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$La_6Ba_3[Si_{17}N_{29}O_2]Cl$—An Oxonitridosilicate Chloride with Exceptional Structural Motifs

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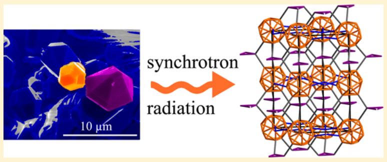
Supporting Information



ABSTRACT: The oxonitridosilicate chloride $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ was synthesized by a high-temperature reaction in a radiofrequency furnace starting from $LaCl_3$, BaH_2, and the ammonolysis product of Si_2Cl_6. Diffraction data of a micrometer-sized single crystal were obtained using microfocused synchrotron radiation at beamline ID11 of the ESRF. EDX measurements on the same crystal confirm the chemical composition. The crystal structure [space group $P6_3/m$ (no. 176), $a = 9.8117(14)$, $c = 19.286(6)$ Å, $Z = 2$] contains an unprecedented interrupted three-dimensional network of vertex-sharing SiN_4 and SiN_3O tetrahedra. The SiN_4 tetrahedra form *dreier* rings. Twenty of the latter condense in a way that the Si atoms form icosahedra. Each icosahedron is connected to others via six SiN_4 tetrahedra that are part of *dreier* rings and via six Q^3-type SiN_3O tetrahedra. Rietveld refinements confirm that the final product contains only a small amount of impurities. Lattice energy (MAPLE) and bond-valence sum (BVS) calculations show that the structure is electrostatically well balanced. Infrared spectroscopy confirms the absence of N−H bonds.

■ INTRODUCTION

Silicon and oxygen are the most abundant elements in the earth's crust, and more than 1000 representatives of silicate structures are known. Among others, silicates find applications in ceramics and glass industries. Nonoxidic ceramics exhibit pronounced covalent bonding character which results generally in high mechanical, thermal, and chemical stability.[1] In this context, (oxo)nitridosilicates turned out to be a promising extension of the classical silicate materials class.[2] In addition, compounds like Li_2SiN_2, Li_8SiN_4, and $Li_{14}Ln_5[Si_{11}N_{19}O_5]O_2F_2$, with Ln = Ce and Nd, emerged as lithium ion conductors, which makes them interesting for potential applications in lithium batteries.[3−7] Moreover, nitridosilicates such as $M_2Si_5N_8$ with M = Ca and Sr seem suitable as nonlinear optical (NLO) materials.[8] Nowadays, Eu^{2+}-doped (oxo)nitridosilicates are indispensable luminescence materials for phosphor-converted light-emitting diodes (pc-LEDs).[9,10] The reason for the diverse and tunable properties of these compounds lies in their broad structural variety. The structural entities of oxosilicates are largely limited to SiO_4 tetrahedra with either terminal $O^{[1]}$ or singly bridging $O^{[2]}$ atoms. In contrast, (oxo)nitridosilicates are typically built up from $Si(O,N)_4$ tetrahedra with $N^{[1]}$, $N^{[2]}$, $N^{[3]}$, and $N^{[4]}$ atoms bridging up to four neighboring tetrahedral centers. This variability allows for a wide range of additional structural possibilities. Moreover, except for fibrous SiO_2,[11] whose existence has not yet been proven unequivocally, SiO_4 tetrahedra share only common vertices, whereas nitridosilicates can contain both vertex- and edge-sharing tetrahedra.[12] Due to these structural possibilities and the resulting outstanding properties, the search for novel (oxo)nitridosilicates has been pursued frequently. Synthetic approaches like high-temperature syntheses, flux methods, and precursor routes enabled suitable access to this compound class.[13−15] However, syntheses often lead to inhomogeneous samples containing microcrystalline compounds. This situation impedes structure determination by means of conventional single-crystal or powder X-ray diffraction. However, diffraction data of micrometer-sized single crystals can be acquired using synchrotron radiation as recently developed Be and Al lenses allow unprecedented brilliance by microfocusing.[16−19] This approach leads to the structure elucidation of the novel compound $La_6Ba_3[Si_{17}N_{29}O_2]Cl$, one of the few oxonitridosilicate chlorides among $Nd_{10}Si_{10}O_9N_{17}Cl$,[20] $Ln_4Si_4O_{3+x}N_{7-x}Cl_{1-x}O_x$ (Ln = Ce, Pr, Nd; $x \approx 0.2$),[21] and $Ba_3Si_3N_5OCl$.[22]

