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Structure of the Lanthanum Chlorosilicate $La_3(SiO_4)Cl_5$

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Abstract. Trilanthanum pentachloride orthosilicate, $M_r = 686{\cdot}08$, orthorhombic, $Pnma$, $a = 16{\cdot}225\ (2)$, $b = 4{\cdot}262\ (1)$, $c = 14{\cdot}238\ (2)$ Å, $V = 984{\cdot}6\ (3)$ Å^3, $Z = 4$, $D_x = 4{\cdot}63$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 14{\cdot}3$ mm^{-1}, $F(000) = 1208$, $T = 298$ K, $R = 0{\cdot}054$ for 1187 independent reflections with $I > 5\sigma(I)$. The three-dimensional assembly of $LaCl_7$ groups forms holes in which isolated SiO_4 tetrahedra with 'up–down' orientation disorder are located. Coordination are: $LaCl_7O_3$ for La cations, La_4Cl tetrahedral type for Cl(1), Cl(2), Cl(3) and Cl(4) anions, and La_5Cl pyramidal type for Cl(5). Isostructural compounds are $Ln_3(SiO_4)Cl_5$ with Ln = Ce, Pr, Nd.

Introduction. Investigation of the $LaCl_3$–La_2O_3–SiO_2 system shows the existence of three ternary phases: $La_3(SiO_4)_2Cl$, $La(SiO_3)Cl$ and $La_3(SiO_4)Cl_5$. These halosilicates are favourable host lattices for high luminescence efficiency of rare-earth ions under UV excitation. The structure of $La_3(SiO_4)_2Cl$ has been recently determined (Gravereau, Es-Sakhi & Fouassier, 1988). The present paper reports an X-ray study of a single crystal of $La_3(SiO_4)Cl_5$.

Experimental. $La_3(SiO_4)Cl_5$ was obtained in powder form from a mixture of LaOCl, $LaCl_3$ and SiO_2, heated at 1123 K for about 60 h in a platinum crucible placed in a sealed silica tube:

$$2LaOCl + LaCl_3 + SiO_2 \rightarrow La_3(SiO_4)Cl_5.$$

Crystals were grown by slow cooling (3 K h^{-1}) from 1273 to 1073 K in the presence of an excess of $LaCl_3$ (200 mol %). The selected single crystal has a needle shape (30 × 740 × 30 μm) and {100}, {001}, {101} truncations. Orthorhombic symmetry was determined with photographs (Laue, Weissenberg, precession). Cell parameters refined with 27 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; 8270 reflections; $(\sin\theta)/\lambda < 0{\cdot}81$ Å^{-1}, $-25 \le h \le 26$, $-6 \le k \le 0$, $-23 \le l \le 22$; scan width (°): $0{\cdot}90 + 1{\cdot}04\ \mathrm{tg}\theta$; counter slit width (mm): $0{\cdot}13 + 0{\cdot}60\ \mathrm{tg}\theta$. Three standard reflections checked every 100 reflections, with no systematic variation observed and a maximum relative deviation of 6%. Data corrected for Lorentz–polarization effects and for absorption using *SHELX76* (Sheldrick, 1976), crystal shape and size, and incident- and diffracted-beam direction cosines ($0{\cdot}63 < T < 0{\cdot}70$). Merging equivalents for which $I/\sigma(I) > 3$ gave 1545 unique reflections ($R_{\mathrm{int}} = 0{\cdot}042$).

Systematic absences $k + l = 2n + 1$ for $0kl$ and $h = 2n + 1$ for $hk0$ consistent with space groups $Pnma$ and $Pn2_1a$ [inconsistencies: 0 with $I/\sigma(I) > 5$, 5 with $5 > I/\sigma(I) > 3$]. 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 $Pnma$ group by heavy-atom methods with *SHELX76* and IBM 3090-400 computer of the Computer Center of Montpellier. Three sites of La atoms found by Patterson-function deconvolution on mirror m ($R = 0{\cdot}25$). Five sites for Cl atoms, also on mirror m, located with difference Fourier syntheses. SiO_4 tetrahedron found with a face in mirror m which generated two symmetrically incompatible sites for Si atoms. A partial occupancy (50%) of an $8(d)$ site by Si atoms must be assumed with this space group. Using this $Pnma$ hypothesis, refinement of anisotropic thermal parameters for La and Cl atoms leads to correct values.

