

The lanthanoid(III) chloride *cyclo*-tetrasilicates $M_6Cl_{10}[Si_4O_{12}]$ ($M = Sm, Gd-Dy$): Synthesis, structure and IR investigations

Ingo Hartenbach^a, Stefan Jagiella^b, Thomas Schleid^{a,*}

^aInstitute for Inorganic Chemistry, University of Stuttgart, D-70569 Stuttgart, Germany

^bInstitute for Physical Chemistry, University of Stuttgart, D-70569 Stuttgart, Germany

Received 22 December 2005; received in revised form 27 January 2006; accepted 28 January 2006

Available online 9 March 2006

Dedicated to Professor Hans-Georg von Schnering on the occasion of his 75th birthday

Abstract

The chloride derivatized lanthanoid(III) *cyclo*-tetrasilicates of the composition $M_6Cl_{10}[Si_4O_{12}]$ ($M = Sm, Gd-Dy$) crystallize monoclinically in space group $C2/m$ ($a = 1062-1065$, $b = 1036-1052$, $c = 1163-1187$ pm, $\beta \approx 103^\circ$, $Z = 2$). They are obtained by the reaction of the sesquioxides M_2O_3 (or the combination of Tb_4O_7 and Tb in 3:2-molar ratio for the terbium case), the corresponding trichlorides MCl_3 , and SiO_2 (silica gel) in stoichiometric ratios with double the amount of MCl_3 as flux in evacuated silica tubes ($7d$ at $850^\circ C$) as transparent, *pseudo*-octagonal, pillar-shaped single crystals with the colour of the respective lanthanoid trication M^{3+} . Their crystal structure can be considered as a layered arrangement in which cationic $\infty_2\{(M2)_5Cl_9\}^{6+}$ layers are alternately piled with anionic ones of the kind $\infty_2\{(M1)Cl[Si_4O_{12}]\}^{6-}$. In the latter, the $(M1)^{3+}$ cations show a slightly distorted hexagonal bipyramidal environment built up by two Cl^- and six O^{2-} anions (CN = 8), whereas the $(M2)^{3+}$ cations exhibit a coordination number of only seven (five Cl^- and two O^{2-} anions in the shape of a distorted pentagonal bipyramid). The *cyclo*-tetrasilicate units consist of four corner-linked $[SiO_4]^{4-}$ tetrahedra in *all*-ecliptical conformation each, fused to eight-membered rings, which contain two almost linear (178°) and two bent (142°) Si–O–Si bridges. This particular *cyclo*- $[Si_4O_{12}]^{8-}$ situation could be confirmed by theoretical and experimental infrared-spectroscopic investigations. © 2006 Elsevier Inc. All rights reserved.

Keywords: Oxosilicates; Lanthanoid compounds; Crystal structure; IR spectroscopy

1. Introduction

The crust of planet earth is mainly built up by compounds, which contain vertex-shared oxosilicate tetrahedra $[SiO_4]^{4-}$ forming zero-, one-, two-, and three-dimensional units with the shape of chain fragments, chains, bands, sheets, and frameworks. Besides all this finite and infinite building blocks, cyclic oxosilicate entities are very common as well, e.g. in the mineral *benitoite* ($BaTi[Si_3O_9]$) [1] as *cyclo*-trisilicate or in *beryl* ($Be_3Al_2[Si_6O_{18}]$) [2] as *cyclo*-hexasilicate units. Six- and twelve-membered rings seem to be the most common groups among the *cyclo*-oxosilicates, although some *cyclo*-tetrasilicates are also already known in

mineralogy (e.g. *nagashimalite* [3], *baotite* [4], *verplanckite* [5], and *taramelite* [6]). Considering synthetic ringsilicates $\infty_n([SiO_3]^{2-})_n$, the majority of the compounds show $n = 3$ and 6 as well, but a couple of structures with $[Si_4O_{12}]^{8-}$ units are also established. However, in combination with rare-earth metal cations and chloride anions the number of compounds reduces to two, namely $Eu_8Cl_8[Si_4O_{12}]$ [7] and $Y_6Cl_{10}[Si_4O_{12}]$ [8]. So the title compounds $M_6Cl_{10}[Si_4O_{12}]$ ($M = Sm, Gd-Dy$) [9], which crystallize isostructural to $Y_6Cl_{10}[Si_4O_{12}]$, represent the first lanthanoid(III) chloride *cyclo*-oxotetrasilicates. With the smaller halide F^- as derivatizing anion another rare-earth metal *cyclo*-oxosilicate exists; however, $La_3F_3[Si_3O_9]$ [10] only consists of *cyclo*-trisilicate units. This compound along with other fluoride oxosilicates like the *thalenite*-type $M_3F[Si_3O_{10}]$ series ($M = Y, Dy-Er$) [11] which displays *catena*-trisilicate groups, $Er_4F_2[Si_2O_7][SiO_4]$ [12] which contains both

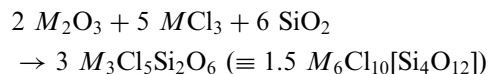
*Corresponding author. Fax: +49 711 685 4241.

E-mail addresses: hartenbach@iac.uni-stuttgart.de (I. Hartenbach), schleid@iac.uni-stuttgart.de (Th. Schleid).

