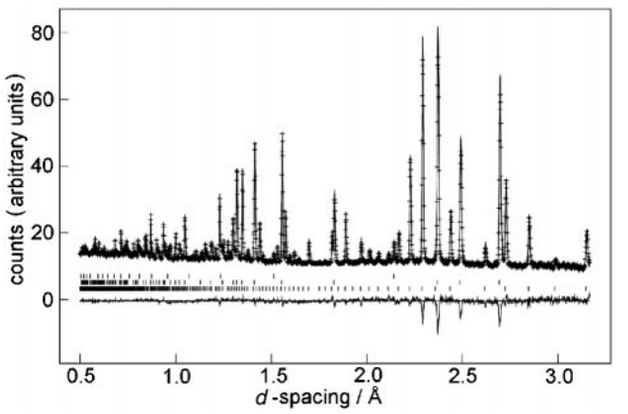

Fig. 2 Observed (crosses) and calculated (line) TOF neutron powder diffraction pattern as well as the difference profile of the Rietveld refinement. The lower row of vertical lines indicates possible peak positions of $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$ (upper row: vanadium of the sample container; middle row: AlN impurities).

4 Results and discussion of the structure refinements

The sialons $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) are the first representatives of a new structure type. In the solid the structure consists of a three-dimensional network of corner sharing $SiON_3$, $AlON_3$, and SiN_4 tetrahedra (all Q^4 type). According to Pauling's rules[29] in sions and sialons nitrogen normally prefers sites in which the N atoms in comparison with the O atoms are directly bound to the same or a higher number of neighbouring Si or Al atoms.[17] Therefore, the N atoms in $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) are connecting two ($N^{[2]}$) or three tetrahedral centres ($N^{[3]}$) while the oxygen atoms are only connecting two ($O^{[2]}$) of them or they are isolated ($O^{[0]}$). According to the formula $Sr_3Ln_{10}[Si_{18}Al_{12}O_{12}N_{36}]O_6$ the

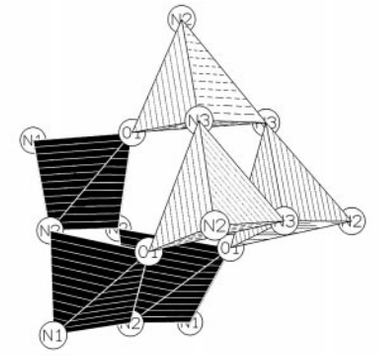

Fig. 3 Double three-rings of $SiON_3$ (black) and $AlON_3$ tetrahedra (grey) are the characteristic building blocks of the $^3_\infty[(Si^{[4]}_{18}Al^{[4]}_{12}O^{[2]}_{12}N^{[2]}_{12}N^{[3]}_{24})]$ network in $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd).

Table 3 Crystallographic data of $Sr_3Ce_{10}Si_{18}Al_{12}O_{18}N_{36}$ (e.s.d.s in parentheses)

Crystal data	
$Sr_3Ce_{10}Si_{18}Al_{12}O_{18}N_{36}$	$F(000)=2996$
$M=3285.8$ g mol^{-1}	$D_c=4.554$ g cm^{-3}
cubic	Mo-K$_\alpha$ radiation ($\lambda=71.073$ pm)
space group $I\bar{4}3m$ (No. 217)	$\mu=13.372$ mm^{-1}
$a=1338.2(2)$ pm	$T=296(2)$ K
$V=2396.4(7)\times10^6$ pm^3	$0.10\times0.12\times0.15$ mm^3
$Z=2$	orange
Data collection	
Siemens P4 diffractometer	measured octants: $h\ k\ l$ and $\bar{h}\ \bar{k}\ \bar{l}$ with
ω-scans	$h=-18\rightarrow18$
Absorption correction: Ψ-scans	$k=-18\rightarrow18$
$T_{min}=0.1798$; $T_{max}=0.3177$	$l=-18\rightarrow18$
$R_{int}=0.0721$	688 independent reflections
$\Theta_{max}=30^\circ$	688 observed reflections ($F_o^2\geqslant0\sigma(F_o^2)$)
Refinement	
refinement on F^2	program used to refine structure: SHELXL-93[23]
$R1=0.0333$	$w^{-1}=\sigma^2F_o^2+(xP)^2+yP$; $P=(F_o^2+2F_c^2)/3$
$wR2=0.0740$	weighting (x/y) 0.0414/19.9850
GOF = 1.116	extinction coefficient: 0.0001(1)
3875 measured reflections	Flack parameter: 0.01(3)
57 parameters	min/max resid. electron dens.: $-0.873/2.488$ e Å^{-3}

title compounds may be described as strontium lanthanoide oxonitridoaluminosilicate oxides.

