and anisotropic temperature factors were refined, the final values being given in Table 2. The refinement gave $R_p = 5{\cdot}09$, $R_{wp} = 5{\cdot}79$ ($R_E = 5{\cdot}83$) and $\chi^2 = 0{\cdot}99$ [R factors as defined by Rietveld (1969)]. The observed, calculated and difference profiles, plotted to the same scale, are shown in Fig. 1.

The structure consists of chains of face-sharing and alternating PtO$_6$ and Ba(1)O$_6$ polyhedra. The platinum is octahedrally coordinated but the barium is in a distorted trigonal prismatic site. The chains are held together by barium [Ba(2)] in an irregular eight-coordinated site (Table 3). The occurrence of isolated octahedral platinum in oxides is rare (Schwartz & Prewitt, 1984), and has been suggested to be responsible for the ready hydrolysis of compounds of this type (Randall & Katz, 1959). The structure and packing of these chains can be seen in Figs. 2 and 3, respectively. The model is essentially the same as that found for Sr$_4$PtO$_6$ and the rhombohedral form of Ca$_4$PtO$_6$ (McDaniel, 1972). It is also related to the newly discovered compound Sr$_3$CuPtO$_6$ (Wilkinson, Cheetham, Kunnmann & Kvick, 1989).

Examination of Schneider & McDaniel's reported powder X-ray data shows that the agreement with the pattern calculated on the basis of their hexagonal unit cell is good, implying that their sample was monophasic. We conclude that there must be two modifications of Ba$_4$PtO$_6$. It is not clear why we obtained a different phase from that of Schneider & McDaniel, there being several possibilities. The annealing procedure we adopted is rather different to that originally reported; 3 days at 1370 K as opposed to 3 days at 1070 K followed by 30 minutes at 1370 K. Hence it is possible that Schneider & McDaniel's sample had not come to equilibrium at the higher temperature before being quenched. Another possibility is that the rhombohedral phase has been stablized relative to the hexagonal one by the presence of impurities commonly found in commerical PtO$_2$. The nature of the brown material produced where the pellets made contact with the platinumn foil is not yet known, but X-ray microanalysis indicates the presence of a phase with a higher platinum content than the title compound.

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Structure of CsAlTiO$_4$ – a Compound with TiO$_4$ Tetrahedra

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Abstract. Caesium aluminium orthotitanate, $M_r = 271{\cdot}79$, orthorhombic, *Imma*, $a = 8{\cdot}978\,(4)$, $b = 5{\cdot}740\,(1)$, $c = 9{\cdot}969\,(2)$ Å, $V = 513{\cdot}74$ Å^3, $Z = 4$, D_m not measured (insufficient material), $D_x = 3{\cdot}51$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}7107$ Å, $\mu = 8{\cdot}66$ mm^{-1}, $F(000) = 488$, $T = 293$ K, final $R = 0{\cdot}032$ for 377 counter-measured reflections. The structure consists of six-membered rings of tetrahedra (disordered Al and Ti) formed from corner sharing of infinite strings of tetrahedra where adjacent strings point in opposite directions, up or down. The Cs$^+$ ions are located in cavities formed by the rings of tetrahedra. This appears to be only the second report of a titanium(IV) compound in which TiO$_4$ tetrahedra are present. The mean Al(Ti)—O and Cs—O distances are 1·764 and 3·510 respectively.

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Introduction. An interest in compounds likely to be important in the formation of 'SYNROC' – a means proposed for the disposal of high-level radioactive waste (Ringwood, Kesson, Ware, Hibberson & Major, 1979) – led to work on the systems $BaO:Al_2O_3:TiO_2$, $BaO:MgO:TiO_2$ and $Cs_2O:Al_2O_3:TiO_2$ (Roth & Waring, 1982), and to the independent determination of several structures deriving from the first of these systems (Fallon & Gatehouse, 1983; Fallon, Gatehouse & Wright, 1985). Recently, after partial refinement of the structure of $CsAlTiO_4$ using a powder sample and the Rietveld method, a sample heated in a furnace at 1773 K for a period of 4 weeks in a sealed platinum tube provided single-crystal fragments. The structure of this compound is reported here.

