DOI: 10.1002/zaac.200500368

$Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$ with x ≈ 1 − an Oxonitridoaluminosilicate Chloride

Alexandra Lieb, Rainer Lauterbach, and Wolfgang Schnick*

München, Department Chemie und Biochemie der Ludwig-Maximilians-Universität

Received September 9th, 2005.

Abstract: The oxonitridoaluminosilicate chloride $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$ was obtained by the reaction of praseodymium metal, the respective chloride, AlN and $Al(OH)_3$ with "$Si(NH)_2$" in a radiofrequency furnace at temperatures around 1900°C. The crystal structure was determined by single-crystal X-ray diffraction (*Pbam*, no. 55, Z = 2,*a* = 10.5973(8) Å, *b* = 11.1687(6) Å, *c* = 11.6179(7) Å, *R*1 = 0.0337). The sialon crystallizes isotypically to the oxonitridosilicate halides $Ce_{10}[Si_{10}O_9N_{17}]Br$, $Nd_{10}[Si_{10}O_9N_{17}]Br$ and $Nd_{10}[Si_{10}O_9N_{17}]Cl$, which represent a new layered structure type. The structure refinement was performed utilizing an O/N-distribution model according to *Paulings* rules, i.e. nitrogen was positioned on all bridging sites and mixed O/N-occupation was assumed on the terminal sites resulting in charge neutrality of the compounds. The Si and Al atoms were refined equally distributed on their three crystallographic sites, due to their poor distinguishability by X-ray analysis. The tetrahedra layers of the structure consist of condensed $[(Si,Al)N_2(O,N)_2]$ and $[(Si,Al)N_3(O,N)]$ tetrahedra of Q^2 and Q^3 type. The chemical composition of the compound was derived from electron probe micro analyses (EPMA).

Keywords: Praseodymium; Chloride; Oxonitridoaluminosilicate; Sialon; Crystal structure; Electron probe micro analysis (EPMA)

1 Introduction

With respect to their composition oxonitridosilicates represent an intermediate class of compounds between oxosilicates and nitridosilicates. Further partial substitution of silicon with aluminum leads to the oxonitridoaluminosilicates (so-called sialons). For application such sialons are often synthesized by hot press techniques and the first members of this class of compounds were made from the reaction of Si_3N_4 and Al_2O_3 [1−3]. The crystallographic structures of these sialons derive mainly from those of α- and β-Si_3N_4. In the meantime several sialons with anionic networks and additional cations have been synthesized and characterized. Some of these sialons are isotypic to known nitrido- and oxonitridosilicate structures, like $SrEr[SiAl_3O_3N_4]$ [4] (isotypic to $MYb[Si_4N_7]$ with M = Sr, Ba [5, 6]), $Nd_3[Si_5AlON_{10}]$ [7] (isotypic to $Ln_3Si_6N_{11}$ with Ln = La, Ce, Pr, Nd, Sm [8−10]), $Y_2Si_{3-x}Al_xO_{3+x}N_{4-x}$ [11] (isotypic to melilite $Y_2Si_4O_3N_4$) or $Sr_2Al_xSi_{12-x}N_{16-x}O_{2+x}$ with x ≈ 2 [12] (isotypic to $BaSi_6N_8O$ [13]).

Such compounds are considered to be very interesting for doping with suitable rare earth metals to create luminescent materials with high stability and efficiency [14, 15]. The implantation of aluminum and oxygen in the nitridosilicate networks and the occurrence of additional anions in the coordination sphere of the metals can be used to tune the optical properties of the doping metal by changes in its ligand field. This strategy is supported by the existence of significant phase widths in these compounds.

In this paper we present a sialon compound that is isotypic to an oxonitridosilicate, showing the possibility of aluminum incorporation in these systems. In addition it represents the first chlorine containing oxonitridoaluminosilicate (sialon).

2 Synthesis

2.1 Synthesis of AlN

Single-phase and crystalline AlN was obtained by the reaction of Al (purity > 99.9 %, Fluka) with a continuous stream of pure nitrogen. Five reaction cycles of 2 h each at 900°C (heating rate 1°C / min, cooling rate 20°C / min) with subsequent grinding of the sintered product were performed. The purity of the product was checked by X-ray powder diffraction [16], and the absence of N−H groups was determined by IR-spectroscopic investigations. The AlN deriving from this procedure is considered to be more reactive than the commercially available crystalline compound.

