Richtung des $CaCu_2O_3$ entsprechen [010] und [001] der vorliegenden Verbindung. Die geraden CuO_2-Ketten kommen in den bisher bekannten Oxocupraten der Erdalkalimetalle nicht vor, sie treten vielmehr in Alkalimetall-Oxocupraten Li_2CuO_2 (Hoppe & Rieck, 1970), $NaCuO_2$ (Hestermann & Hoppe, 1969*b*) sowie $KCuO_2$, $RbCuO_2$ und $CsCuO_2$ (Hestermann & Hoppe, 1969*a*) auf. Die $Cu^{III}—O$-Abstände 1,85 und 1,84 Å in $NaCuO_2$ bzw. $KCuO_2$ sind merklich kürzer als der $Cu^{II}—O$-Abstand 1,966 Å in Li_2CuO_2. Der Unterschied zwischen $Cu^{II}O_2$- und $Cu^{III}O_2$-Ketten kommt auch in den durchschnittlichen Längen ihrer Kettenglieder deutlich zum Ausdruck. So liegen diese Längen zwischen 2,71 und 2,748 Å für die $Cu^{III}O_2$-Ketten der ebengenannten Verbindungen, während die entsprechende Länge des Li_2CuO_2 2,863 Å ist. Werden diese Werte mit 2,755 Å der vorliegenden CuO_2-Ketten verglichen, so erscheint die Annahme naheliegend, daß die dreiwertigen Cu-Atome überwiegend in diesen Ketten eingelagert sind.

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$La_3(SiO_4)_2Cl$: a New Structural Type of Rare-Earth Chloroorthosilicate

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Abstract. Trilanthanum chloride bis(orthosilicate), $M_r = 636{\cdot}35$, monoclinic, $C2/c$, $a = 14{\cdot}512\,(2)$, $b = 6{\cdot}526\,(1)$, $c = 8{\cdot}844\,(2)$ Å, $\beta = 98{\cdot}35\,(1)°$, $V = 828{\cdot}7\,(3)$ Å^3, $Z = 4$, $D_m = 5{\cdot}01$, $D_x = 5{\cdot}10$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 15{\cdot}9$ mm^{-1}, $F(000) = 1120$, $T = 298$ K, $R = 0{\cdot}032$ for 1610 independent reflections with $I > 3\sigma(I)$. Isostructural compounds are $Ln_3(SiO_4)_2Cl$ with Ln = Ce, Pr, Nd and $Ln_3(SiO_4)_2Br$ with Ln = La, Ce. The new chloroorthosilicate structural type shows some common features with that of $Yb_3(SiO_4)_2Cl$, previously determined, $(LnCl)_n$ planes alternating with two successive $[Ln(SiO_4)]_n$ planes, square coordination for Cl. The arrangements of cations and anions in the mixed planes differ, leading to higher coordination for the lanthanum ions.

Introduction. The structure of a rare-earth chlorosilicate, $Yb_3(SiO_4)_2Cl$, has been previously determined (Ayasse & Eick, 1973). Its symmetry is orthorhombic, the space group $Pnma$. Isostructural phases have been reported for Y and Gd; they show interesting luminescent properties when doped with Ce^{3+} (Yamada, Kano & Tanabe, 1978). Investigation of the Ln_2O_3–SiO_2–LnOCl systems (Ln: lanthanide) reveals the existence of a different structure type for the largest rare-earth ions: La, Ce, Pr, Nd. With Br a homologous phase was obtained only for Ln = La, Ce. The present paper reports an X-ray structural study on a single crystal of $La_3(SiO_4)_2Cl$. The new crystal structure is compared with that of $Yb_3(SiO_4)_2Cl$.

Experimental. $Ln_3(SiO_4)_2X$ (La, Ce, Pr, Nd, X = Cl; La, Ce, X = Br) powder samples were prepared by solid-state reaction between silica, rare-earth oxide and oxyhalide. The technique is described below using $La_3(SiO_4)_2Cl$ as an example.