■ EXPERIMENTAL SECTION

Synthesis. For the synthesis of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$, $LaCl_3$ (23.2 mg, 0.095 mmol, 99.99%, Alfa Aesar), "$Si_2(NH)_3{\cdot}6NH_4Cl$"[23] (100.0 mg, 0.237 mmol), and BaH_2 (66.7 mg, 0.479 mmol, 99.7%, Materion) were thoroughly ground in an agate mortar and filled into a tungsten crucible. These steps were performed under argon atmosphere in a glovebox (Unilab, MBraun, Garching; O_2 < 1 ppm; H_2O < 1 ppm). Then the crucible was placed into a radiofrequency furnace (type AXIO 10/450, max electrical output 10 kW, Hüttinger Elektronik, Freiburg),[13] heated under N_2 atmosphere to 900 °C within 5 min, subsequently heated to 1600 °C within 4 h, and finally quenched to room temperature by switching off the furnace. The reaction affords an inhomogeneous sample with small, turquoise crystals of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ which are resistant to hydrolysis. To remove soluble byproducts the sample was washed with water. Addition of CeF_3 or EuF_3 (0.4 mg, 0.002 mmol, 99.99%, Alfa Aesar/0.4 mg, 0.002 mmol, 99.99% Aldrich) as doping agent to the reaction mixture results

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in no marked change of color and does not lead to luminescence of the crystals of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$.

Elemental Analysis and Spectroscopy. The chemical composition and morphology of the crystals were analyzed with a LEO 1530 field-emission scanning electron microscope (SEM) operated at 20 kV and equipped with an energy-dispersive Si/Li detector 7418 (Oxford Instruments). To provide electrical conductivity on the sample surface it was coated with carbon (electron beam evaporator CED 030, Balzers). Fourier transform infrared (FTIR) spectroscopy was carried out with a PerkinElmer BXII spectrometer mounting ATR (attenuated total reflection) technology.

Crystal Structure Analysis. For single-crystal structure investigations, crystals of $La_6Ba_3[Si_{17}N_{29}O_2]Cl:Ce^{3+}$ were mounted on Kapton foil sample holders (micromount, MiTeGen, Ithaca). X-ray diffraction data were collected at beamline ID11 of the ESRF in Grenoble (Ge(111) double-crystal monochromator, Frelon 2K CCD detector).[24] The beam ($\lambda = 0.33510$ Å) was focused to ~4.5 μm in the horizontal direction and ~2 μm in the vertical direction with a beryllium lens system.[16] The reflections of the dominant crystal in an aggregate were indexed with SMART,[25] integrated with SAINT,[26] and semi-empirically absorption corrected using SADABS.[27] In addition, a correction was applied in order to account for the systematic error owing to the diffraction-angle dependence of the beam path length through the CCD phosphor.[28] The structure was solved by direct methods and refined by full matrix least-squares methods with SHELX.[29] Powder X-ray diffraction data were collected with a STOE STADI P diffractometer (Mo Kα_1 radiation, $\lambda = 0.70930$ Å, Ge(111) monochromator, MYTHEN 1K detector) in modified Debye–Scherrer geometry. Rietveld refinement was carried out using the TOPAS-Academic package.[30]

■ RESULTS AND DISCUSSION

Synthesis and Sample Characterization. $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ was synthesized at high temperature, the driving force presumably being the decomposition of BaH_2 around 675 °C[31] and its reaction to $BaCl_2$ with chlorine originating from $LaCl_3$. Among other intermediates, probably La metal is formed, which reacts with the remaining Ba, $LaCl_3$, and the precursor "$Si_2(NH)_3\cdot 6NH_4Cl$" to form turquoise crystals of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ (Figure 1). The incorporated O supposably originates from contamination of commercially acquired starting materials.

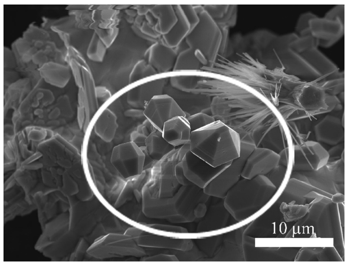

Figure 1. SEM image of crystals of $La_6Ba_3[Si_{17}N_{29}O_2]Cl:Ce^{3+}$ (white circle).