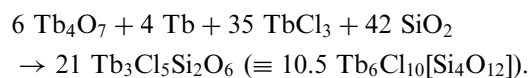
disilicate units and *ortho*-silicate anions, and mixed-valent *apatite*-type $\text{Eu}_5\text{F}[\text{SiO}_4]_3$ [13] which shows only *ortho*-silicate tetrahedra [13] do not only offer an interesting structural chemistry, but also amazing luminescence properties by using these compounds as host lattices (especially the La^{3+} and Y^{3+} compounds) for doping in small amounts of suitable lanthanoid trications such as Eu^{3+} . $\text{La}_3\text{F}_3[\text{Si}_3\text{O}_9]$ doped with Ce^{3+} has already proven to be a powerful UV-luminescent material [14] and most fluoride oxosilicates look very promising in exhibiting similar properties (e.g. visible and IR-luminescent $\text{Y}_3\text{F}[\text{Si}_3\text{O}_{10}]:\text{M}^{3+}$ with $M = \text{Nd}, \text{Eu}, \text{Tb}, \text{Dy}, \text{Er},$ and Yb [15]). Whether the rare-earth metal chloride oxosilicates are possible luminescent materials too must be evidenced in the future.

2. Experimental

The lanthanoid(III) chloride *cyclo*-tetrasilicates $\text{M}_6\text{Cl}_{10}[\text{Si}_4\text{O}_{12}]$ ($M = \text{Sm}, \text{Gd}, \text{Dy}$) were synthesized using the lanthanoid sesquioxides (M_2O_3 : ChemPur, 99.9%), the corresponding trichlorides (MCl_3 : ChemPur, 99.9%) and silicon dioxide (SiO_2 as silica gel: Merck, p.a.) according to



with a double excess of the respective lanthanoid trichloride as source for the chloride anions and fluxing agent as well. Due to the *non*-commercial availability of Tb_2O_3 , the synthesis of $\text{Tb}_6\text{Cl}_{10}[\text{Si}_4\text{O}_{12}]$ was carried out with Tb_4O_7 (ChemPur, 99.9%) and elemental terbium (Tb: ChemPur, 99.9%) in the molar ratio of 3:2 according to



All the above-mentioned mixtures were sealed in evacuated silica ampoules and heated at 850 °C for 10

days. The reactions lead to air- and water-resistant, transparent, *pseudo*-octagonal, pillar-shaped single crystals with the colour of the respective lanthanoid trication (Sm^{3+} : pale yellow; Gd^{3+} , Tb^{3+} : colourless; Dy^{3+} : very pale green). After removing the chloride flux by washing the bulk with water, the phase purity of the remaining products was determined by X-ray powder diffraction (Fig. 1) and even the IR spectra did not show any major *non*-crystalline by-product as well. The crystal structures were determined by X-ray diffraction of selected single crystals on a Stoe IPDS-I single-crystal diffractometer at room temperature. The results of the structure determinations along with important internuclear distances and angles can be taken from Tables 1–3 [16–19]. Further details of the crystal structure investigations are available at the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247/808 666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-416001 for $\text{Sm}_6\text{Cl}_{10}[\text{Si}_4\text{O}_{12}]$, CSD-416000 for $\text{Gd}_6\text{Cl}_{10}[\text{Si}_4\text{O}_{12}]$, CSD-415998 for $\text{Tb}_6\text{Cl}_{10}[\text{Si}_4\text{O}_{12}]$, and CSD-415999 for $\text{Dy}_6\text{Cl}_{10}[\text{Si}_4\text{O}_{12}]$. The X-ray powder diffraction measurements were carried out using a Stoe STADI P diffractometer with a position sensitive detector (PSD) using monochromatized $\text{Cu-K}\alpha$ radiation ($\lambda = 154.06 \text{ pm}$). IR spectra were collected with a Perkin-Elmer Paragon TC1000 spectrometer in the range of 3000–250 wavenumbers. The calculation of the harmonic vibrational frequencies was carried out with the program Gaussian 98 [20], where the hybrid density functional B3-LYP with a 6-31G(d) basis set found application.

3. Structure description and discussion

The chloride derivatized lanthanoid(III) *cyclo*-oxotetrasilicates $\text{M}_6\text{Cl}_{10}[\text{Si}_4\text{O}_{12}]$ ($M = \text{Sm}, \text{Gd-Dy}$) crystallize monoclinically in the space group $C2/m$ ($a = 1062\text{--}1065$,

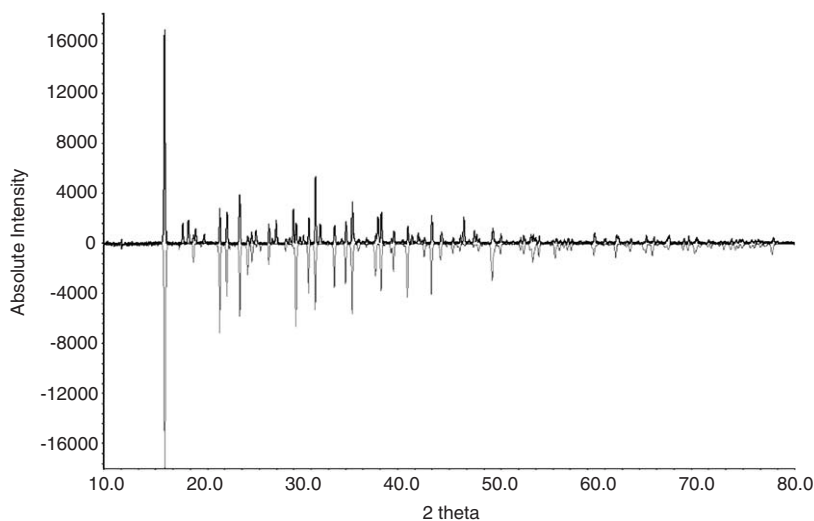


Fig. 1. Experimental powder pattern of $\text{Tb}_6\text{Cl}_{10}[\text{Si}_4\text{O}_{12}]$ (black curve with positive intensities) compared to the calculated one (gray curve with negative intensities).