2.2 Synthesis of Al_2O_3

Al_2O_3 was used as an oxygen source for the sialon syntheses and made by alkaline precipitation of dissolved aluminum with NH_3. Therefore pure Al (2.4 g / 9 mmol, Fluka, purity > 99 %) was dissolved and refluxed for 60 min in pure, concentrated HCl. NH_3

---

* Prof. Dr. W. Schnick
Department Chemie und Biochemie
Lehrstuhl für Anorganische Festkörperchemie
Ludwig-Maximilians-Universität München
Butenandtstraße 5−13 (D)
D-81377 München, Germany
Fax: +49-(0)89-2180-77440
E-Mail: wolfgang.schnick@uni-muenchen.de

Table 1 Crystallographic data and details of the single crystal X-ray data collection for $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$.

Diffractometer, monochromator	STOE IPDS, graphite
Radiation	$Mo_{K\alpha}$ (λ = 0.71073 Å)
Temperature / K	293(2)
Space group, crystal system	*Pbam*, orthorhombic
Lattice parameters, *a* / Å	10.5973(8)
b / Å	11.1687(6)
c / Å	11.6179(7)
Cell volume, *V* / Å^3	1375.07(15)
Formula units	Z = 2
Crystal size / mm^3	0.300 x 0.167 x 0.148
Crystal color	light green
Calculated density / g cm^{-3}	5.092
Diffraction range / °	6.39 < 2θ < 63.04
Measured reflections	15467
Independent reflections	2384
Observed reflections	2222
Refined Parameters	122
R_{int}	0.0768
F(000)	1876
Extinction coefficient, c	0.00169(11)
Absorption correction	semi-empirical, multi-scan
Absorption coefficient / mm^{-1}	17.939
Min. / max. transmission	0.027 / 0.070
Min. / max. residual electron density / e / Å^3	−2.574 / 2.818
GooF	1.206
R_1 (all data) [I 2σ(I)]	0.0337 [0.0305]
wR_2 (all data) [I 2σ(I)]	0.0775 [0.0763]

subsequently was mixed to the solution until $Al(OH)_3$, as a white voluminous precipitate was formed. It was separated from the solution and washed with destilled water. The product was dried at 150°C under vacuum for 48 h. IR-spectroscopic investigations and X-ray powder diffraction substantiated the purity of the derived Al_2O_3 [17].

2.3 Synthesis of $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$

A mixture of Pr (120 mg / 0.85 mmol, Chempur, 99.9 %, powder), "$Si(NH)_2$" (58 mg / 1 mmol) (synthesized according to ref. [18]), $PrCl_3$ (50 mg / 0.2 mmol, Chempur, 99.9 %, ultradry), Al_2O_3 (30 mg / 0.3 mmol) and AlN (50 mg / 1.2 mmol) was thoroughly mixed and transferred into a tungsten crucible in a glove box (argon atmosphere). The crucible then was positioned in a water-cooled silica glass reactor of a radiofrequency furnace. It was heated under a pure nitrogen atmosphere to 1500°C within 1 h, then to 1900°C within 1 h, maintained at that temperature for 1 h and subsequently cooled to 1200°C within 60 h. Finally, the product was quenched to room temperature. Further details about the experimental setup are given in ref. 4.

The reaction yielded a light green crystalline product, together with small amounts of $Pr_2Si_{2.5}Al_{0.5}O_{3.5}N_{3.5}$ [19], $Pr_3Si_6N_{11}$ [20] and $Pr_4Si_2O_7N_2$ [21, 22] as crystalline by-products. In addition, amorphous by-products could be found, but not identified.

3 Single-crystal X-ray analysis

X-ray diffraction data of $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$ was collected using an IPDS-I diffractometer (STOE, Darmstadt) using Mo-K_α radiation. According to the observed reflection conditions (0*kl* with *k* = 2*n*, *h*0*l* with *h* = 2*n*, *h*00 with *h* = 2*n* and 0*k*0 with *k* = 2*n*) of the orthorhombic lattice, the space group *Pbam* (no. 55) was determined. The structure was solved by direct methods using SHELXTL [23] and refined with anisotropic thermal displacement parameters for all atoms. Due to their poor distinguishability by X-ray analysis, the Si and Al atoms were refined equally distributed on their three crystallographic sites, employing the respective amounts of Si and Al according to the EPMA analysis. The refinement of the light atoms (O, N) was performed, according to *Paulings* rules [24], assuming N on all bridging positions and mixed O/N-occupancies of the terminal sites, thus leading to charge neutrality of the compounds. Relevant crystallographic data and details of the X-ray data collection are shown in Table 1. Table 2 gives the positional and isotropic displacement parameters for all atoms. Table 3 lists the anisotropic displacement parameter and Table 4 lists selected interatomic distances and angles.