Crystal structure investigations were performed on a crystal of a sample doped with Ce^{3+} (see above). Consequently, the same crystal was used for EDX analysis, which yields an average composition of La/Ba/Si/Cl/Ce = 6.0:3.5:13.3:1.0:0.14 (normalized according to the La content; four-point measurements at different positions; the atomic content of N and O was excluded as they are underdetermined, due to the limitations of the method). The heavy element ratios are in good agreement with the sum formula obtained from single-crystal structure refinement, which is consistent with bond-valence sum (BVS) and MAPLE (Madelung part of lattice energy) calculations (see below). The absence of N–H and O–H groups was confirmed by infrared spectroscopy (Figure S2, Supporting Information). Consequently, the combination of the results of EDX measurements and infrared spectroscopy excludes the presence of elements other than La, Ba, Si, N, O, Cl, and Ce. In order to determine the bulk phase composition of the washed sample, a Rietveld refinement of powder X-ray diffraction data was performed (Figure S1, Table S1). It shows that the sample contains $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ as the main phase and $BaCl_2$ as byproduct. A few weak reflections cannot be ascribed to any known compound.

Crystal Structure of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$. Due to the limited scattering power of the micrometer-sized crystals, microfocused synchrotron radiation was used for single-crystal investigations. As it was impossible to isolate and handle such tiny single crystals, the investigated sample consisted of several fragments; however, the reflections of one individual could be selected in a straightforward fashion and yielded a data set with high quality. The crystal structure of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ was solved and refined in space group $P6_3/m$ (no. 176) with a = 9.8117(14) Å and c = 19.286(6) Å. In the refinement as well as for BVS and MAPLE calculations, Ce^{3+} was neglected because of its insignificant contribution to the scattering density. The distribution of La and Ba as well as of N and O was fixed as indicated by MAPLE and BVS calculations; for detailed explanations see the sections on Bond-Valence Sum Calculations and MAPLE Calculations below. The crystallographic data of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ are summarized in Table 1, and the atomic parameters are listed in Table 2. All atoms were refined anisotropically (Table S2 in the Supporting Information).[32]

Table 1. Crystallographic Data and Details of the Structure Refinement of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ at Room Temperature

formula	$La_6Ba_3[Si_{17}N_{29}O_2]Cl$
cryst syst	hexagonal
space group	$P6_3/m$ (no. 176)
a (Å)	9.8117(14)
c (Å)	19.286(6)
cell volume (Å^3)	1607.9(7)
Z	2
density (g·cm^{-3})	4.54
μ (mm^{-1})	1.611
radiation	synchrotron ($\lambda = 0.33510$ Å, ID11 at ESRF)
$F(000)$	1968
θ range (deg)	$1.96 \leq \theta \leq 14.70$
total no. of reflns	21 886
no. of independent reflns	1985 [R(int) = 0.0304]
no. of refined params	95
extinction param	0.0031
GOF	1.30
$R1$ (all data/for $F^2 > 2\sigma(F^2)$)	0.0171/0.0169
$wR2$ (all data/for $F^2 > 2\sigma(F^2)$)	0.0397/0.0396
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (in e/Å^3)	1.755; −1.051

In contrast to the oxonitridosilicate chlorides $Nd_{10}Si_{10}O_9N_{17}Cl$ and $Ln_4Si_4O_{3+x}N_{7-x}Cl_{1-x}O_x$ (Ln = Ce, Pr, Nd; $x \approx 0.2$), which represent layer silicates,[20,21] and $Ba_3Si_3N_5OCl$, which consists of a zeolite-like framework,[22] the crystal structure of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ is characterized by an unprecedented interrupted three-dimensional network. It

Table 2. Atomic Coordinates, Isotropic Displacement Parameters, and Site Occupancies of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ at Room Temperature[a]

atom		x	y	z	U_{eq} [Å^2]	s.o.f
La1	12*i*	0.53306(2)	0.47894(2)	0.39098(2)	0.00793(5)	1
Ba2	6*h*	0.16199(3)	0.29913(3)	1/4	0.01178(6)	1
Si1	6*h*	0.75300(9)	0.54355(9)	1/4	0.00492(13)	1
Si2	4*f*	2/3	1/3	0.50460(5)	0.00530(16)	1
Si3	12*i*	0.20747(6)	0.12253(6)	0.38315(3)	0.00472(10)	1
Si4	12*i*	0.67463(7)	0.81638(6)	0.46847(3)	0.00492(10)	1
N1	4*e*	0	0	0.36301(16)	0.0058(5)	1
N2	12*i*	0.7991(2)	0.7374(2)	0.45792(9)	0.0062(3)	1
N3	12*i*	0.2345(2)	0.3081(2)	0.39609(9)	0.0067(3)	1
N4	12*i*	0.5059(2)	0.3480(2)	0.52299(10)	0.0080(3)	1
N5	12*i*	0.7942(2)	0.6655(2)	0.32130(9)	0.0087(3)	1
N6	6*h*	0.5486(3)	0.4142(3)	1/4	0.0080(4)	1
O7	4*f*	2/3	1/3	0.41468(14)	0.0086(4)	1
Cl1	4*f*	1/3	2/3	0.2718(3)	0.0542(16)	1/2