The mean bond lengths from the tetrahedral centres T (T = Si, Al) show a significant differentiation T–N > T–O and $Si–N^{[3]} > Si–N^{[2]}$ ($Si–N^{[2]}$: 170.2(8)–172.4(4) pm; $Si–N^{[3]}$: 173.9(6)–176.5(4) pm; $Al–N^{[3]}$: 177.8(6)–179.5(5) pm; $Si–O^{[2]}$: 166.1(6)–168.2(8) pm; $Al–O^{[2]}$: 170.5(4)–171.1(6) pm). The bond angles at the $N^{[2]}$ atoms are in the range 111.6(4)–112.2(5)°, for the $O^{[2]}$ atoms in the range 161.8(3)–162.2(5)°. The sums of the bond angles at the $N^{[3]}$ atoms amount to 356–358°. The molar ratio T : X (T = Si, Al; X = O, N) for the Si–Al–O–N network of $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) amounts to 0.63. Accordingly these sialons may be classified as highly condensed (*i.e.* they exhibit a degree of condensation T : X > 0.5, which is the maximum value of pure oxosilicates).

Typical of the crystal structure are double three-rings of three $SiON_3$ and three $AlON_3$ tetrahedra. Within these units each $SiON_3$ is connected to a $AlON_3$ tetrahedron through an O atom. Thus within the double three-ring the bridges Si–N–Si, Al–N–Al, and Al–O–Si occur (Fig. 3). The Si_3N_3 and Al_3N_3 rings of these units exhibit the chair conformation, the resulting four-rings $Al_2Si_2N_2O_2$ the saddle conformation. Furthermore,

Table 4 Crystallographic data of $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$ (e.s.d.s in parentheses)

Crystal data	
$Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$	$F(000)=3016$
$M=3293.70$ g mol^{-1}	$D=4.602$ g cm^{-3}
cubic	Mo-K$_\alpha$ radiation ($\lambda=71.073$ pm)
space group $I\bar{4}3m$ (No. 217)	$\mu=14.155$ mm^{-1}
$a=1334.54(6)$ pm	$T=293(2)$ K
$V=2376.8(2)\times10^6$ pm^3	$0.14\times0.16\times0.21$ mm^3
$Z=2$	dark green
Data collection	
Siemens P4 diffractometer	measured octants: $h\ k\ l$ and $\bar{h}\ \bar{k}\ \bar{l}$ with
ω-scans	$h=-24\rightarrow24$
absorption correction: Ψ-scans	$k=-24\rightarrow24$
$T_{min}=0.0210$; $T_{max}=0.0711$	$l=-24\rightarrow24$
$R_{int}=0.0561$	1393 independent reflections
$\Theta_{max}=40^\circ$	1393 observed reflections ($F_o^2\geqslant0\sigma(F_o^2)$)
Refinement	
refinement on F^2	program used to refine structure: SHELXL-93[23]
$R1=0.0296$	$w^{-1}=\sigma^2F_o^2+(xP)^2+yP$; $P=(F_o^2+2F_c^2)/3$
$wR2=0.0645$	weighting (x/y) 0.0331/1.0807
GOF = 1.093	extinction coefficient: 0.00063(9)
8052 measured reflections	Flack parameter: 0.01(2)
57 parameters	min/max resid. electron dens.: $-0.844/2.770$ e Å^{-3}
Neutron Powder Diffraction	
TOF powder diffractometer: POLARIS/ISIS	
$2\theta=145^\circ$	χ^2: 4.47
$a=1335.63(1)$ pm	$R_P=0.030$
$T=298$ K	$wR_P=0.017$
range [d-spacing]: 0.48–3.09 Å	$R_F=0.043$
no. of data points: 3196	
no. of observed reflections: 1092	
refined parameters:	
32 structure parameters	
16 profile parameters	