Table 2 Atomic coordinates and isotropic displacement parameters (Å^2) for $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$ determined by single-crystal X-ray diffraction with standard deviations in parentheses. U_{eq} is defined as one third of the trace of the U_{ij} tensor.

Atom	Wyck	*x*	*y*	*z*	*s.o.f.*	U_{eq}
Pr1	8i	0.64361(3)	0.10332(3)	0.23600(3)	1	0.01299(9)
Pr2	4h	0.87184(4)	0.12186(4)	$^1/_2$	1	0.01570(11)
Pr3	4e	1	0	0.16798(3)	1	0.01195(10)
Pr4	4g	0.61397(4)	−0.12821(4)	0	1	0.01487(10)
(Si,Al)1	8i	0.88540(13)	0.25798(13)	0.24679(11)	0.9, 0.1	0.0102(3)
(Si,Al)2	8i	0.65176(13)	0.35658(13)	0.36513(12)	0.9, 0.1	0.0101(2)
(Si,Al)3	4g	0.78249(19)	0.11073(17)	0.0000	0.9, 0.1	0.0105(3)
N1	8i	0.8337(4)	0.1835(4)	−0.1231(4)	1	0.0127(8)
N2	8i	1.0259(4)	0.1941(4)	0.2862(4)	1	0.0161(8)
N3	8i	0.7716(4)	0.2529(4)	0.3527(4)	1	0.0128(7)
N4	4h	0.6015(6)	0.3917(6)	$^1/_2$	1	0.0140(11)
(N,O)5	8i	0.6815(4)	0.4921(4)	0.3097(3)	0.17, 0.83	0.0144(7)
(N,O)6	8i	0.9186(4)	0.3984(3)	0.2040(3)	0.17, 0.83	0.0121(7)
(N,O)7	4g	0.8506(5)	−0.0268(5)	0	0.17, 0.83	0.0148(10)
(N,O)8	4g	0.6199(6)	0.0894(6)	0	0.17, 0.83	0.0195(11)
Cl1	4h	0.5755(5)	0.0491(5)	$^1/_2$	0.480(12)*	0.0304(15)

*This value equals 0.5, within the uncertainties of the refinement.

Table 3 Anisotropic displacement parameters (Å^2) for $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$ determined by single-crystal X-ray diffraction with standard deviations in parentheses. The anisotropic displacement factor exponent is of the form $-2p^2[(ha^*)^2U_{11} + \cdots 2hka^*b^*U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pr1	0.01035(13)	0.01114(15)	0.01749(15)	−0.00146(9)	−0.00038(9)	−0.00002(8)
Pr2	0.0191(2)	0.0159(2)	0.01216(19)	0	0	0.00562(14)
Pr3	0.01289(17)	0.01283(19)	0.01013(17)	0	0	0.00105(13)
Pr4	0.0248(2)	0.01098(19)	0.00888(17)	0	0	0.00217(14)
(Si,Al)1	0.0100(5)	0.0113(6)	0.0092(6)	0.0003(5)	−0.0002(4)	−0.0002(5)
(Si,Al)2	0.0106(5)	0.0103(6)	0.0093(6)	−0.0004(5)	−0.0002(4)	0.0001(4)
(Si,Al)3	0.0121(8)	0.0109(8)	0.0086(8)	0	0	−0.0001(6)
N1	0.0173(19)	0.0128(19)	0.0079(17)	0.0022(14)	0.0011(14)	−0.0014(15)
N2	0.0140(19)	0.016(2)	0.019(2)	−0.0013(17)	−0.0027(16)	0.0018(16)
N3	0.0121(17)	0.0142(19)	0.0121(18)	−0.0006(15)	−0.0004(14)	0.0018(14)
N4	0.017(3)	0.016(3)	0.010(3)	0	0.	0.005(2)
(N,O)5	0.0131(16)	0.0134(17)	0.0168(18)	0.0029(14)	0.0019(13)	−0.0014(13)
(N,O)6	0.0128(16)	0.0118(17)	0.0116(16)	−0.0001(13)	0.0004(13)	−0.0003(12)
(N,O)7	0.018(3)	0.015(3)	0.012(2)	0	0	0.0020(19)
(N,O)8	0.015(2)	0.016(3)	0.028(3)	0	0	−0.001(2)
Cl1	0.035(3)	0.036(3)	0.021(2)	0	0	0.005(2)

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), e-mail: crysdata@FIZ-karlsruhe.de, on quoting the depository

Table 4 Selected interatomic distances /Å and angles /° in the structure of $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$ determined by single-crystal X-ray diffraction with standard deviations in parentheses.