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Table 1. *Positional parameters and isotropic thermal parameters and alternative solutions for* Cl-*atom parameters*

$$B_{eq} = 8\pi^2/3 \sum_{i=1}^{3} \sum_{j=1}^{3} a_i^* a_j^* U_{ij}(\mathbf{a}_i.\mathbf{a}_j) \text{ for La, Cl and Si.}$$

	Position	Site symmetry	x	y	z	B_{eq} or B_{iso}(Å^2)
La(1)	8(f)	1	0·18452 (2)	0·39635 (5)	0·16975 (3)	0·47
La(2)	4(e)	2	$\frac{1}{2}$	0·4315 (1)	$\frac{1}{4}$	0·55
Cl	4(e)	2	0	0·4731 (4)	$\frac{1}{4}$	2·56
Si	8(f)	1	0·3417 (1)	0·4441 (3)	0·4736 (2)	0·46
O(1)	8(f)	1	0·0785 (3)	0·1206 (7)	0·0330 (5)	0·63 (6)
O(2)	8(f)	1	0·2590 (3)	0·0542 (7)	0·0809 (5)	0·56 (6)
O(3)	8(f)	1	0·3551 (3)	0·2649 (8)	0·3539 (5)	0·84 (6)
O(4)	8(f)	1	0·1546 (3)	0·1190 (7)	0·3485 (5)	0·73 (6)

				Site occupation	U_{ij} †(Å^2 × 10^4)					
	x	y	z	factor	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Case I:										
Cl site 4(e)	0	0·4731 (4)	$\frac{1}{4}$	1	194 (12)	140 (11)	707 (23)	0	290 (14)	0
Case II:										
Cl site 8(f)	0·0060 (2)	0·4730 (4)	0·2720 (3)	$\frac{1}{2}$	108 (12)	145 (11)	244 (22)	−8 (11)	84 (14)	5 (14)

† $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2lhc^*a^*U_{13} + 2hka^*b^*U_{12})]$.

The starting materials were La_2O_3 (99·99%), LaOCl and SiO_2 (precipitated from an Na_2SiO_3 solution) in the proportions $1{:}1{:}2+x$.

They were ground in an agate mortar inside an argon dry box. The powders placed in a platinum tube sealed under argon atmosphere were heated at 1570 K for 5 h. With the stoichiometric proportions (1:1:2) the reaction is incomplete and leads predominantly to the formation of silicates ($La_2Si_2O_7$, $La_{14/3}Si_3O_{13}$ and La_2SiO_5). The latter are very inert towards LaOCl even at very high temperature (~1670 K). An excess of silica (minimum $x = 0\cdot5$) prevents their formation:

$$La_2O_3 + LaOCl + 2\cdot5SiO_2 \rightarrow La_3(SiO_4)_2Cl + 0\cdot5SiO_2 \text{ (amorphous).}$$

The single crystal was obtained by heating a mixture containing an excess of LaOCl at 1670 K.

Measurement of the density of $La_3(SiO_4)_2Cl$ was carried out for two samples with different silica contents (100 and 50% in mol). The densities obtained (4·55 and 4·75 Mg m^{-3}) were in agreement with those calculated (4·60 and 4·83 Mg m^{-3}) using values of 2·30 and 5·10 Mg m^{-3} for SiO_2 and $La_3(SiO_4)_2Cl$ ($Z = 4$).

Translucent colourless single crystal with a parallelepipedic primitive shape (50 × 90 × 140 μm) and {111} crystal-form truncations. Monoclinic symmetry determined with photographs (Laue, Weissenberg, precession). Cell parameters refined with 35 reflections from X-ray powder diffraction pattern (graphite-monochromated Cu $K\alpha$ radiation and Si as internal standard).

Data collection with an Enraf–Nonius CAD-3 diffractometer: graphite-monochromated Mo $K\alpha$ radiation; ω scan; 7262 reflections; $(\sin\theta)/\lambda < 0\cdot81$ Å^{-1}, $-23 < h < 23$, $0 < k < 10$, $-14 < l < 14$; scan width $(0\cdot64 + 0\cdot79\tan\theta)°$; counter slit width $(0\cdot09 + 0\cdot22\tan\theta)$ mm. Three standard reflections every 100 reflections, with no systematic variation observed and a maximum relative deviation of 5%. Data corrected for Lorentz–polarization effects and for absorption using *SHELX*76 (Sheldrick, 1976), crystal shape and size, and incident- and diffracted-beam direction cosines ($0\cdot225 < T < 0\cdot485$). Equivalent reflections for which $I/\sigma(I) > 3$ averaged to give 1626 unique reflections ($R_{int} = 2\cdot2$ and 1·9% before and after absorption correction).

