

O2—Cu—F3	87.8 (6)	D11—O1—D12	105.5 (13)
O2—Cu—F3 ⁱ	92.2 (8)	D21—O2—D22	107.4 (15)
F1—Si—F2	90.3 (6)	Cu—F3—Si	153 (4)
F1—Si—F2 ⁱⁱ	89.7 (7)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, -y, 1-z$.

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1—D11...F2 ⁱ	0.962 (8)	1.720 (9)	2.676 (12)	172.2 (6)
O1—D12...F2 ⁱⁱ	0.953 (8)	1.787 (9)	2.740 (12)	178.8 (6)
O2—D21...F1 ⁱⁱⁱ	0.952 (10)	1.786 (14)	2.737 (18)	177.0 (6)
O2—D22...F1 ^{iv}	0.957 (8)	1.764 (10)	2.718 (14)	173.7 (5)

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

The rate of deuteration of the crystals was obtained from the occupation parameters of the D-atom sites, which were constrained to the same value: we obtained 0.749 (9), which leads to a deuteration rate of 0.839 (3). From the coordinates obtained by Clark, Fleming & Lynton (1969) and with the D atoms located from a difference synthesis, the structure was refined by the full-matrix least-squares method based on F^2 . Using a type II anisotropic extinction correction (Coppens & Hamilton, 1970), the coefficients z_{11} , z_{22} , z_{33} , z_{23} , z_{13} and z_{12} ($z_{ij} = W'_{ij} \times 10^{-4}$) obtained were 0.0063 (9), 0.0070 (11), 0.0201 (41), -0.0057 (15), -0.0010 (9) and -0.0002 (5), respectively, which leads to values of 0.230, 0.187 and 0.096 μm for the principal axes of the ellipsoid of the average crystallite shape.

The computer programs used were *SHELXL93* (Sheldrick, 1993) and *ORXFLS4* (Busing, Martin, Levy, Brown, Ellison, Hamilton, Ibers, Johnson & Thiessen, 1977) on PC and *CI-XP* computers.

We are very grateful to A. Forget and D. Colson for the preparation of the crystals.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: BR1141). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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La₃(Si₂O₇)Cl₃

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Abstract

The crystal structure of trilanthanum trichloride pyrosilicate, La₃(Si₂O₇)Cl₃, has been determined. The main building units are La(1)Cl₄O₅, La(2)Cl₅O₅ and La(3)Cl₃O₆ polyhedra, and Si₂O₇ pyrosilicate groups.

Comment

The structures of the lanthanum chloride silicates La₃(SiO₄)₂Cl (Gravereau, Es-Sakhi & Fouassier, 1988) and La₃(SiO₄)Cl₅ (Gravereau, Es-Sakhi & Fouassier, 1989) have been determined previously. These compounds show interesting luminescent properties.

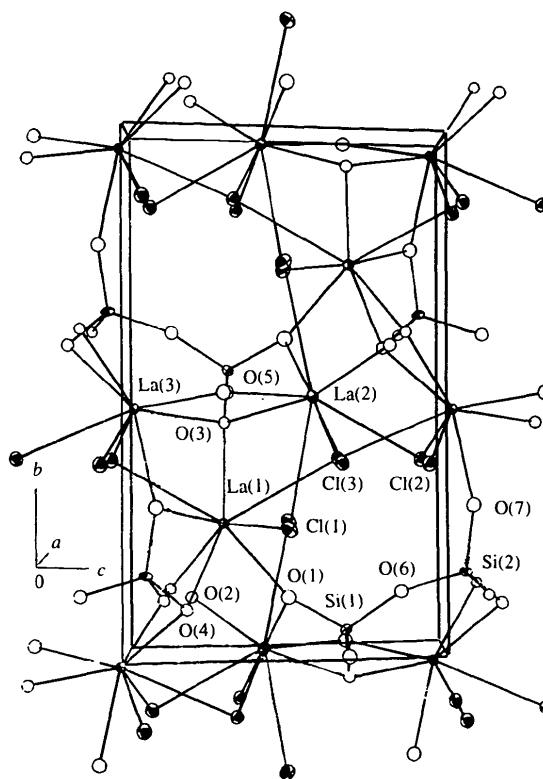


Fig. 1. The crystal structure of La₃(Si₂O₇)Cl₃ with ellipsoids at the 50% probability level.