Table 1
Crystallographic data for the chloride oxosilicates $M_6Cl_{10}[Si_4O_{12}]$ ($M = Sm, Gd-Dy$) and their determination

$M_6Cl_{10}[Si_4O_{12}]$	$M = Sm$	$M = Gd$	$M = Tb$	$M = Dy$
Crystal system, space group	Monoclinic, $C2/c$ (no. 12)			
Formula units	2			
Lattice constants				
a (pm)	1064.79(8)	1063.34(8)	1062.83(8)	1062.17(8)
b (pm)	1052.06(7)	1042.71(6)	1039.42(6)	1035.68(6)
c (pm)	1186.68(9)	1173.87(9)	1168.91(9)	1163.46(9)
β (deg)	103.152(9)	103.008(9)	103.211(9)	103.150(8)
Calculated density (D_x) (g cm $^{-3}$)	4.005	4.196	4.260	4.354
Molar volume (V_m) (cm 3 mol $^{-1}$)	389.77	381.84	378.53	375.27
$F(000)$	1388	1412	1424	1436
Diffractometer, wavelength	IPDS-I (Stoe), Mo- $K\alpha$: $\lambda = 71.07$ pm			
Index range				
$\pm h$	16	16	16	16
$\pm k$	14	14	14	15
$\pm l$	18	17	17	17
θ range				
θ_{min}	3.51	3.53	3.54	3.55
θ_{max}	32.8	32.9	33.0	32.9
Absorption coefficient (μ) (mm $^{-1}$)	14.65	16.75	17.95	19.07
Data corrections	Background, polarization, and Lorentz factors; numerical absorption correction: program <i>HABITUS</i> [16]			
T_{min} , T_{max}	0.257, 0.353	0.185, 0.347	0.304, 0.360	0.309, 0.519
Collected, unique reflections	10 673, 2332	9126, 2353	9246, 2348	11 938, 2414
R_{int} , R_σ	0.031, 0.023	0.043, 0.037	0.056, 0.047	0.040, 0.031
Structure solution and refinement	Program package <i>SHELX-97</i> [17]			
Scattering factors	International Tables, Vol. C [18]			
R_1 , reflections with $ F_o \geq 4\sigma(F_o)$	0.028, 1701	0.054, 1400	0.032, 1020	0.029, 1389
R_1 , wR_2 for all reflections	0.044, 0.065	0.086, 0.156	0.096, 0.077	0.057, 0.074
Goodness of fit (GooF)	0.977	0.962	0.819	0.858
Residual electron density, max. ($\rho/e^- \times 10^{-6}$ pm $^{-3}$) min.	3.01 at Cl2 -1.42	4.37 at Cl1 -3.50	2.26 at O3 -1.40	2.25 at Cl4 -2.19

$b = 1036-1052$, $c = 1163-1187$ pm, $\beta \approx 103^\circ$) with two formula units per unit cell. The crystal structure contains two crystallographically independent rare-earth metal trications. $(M1)^{3+}$ shows a coordination number of eight with a figure of a slightly distorted hexagonal bipyramid consisting of two Cl^- and six O^{2-} anions (Fig. 2, top). The coordination sphere about the $(M2)^{3+}$ cations (CN = 7) can be described as distorted pentagonal bipyramid built up by five chlorine and two oxygen atoms (Fig. 2, bottom). The metal-chlorine distances ($d(M^{3+}-Cl^-) = 265-289$ pm, see Table 3) fall into the usual range as those of other compounds containing lanthanoid trications and chloride anions (e.g. $SmCl_3$: $d(Sm^{3+}-Cl^-) = 285-292$ pm [21], $DyCl_3$: $d(Dy^{3+}-Cl^-) = 266-292$ pm [22]). The same is true for the distances between the metal and the oxygen atoms ($d(M^{3+}-O^{2-}) = 222-240$ plus 288 pm, see Table 3) compared with other rare-earth metal(III) oxocompounds (e.g. $B-Sm_2O_3$: $d(Sm^{3+}-O^{2-})$: 229–256 pm [23], $C-Dy_2O_3$: $d(Dy^{3+}-O^{2-})$: 224–235 pm [24]) although the largest $(M1)^{3+}-O(1)^{2-}$ distance of about 288 pm has to be considered rather huge, but the contribution of the $O(1)^{2-}$ ligand to the coordination sphere of $(M1)^{3+}$ is not negligible, judging from the ECoN basis [25] (contribution of δ -ECoN(O1) = 0.08–0.13 to ECoN(M1) =

6.37–6.55, see Table 4). The four crystallographically independent chloride anions show coordination numbers of two (Cl1–Cl3) and three (Cl4) exhibiting an angled twofold or a *non-planar* trigonal M^{3+} environment, respectively (see Fig. 3).

The *cyclo-oxotetrasilicate* unit $[Si_4O_{12}]^{8-}$ is built up by four vertex-shared $[SiO_4]^{4-}$ tetrahedra in *all-ecliptic* conformation fused to an eight-membered ring (Fig. 4), which seems to be quite common among mineralic as well as artificially synthesized compounds containing these very groups. Their special conformation, however, is different from that one of *cyclo-tri-* or *-hexasilicates*, which usually appear in a staggered fashion. The centers of gravity of the *cyclo-tetrasilicate* units in the chloride oxosilicates $M_6Cl_{10}[Si_4O_{12}]$ ($M = Sm, Gd-Dy$) represent inversion centers in the unit cell (Fig. 5), so this group contains full $2/m$ symmetry (but *no* $4/m$ symmetry as observed in tetragonal $Eu_8Cl_8[Si_4O_{12}]$ [7]). Thus two different Si–O–Si bridging angles are observed ($\sphericalangle(Si-O-Si) = 177-179^\circ$ and $\sphericalangle(Si-O-Si) = 140-143^\circ$), a fact that results in the splitting of the Si–O–Si vibrations into 1465 and 1377 cm^{-1} , respectively (see Fig. 6 for the example of $Gd_6Cl_{10}[Si_4O_{12}]$). This observation contradicts a $[Si_4O_{12}]^{8-}$ unit with fourfold symmetry, where these vibrations ought