Systematic absences $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$ consistent with two possible space groups $C2/c$ and Cc [inconsistencies: 0 with $I/\sigma(I) > 4$, 16 with $4 > I/\sigma(I) > 3$]. Atomic scattering factors for La^{3+}, Si^{4+}, O$^-$ and Cl$^-$ and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Structure solved in the $C2/c$ group by heavy-atom methods with *SHELX*76 and IBM 3090-400 computer of the Computing Center of Montpellier. Sites of La atoms found by Patterson-function deconvolution ($R = 0\cdot20$), and Cl, Si and O atoms located with several difference Fourier syntheses. Calculations, with individual isotropic thermal parameters, a weighting scheme $w = 1/\sigma^2(F_o)$ and an empirical isotropic extinction parameter x [$F_c = F(1-10^{-4}xF^2/\sin\theta)$], converging to $R = 0\cdot055$, $wR = 0\cdot074$. The structure refined to $R = 0\cdot032$ and $wR = 0\cdot050$ with anisotropic thermal factors for La, Cl and Si atoms: extinction parameter $x = 7\cdot2\,(6) \times 10^{-4}$; max. shift/e.s.d. in last cycle $< 0\cdot002$; residual electron density less than 3·8 e Å^{-3} near La(1) and La(2) atoms, and less than 1·5 e Å^{-3} near Cl, Si and O atoms.* Calculations with the

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* Lists of structure factors and anisotropic thermal parameters for $La_3(SiO_4)_2Cl$ have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51191 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected distances* (Å) *and angles* (°)

La(1)—O(1)	1 × 2·555 (4)	Cl—La(1)	2 × 2·911 (1)
—O(2)	1 × 2·649 (4)	—La(1^{v})	2 × 4·335 (2)
—O(2^{i})	1 × 2·464 (4)	—La(2^{i})	1 × 2·992 (3)
—O(2^{iv})	1 × 2·494 (4)	—La(2^{iii})	1 × 3·534 (3)
—O(3)	1 × 2·889 (5)		
—O(3^{i})	1 × 2·475 (5)	Si—O(1^{i})	1 × 1·641 (5)
—O(4)	1 × 2·482 (5)	—O(2^{i})	1 × 1·636 (5)
—O(4^{i})	1 × 2·774 (5)	—O(3)	1 × 1·609 (5)
—Cl	1 × 2·911 (1)	—O(4^{vi})	1 × 1·619 (5)
La(2)—O(1^{i})	2 × 2·671 (5)	O(1^{i})—Si—O(2^{i})	106·6 (2)
—O(1^{ii})	2 × 2·617 (4)	—O(3)	109·5 (2)
—O(3)	2 × 2·647 (5)	—O(4^{vi})	106·8 (2)
—O(4^{i})	2 × 2·593 (5)	O(2^{i})—Si—O(3)	108·2 (2)
—Cl^{iii}	1 × 2·992 (3)	—O(4^{vi})	107·4 (2)
—Cl^{i}	1 × 3·534 (3)	O(3)—Si—O(4^{vi})	117·7 (3)

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (v) $-x, 1-y, -z$; (vi) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

non-centrosymmetric group *Cc* did not improve the model. Atomic parameters in *C*2/*c* are given in Table 1.

The results show a strong thermal anisotropy for Cl atoms with largest mean square of the amplitude of vibration in the **c*** direction ($U_{33} \simeq 0{\cdot}071$ Å^2). Another solution can be refined, considering slight delocalization along **c** of Cl atoms beside the twofold axis, with a statistical distribution in an 8(*f*) site. Because of this, positional parameters and anisotropic thermal parameters have to be refined separately. Reliability coefficients so obtained ($R = 0{\cdot}033$ and $wR = 0{\cdot}050$) are close to those with Cl in 4(*e*). Results for both solutions are compared in Table 1. As the structural description is in good agreement with possible strong thermal vibrations of Cl atoms along **c**, it will be based on the model of case I. Selected bond lengths and angles are given in Table 2.