At this stage we looked for an ordered model in subgroups of $Pnma$ without a mirror perpendicular to **b**: $Pn2_1a$, $P2_12_12_1$ and $P2_1/c$.

Relative orientations of SiO_4 tetrahedra in these different subgroups can be seen in Fig. 1 (in the monoclinic $P2_1/c$ space group: $b \rightarrow a$). The main

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features of the calculations in these subgroups, compared with results in *Pnma*, are the following:

– *R* factors and residual electron density are not significantly improved.

– values of isotropic thermal parameters are less satisfying for Si and O atoms and in all cases it is now impossible to refine anisotropic parameters even for La atoms only.

– fractional coordinates *x* and *z* (*z* and *y* in $P2_1/c$) keep the same values but *y* values (except for La atoms) are very inaccurate with important fluctuations.

The possibility of a twin mirror perpendicular to the *b* axis has also to be taken into consideration. If the La and Cl sites are not exactly in the same plane, a twin mirror would induce strong anisotropy along [010] for these atoms. This is not observed, the anisotropic thermal parameters obtained in the *Pnma* refinement having satisfactory U_{22} values, of the same order of magnitude as U_{11} and U_{33} values.

On the basis of these results we have kept the hypothesis of the space group *Pnma* assuming an 'up–down' disorder for SiO_4 tetrahedra (above or below *m*). This is also justified by the weakness of interactions between SiO_4 groups in the plane perpendicular to **b** (Fig. 1), due to the high number and large size of La and Cl atoms. If disorder is not complete, it affects weak reflections and anisotropic thermal parameters lose a part of their physical significance. The final refinement was carried out with the following conditions: 1187 reflections for which $I > 5\sigma(I)$, individual isotropic thermal parameters, a weighting scheme $w = 1/\sigma^2(F_o)$, an empirical isotropic extinction parameter x [$F_c = F(1 - 10^{-4}\,xF^2/\sin\theta)$]: $R = 0{\cdot}054$, $wR = 0{\cdot}086$; $x = 12{\cdot}7\,(5) \times 10^{-4}$; max. shift/e.s.d. in last cycle $< 0{\cdot}007$; electron density map featureless, with maxima near La atoms.* Atomic parameters in *Pnma* are given in Table 1. Selected bond lengths and angles are given in Table 2.

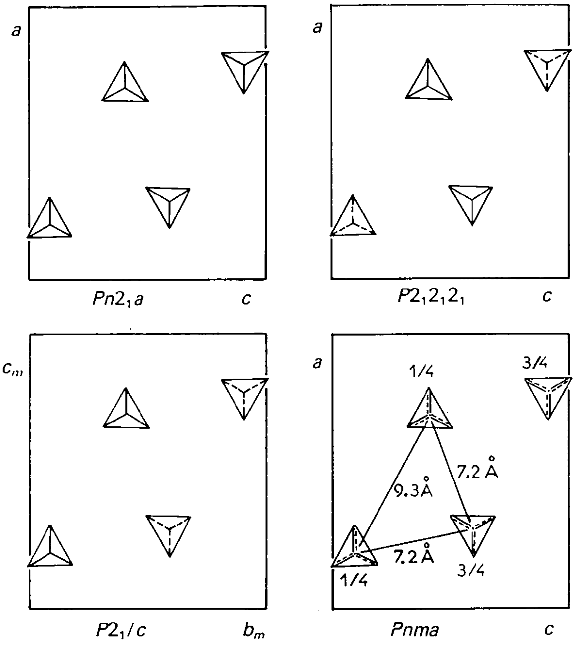

Fig. 1. Relative 'up' (full lines) and 'down' (dash lines) orientations for SiO_4 tetrahedra in *Pnma* subgroups $Pn2_1a$, $P2_12_12_1$ and $P2_1/c$ and in space group *Pnma* (with distances between the projections of the Si atoms on the mirror planes).