In the title compound, atoms La(1), La(2) and La(3) have different coordination environments, *i.e.* Cl₄O₅, Cl₅O₅ and Cl₃O₆, respectively. The Cl atoms have La₄ environments and show *nido*-trigonal bipyramidal coordination. The Si atoms come from the silica tube and together with seven O atoms form a pyrosilicate slab with an Si—O—Si angle of 150(1)°, which is almost the same as that found in Eu₂Si₂O₇ (Siegrist, Petter & Hulliger, 1982).

Three types of chain are found along the *a* direction in the title compound: an La(1) chain formed through sharing Cl(1) atoms, with alternating La(1)—Cl(1) lengths of 2.898(6) and 3.304(7) Å; an La(2) chain formed through sharing Cl(3) atoms, with alternating La(2)—Cl(3) lengths of 3.009(7) and 3.218(7) Å; and an La(3) chain formed through sharing Cl(2) atoms, with alternating La(3)—Cl(2) lengths of 2.980(7) and 3.070(7) Å.

The La(2) and La(3) chains combine by sharing Cl(3) atoms to form La(2)—La(3) double chains, and these double chains are connected to one another by sharing six O atoms of the [Si₂O₇] pyrosilicate group, resulting in an [La₂Cl₂Si₂O₆] sheet in the *ac* plane. These sheets stack along the *b* direction to form the three-dimensional framework of the title compound and other [LaClO] units are accommodated between the adjacent [La₂Cl₂Si₂O₆] sheets.

Experimental

La₃(Si₂O₇)Cl₃ was obtained while preparing a lanthanum vanadium compound by reaction of LaCl₃ [from dehydrating LaCl₃·7H₂O (AR) at 473 K in a vacuum, a trace amount of H₂O may be left] and metallic vanadium (SP) powder. A pressed pellet containing 95 mg LaCl₃ and 19.6 mg V was sealed in an evacuated silica tube. The tube was heated at 473 K for 24 h, then slowly heated to 1223 K at a rate of 5 K h⁻¹, held at that temperature for 162 h, then slowly cooled to 1073 K at a rate of 6.3 K h⁻¹ and finally cooled to room temperature. The title compound appeared as translucent colorless plate-like crystals.

Crystal data

La ₃ (Si ₂ O ₇)Cl ₃	Mo Kα radiation
<i>M_r</i> = 691.26	λ = 0.71073 Å
Monoclinic	Cell parameters from 25 reflections
<i>P</i> 2 ₁	θ = 10–11°
<i>a</i> = 5.364(8) Å	μ = 14.03 mm ⁻¹
<i>b</i> = 12.148(9) Å	<i>T</i> = 293 K
<i>c</i> = 7.922(4) Å	Plate
β = 108.87(6)°	0.40 × 0.08 × 0.04 mm
<i>V</i> = 488.5(9) Å ³	Colorless
<i>Z</i> = 2	
<i>D_x</i> = 4.70 Mg m ⁻³	
<i>D_m</i> not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	2084 observed reflections
ω/2θ scans	[<i>I</i> > 3.0σ(<i>I</i>)]
	<i>R_{int}</i> = 0.086

Absorption correction: spherical and ψ scan (North, Phillips & Mathews, 1968)	θ _{max} = 35.0°
<i>T_{min}</i> = 0.11, <i>T_{max}</i> = 0.27	<i>h</i> = 0 → 8
2424 measured reflections	<i>k</i> = 0 → 19
2242 independent reflections	<i>l</i> = -12 → 12
	3 standard reflections
	frequency: 120 min
	intensity decay: 0.6%

Refinement

Refinement on <i>F</i>	(Δ/σ) _{max} = 0.0052
<i>R</i> = 0.0605	Δρ _{max} = 4.54 e Å ⁻³
<i>wR</i> = 0.0918	Δρ _{min} = -3.69 e Å ⁻³
<i>S</i> = 1.50	Extinction correction: none
2084 reflections	Atomic scattering factors from Cromer & Waber (1974)
100 parameters	
<i>w</i> = 1/[σ ² (<i>F</i>) + (0.030 <i>F</i>) ² + 1.0] - <i>F</i>	