[a] For anisotropic displacement parameters, cf. Table S2 in the Supporting Information.

consists of vertex-sharing Q^4- and Q^3-type SiN_4/SiN_3O tetrahedra with a ratio of Q^4/Q^3 = 15/2 (Figure 2), which results in a degree of condensation $\kappa = n(Si):n(N,O) = 0.55$. The Q^3-type tetrahedra exhibit one terminal $O^{[1]}$ and three singly bridging $N^{[2]}$ atoms, whereas the Q^4-type tetrahedra consist of four $N^{[2]}$ or two $N^{[2]}$ and two $N^{[3]}$ (interconnection of three tetrahedra) atoms.

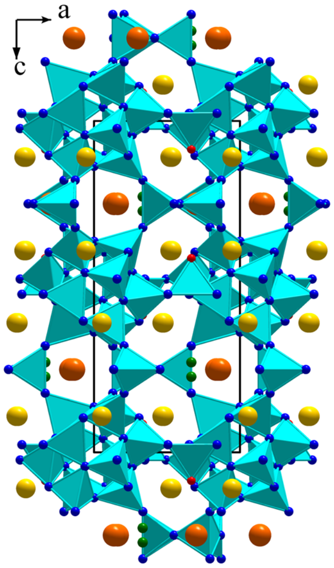

Figure 2. Crystal structure of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ in projection along [010] with $Si(N,O)_4$ tetrahedra (turquoise), N (blue), O (red), La (yellow), Ba (orange), and semi-occupied Cl positions (green); the unit cell is displayed.

The Q^4-type SiN_4 tetrahedra form *dreier* rings,[33,34] 20 of which condense in a way that the Si atoms form icosahedra (note that in skeletal representations not all edges of this polyhedron correspond to Si−N−Si bonds due to the presence of $N^{[3]}$ atoms, Figure 3e). Each icosahedron is connected to others via six SiN_4 tetrahedra that are part of *dreier* rings and via six Q^3-type SiN_3O tetrahedra (Figure 3a, 3b, 3d, and 3e).

In addition, the structure is characterized by *sechser* and *siebener* rings, which are built up by the tetrahedra of the Si atoms of the icosahedra and the Q^3-type tetrahedra. Six edges of the icosahedron are part of the *sechser* rings, and 18 edges are part of the *siebener* rings (Figure 3f and 3g). The novel topology of the framework is characterized by the point symbol $\{3.6.7^4\}_3\{3^5.4^5.6^2.7^3\}_{12}\{6^3\}_2$ as calculated with the program TOPOS.[35] Despite the complexity of the network it is a hierarchical derivative[36,37] of the simple NiAs structure type,[38] with the centers of the icosahedra on the Ni and the centers of the *dreier* rings on the As positions (Figure 3c).