Pr1−(O,N)5	2.390(4)	Pr2−N4	2.439(7)
Pr1−(O,N)6 (2 x)	2.411(4)	Pr2−N3 (2 x)	2.490(4)
Pr1−(O,N)6	2.413(4)	Pr2−N4	2.587(7)
Pr1−N3	2.543(4)	Pr2−(O,N)5	2.704(4)
Pr1−N1	2.565(4)	Pr2−(O,N)5	2.704(4)
Pr1−N2	2.649(5)	Pr2−N2 (2 x)	3.08(5)
Pr1−(O,N)8	2.7577(7)	Pr2−Cl1	3.244(6)
Pr1−Cl1	3.2085(17)		
Pr3−(O,N)7 (2 x)	2.531(4)	Pr4−(O,N)6 (2 x)	2.413(4)
Pr3−(O,N)5 (2 x)	2.534(4)	Pr4−(O,N)8	2.431(6)
Pr3−N2 (2 x)	2.581(5)	Pr4−(O,N)8	2.516(6)
Pr3−N1 (2 x)	2.753(5)	Pr4−N1 (2 x)	2.603(4)
		Pr4−(O,N)7	2.751(6)
(Si,Al)1−(O,N)6	1.682(4)	(Si,Al)2−(O,N)5	1.674(4)
(Si,Al)1−N2	1.713(5)	(Si,Al)2−N4	1.701(3)
(Si,Al)1−N3	1.724(4)	(Si,Al)2−N2	1.715(5)
(Si,Al)1−N1	1.748(4)	(Si,Al)2−(O,N)5	1.725(5)
(Si,Al)3−(O,N)7	1.698(6)	Cl1−Cl1*	1.940(11)
(Si,Al)3−N1	1.732(4)		
(Si,Al)3−N1	1.732(4)		
(Si,Al)3−(O,N)8	1.739(6)		
(O,N)6−(Si,Al)1−N2	106.6(2)	(O,N)5−(Si,Al)2−N4	101.9(3)
(O,N)6−(Si,Al)1−N3	112.8(2)	(O,N)5−(Si,Al)2−N2	103.8(2)
N2−(Si,Al)1−N3	113.8(2)	N4−(Si,Al)2−N2	109.0(3)
(O,N)6−Si1−N1	105.4(2)	(O,N)5−(Si,Al)2−N3	115.8(2)
N2−(Si,Al)1−N1	107.1(2)	N4−(Si,Al)2−N3	117.5(3)
N3−(Si,Al)1−N1	110.6(2)	N3−(Si,Al)2−N3	107.9(2)
(O,N)7−(Si,Al)3−N1 (2x)	106.95(19)	(Si,Al)3−N1−(Si,Al)1	179.6(3)
N1−(Si,Al)3−N1	111.3(3)	(Si,Al)1−N2−(Si,Al)2	163.0(3)
(O,N)7−(Si,Al)3−(O,N)8	107.3(3)	(Si,Al)1−N3−(Si,Al)2	123.5(3)
(O,N)8−(Si,Al)3−N1 (2x)	111.98(19)	(Si,Al)2−N4−(Si,Al)2	134.3(4)

*Distance between symmetrically equivalent split positions.

number CSD-391345, the name of the author(s) and citation of the paper.

4 EPMA-analysis

Quantitative chemical analyses on the microscale by electron probe micro analysis (EPMA) were carried out with a Jeol JXA-8900 R superprobe using an accelerating voltage of 15 kV, a beam current of 80 nA and a 3 µm measuring spot. The total volume analyzed was approximately 10−15 µm^3. The microprobe is equipped with synthetic multilayer spectrometer crystals with large *d*-spacing for quantitative wavelength dispersive analysis of light elements. For N and O analysis, the LDE1 crystal with 2*d* = 600 nm was used. Matrix correction was carried out with the CITZAF program [25]. For the analysis, the samples were mounted with epoxy resin into cylindrical holes in an epoxy pellet of 25 mm diameter and polished with a final diamond powder grain size of 0.25 µm. In addition, the samples have been coated with carbon. Since the quantitative analysis of light elements such as N and O, and also of Cl are not a routine EPMA technique (see [26, 27]), significant care was taken to minimize errors that may occur during measurements of these low-energy X-ray emission lines. In addition, the analysis of light elements becomes more difficult in the presence of lanthanide elements in high concentrations in the analyzed oxonitridoaluminosilicate. Praseodymium produces a large number of emission lines which may overlap with the N, O or Cl Kα lines. Further details of the measurements can be taken from ref. [28]. The used standards are listed in Table 5.