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

<i>U</i> _{iso} for O atoms, <i>U</i> _{eq} = (1/3)Σ _{<i>i</i>} Σ _{<i>j</i>} <i>U</i> _{<i>ij</i>} <i>a_i[*]a_j[*]a_k</i> for all others.				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} / <i>U</i> _{eq}
La(1)	0.4336 (2)	0.25	0.2997 (1)	0.0060 (2)
La(2)	0.9801 (2)	0.4943 (1)	0.5795 (1)	0.0071 (2)
La(3)	0.7144 (2)	0.4704 (1)	1.0289 (1)	0.0051 (2)
Cl(1)	0.989 (1)	0.2460 (5)	0.5067 (8)	0.0121 (9)
Cl(2)	0.163 (1)	0.3689 (5)	-0.0592 (7)	0.011 (1)
Cl(3)	0.543 (1)	0.3751 (5)	0.6639 (7)	0.010 (1)
Si(1)	0.392 (1)	0.5447 (5)	0.3161 (8)	0.005 (1)
Si(2)	0.782 (1)	0.1567 (5)	0.0653 (8)	0.006 (1)
O(1)	0.442 (3)	0.105 (2)	0.505 (2)	0.013 (3)
O(2)	0.641 (3)	0.090 (1)	0.187 (2)	0.009 (3)
O(3)	0.585 (3)	0.445 (1)	0.306 (2)	0.008 (3)
O(4)	0.089 (3)	0.118 (1)	0.127 (2)	0.007 (2)
O(5)	0.104 (3)	0.503 (2)	0.310 (2)	0.011 (3)
O(6)	0.378 (3)	0.617 (2)	0.138 (2)	0.010 (3)
O(7)	0.733 (3)	0.284 (2)	0.095 (2)	0.011 (3)

Table 2. Selected geometric parameters (Å, °)

La(1)—Cl(1 ⁱ)	3.304 (7)	La(2)—O(5 ⁱⁱ)	2.44 (2)
La(1)—Cl(1)	2.898 (6)	La(3)—Cl(2 ⁱⁱⁱ)	3.070 (7)
La(1)—Cl(2)	3.100 (6)	La(3)—Cl(2 ⁱⁱⁱ)	2.980 (7)
La(1)—Cl(3)	3.144 (6)	La(3)—Cl(3)	2.970 (6)
La(1)—O(1)	2.38 (2)	La(3)—O(2 ^v)	2.56 (1)
La(1)—O(2)	2.55 (2)	La(3)—O(3 ^{vi})	2.53 (2)
La(1)—O(3)	2.49 (2)	La(3)—O(4 ^{vii})	2.58 (2)
La(1)—O(4)	2.50 (1)	La(3)—O(5 ^{viii})	2.54 (1)
La(1)—O(7)	2.66 (2)	La(3)—O(6 ^{ix})	2.86 (2)
La(2)—Cl(1)	3.075 (7)	La(3)—O(7 ^x)	2.31 (2)
La(2)—Cl(1 ⁱⁱ)	3.148 (7)	Si(1)—O(1 ^x)	1.59 (2)
La(2)—Cl(2 ⁱⁱⁱ)	3.108 (6)	Si(1)—O(3)	1.61 (2)
La(2)—Cl(3)	3.009 (7)	Si(1)—O(5)	1.61 (2)
La(2)—Cl(3 ^{iv})	3.218 (7)	Si(1)—O(6)	1.64 (2)
La(2)—O(1 ^v)	2.53 (2)	Si(2)—O(2)	1.62 (2)
La(2)—O(2 ^{vi})	2.54 (1)	Si(2)—O(4 ^{vii})	1.63 (2)
La(2)—O(3)	2.57 (1)	Si(2)—O(6 ^{viii})	1.64 (2)
La(2)—O(4 ^{vii})	2.89 (2)	Si(2)—O(7)	1.60 (2)
O(1 ^v)—Si(1)—O(3)	102.2 (9)	O(2)—Si(2)—O(4 ^{vii})	107.2 (9)
O(1 ^v)—Si(1)—O(5)	115 (1)	O(2)—Si(2)—O(6 ^{viii})	103.9 (9)
O(1 ^v)—Si(1)—O(6)	112 (1)	O(2)—Si(2)—O(7)	106 (1)
O(3)—Si(1)—O(5)	112 (1)	O(4 ^{vii})—Si(2)—O(6 ^{viii})	111 (1)
O(3)—Si(1)—O(6)	102 (1)	O(4 ^{vii})—Si(2)—O(7)	115.7 (9)
O(5)—Si(1)—O(6)	111.3 (9)	O(6 ^{viii})—Si(2)—O(7)	112.0 (9)