Discussion. La^{3+} cations and Cl$^-$ or SiO$_4^{4-}$ anions are equally distributed in planes parallel to *yz* (Fig. 1). Double [La(1)(SiO$_4$)]$_n$ layers ($x \sim \frac{1}{6}, \frac{1}{3}$ or $\frac{2}{3}, \frac{5}{6}$) alternate with [La(2)Cl]$_n$ layers ($x = 0, \frac{1}{2}$).

The La(1) and La(2) ions have O$_8$Cl and O$_8$Cl$_2$ environments respectively. The anionic polyhedron around La(1) is irregular. The O atoms around La(2) form a distorted antiprism with the Cl atoms out of the distorted square faces. The site of La(2) can also be considered as a distorted octahedron consisting of four SiO$_4$ groups and two Cl atoms.

Along the *z* direction the oxygen polyhedra around La(1) form chains with corner-sharing O(2) atoms. Each La(1)O$_8$ polyhedron is connected to three La(1) polyhedra of the neighbouring [La(1)(SiO$_4$)]$_n$ plane, two by face sharing [O(2)O(3)O(4)] and one by a common edge [O(2)O(2)].

Along **z**, the La(2)O$_8$ polyhedra are linked by edge sharing [O(1)O(1)]. Each La(2)O$_8$ polyhedron is linked to four La(1)O$_8$ polyhedra of each [La(1)(SiO$_4$)]$_n$ double sheet, two by edge sharing [O(1)O(4) and O(3)O(4)] and two by a common apex [O(1) or O(3)].

The assembly of SiO$_4$ groups and lanthanum polyhedra forms tunnels parallel to the *z* direction, which accommodate the Cl atoms (Fig. 2). The Cl atoms are coordinated to two La(1) and two La(2) atoms located at the corners of a distorted square, with Cl–La distances between 2·911 and 3·534 Å. Two other La(1) atoms are situated at 4·335 Å, forming an

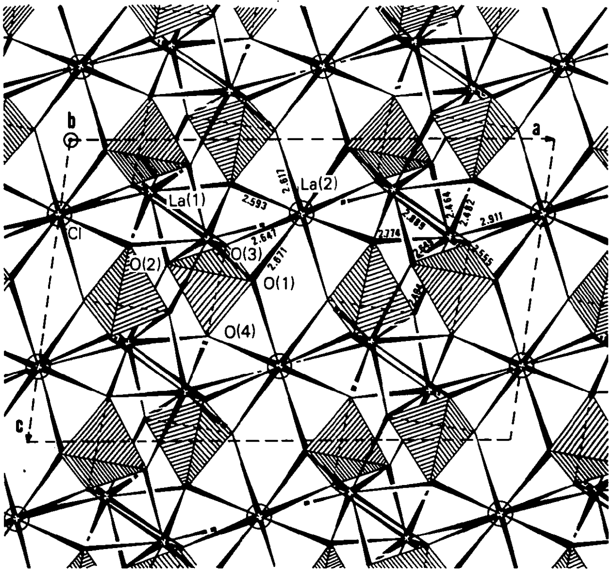

Fig. 1. Projection of the La$_3$(SiO$_4$)$_2$Cl structure along the *b* axis (atoms with $\frac{1}{4} < y < \frac{3}{4}$ are represented). The tetrahedra represent the SiO$_4$ groups, the small circles the La atoms, the larger ones the Cl atoms.