Table 5 Crystallographic data of $Sr_3Nd_{10}Si_{18}Al_{12}O_{18}N_{36}$ (e.s.d.s in parentheses)

Crystal data	
$Sr_3Nd_{10}Si_{18}Al_{12}O_{18}N_{36}$	$F(000)=3036$
$M=3327.00$ g mol^{-1}	$D=4.666$ g cm^{-3}
cubic	Mo-K$_\alpha$ radiation ($\lambda=71.073$ pm)
space group $I\bar{4}3m$ (No. 217)	$\mu=14.885$ mm^{-1}
$a=1332.85(6)$ pm	$T=293(2)$ K
$V=2367.8(2)\times10^6$ pm^3	$0.10\times0.12\times0.13$ mm^3
$Z=2$	blue violet
Data collection	
Siemens P4 diffractometer	measured octants: $h\ k\ l$ and $\bar{h}\ \bar{k}\ \bar{l}$ with
ω-scans	$h=-18\rightarrow18$
absorption correction: Ψ-scans	$k=-18\rightarrow18$
$T_{min}=0.0216$; $T_{max}=0.0534$	$l=-18\rightarrow18$
$R_{int}=0.0759$	680 independent reflections
$\Theta_{max}=30^\circ$	680 observed reflections ($F_o^2\geqslant0\sigma(F_o^2)$)
Refinement	
refinement on F^2	program used to refine structure: SHELXL-93[23]
$R1=0.0271$	$w^{-1}=\sigma^2F_o^2+(xP)^2+yP$; $P=(F_o^2+2F_c^2)/3$
$wR2=0.0501$	weighting (x/y) 0.0215/8.7902
GOF = 1.117	extinction coefficient: 0.00056(8)
3879 measured reflections	Flack parameter: 0.00(2)
57 parameters	min/max resid. electron dens.: $-0.546/1.797$ e Å^{-3}

the double three-rings are connected *via* SiN_4 tetrahedra forming a three dimensional network $^3_\infty[(Si^{[4]}_{18}Al^{[4]}_{12}O^{[2]}_{12}N^{[2]}_{12}N^{[3]}_{24})]$ (Fig. 4).

Among the $O^{[2]}$, $N^{[2]}$, and $N^{[3]}$ atoms, which are bridging two or three tetrahedral centres there are $(O^{[0]})^{2-}$ ions which are not directly bound to Si or Al. These O(2) ions are tetrahedrally coordinated by four metal cations. A free refinement of the respective site occupation factors revealed that the respective metal positions are statistically occupied by Ln^{3+} and Sr^{2+} with a molar ratio 5 : 1. The exact site occupation factors gave a ratio of 0.415(15) : 0.085(15), which is very similar to the ratio of 0.417 : 0.083 calculated from the idealised stoichiometric formulae. In spite of this accordance a certain phase width cannot be excluded. Charge compensation by variation not only of the O/N ratio but also of the Al/Si ratio would be possible. However, in accordance with the powder neutron

Table 6 Atomic coordinates and thermal displacement parameters for $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) (e.s.d.s in parentheses)