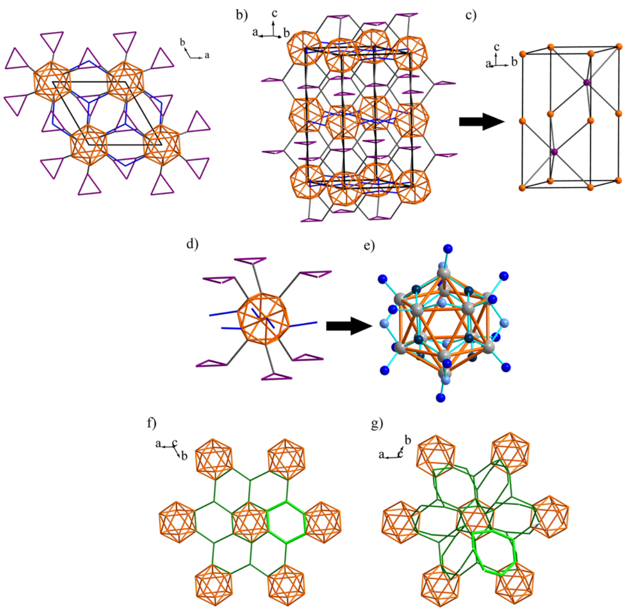

Figure 3. (a and b) Topological representations of $La_6Ba_3[Si_{17}N_{29}O_2]$-Cl; (c) simplification of the topology of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ as a variant of the NiAs structure type (centers of icosahedra orange; centers of *dreier* rings violet); (d) icosahedra (orange) connected via six *dreier* rings (violet) and six Q^3-type tetrahedra (blue) as characteristic buildings blocks of the silicate network; (e) interconnection of the Si atoms of one icosahedron (Si gray; $N^{[3]}$ dark blue; $N^{[2]}$ blue/light blue); due to the presence of $N^{[3]}$ atoms only each $Si-N^{[2]}-Si$ bond corresponds to an edge of the icosahedron; (f and g) topological representation of the *sechser* and *siebener* rings (green); each connecting line of the *dreier*, *sechser*, and *siebener* rings represents a Si−N−Si bond.

$La_6Ba_3[Si_{17}N_{29}O_2]Cl$ contains a half-occupied Cl split position (Table 2). This site is coordinated by three Ba atoms forming a decentered trigonal coordination sphere (Figure 4a). A similar coordination of Cl atoms was observed in other oxo- and oxonitridosilicates, e.g., $Nd_{10}[Si_{10}O_9N_{17}]Cl$[20] and $Tb_3Cl_5[SiO_4]$.[39] Additionally, the refined crystal structure exhibits two crystallographically independent heavy-atom sites. BVS as well as MAPLE calculations (Table 3 and 4) indicate one La and one Ba site (Table 2). La is 7-fold coordinated by six N and one O atom, which results in a distorted single-capped octahedron (Figure 4b). The Ba site is irregularly coordinated by nine N atoms and the Cl split position (50%/50%) (Figure 4c).

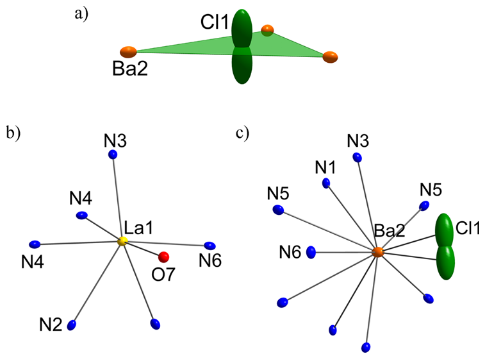

Figure 4. Coordination sphere of the Cl split position (a) and the heavy-atom sites (b and c) of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ (anisotropic displacement ellipsoids with 60% probability).

Table 3. Bond-Valence Sums for $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ and Expected Oxidation States

	BVS	oxidation state
La1	3.05	+3
Ba2	2.14	+2
Si1	3.82	+4
Si2	4.02	+4
Si3	3.78	+4
Si4	3.89	+4
Cl	0.46	−1[i]
$N1^{[3]}$	2.66	−3
$N2^{[3]}$	3.08	−3
$N3^{[2]}$	2.97	−3
$N4^{[2]}$	3.07	−3
$N5^{[2]}$	3.02	−3
$N6^{[2]}$	2.54	−3
$O7^{[1]}$	2.20	−2

[i] sof =1/2

The distances Si−N [1.6914(18)−1.8145(9) Å] and Si−O [1.734(3) Å] are in good agreement with other (nitrido)-silicates as well as the La−N [2.5361(19)−2.8796(18) Å] and Ba−N [2.8725(19)−3.374(3) Å] distances.[40−43] The La−O [2.4168(6) Å] and Ba−Cl [3.1535(8) Å] distances correspond to those in other lanthanum or barium compounds.[44,45] Additionally, all mentioned distances are in good agreement with the sum of the ionic radii.[46]

Bond-Valence Sum Calculations. As mentioned before, BVS calculations[47] were performed in order to reasonably assign sites to N or O and La or Ba, respectively, despite their very similar X-ray scattering factors. Charge neutrality alone can be preserved by arbitrary exchange of LaN and BaO units and thus is not a sufficient constraint in structure refinements. Pauling's rules[48] and the fact that $X^{[3]}$ (X = N,O) is usually not occupied by O served as a basis. Consequently, the bridging anion positions were assumed to be occupied by N and the terminal anion positions by O. This assumption is corroborated by neutron powder diffraction of other oxonitridosilicates, where a similar contribution of N and O was observed.[21] On the basis of this O/N distribution, the BVS of the cations and anions were determined (Table 3) and indicate one La and one Ba site. This leads to a charge-neutral formula, which is additionally corroborated by EDX measurements.