Table 1. *Positional and isotropic thermal parameters*

	Position	Site symmetry	*x*	*y*	*z*	B_{iso}(Å^2)
La(1)	4(*c*)	.*m*.	0·12690 (8)	$\frac{1}{4}$	0·58361 (9)	0·57 (2)
La(2)	4(*c*)	.*m*.	0·36772 (8)	$\frac{1}{4}$	0·75075 (9)	0·59 (2)
La(3)	4(*c*)	.*m*.	0·37313 (8)	$\frac{1}{4}$	0·42994 (9)	0·56 (2)
Cl(1)	4(*c*)	.*m*.	0·4886 (4)	$\frac{1}{4}$	0·5941 (4)	0·98 (9)
Cl(2)	4(*c*)	.*m*.	0·1804 (4)	$\frac{1}{4}$	0·7790 (4)	1·05 (9)
Cl(3)	4(*c*)	.*m*.	0·1979 (4)	$\frac{1}{4}$	0·3923 (4)	0·86 (9)
Cl(4)	4(*c*)	.*m*.	0·4447 (4)	$\frac{1}{4}$	0·9431 (5)	1·01 (9)
Cl(5)	4(*c*)	.*m*.	0·4775 (5)	$\frac{1}{4}$	0·2178 (5)	1·67 (12)
Si	8(*d*)	1	0·2093 (5)	0·676 (3)	0·5893 (6)	0·50 (13)
O(1)	4(*c*)	.*m*.	0·1917 (10)	$\frac{3}{4}$	0·5925 (11)	0·7 (2)
O(2)	4(*c*)	.*m*.	0·3375 (11)	$\frac{3}{4}$	0·6860 (12)	0·8 (3)
O(3)	4(*c*)	.*m*.	0·3417 (10)	$\frac{3}{4}$	0·4911 (11)	0·5 (2)
O(4)	8(*d*)	1	0·2915 (11)	0·295 (8)	0·5885 (13)	0·7 (3)

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

La(1)—O(1)	2 × 2·380 (7)	Cl(1)—La(2)	1 × 2·970 (6)
—O(4)	1 × 2·679 (18)	—La(3)	1 × 2·995 (6)
—Cl(2)	1 × 2·914 (6)	—La(3^{iv})	2 × 3·113 (6)
—Cl(3)	1 × 2·957 (6)		
—Cl(4^{i})	1 × 2·980 (6)	Cl(2)—La(1)	1 × 2·914 (6)
—Cl(4^{ii})	2 × 3·146 (6)	—La(2)	1 × 3·066 (6)
—Cl(5^{iii})	2 × 3·326 (7)	—La(3^{iii})	2 × 3·149 (6)
La(2)—O(2)	2 × 2·373 (8)	Cl(3)—La(1)	1 × 2·957 (6)
—O(4)	1 × 2·627 (18)	—La(2^{ii})	2 × 3·121 (6)
—Cl(1)	1 × 2·970 (6)	—La(3)	1 × 2·894 (6)
—Cl(2)	1 × 3·066 (6)		
—Cl(3^{iii})	2 × 3·121 (6)	Cl(4)—La(1^{v})	1 × 2·980 (6)
—Cl(4)	1 × 3·010 (7)	—La(1^{iii})	2 × 3·146 (6)
—Cl(5^{iv})	2 × 3·323 (7)	—La(2)	1 × 3·010 (7)
La(3)—O(3)	2 × 2·358 (7)	Cl(5)—La(1^{ii})	2 × 3·326 (7)
—O(4)	1 × 2·624 (18)	—La(2^{iv})	2 × 3·323 (7)
—Cl(1)	1 × 2·995 (6)	—La(3)	1 × 3·463 (7)
—Cl(1^{iv})	2 × 3·113 (6)		
—Cl(2^{ii})	2 × 3·149 (6)		
—Cl(3)	1 × 2·894 (6)	O(1)—Si—O(2)	113·8 (9)
—Cl(5)	1 × 3·463 (7)	—O(3)	118·6 (9)
		—O(4)	101·9 (8)
Si—O(1)	1 × 1·631 (18)	O(2)—Si—O(3)	116·5 (9)
—O(2)	1 × 1·607 (19)	—O(4)	101·4 (8)
—O(3)	1 × 1·659 (18)	O(3)—Si—O(4)	100·3 (9)
—O(4)	1 × 1·626 (38)		

Symmetry code: (i) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (ii) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (iii) $\frac{1}{2} - x, -y, z + \frac{1}{2}$; (iv) $1 - x, \frac{1}{2} + y, 1 - z$; (v) $\frac{1}{2} + x, y, \frac{3}{2} - z$.

Discussion. La^{3+} cations and Cl^- anions are distributed in mirrors perpendicular to **b** with $y = \frac{1}{4}, \frac{3}{4}$ (Fig. 2).