Table 2

Atomic coordinates and equivalent isotropic thermal displacement parameters U_{eq}^a for the chloride oxosilicates $M_6\text{Cl}_{10}[\text{Si}_4\text{O}_{12}]$ ($M = \text{Sm}, \text{Gd-Dy}$)

Atom	Wyckoff position	x/a	y/b	z/c	U_{eq} (pm ²)
Sm₆Cl₁₀[Si₄O₁₂]					
Sm1	4e	1/4	1/4	0	103(1)
Sm2	8j	0.33338(2)	0.25161(2)	0.33177(2)	71(1)
Cl1	4i	0.3172(2)	0	0.0040(2)	285(3)
Cl2	4i	0.7698(2)	0	0.3321(2)	316(4)
Cl3	4i	0.3830(2)	0	0.3587(2)	349(4)
Cl4	8j	0.10595(8)	0.2136(1)	0.42063(7)	189(2)
Si	8j	0.03606(9)	0.1445(1)	0.14192(8)	49(2)
O1	4g	0	0.1463(5)	0	216(9)
O2	4i	0.0468(4)	0	0.1866(3)	139(8)
O3	8j	0.1733(2)	0.2151(3)	0.1717(2)	99(5)
O4	8j	0.4144(2)	0.2842(3)	0.1720(2)	97(5)
Gd₆Cl₁₀[Si₄O₁₂]					
Gd1	4e	1/4	1/4	0	86(2)
Gd2	8j	0.33269(3)	0.25060(3)	0.33128(3)	59(1)
Cl1	4i	0.3190(4)	0	0.0056(3)	313(8)
Cl2	4i	0.7768(4)	0	0.3378(3)	346(9)
Cl3	4i	0.3787(4)	0	0.3540(3)	372(9)
Cl4	8j	0.1063(2)	0.2221(3)	0.4218(2)	238(5)
Si	8j	0.0359(2)	0.1463(2)	0.1440(2)	99(4)
O1	4g	0	0.1427(9)	0	214(20)
O2	4i	0.0419(8)	0	0.1903(7)	213(20)
O3	8j	0.1718(6)	0.2311(6)	0.1743(6)	173(14)
O4	8j	0.4136(7)	0.2698(7)	0.1704(7)	207(15)
Tb₆Cl₁₀[Si₄O₁₂]					
Tb1	4e	1/4	1/4	0	191(1)
Tb2	8j	0.33296(3)	0.25085(5)	0.33139(3)	143(1)
Cl1	4i	0.3161(5)	0	0.0022(5)	351(8)
Cl2	4i	0.7799(5)	0	0.3397(5)	476(11)
Cl3	4i	0.3821(5)	0	0.3520(5)	537(13)
Cl4	8j	0.1057(2)	0.2225(3)	0.4203(2)	422(11)
Si	8j	0.0366(2)	0.1450(3)	0.1438(2)	141(4)
O1	4g	0	0.1422(9)	0	448(31)
O2	4i	0.0454(8)	0	0.1916(8)	223(18)
O3	8j	0.1730(7)	0.2271(8)	0.1712(6)	360(26)
O4	8j	0.4139(7)	0.2717(8)	0.1721(6)	347(24)
Dy₆Cl₁₀[Si₄O₁₂]					
Dy1	4e	1/4	1/4	0	183(1)
Dy2	8j	0.33298(2)	0.25107(3)	0.33123(2)	125(1)
Cl1	4i	0.3170(3)	0	0.0032(3)	335(5)
Cl2	4i	0.7789(3)	0	0.3368(3)	391(6)
Cl3	4i	0.3782(3)	0	0.3568(3)	424(7)
Cl4	8j	0.1055(1)	0.2207(2)	0.4210(1)	268(4)
Si	8j	0.0360(1)	0.1460(2)	0.1440(1)	122(3)
O1	4g	0	0.1418(8)	0	420(22)
O2	4i	0.0481(6)	0	0.1933(5)	175(11)
O3	8j	0.1728(4)	0.2193(5)	0.1720(4)	195(9)
O4	8j	0.4136(4)	0.2798(5)	0.1713(4)	203(9)

^a $U_{\text{eq}} = \frac{1}{3}[U_{22} + (1/\sin^2 \beta)(U_{11} + U_{33} + 2U_{13} \cos \beta)]$ [19].

to be degenerated. A frequency calculation on the basis of a hypothetical electroneutral $[\text{Si}_4\text{O}_4\text{F}_8]$ model unit with four-fold symmetry gives a value of 1427 cm^{-1} for the corresponding degenerated vibrations. The $\text{Si}^{4+}-\text{O}^{2-}$

Table 3

Important internuclear distances (d in pm) and angles (\sphericalangle in deg) in the chloride oxosilicates $M_6\text{Cl}_{10}[\text{Si}_4\text{O}_{12}]$ ($M = \text{Sm}, \text{Gd-Dy}$)