Ln	Atom	Wyckoff symbol	SOF	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ce	Ce(1)	24g	0.415(15)	0.3706(1)	x	0.0496(3)	0.0148(5)	U_{11}	0.0099(6)	0.0001(3)	U_{23}	−0.0048(6)	0.0132(3)
	Sr(1)	24g	0.085(15)	0.3706(1)	x	0.059(2)	0.044(10)	U_{11}	0.012(7)	−0.001(3)	U_{23}	−0.023(9)	0.034(8)
	Sr(2)	2a		0	0	0	0.22(1)	U_{11}	U_{11}	0	0	0	0.22(1)
	Si(1)	24g		0.1502(1)	x	0.3100(2)	0.0100(6)	U_{11}	0.0097(9)	−0.0004(5)	U_{23}	0.0006(7)	0.0099(4)
	Si(2)	12e		0.3000(3)	0	0	0.010(1)	0.0081(8)	U_{22}	−0.001(1)	0	0	0.0088(6)
	Al(1)	24g		0.2054(1)	x	0.9546(2)	0.0066(6)	U_{11}	0.007(1)	0.0000(6)	U_{23}	−0.0011(8)	0.0068(5)
	O(1)	24g		0.2138(4)	x	0.3978(6)	0.034(3)	U_{11}	0.020(3)	0.000(2)	U_{23}	−0.012(3)	0.029(2)
	O(2)	12d		¼	½	0	0.013(4)	0.025(3)	U_{22}	0	0	0	0.021(2)
	N(1)	24g		0.0720(4)	x	0.3762(6)	0.014(2)	U_{11}	0.012(3)	0.001(2)	U_{23}	−0.005(2)	0.014(1)
	N(2)	24g		0.2324(4)	x	0.0823(5)	0.013(2)	U_{11}	0.010(3)	0.001(2)	U_{23}	0.005(3)	0.012(1)
	N(3)	24g		0.9228(5)	$-x+1$	0.2287(8)	0.017(2)	U_{11}	0.033(5)	0.013(3)	$-U_{23}$	−0.002(3)	0.022(2)
Pr	Pr(1)	24g	0.415(10)	0.37033(4)	x	0.04848(8)	0.0233(1)	U_{11}	0.0157(3)	−0.0001(1)	U_{23}	−0.0071(2)	0.02076(9)
	Sr(1)	24g	0.085(15)	0.3709(5)	x	0.0625(7)	0.061(4)	U_{11}	0.012(2)	0.001(1)	U_{23}	−0.039(4)	0.044(3)
	Sr(2)	2a		0	0	0	0.156(4)	U_{11}	U_{11}	0	0	0	0.156(4)
	Si(1)	24g		0.15021(6)	x	0.31014(9)	0.0154(3)	U_{11}	0.0154(4)	0.0001(2)	U_{23}	−0.0004(3)	0.0154(2)
	Si(2)	12e		0.3002(1)	0	0	0.0149(6)	0.0148(4)	U_{22}	−0.0007(5)	0	0	0.0148(3)
	Al(1)	24g		0.20544(6)	x	0.95438(9)	0.0123(3)	U_{11}	0.0119(4)	−0.0002(2)	U_{23}	0.0002(3)	0.0122(2)
	O(1)	24g		0.2135(2)	x	0.3979(3)	0.041(2)	U_{11}	0.023(2)	−0.0002(9)	U_{23}	−0.018(2)	0.035(1)
	O(2)	12d		¼	½	0	0.026(2)	0.031(2)	U_{22}	0	0	0	0.029(1)
	N(1)	24g		0.0720(2)	x	0.3770(3)	0.0207(9)	U_{11}	0.018(1)	−0.0006(8)	U_{23}	−0.006(1)	0.0197(6)
	N(2)	24g		0.2322(2)	x	0.0823(3)	0.0200(9)	U_{11}	0.015(1)	0.0014(8)	U_{23}	0.003(1)	0.0184(6)
	N(3)	24g		0.9225(2)	$-x+1$	0.2288(4)	0.021(1)	U_{11}	0.033(2)	0.010(1)	$-U_{23}$	−0.003(1)	0.0251(8)
Nd	Nd(1)	24g	0.415(15)	0.37036(7)	x	0.0475(2)	0.0254(3)	U_{11}	0.0149(6)	0.0001(2)	U_{23}	−0.0066(3)	0.0219(2)
	Sr(1)	24g	0.085(15)	0.3706(6)	x	0.063(1)	0.060(6)	U_{11}	0.013(5)	0.001(2)	U_{23}	−0.058(5)	0.045(5)
	Sr(2)	2a		0	0	0	0.150(4)	U_{11}	U_{11}	0	0	0	0.150(4)
	Si(1)	24g		0.15038(9)	x	0.3106(1)	0.0150(5)	U_{11}	0.0169(7)	0.0004(4)	U_{23}	−0.0012(6)	0.0156(3)
	Si(2)	12e		0.3008(2)	0	0	0.013(1)	0.0159(7)	U_{22}	−0.0011(9)	0	0	0.0150(5)
	Al(1)	24g		0.2054(1)	x	0.9548(2)	0.0120(5)	U_{11}	0.0112(8)	−0.0001(5)	U_{23}	0.0003(6)	0.0117(3)
	O(1)	24g		0.2132(3)	x	0.3980(5)	0.048(3)	U_{11}	0.028(3)	−0.002(2)	U_{23}	−0.028(3)	0.041(2)
	O(2)	12d		¼	½	0	0.032(4)	0.031(3)	U_{22}	0	0	0	0.032(2)
	N(1)	24g		0.0720(3)	x	0.3779(3)	0.022(2)	U_{11}	0.019(3)	−0.002(2)	U_{23}	−0.004(2)	0.021(1)
	N(2)	24g		0.2327(3)	x	0.0825(4)	0.019(2)	U_{11}	0.016(2)	0.005(2)	U_{23}	0.003(2)	0.018(1)
	N(3)	24g		0.9229(4)	$-x+1$	0.2292(6)	0.021(2)	U_{11}	0.037(4)	0.012(2)	$-U_{23}$	−0.005(2)	0.026(1)