Symmetry codes: (i) *x* - 1, *y*, *z*; (ii) 2 - *x*, ½ + *y*, 1 - *z*; (iii) 1 + *x*, *y*, 1 + *z*; (iv) 1 + *x*, *y*, *z*; (v) 1 - *x*, ½ + *y*, 1 - *z*; (vi) *x*, *y*, 1 + *z*; (vii) 1 - *x*, *y* - ½, -*z*.

Data collection: CAD-4 Operations Manual (Enraf–Nonius, 1977). Cell refinement: CAD-4 Operations Manual. Data reduction: MolEN (Fair, 1990). Program(s) used to solve

structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Nd₄V₅Si₄O₂₂

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Abstract

The title compound, tetraneodymium pentavanadium octaoxygen bis(pyrosilicate), has a quasi-two-dimensional chevkinite-type structure, consisting of rutile-like vanadium–oxygen layers with V–V distances of 2.794 (2) Å.

Comment

Lanthanide oxosilicates containing early transition metals are rare. Wang & Hwu (1992) first prepared La₄Ti₉Si₄O₃₀, which shows a perrierite-related structure; La₂Ti₂SiO₉ has also been reported (Benbental, Mosset & Trombe, 1994). Recently, we prepared Pr₄V₅Si₄O₂₂ (Chen, Guo, Zhuang, Huang & Zhang, 1995) as the first praseodymium oxosilicate containing vanadium; it has a quasi-two-dimensional chevkinite-type structure.

Nd₄V₅Si₄O₂₂ is isostructural with Pr₄V₅Si₄O₂₂, consisting of rutile-like vanadium–oxygen layers and neodymium–oxygen layers formed by [Nd₂O₁₃] dimers. In this compound, the V–V distance across the shared octahedral edges along the rutile-like vanadium–oxygen chains is 2.794 (2) Å, the Nd–Nd distance within the

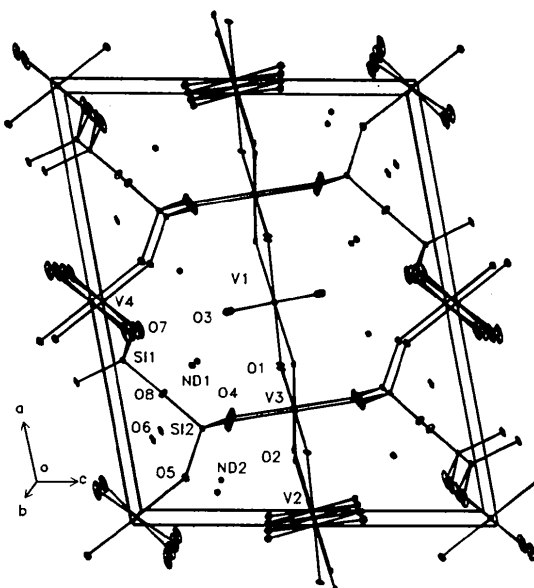


Fig. 1. The crystal structure of Nd₄V₅Si₄O₂₂ with displacement ellipsoids at the 50% probability level (all bonds to Nd atoms are omitted).

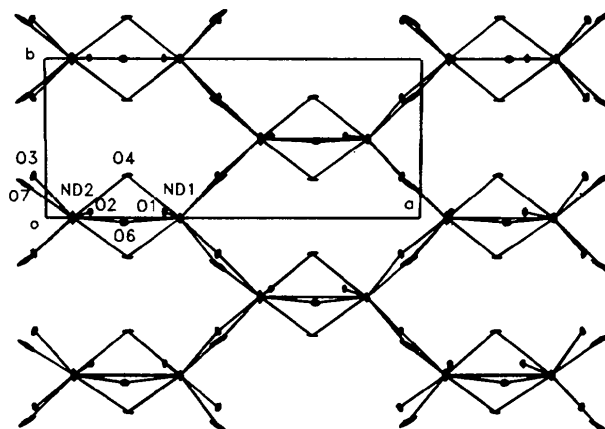


Fig. 2. A view down the *c* axis showing the [Nd₂O₁₃] dimers.