	$M = \text{Sm}$ d (pm)	$M = \text{Gd}$ d (pm)	$M = \text{Tb}$ d (pm)	$M = \text{Dy}$ d (pm)
$M1-\text{O}4$ (2 ×)	239.5	234.6	235.2	234.8
$M1-\text{O}3$ (2 ×)	239.0	238.4	234.1	235.0
$M1-\text{O}1$ (2 ×)	287.7	288.4	288.4	288.2
$M1-\text{Cl}1$ (2 ×)	272.3	270.5	269.0	268.3
$M2-\text{O}3$ (1 ×)	227.8	222.4	223.7	223.6
$M2-\text{O}4$ (1 ×)	228.1	225.3	223.3	223.8
$M2-\text{Cl}2$ (1 ×)	270.0	267.2	265.7	264.5
$M2-\text{Cl}3$ (1 ×)	270.4	266.1	265.9	264.9
$M2-\text{Cl}4$ (1 ×)	287.7	287.8	286.1	286.0
$M2-\text{Cl}4'$ (1 ×)	288.1	285.7	285.5	285.9
$M2-\text{Cl}4''$ (1 ×)	288.5	283.8	283.9	282.2
$\text{Si}-\text{O}2$ (1 ×)	160.6	161.6	160.3	161.2
$\text{Si}-\text{O}4$ (1 ×)	160.6	165.3	166.0	160.3
$\text{Si}-\text{O}3$ (1 ×)	160.5	166.3	164.9	160.6
$\text{Si}-\text{O}1$ (1 ×)	164.0	164.7	163.7	163.2
	\sphericalangle (deg)	\sphericalangle (deg)	\sphericalangle (deg)	\sphericalangle (deg)
$\text{O}1-\text{Si}-\text{O}4$	102.2	101.2	101.6	101.8
$\text{O}1-\text{Si}-\text{O}3$	102.1	102.8	101.6	102.2
$\text{O}1-\text{Si}-\text{O}2$	109.4	107.8	108.8	108.8
$\text{O}2-\text{Si}-\text{O}4$	111.7	114.2	114.0	112.5
$\text{O}2-\text{Si}-\text{O}3$	111.9	117.6	116.1	112.1
$\text{O}3-\text{Si}-\text{O}4$	118.4	111.2	112.8	118.1
$\text{Si}-\text{O}2-\text{Si}'$	142.5	141.5	140.2	139.5
$\text{Si}-\text{O}1-\text{Si}'$	178.7	177.4	178.0	177.0

distances range in an interval between 160 and 166 pm, which corresponds very well with other compounds containing oxosilicate units (e.g. $A\text{-Sm}_2[\text{Si}_2\text{O}_7]$: $d(\text{Si}^{4+}-\text{O}^{2-}) = 158\text{--}166 \text{ pm}$ [26], $B\text{-Dy}_2\text{Si}_2\text{O}_7$ ($\equiv \text{Dy}_4\text{-}[\text{Si}_3\text{O}_{10}][\text{SiO}_4]$): $d(\text{Si}^{4+}-\text{O}^{2-}) = 158\text{--}171 \text{ pm}$ [27]) or even with SiO_2 itself (e.g. SiO_2 as α -quartz: $d(\text{Si}^{4+}-\text{O}^{2-}) = 159\text{--}164 \text{ pm}$ [28]). The same holds for the $\text{O}-\text{Si}-\text{O}$ angles with values of $102\text{--}118^\circ$ (for comparison: SiO_2 as α -quartz: $\sphericalangle(\text{O}-\text{Si}-\text{O}) = 107\text{--}110^\circ$ [28], $A\text{-Sm}[\text{Si}_2\text{O}_7]$: $\sphericalangle(\text{O}-\text{Si}-\text{O}) = 101\text{--}118^\circ$ [25], $B\text{-Dy}_2\text{Si}_2\text{O}_7$ ($\equiv \text{Dy}_4\text{-}[\text{Si}_3\text{O}_{10}][\text{SiO}_4]$): $\sphericalangle(\text{O}-\text{Si}-\text{O}) = 99\text{--}117^\circ$ [27]).

The whole crystal structure can be considered as layered arrangement in which anionic layers ${}_{\infty}^2\{[(M1)(Cl1)[\text{Si}_4\text{O}_{12}]]^{6-}\}$ are alternately piled with cationic ones according to ${}_{\infty}^2\{[(M2)_5\text{Cl}_9]^{6+}\}$ (see Fig. 5). Although these $M_6\text{Cl}_{10}[\text{Si}_4\text{O}_{12}]$ -type compounds remain stable when exposed to moist air and water, they are not very resistant against mechanical stress. So little pressure with a dissection pin leads to breaking of the brittle crystals. The presumable reason for this behavior may result from the chloride-rich double layers ${}_{\infty}^2\{[(M2)_5\text{Cl}_9]^{6+}\}$, in which some of the chloride anions show distances (e.g. $d\{(\text{Cl}4)^- \cdots (\text{Cl}4)^-\} = 322$ and 325 pm) of less than their double “crystal radius” of 167 pm or “ionic radius” of 181 pm [29] and thus a repulsive force within these sheets is evident. The ionic radii of the rare-earth cations range