Table 5 Parameters of the EPMA measurements.

Element, X-ray line	Standard	Spectrometer crystal	Measuring time on peak / sec	Measuring time on background / sec
Pr, Lα	$Pr_3Si_6N_{11}$ [20]	PET	60	30+30
Si, Kα	$Ce_3Si_6N_{11}$ [34]	TAP	90	90
Al, Kα	Al_2O_3 [35]	TAP	60	60
N, Kα	$Ce_3Si_6N_{11}$	LDE1	120	60+60
O, Kα	Albite [35]	LDE1	40	40
Cl, Kα	Scapolite [36]	PETH	180	90+90

5 Results and Discussion

5.1 EPMA

Using EPMA, a single crystal of $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$, was investigated (19 spots). The averaged results are given in Table 6. The low values of 1 sigma indicate high homogeneity of the crystal. The total of the analyses is 102.1 %, thus indicating a good quality of the analyses of light elements in a difficult matrix. Due to measurement uncertainty the atomic composition of such a system can not be obtained exactly. Given that there are no defects in the Si−Al−O−N substructure a formula $[Si_{10-x}Al_xO_{9+x}N_{17-x}]^{29-}$ with $0.99 \leq x \leq 1.17$, conforming to charge neutrality, can be derived. The value for N, which is known to be slightly too high for reasons of measurement artifacts, has not been taken into account for the calculation. The resulting averaged elemental composition $Pr_{10}[Si_9AlO_{10}N_{16}]Cl$ (x = 1) was implemented in the single-crystal X-ray refinement.

Table 6 Quantitative results of the EPMA analyses of $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$ with x ≈ 1 (19 measuring spots).

		Pr	Si	Al	O	N	Cl	Total
Wt-%	average	68.06	11.98	1.43	7.73	11.2	1.73	102.1
	1 sigma	0.09	0.03	0.02	0.05	0.10	0.01	0.18
At-%	average	21.07	18.60	2.30	21.1	34.8	2.12	
	1 sigma	0.08	0.09	0.02	0.11	0.20	0.01	
stoichiom. formula		10	8.83	1.09	10.01	16.53	1.01	

5.2 Crystal structure

The title compound $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$ is an isotypic sialon to $Ln_{10}[Si_{10}O_9N_{17}]X$ with Ln = Ce, Nd and X = Cl, Br [29], which represent a new layered structure type. The cell parameters of the praseodymium sialon are 10.5973(8) Å, *b* = 11.1687(6) Å, *c* = 11.6179(7) Å. They show an intermediate dimension compared to the cerium

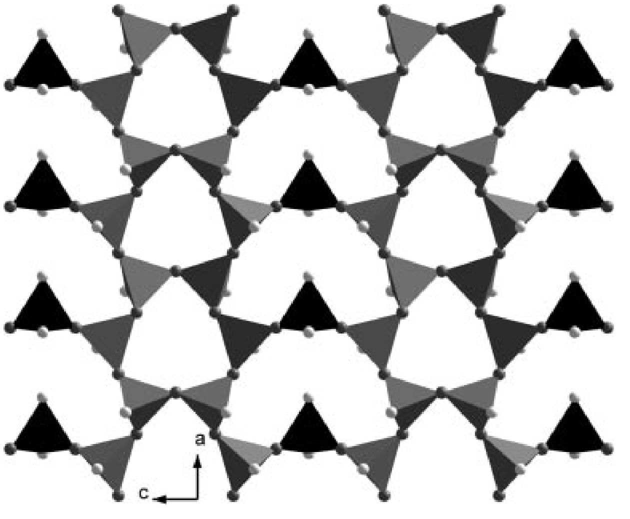

Fig. 1 Anionic layer $[Si_{10-x}Al_xO_{9+x}N_{17-x}]^{29-}$ of $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$. Tetrahedra of Q^3 type: gray, tetrahedra of Q^2 type: black, N: medium gray spheres, mixed O/N: white spheres. View along [010].