[n]The anisotropic temperature factor is given as $\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{13}hla^*c^*)]$; SOF: site occupation factor.

Table 7 Selected interatomic distances [pm] and angles [°] for $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) (e.s.d.s in parentheses)

		Ce	Pr	Nd
Ln(1)	–O(2)$^{[0]}$	245.8(1) 2×	244.78(3) 2×	244.14(6) 2×
	–N(1)$^{[2]}$	256.2(9)	253.4(4)	250.9(7)
	–O(1)$^{[2]}$	258.4(9)	255.7(4)	254.0(7)
	–N(2)$^{[3]}$	265.1(9)	264.6(4)	263.6(6)
	–N(1)$^{[2]}$	297.3(5) 2×	297.1(2) 2×	296.7(4) 2×
	–O(1)$^{[2]}$	306.0(3) 2×	306.04(9) 2×	306.6(2) 2×
	–N(3)$^{[3]}$	313(1)	313.1(6)	313.6(8)
Sr(1)	–O(2)$^{[0]}$	250(1) 2×	250.3(3) 2×	250.2(6) 2×
	–N(2)$^{[3]}$	263(3)	263(1)	261(1)
	–N(1)$^{[2]}$	268(3)	270(1)	269(2)
	–O(1)$^{[2]}$	269(3)	271(1)	271(2)
	–N(1)$^{[2]}$	293(3) 2×	290.5(9) 2×	290(1) 2×
	–O(1)$^{[2]}$	297(2) 2×	293.3(8) 2×	292(1) 2×
	–N(3)$^{[3]}$	301(3)	295(1)	294(2)
Sr(2)	–N(3)$^{[3]}$	339(1) 12×	338.6(6) 12×	338.3(8) 12×
Si(1)	–O(1)$^{[2]}$	168.2(8)	167.3(4)	166.1(6)
	–N(1)$^{[2]}$	172.5(7)	172.4(4)	172.9(6)
	–N(2)$^{[3]}$	176.5(4) 2×	176.1(2) 2×	176.1(3) 2×
Si(2)	–N(1)$^{[2]}$	170.2(8) 2×	170.3(4) 2×	170.2(6) 2×
	–N(3)$^{[3]}$	174.5(8) 2×	174.5(4) 2×	173.9(6) 2×
Al(1)	–O(1)$^{[2]}$	170.8(8)	170.5(4)	171.1(6)
	–N(2)$^{[3]}$	178.4(8)	178.1(4)	177.8(6)
	–N(3)$^{[3]}$	179.5(4) 2×	178.7(2) 2×	179.0(3) 2×
Si(1)	–O(1)$^{[2]}$–Al(1)	162.2(5)	161.8(3)	161.8(4)
Si(1)	–N(1)$^{[2]}$–Si(2)	112.2(5)	111.8(2)	111.6(4)
Si(1)	–N(2)$^{[3]}$–Al(1)	119.0(2) 2×	119.2(1) 2×	119.0(2) 2×
Si(1)	–N(2)$^{[3]}$–Si(1)	118.0(4)	118.0(2)	118.1(3)
		Σ = 356.0	Σ = 356.4	Σ = 356.1
Si(2)	–N(3)$^{[3]}$–Al(1)	121.4(2) 2×	121.4(1) 2×	121.4(2) 2×
Al(1)	–N(3)$^{[3]}$–Al(1)	115.1(5)	115.1(2)	115.0(3)
		Σ = 357.9	Σ = 357.9	Σ = 357.8