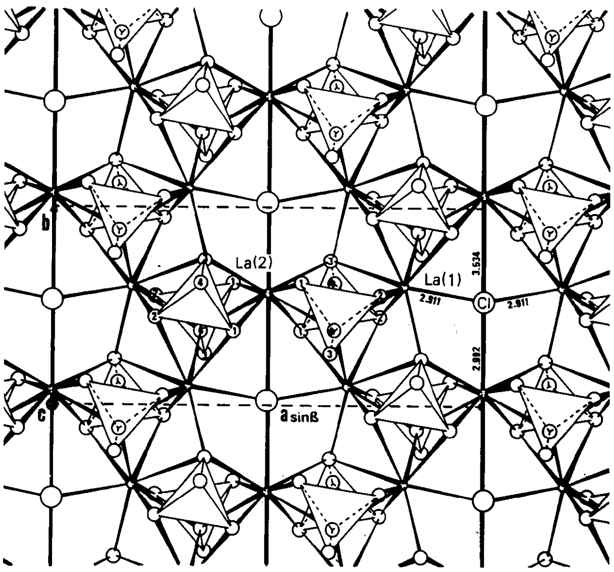

Fig. 2. Projection of the La$_3$(SiO$_4$)$_2$Cl structure along the *c* axis (only half the La and Cl atoms are represented).

elongated octahedron with the four nearest-neighbouring La atoms. The accommodation of Cl atoms in tunnels running in the z direction explains the high value of the U_{33} anisotropic thermal parameter.

The close similarity of the powder patterns of the $Ln_3(SiO_4)_2Cl$ (Ln = Ce, Pr, Nd) and $Ln_3(SiO_4)_2Br$ (Ln = La, Ce) phases shows that these halosilicates are isostructural with $La_3(SiO_4)_2Cl$. Their lattice constants will be published elsewhere, with those of other phases in the Ln_2O_3–SiO_2–$LnCl_3$ systems. From samarium in the lanthanide series the chlorosilicates belong to the $Yb_3(SiO_4)_2Cl$ type.

The two structures have common features: (1) the existence of double layers $[Ln(SiO_4)]_n$ alternating with $(LnCl)_n$ layers; (2) the presence of tunnels accommodating the Cl atoms; (3) the square coordination of Cl.

However, the arrangement of ions in the $[Ln(SiO_4)]_n$ and $(LnCl)_n$ planes differs. A higher coordination for La^{3+} is obtained by the increasing number of SiO_4 groups connected by edge sharing to the rare-earth coordination polyhedra: three for La(1) and four for La(2) compared with two for Yb(1) and Yb(2).

The SiO_4 tetrahedra are more regular for the La chlorosilicate than for the Yb phase. The Si—O bonds range from 1·61 to 1·64 Å (⟨Si—O⟩: 1·626 Å) in the La phase and from 1·56 to 1·64 Å (⟨Si—O⟩: 1·605 Å) in the Yb phase, and the O—Si—O angles from 106·6 to 117·7° (⟨O—Si—O⟩: 109·4°) and from 101·1 to 118·3° (⟨O—Si—O⟩: 109·4°), respectively. The four independent O atoms are bonded to one Si and three La atoms, resulting in close values of the electrostatic valence. That is not the case for the Yb phase, since the number of bonds with Yb is two for O(1) and O(2), three for O(3) and O(4). This results particularly in an increase of the O(1)—Si—O(2) angle and a decrease of the O(3)—Si—O(4) angle.

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Structure of Dilithium Dimagnesium Trisulfate

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Abstract. $Li_2Mg_2(SO_4)_3$, $M_r = 350·69$, orthorhombic, *Pbcn*, $a = 12·165\ (2)$, $b = 8·538\ (1)$, $c = 8·689\ (1)$ Å, $V = 902·5\ (4)$ Å^3, $Z = 4$, $D_m = 2·50$, $D_x = 2·581$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 0·32$ mm^{-1}, $F(000) = 696$, $T = 293$ K, final $R = 0·026$ for 1494 reflections. The structure contains almost regular SO_4 tetrahedra linked by Mg cations which have distorted octahedral coordination; Li cations are in tetrahedral cavities. This compound, with the small Li cation, belongs to a new family of double sulfates which is structurally different from the langbeïnite family stabilized by larger univalent cations.

Introduction. The high-temperature form (cubic) of the lithium sulfate Li_2SO_4 exhibits high ionic conductivity (Kvist & Lunden, 1965; Benrath & Drekopf, 1921)

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