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51993 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

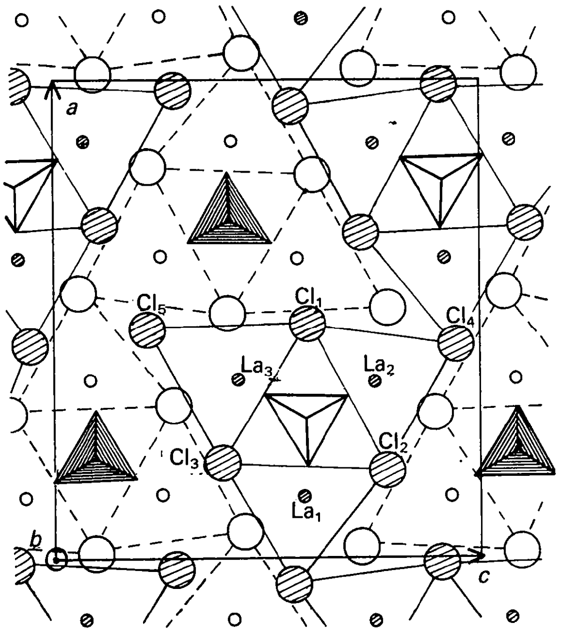

Fig. 2. Projection of the $La_3(SiO_4)Cl_5$ structure along the b axis (atoms striped and joined by full lines at $y = \frac{1}{4}$, atoms joined by dashed lines at $y = -\frac{1}{4}$).

The La(1), La(2) and La(3) ions have similar Cl_7O_3 environments: three Cl atoms at the apices of a nearly equilateral triangle in the 'mirror', a Cl_4O_2 trigonal prism with triangular faces symmetrical with respect to the 'mirror' and one O atom [O(4)] more distant than the two other O atoms.

In planes $y = \frac{1}{4}$, $\frac{3}{4}$ we can characterize triangular La_3Cl_6 groups formed by three $LaCl_3$ groups sharing apices. Each La_3Cl_6 triangle shares two apices with two other similar triangles to constitute $(La_3Cl_5)_n$ chains parallel to **a**. The apex of the La_3Cl_6 triangle not shared in this chain is occupied by Cl(5). Pseudo-hexagonal holes appear between two consecutive chains in the mirror in which triangular bases of SiO_4 tetrahedra are located (Fig. 2).

The Cl(1), Cl(2), Cl(3), and Cl(4) anions have a cationic tetrahedral environment (La_4Cl). This halogen coordination can be found in halogenoaluminosilicates of sodalite $Na_4(AlSiO_4)_3X$ (Löns & Schulz, 1967). The Cl(5) anion has a fivefold pyramidal coordination (La_5Cl) with greater Cl—La distances, resulting in a greater value of the thermal parameter (Table 1).

Because of the low value of the b parameter, consecutive SiO_4 tetrahedra along [010] keep the same orientation. So it can be assumed that orientation disorder occurs between such 'SiO_4 rows' parallel to **b**. In planes $y \simeq \frac{1}{4}$, $\frac{3}{4}$ distances between tetrahedra shown in Fig. 1 are great so the two possible orientations for a tetrahedron lead to a weak variation of lattice energy, making possible the existence of some disorder. Orientational disorders of oxygen tetrahedra have been observed, for instance for SO_4 in Na_2SO_4 (Eysel, Höfer, Keester & Hahn, 1985).

The similarity of the powder patterns indicates that $Ln_3(SiO_4)Cl_5$ compounds with Ln = La, Ce, Pr, Nd are isostructural.

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Dimerer Cadmium(II)-komplex mit Dihydrazidothiophosphorsäurephenylester als zweizähnigem *S*,*N*-Chelatligand

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Abstract. Di-μ-chloro-bis{chloro[*O*-phenyl bis(*N*,*N'*-dimethylhydrazido)thiophosphate-*S*,*N*]cadmium(II)}, $[Cd_2Cl_2(C_{10}H_{19}N_4OPS)_2]$, $M_r = 915{\cdot}28$, monoclinic, $P2_1/c$, $a = 12{\cdot}497\,(5)$, $b = 7{\cdot}968\,(6)$, $c = 18{\cdot}144\,(11)$ Å, $\beta = 91{\cdot}44\,(4)°$, $V = 1806\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}683$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 17{\cdot}04$ mm^{-1}, $F(000) = 912$, $T = 293$ K, $R = 0{\cdot}043$ for 2582 unique contributing reflections. The title compound crystallizes from a solution of *O*-phenyl bis(*N*,*N'*-dimethylhydrazido)thiophosphate (dhtp)

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