diffraction refinement of $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$ the deviation from the ideal formula should be small. Six of the tetrahedra $O(Ln_{3.33}Sr_{0.67})$ (Ln = Ce, Pr, Nd) are sharing common corners forming rings (Fig. 5). The bond length Ln–O$^{[0]}$ varies in the range 244–246 pm (Sr–O$^{[0]}$: 250 pm) The position of (Ln(1)/Sr(1)) is tenfold coordinated by five O and five N (Ln(1)–O: 244–307 pm; Sr(1)–O: 250–297 pm; Ln(1)–N: 251–314 pm; Sr(1)–N: 261–301 pm). Sr(2) is coordinated by twelve N atoms forming regularly truncated tetrahedra (Sr(2)–N: 338–339 pm) (Fig. 5). The strongly enlarged thermal displacement ellipsoids of Sr(2) indicates a disorder around this special Wyckoff position (2a) (0 0 0), however no convincing disorder model was yielded during the structure refinement.

The Si and Al atoms of the sialons $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) form a Frank Kasper like polyhedron (Fig. 6) with 30 tetrahedral centres. A direct connection of the tetrahedral centres of the neighbouring Frank Kasper like

Table 8 Atomic coordinates, isotropic displacement parameters [pm^2], and refined site occupation factors (SOF) for $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) determined by neutron powder diffraction. U_{eq} is defined as $\exp(-8\pi^2 U_{eq}\sin^2\theta/\lambda)$

	x	y	z	U_{eq}	SOF
Pr(1)	0.3734(4)	x	0.0531(6)	137(15)	0.44(2)
Sr(1)	0.3734(4)	x	0.0531(6)	137(15)	0.06(2)
Sr(2)	0	0	0	1203(208)	0.042(4)
Si(1)	0.1492(5)	x	0.3078(6)	41(14)	0.5
Si(2)	0.2986(8)	0	0	17(20)	0.25
Al(1)	0.2058(5)	x	0.9526(7)	23(15)	0.5
O(1)	0.2126(3)	x	0.3982(4)	31(10)	0.49(2)
N(1)*					0.01(2)
O(2)	¼	½	0	289(27)	0.27(2)
N(2)*					−0.02(2)
O(3)*					0.04(2)
N(3)	0.0715(2)	x	0.3749(2)	52(6)	0.46(2)
O(4)*					0.03(2)
N(4)	0.2331(2)	x	0.0840(3)	52(6)	0.47(2)
O(5)*					0.04(2)
N(5)	0.9217(3)	$-x+1$	0.7298(3)	133(6)	0.46(2)

[a]*Pr(1), Sr(1), O(n), and N(n), respectively, have been positioned on the identical crystallographic site and the fractional occupancy factors have been dependently refined. The atoms indicated obtained a SOF near zero.