Table 4. Partial MAPLE Values and MAPLE Sums [kJ/mol] for $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ as Well As Typical Partial MAPLE Values

$La_6Ba_3[Si_{17}N_{29}O_2]Cl$		typical partial MAPLE values[2,52−56]
La1	4032	Ln^{3+}: 3500−5100
Ba2	1708	Ba^{2+}: 1500−2000
Si1	10264	Si^{4+}: 9000−10200
Si2	9978	
Si3	9677	
Si4	9776	
Cl	289	Cl^-: 307−357
$N1^{[3]}$	5835	$N^{[3]3-}$: 5000−6200
$N2^{[3]}$	6084	
$N3^{[2]}$	5427	$N^{[2]3-}$: 4600−6000
$N4^{[2]}$	5396	
$N5^{[2]}$	5281	
$N6^{[2]}$	5100	
$O7^{[1]}$	2494	$O^{[1]2-}$: 2000−2800

$\sum = 362\,093$

$2/3La_2O_3 + 14/3LaN + 1/2BaCl_2 + 5/6Ba_3N_2 + 17/3\beta\text{-}Si_3N_4 \rightarrow La_6Ba_3[Si_{17}N_{29}O_2]Cl$

$9461 + 38\,470 + 1103 + 10\,129 + 301\,963 \rightarrow 361\,127;\ \Delta = 0.27\%$

MAPLE Calculations. In order to further confirm the electrostatic consistency of the crystal structure, lattice energies were calculated using the MAPLE concept (Table 4).[46,49−51] This solely takes into account electrostatic interactions, which depend on the coordination spheres, the charge, and the distances of the constituting ions. As the MAPLE software cannot consider partially occupied positions, an idealized structure model of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ was set up by shifting Cl from Wyckoff position 4*f* (point symmetry: 3..; $x = 1/3$, $y = 2/3$, $z = 0.2718$) to a fully occupied "average" Wyckoff position 2*c* (point symmetry: $\bar{6}$..; $x = 1/3$, $y = 2/3$, $z = 1/4$). The calculated partial MAPLE values of La, Ba, Si, N, and O are consistent with the characteristic ranges.[2,52−55] The partial MAPLE value of Cl is slightly smaller than reference values.[56,57] Therefore, as the exchange of the La and Ba position with consideration of charge neutrality leads to MAPLE values outside of the characteristic ranges, the occupation of the atoms sites is corroborated. The minor deviation of 0.27% of the overall MAPLE value of $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ and the sum of those of the binary compounds that formally constitute $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ confirms the electrostatic balance of the refined crystal structure.

■ CONCLUSION

A high-temperature reaction yielded a novel oxonitridosilicate chloride $La_6Ba_3[Si_{17}N_{29}O_2]Cl$, characterized by an unprecedented tetrahedra network. The structure elucidation shows how microfocused synchrotron radiation is well suited to precisely determine the structure of microcrystals even with

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complex structures which could not be characterized by conventional single-crystal or powder X-ray diffraction. This approach is a powerful tool as knowledge of the structure could foster the development of syntheses to phase-pure samples and by comprehension of the relation between structures and properties which is necessary for a systematic improvement of properties. The usefulness of BVS and MAPLE calculations was demonstrated by applying these methods for a reasonable assignment of N and O as well as of Ba and La. Using BaH_2 as a starting material appears essential as it decomposes and presumably reacts with $LaCl_3$ to $BaCl_2$ and finely dispersed and reactive La. Furthermore, the use of the precursor "$Si_2(NH)_3·6NH_4Cl$" seems to play an important role to obtain novel (oxo)nitridosilicates as this starting material provides another stoichiometric proportion of Si and N and another oxidation state of Si as the common precursors Si_3N_4 and $Si(NH)_2$.[58] Consequently, this combination of starting materials appears to be a promising route which might lead to the discovery of further new (oxo)nitridosilicates with intriguing structural features and properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01368.

Rietveld refinement, crystallographic data of the Rieveld refinement, table of anisotropic displacement parameters, and IR spectrum (PDF)

Crystallographic information file (CIF)

Checkcif Report for $La_6Ba_3[Si_{17}N_{29}O_2]Cl$ (PDF)

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Author Contributions

The manuscript was written with contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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