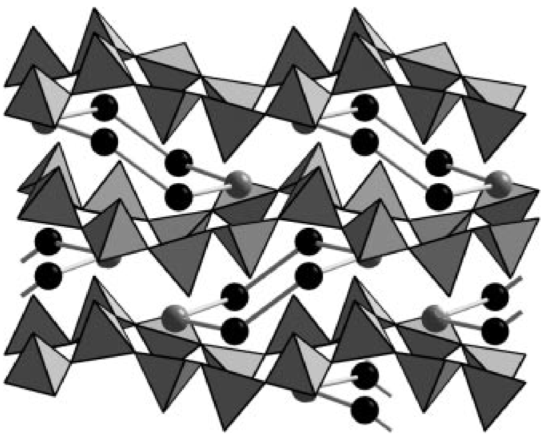

Fig. 2 Formfitting six membered rings of Pr1 and Pr2 atoms and their position between the oxonitridoaluminosilicate layers. Pr3 and Pr4 are omitted. Pr1: black spheres, Pr2: gray spheres. View along [001].

and the neodymium oxonitridosilicates ($Ce_{10}[Si_{10}O_9N_{17}]Br$: a = 10.6117(9) Å, *b* = 11.2319(10) Å, *c* = 11.6288(8) Å; $Nd_{10}[Si_{10}O_9N_{17}]Br$: a = 10.523(2) Å, *b* = 11.101(2) Å, *c* = 11.546(2) Å), owing to the medium sized Pr^{3+} ions, compared to the smaller Nd^{3+} and the larger Ce^{3+} ions.

The anionic layers $[Si_{10-x}Al_xO_{9+x}N_{17-x}]^{29-}$ (Fig. 1) are made up of $[(Si,Al)N_2(O/N)_2]$ and $[(Si,Al)N_3(O/N)]$ units representing Q^2 and Q^3 type tetrahedra. According to *Liebau* the $[Si_{10-x}Al_xO_{9+x}N_{17-x}]^{29-}$ layer of the title compound has to be specified as an open-branched vierer single chain layer [30−32]. A more detailed description of the topology can be found in ref. 29. The Pr^{3+} ions are located on four different crystallographic sites. Pr1 and Pr2 form six-membered rings in chair conformation situated formfitting between the six-membered tetrahedra rings of the silicate layers (Fig. 2). These cations are coordinated by O, N and the chloride ions (Fig. 3). The chloride ions are statistically disordered on two neighboring and symmetrically equivalent positions in the center of the Pr1/Pr2-rings. The distance between the two positions is 1.940(11) Å and can be compared to the Cl−Cl distance (1.931(8) Å) in $Nd_{10}[Si_{10}O_9N_{17}]Cl$. Due to the split position (occupancy factor = 0.5) only one of the chloride ions is present at a time. The chloride ion has three shorter and five longer distances to the surrounding praseodymium cations and it is therefore assumed to be predominantly coordinated by three lanthanide atoms forming a decentered trigonal coordination sphere (Fig. 4). Since several anions (O, N) are located between the three closer and the five more distant praseodymium cations, the threefold coordination of the halide atoms is more likely than an enlarged cationic coordination sphere. A similar threefold coordination of halide atoms has already been found in lanthanide oxosilicate

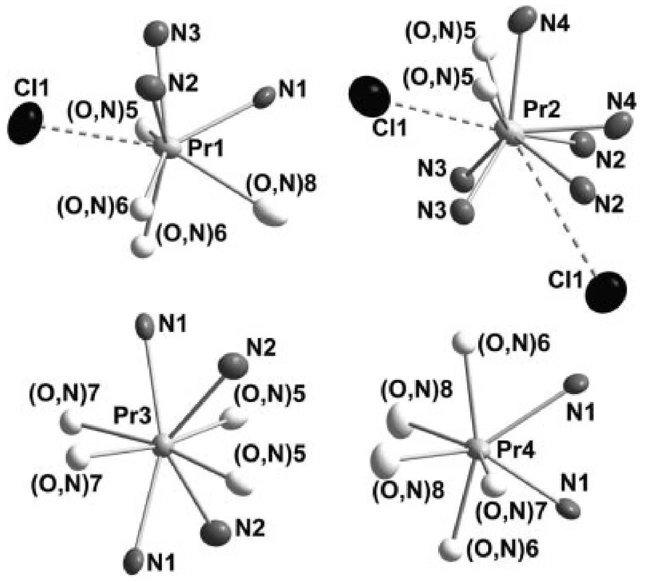

Fig. 3 Coordination spheres of the four crystallographically different Pr atoms. Displacement ellipsoids are drawn at the 90 % probability level.