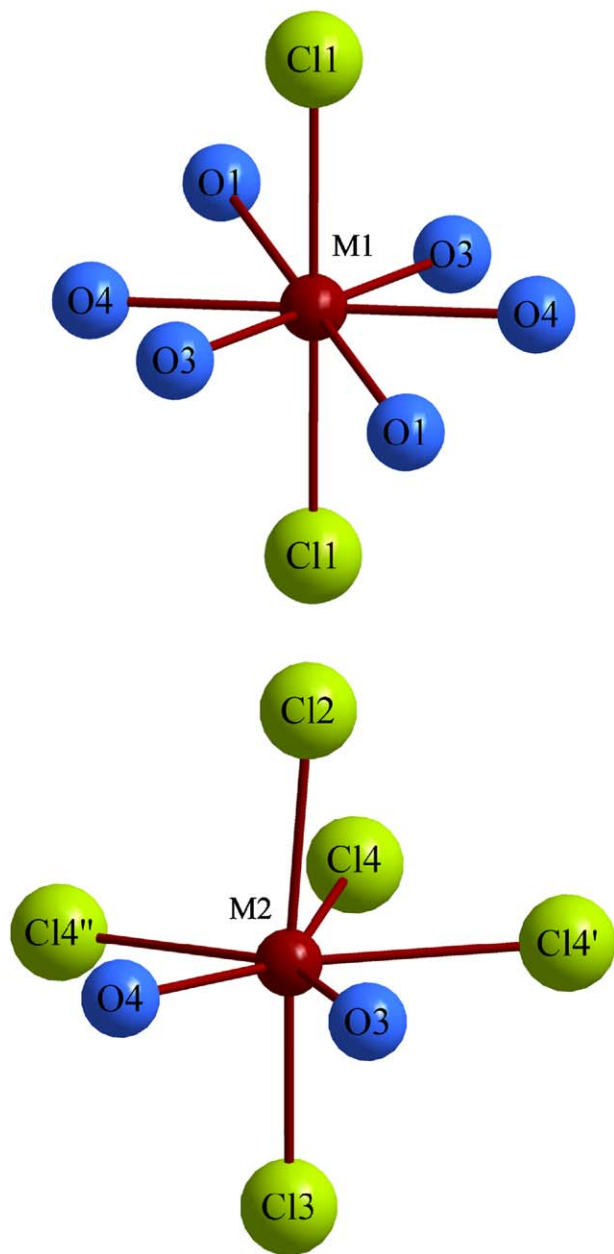


Fig. 2. Coordination polyhedron about the $(M1)^{3+}$ (top) and the $(M2)^{3+}$ cations (bottom) in the crystal structure of the chloride oxosilicates $M_6Cl_{10}[Si_4O_{12}]$ ($M = Sm, Gd-Dy$).

Table 4

Motifs of mutual adjunction in the crystal structure of the chloride oxosilicates $M_6Cl_{10}[Si_4O_{12}]$ ($M = Sm, Gd-Dy$)

	Cl1	Cl2	Cl3	Cl4	O1	O2	O3	O4	CN
M1	2/2	0/0	0/0	0/0	2/2	0/0	2/1	2/1	8
M2	0/0	1/2	1/2	3/3	0/0	0/0	1/1	1/1	7
Si	0/0	0/0	0/0	0/0	1/2	1/2	1/1	1/1	4
CN	2	2	2	3	4	2	3	3	

between 100 pm (for Dy^{3+} [29]) and 108 pm (for Sm^{3+} [29]) according to the lanthanoid contraction. This effect is clearly seen in the decrease of the lattice constants with shrinking

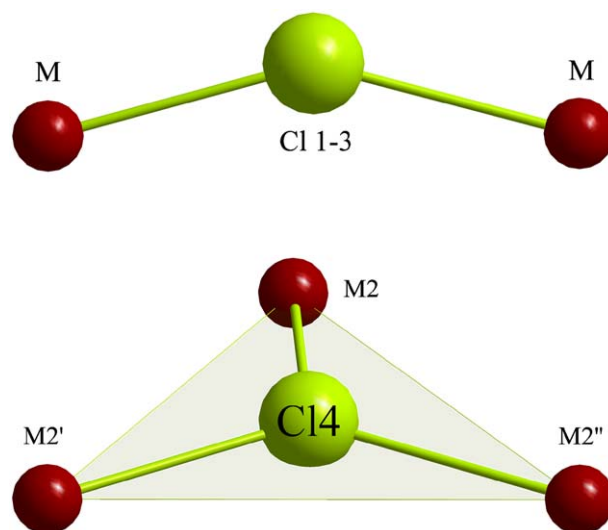


Fig. 3. Cationic environment of the chloride anions in the crystal structure of the chloride oxosilicates $M_6Cl_{10}[Si_4O_{12}]$ ($M = Sm, Gd-Dy$; $M1$ for Cl1 and $M = M2$ for Cl2 and Cl3).

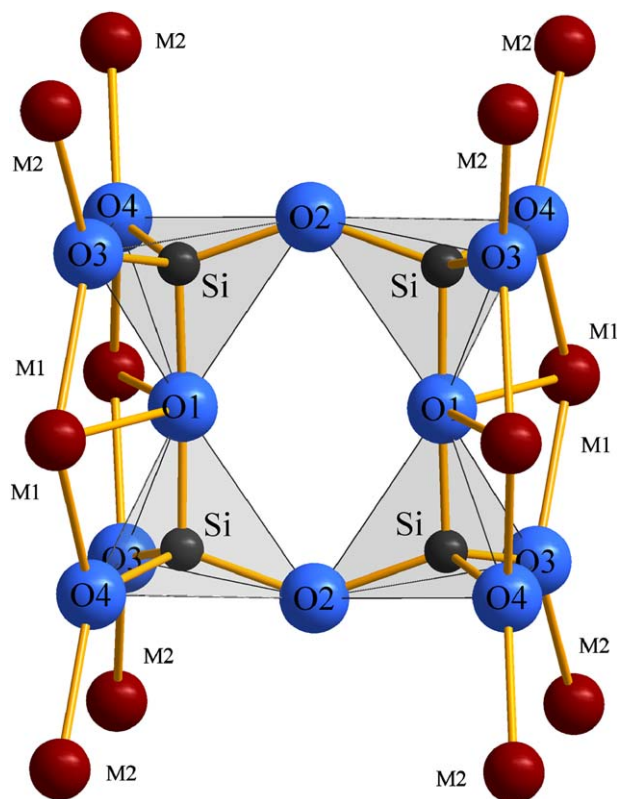


Fig. 4. Cationic surrounding of the *cyclo-oxotetrasilicate* anions $[Si_4O_{12}]^{8-}$ in the crystal structure of the chloride oxosilicates $M_6Cl_{10}[Si_4O_{12}]$ ($M = Sm, Gd-Dy$).