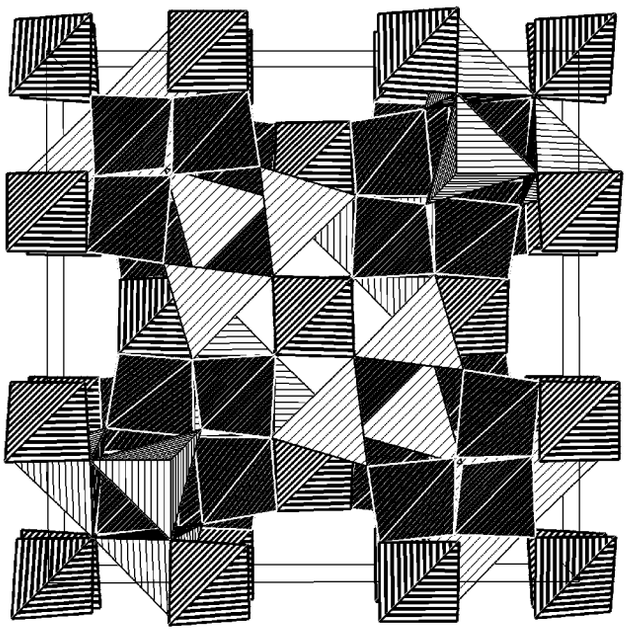

Fig. 4 $^3_\infty[(Si^{[4]}_{18}Al^{[4]}_{12}O^{[2]}_{12}N^{[2]}_{12}N^{[3]}_{24})]$ network of the sialons $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) consisting of $SiON_3$ (black), $AlON_3$ (grey), and SiN_4 tetrahedra (dark hatched).

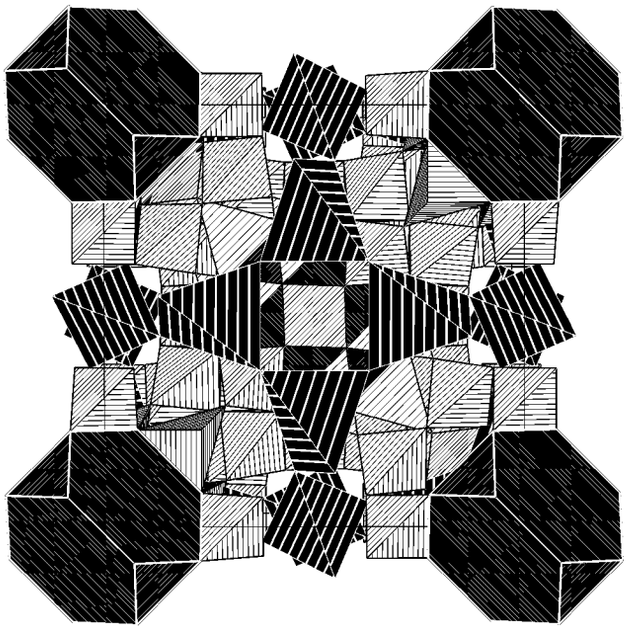

Fig. 5 Crystal structure of the sialons $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) in polyhedral visualisation; SrN_{12} polyhedra (black), $O(Ln_{3.33}Sr_{0.67})$ tetrahedra (dark hatched), $^3_\infty[(Si^{[4]}_{18}Al^{[4]}_{12}O^{[2]}_{12}N^{[2]}_{12}N^{[3]}_{24})]$ network (grey).

Table 9 Results of the MAPLE calculations for $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd) and increment calculations; Δ = difference

$Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$	Ln(1)/Sr(1)	Sr(2)	Si(1)	Si(2)	Al(1)	O(1)	O(2)	N(1)	N(2)	N(3)
Ln = Ce	3590	1833	9327	10174	5970	2765	1876	5328	5881	5186
Ln = Pr	3610	1833	9345	10163	5988	2781	1881	5329	5892	5203
Ln = Nd	3634	1823	9348	10188	5968	2790	1880	5323	5901	5217

MAPLE (10 LnN + 3 SrO + 9 Si_2N_2O + 8 AlN + 2 Al_2O_3)		MAPLE ($Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$)		
Ln = Ce	530957	Ln = Ce	530699	Δ = 0.1%
Ln = Pr	529211	Ln = Pr	531880	Δ = 0.5%
Ln = Nd	528873	Ln = Nd	532416	Δ = 0.6%