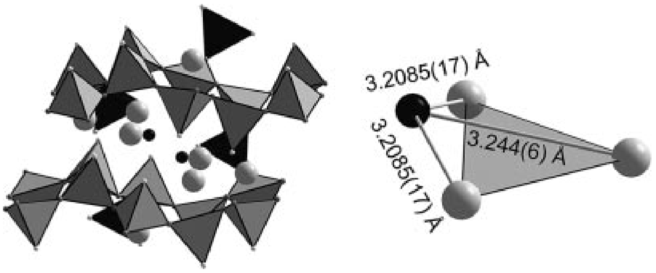

Fig. 4 Possible positions and assumed coordination of the chloride anions in $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$ (split position with an occupancy factor of 0.5). Pr: large gray spheres, chloride: small black spheres, N: small medium gray spheres, mixed O/N: small white spheres. View along [001].

Table 7 Environment of the halide anion represented by selected interatomic distances /Å in the structure of $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$ and $Nd_{10}[Si_{10}O_9N_{17}]Cl$ determined by single-crystal X-ray diffraction with standard deviations in parentheses.

$Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$			$Nd_{10}[Si_{10}O_9N_{17}]Cl$		
Pr1	3.2085(2)	2x	Nd1	3.208(1)	2x
Pr2	3.244(6)		Nd2	3.207(4)	
Pr1	4.207(4)	2x	Nd1	4.196(3)	2x
Pr2	4.262(6)		Nd2	4.263(4)	
Pr2	4.804(6)		Nd2	4.805(3)	
Pr2	5.111(5)		Nd2	5.062(4)	
(O,N)5	3.453(6)	2x	(O,N)5	3.426(4)	2x
N3	3.525(7)	2x	N3	3.504(5)	2x
N4	3.836(9)		N4	3.792(6)	
(O,N)6	3.829(4)	2x	(O,N)6	3.799(3)	2x
N2	3.830(6)	2x	N2	3.821(4)	2x
(Si,Al)2	3.860(5)	2x	(Si,Al)2	3.837(3)	2x
(O,N)6	3.865(4)	2x	(O,N)6	3.838(3)	2x

chlorides, e.g. $Tb_3Cl_5[SiO_4]$ [33]. The interatomic distances between the chloride atoms and their surrounding atoms are listed and compared to the data from $Nd_{10}[Si_{10}O_9N_{17}]Cl$ in Table 7, thus showing the similarity of the chlorine coordination sphere in these compounds. Pr3 and Pr4 do not participate in the coordination of the halide ions and are situated closer to the $[(Si,Al)N_2(O/N)_2]$ Q^2 type tetrahedra. Pr3 and Pr4 are solely coordinated by O and N (Fig. 3).

6 Conclusions

The new compound $Pr_{10}[Si_{10-x}Al_xO_{9+x}N_{17-x}]Cl$ shows, that in addition to the class of oxonitridosilicate halides the class of oxonitridoaluminosilicate chlorides (sialon chlorides) is accessible. This demonstrates the large range of substitution possibilities in the field of silicate chemistry. Substitution can be achieved on the cation positions and the tetrahedra centers (Si,Al) and concerning the ligand atoms (O,N) and additional anions, such as oxygen or halides. Furthermore, it could be shown that the unprecedented silicate layer of $Ln_{10}[Si_{10}O_9N_{17}]X$ (Ln = Ce, Nd and X = Cl, Br) also exists in the sialon system. Hence it is stressed, that the existence of the new layer topology does not depend on the tetrahedra center, but derives mainly from the incorporation of nitrogen and/or the halide. The implantation of bromine, as it is possible concerning the oxonitridosilicates, will be subject of further investigations.

The characterization of the new oxonitridoaluminosilicate chloride was carried out by means of single-crystal X-ray and electron probe micro analyses. The formerly established method for measuring light elements by EPMA [28] could be successfully transferred to the sialon system.

Acknowledgements. The authors would like to thank the Deutsche Forschungsgemeinschaft (SPP 1136 "Substitutionseffekte in Festkörpern", projekt SCHN 377/9) and the Fonds der Chemischen Industrie for generous financial support. Thanks are given to *Dr. Heidi E. Höfer* (Department of Mineralogy, Institut for Petrology and Geochemistry, J.-W. Goethe University of Frankfurt/Main, Germany) for performing the EPMA measurements. Additional thanks are given to *Dr. Oliver Oeckler* (Department of Chemistry and Biochemistry, LMU Munich, Germany) for helpful crystallographic advice.