M^{3+} cation (see Table 1), but considering the conformation of the *cyclo-oxotetrasilicate* unit, no significant changes are observed for the bond lengths or angles. Nonetheless, a strong relationship between the size of the cation and the conformation of these $[Si_4O_{12}]^{8-}$ groups can probably be assumed, since the domain of existence of the $M_6Cl_{10}[Si_4O_{12}]$ series is rather

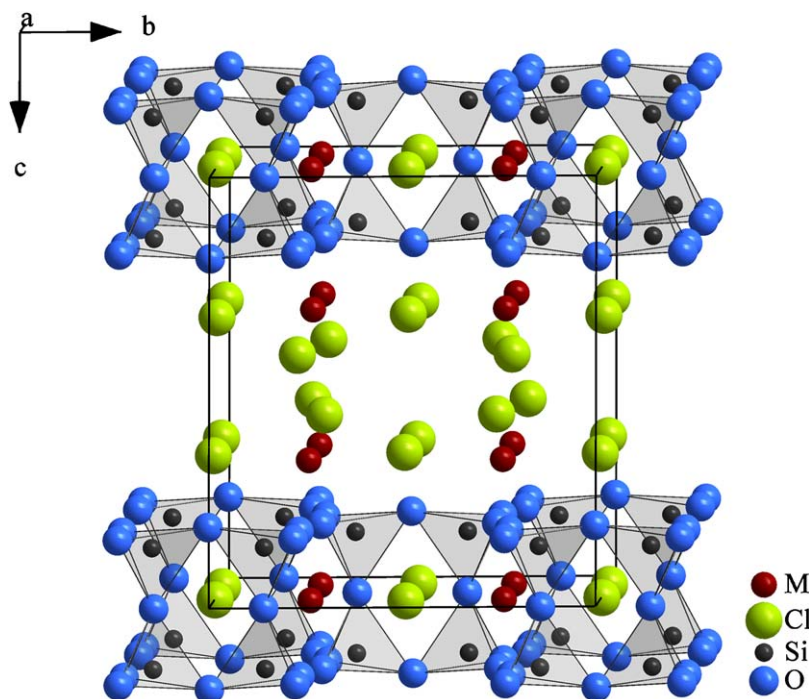


Fig. 5. View at the crystal structure of the chloride oxosilicates $M_6Cl_{10}[Si_4O_{12}]$ ($M = Sm, Gd-Dy$) along [100].

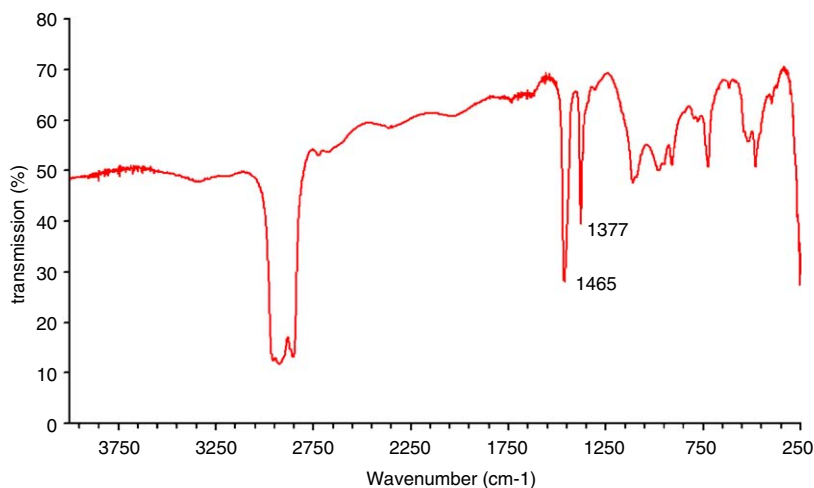


Fig. 6. IR spectrum of $Gd_6Cl_{10}[Si_4O_{12}]$ as typical example for those of all chloride oxosilicates $M_6Cl_{10}[Si_4O_{12}]$ ($M = Sm, Gd-Dy$).

small compared to other chloride derivatized lanthanoid oxosilicates such as the *B*-type $M_3Cl[SiO_4]_2$ representatives (with $M = Nd, Sm, Gd-Yb$) [9,30]. Because the Si–O2–Si angle becomes slightly (but steadily) smaller with the decrease of the rare-earth metal cation's radius the limit is obviously reached with the Dy^{3+} or the Y^{3+} cation [8], respectively. The same is true for the increase of the mentioned ionic radii, since no *cyclo-oxotetrasilicates* of the composition $M_6Cl_{10}[Si_4O_{12}]$ are known for the lighter (but larger) cations La^{3+} through Nd^{3+} . However, the $M^{3+}:Cl^-$ ratio of 3:5 is indeed already realized in the rare-earth metal chloride *ortho*-silicates $M_3Cl_5[SiO_4]$ [9,31,32]. So the research among the lanthanide chloride oxosilicates tends to be a large field apparently, in

which a complete structure field diagram of the different structures is still missing. After establishing the relationships revealed thereby, all these compounds could provide a true basis for enhancing our doping experiments with the chloride derivatized rare-earth metal oxosilicates in order to obtain novel luminescent materials.