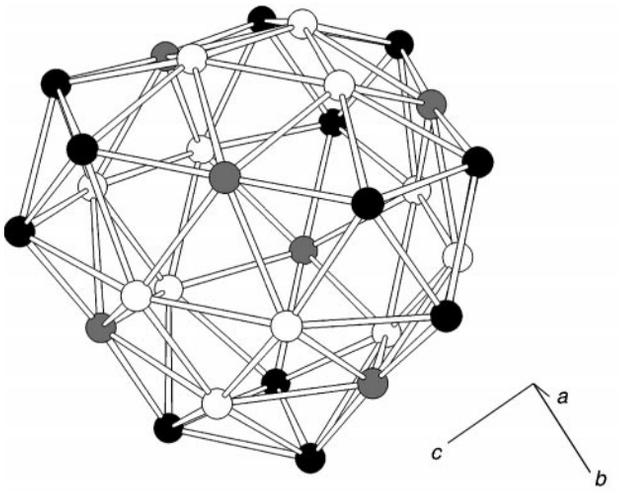

Fig. 6 Frank Kasper like ($Si_{18}Al_{12}$) polyhedra of the sialons $Sr_3Ln_{10}Si_{18}Al_{12}O_{18}N_{36}$ (Ln = Ce, Pr, Nd); Si(1) atoms black, Si(2) atoms grey, Al(1) atoms white; in the center of the polyhedron is the position of Sr(2).

polyhedra yields the arrangement depicted in Fig. 7. The centers of these polyhedra are formed by the Sr(2) atoms.

Further details of the crystal structure investigations reported in this paper may be obtained from the Cambridge Crystallographic Data Centre (CCDC), on quoting the reference number CCDC 1145/214. See http://www.rsc.org/suppdata/jm/a9/a908844j/ for crystallographic files in .cif format.

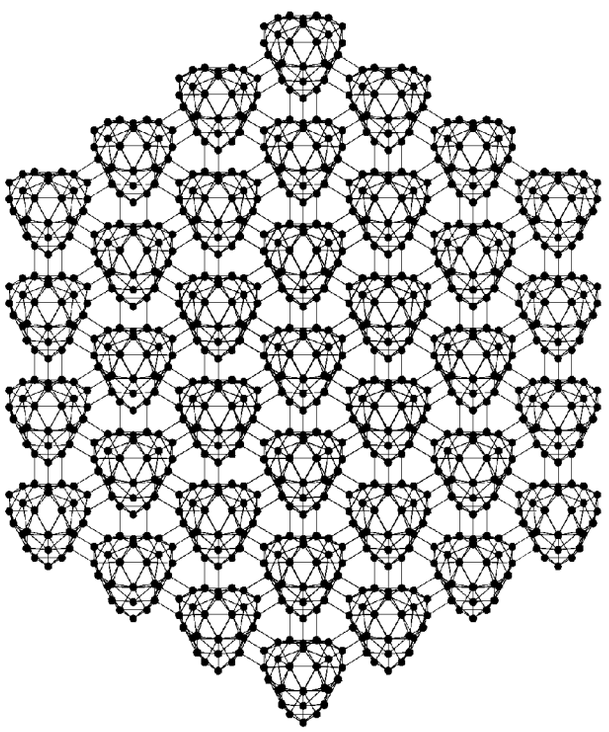

Fig. 7 Frank Kasper like ($Si_{18}Al_{12}$) polyhedra connected by trigonal prisms; view along [111].

5 Single-crystal hardness investigations of $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$

For the first time we performed hardness investigations on sialon single crystals. The usual method to determine the hardness of small single crystals (edge lengths 0.3 mm) is the Vickers method. Isolated single crystals of $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$ were merged for adjustment into a cylindrically formed polymer matrix (diameter: 2 cm). As test load 0.1 N and a time interval of 30 s as suitable parameters were chosen. The hardness investigations (nine independent measurements) exhibit an averaged Vickers hardness for $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$ single crystals of 22.0 GPa. The measured hardness value of $Sr_3Pr_{10}Si_{18}Al_{12}O_{18}N_{36}$ is in the same range as the highest known values for sintered polycrystalline α-sialons[30–33] and α-Al_2O_3.[34]

Recently, we obtained the oxonitridosilicate oxide $Ce_4[Si_4O_4N_6]O$, which contains a hyperbolically layered structure of Q^3 type $SiON_3$ tetrahedra and tetrahedral $[Ce_4O]^{10+}$ ions. The differentiation of O and N was possible by lattice energy calculations with the MAPLE concept and it was confirmed by powder neutron diffraction.[35]

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