References

[1] Y. Oyama, O. Kamigaito, *Jpn. J. Appl. Phys.* **1971**, *10*, 1637.
[2] K. H. Jack, W. I. Wilson, *Nature* **1972**, *238*, 28.
[3] K. H. Jack, *J. Mater. Sci.* **1976**, *11*, 1135.
[4] W. Schnick, H. Huppertz, R. Lauterbach, *J. Mater. Chem.* **1999**, *9*, 289.
[5] H. Huppertz, W. Schnick, *Angew. Chem.* **1996**, *108*, 2115; *Angew. Chem. Int. Ed.* **1996**, *35*, 1983.
[6] H. Huppertz, W. Schnick, *Z. Allg. Anorg. Chem* **1997**, *623*, 212.
[7] R. Lauterbach, W. Schnick, *Z. Anorg. Allg. Chem.* **2000**, *626*, 56.
[8] M. Woike, W. Jeitschko, *Inorg. Chem.* **1995**, *34*, 5105.
[9] T. Schlieper, W. Schnick, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1535.
[10] T. Schlieper, W. Schnick, *Z. Kristallogr.* **1996**, *211*,254.
[11] J. W. H. van Krevel, H. T. Hintzen, R. Metselaar, *Mater. Res. Bull.* **2000**, *35*, 747.
[12] Z. Shen, J. Grins, S. Esmaeilzadeh, H. Ehrenberg, *J. Mater. Chem.* **1999**, *9*, 1019.
[13] F. Stadler, R. Kraut, O. Oeckler, S. Schmid, W. Schnick, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1773.
[14] R. Müller-Mach, G. Müller, M. R. Krames, H. A. Höppe, F. Stadler, W. Schnick, T. Jüstel, P. Schmidt, *Phys. Stat. Sol. (A)* **2005**, *202*, 1727.
[15] H. A. Höppe, H. Lutz, P. Morys, W. Schnick, A. Seilmeier, *J. Phys. Chem. Solids* **2000**, *61*, 2001.
[16] G. A. Geffrey, G. S. Parry, R. L. Mozzi, *J. Chem. Phys.* **1956**, *25*, 1024.
[17] E. J. W. Verwey, *Z. Kristallogr.* **1935**, *91*, 317.
[18] H. Lange, G. Wötting, G. Winter, *Angew. Chem.* **1991**, *103*, 1606; *Angew. Chem. Int. Ed.* **1991**, *30*, 1579.
[19] R. Lauterbach, W. Schnick, *Z. Anorg. Allg. Chem.* **1999**, *625*, 429.
[20] T. Schlieper, W. Schnick, *Z. Kristallogr.* **1996**, *211*, 254.
[21] R. Marchand, A. Jayaweera, P. Verdier, J. Lang, *C. R. Séances Acad. Sci. C* **1976**, *283*, 675.
[22] J. P. Guha, *J. Mater. Sci.* **1980**, *15*, 262.
[23] G. M. Sheldrick, SHELXS97 Program for the Solution of Crystal Structures and SHELXL97 Program for the Refinement of Crystal Structures, Univ. Göttingen **1997**.
[24] P. E. D. Morgan, *J. Mater. Sci.* **1986**, *21*, 4305.
[25] J. T. Armstrong, Caltech 1993, Jeol License of CITZAF Version 3.5.
[26] G. F. Bastin, H. J. M. Heijligers, *Quantitative Electron Probe Microanalysis of Nitrogen*, Internal Report, Eindhoven University of Technology, 1988.
[27] G. F. Bastin, H. J. M. Heijligers, *Quantitative Electron Probe Microanalysis of Oxygen*, Internal Report, Eindhoven University of Technology, 1989.

[28] A. Lieb, M. T. Weller, P. F. Henry, R. Niewa, R. Pöttgen, R.-D. Hoffmann, H.E. Höfer, W. Schnick, *J. Solid State Chem.* **2005**, *178*, 976.

[29] A. Lieb, W. Schnick, *J. Solid State Chem.* **2005**, *178*, in press.

[30] F. Liebau, *Structural Chemistry of Silicates*, Springer, Berlin 1985.

[31] The classification can also be determined by using the programm CRYSTANA via http://www.is.informatik.uni-kiel.de/hjk/crystana.html which is partially based on ref. 30

[32] K. Goetzke, H.-J. Klein, *J. Non-Cryst. Solids* **1991**, *127*, 215.

[33] M. Petter, I. Hartenbach, T. Nikelski, Th. Schleid, *Z. Kristallogr.* **2004**, *219*, 177.

[34] T. Schlieper, W. Schnick, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1535.

[35] A.V. McGuire, C.A. Francis, M. Darby Dyar, *Am. Miner.* **1992**, *77*, 1087.

[36] E. Jarosewich, J.A. Nelen, J.A. Norberg, *Geostandards Newsletter* **1980**, *4*, 43.