Acknowledgments

We thank Dr. Falk Lissner for the measurement of the X-ray single-crystal diffraction data sets, Helmut Lenz (CTA) for the collection of the IR-spectroscopic data, and Prof. Dr. Friedhelm Zabel (Institute for Physical

Chemistry, University of Stuttgart) for providing the calculation capacities. Furthermore we gratefully acknowledge the “Land Baden-Wuerttemberg” (Stuttgart), the “Fonds der Chemischen Industrie” (Frankfurt a. M.), and the “Deutsche Forschungsgemeinschaft” (Bonn) within the “Schwerpunktprogramm 1166: Lanthanoidspezifische Funktionalitäten in Molekül und Material” for considerable financial support.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2006.01.063](https://doi.org/10.1016/j.jssc.2006.01.063).

References

- [1] W.H. Zachariasen, *Z. Kristallogr.* 74 (1930) 139–146.
- [2] W.L. Bragg, *Proc. R. Soc. London Ser. A* 111 (1926) 691–714.
- [3] S. Matsubara, *Mineral. J. (Japan)* 10 (1980) 122–142.
- [4] Yu.V. Nekrasov, V.I. Ponomarev, V.I. Simonov, D.M. Kheiker, *Kristallografiya* 14 (1969) 602–609.
- [5] A.R. Kampf, A.A. Khan, W.H. Baur, *Acta Crystallogr. B* 29 (1973) 2019–2021.
- [6] F. Mazzi, G. Rossi, *Z. Kristallogr.* 121 (1965) 243–257.
- [7] H. Jacobsen, G. Meyer, W. Schipper, G. Blasse, *Z. Anorg. Allg. Chem.* 620 (1994) 451–456.
- [8] I. Hartenbach, Th. Schleid, *Z. Anorg. Allg. Chem.* 627 (2001) 2493–2498.
- [9] I. Hartenbach, *Doctoral Thesis, University of Stuttgart*, 2001.
- [10] H. Müller-Bunz, Th. Schleid, *Z. Anorg. Allg. Chem.* 625 (1999) 1377–1383.
- [11] H. Müller-Bunz, Th. Schleid, *Z. Anorg. Allg. Chem.* 624 (1998) 1082–1084;
H. Müller-Bunz, Th. Schleid, *Z. Anorg. Allg. Chem.* 626 (2000) 845–852.
- [12] H. Müller-Bunz, Th. Schleid, *Z. Anorg. Allg. Chem.* 627 (2001) 218–223.
- [13] C. Wickleder, I. Hartenbach, P. Lauxmann, Th. Schleid, *Z. Anorg. Allg. Chem.* 628 (2002) 1602–1606.
- [14] K.D. Oskam, K.A. Kaspers, A. Meijerink, H. Müller-Bunz, Th. Schleid, *J. Lumin.* 99 (2005) 101–105.
- [15] M. Petter, S. Zhang, C. Wickleder, Th. Schleid, J. Lumin. (2006), in preparation.
- [16] W. Herrendorf, H. Bärnighausen, *HABITUS: program for the optimization of the crystal shape for numerical absorption correction in X-SHAPE (version 1.06, Fa. Stoe, Darmstadt 1999)*, Karlsruhe, Gießen, Germany, 1993, 1996.
- [17] G.M. Sheldrick, *SHELX-97: program package for solution and refinement of crystal structures from X-ray diffraction data*, Göttingen, Germany, 1997.
- [18] Th. Hahn, A.J.C. Wilson (Eds.), *International Tables for Crystallography*, vol. C, Kluwer Academic, Boston, Dordrecht, London, 1992.
- [19] R.X. Fischer, E. Tillmanns, *Acta Crystallogr. C* 44 (1988) 775–776.
- [20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Menucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, V. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, *Gaussian 98, Revision A.7*, Pittsburgh, PA, USA, 1998.
- [21] M. Schulze, *Doctoral Thesis, University of Hannover*, 1991; M. Schulze, W. Urland, unpublished results.
- [22] D. Hake, W. Urland, *Z. Anorg. Allg. Chem.* 586 (1990) 99–105.
- [23] Th. Schleid, G. Meyer, *J. Less-Common Met.* 149 (1989) 73–80.
- [24] A. Bartos, K.P. Lieb, M. Uhrmacher, D. Wiarda, *Acta Crystallogr. B* 49 (1993) 165–169.
- [25] R. Hoppe, *Z. Kristallogr.* 150 (1979) 23–52.
- [26] Yu.I. Smolin, Yu.F. Shepelev, I.K. Butikova, *Kristallografiya* 15 (1970) 256–261.
- [27] M.E. Fleet, X.-Y. Liu, *Z. Kristallogr.* 218 (2003) 795–801.
- [28] G.S. Smith, L.E. Alexander, *Acta Crystallogr.* 16 (1963) 462–471.
- [29] R.D. Shannon, *Acta Crystallogr. A* 32 (1976) 751–767.
- [30] C. Sieke, Th. Schleid, *Z. Kristallogr. Suppl.* 12 (1997) 161; C. Sieke, I. Hartenbach, Th. Schleid, *Z. Anorg. Allg. Chem.* 626 (2000) 2235–2239.
- [31] P. Gravereau, B. Es-Sakhi, C. Fouassier, *Acta Crystallogr. C* 45 (1989) 1677–1679.
- [32] C. Sieke, Th. Schleid, *Z. Kristallogr. Suppl.* 12 (1997) 143; C. Sieke, Th. Schleid, *Z. Anorg. Allg. Chem.* 627 (2001) 761–767.