Experimental. A suitable triangular prismatic piece of crystal ($\sim 0{\cdot}14 \times 0{\cdot}09 \times 0{\cdot}05$ mm) was selected from a preparation in which the relevant mole ratios of $CsNO_3$ ('optical grade'), TiO_2 (Hopkins & Williams) and Al_2O_3 (BDH) were heated initially for 24 h at 1200 K followed by 48 h at 1400 K then slow cooled at 10 K min^{-1} in an open platinum crucible. An allowance was made for the loss of caesium at the reaction temperature (Solomah, Odoj & Freiburg, 1984). Some of this material was subsequently ground and heated in a sealed platinum tube as described above.

Space group *Imma* from systematic absences *hkl* $h+k+l = 2n+1$ and *hk*0 $h = 2n+1$ ($k = 2n+1$); cell parameters determined from 25 reflections ($6 < \theta < 12°$) with a Philips PW1100 automatic four-circle diffractometer equipped with a graphite monochromator as described previously (Canty, Chaichit & Gatehouse, 1980). Three standard reflections measured at 4 h intervals. No decomposition occurred. Data collected using ω-scan technique with a symmetrical scan width of $\pm 0{\cdot}70°$ in ω from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of $0{\cdot}04°\ s^{-1}$. No reflection was sufficiently intense to warrant the insertion of an attenuation filter. Data processed using a program written specifically for the PW1100 diffractometer (Hornstra & Stubbe, 1972). Values of I and $\sigma(I)$ corrected for Lorentz and polarization effects. Absorption correction applied based on indexed crystal faces, max. and min. transmission factors 0·8016 and 0·4776 respectively. 1720 reflections measured to $2\theta = 60°$, 377 unique reflections ($R_{int} = 0{\cdot}048$) [$I \geq 3\sigma(I)$] used in analysis; index range h 0/12, k 0/8, l 0/14. Cs-atom parameters found from Patterson synthesis and remaining atoms from subsequent difference Fourier syntheses. Function minimized in full-matrix least-squares refinement $\sum w(|F_o| - |F_c|)^2$, where w is the weight $\{[\sigma^2(F_o)]^{-1}\}$. All atoms refined anisotropically; 24 variable parameters, final R 0·032 and $wR = 0{\cdot}029$ (for observed reflections); max. Δ/σ in final cycle 0·003. Final difference synthesis had $\Delta\rho$ within 0·75 and $-1{\cdot}83\ e\ Å^{-3}$, both in the vicinity of the Cs atom. Scattering factors for neutral atoms and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). All calculations performed on the Monash University VAX 11/780 computer system. Major programs used: *SHELX76* (Sheldrick, 1976) and *STRUPLO* (Fischer, 1984).

Table 1. *Final coordinates* ($\times 10^5$ *for* Cs, $\times 10^4$ *for other atoms*) *and equivalent isotropic thermal parameters* ($\times 10^4$ *for* Cs *and* Al/Ti, $\times 10^3$ *for* O) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq} (Å^2)†
Cs	0	25000	20287 (6)	288 (2)
Al/Ti	1955 (1)	2500	5814 (1)	155 (3)
O(1)	0	2500	5743 (7)	30 (2)
O(2)	2318 (5)	0	0	36 (1)
O(3)	2500	2500	7500	78 (5)

† $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Al/Ti—O(3)	1·751 (1)	Cs—O(2)	3·237 (3)
—O(1)	1·757 (1)	—O(2^{ii})	3·237 (3)
—O(2)	1·773 (2)	—O(2^{iii})	3·237 (3)
—O(2^{i})	1·773 (2)	—O(2^{iv})	3·237 (3)
		—O(1^{v})	3·630 (5)
O(2)—Al/Ti—O(2^{i})	108·1 (2)	—O(1^{vi})	3·630 (5)
O(3)—Al/Ti—O(1)	108·5 (3)	—O(3^{v})	3·6738 (1)
O(3)—Al/Ti—O(2)	109·7 (1) × 2	—O(3^{vi})	3·6738 (1)
O(1)—Al/Ti—O(2)	110·5 (2) × 2	—O(3^{vii})	3·6738 (1)
		—O(3^{viii})	3·6738 (1)
		—O(1)	3·702 (7)

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

Discussion. Final fractional coordinates and thermal parameters are given in Table 1;* interatomic distances and selected angles are given in Table 2.

The crystal structure of $CsAlTiO_4$ is closely related to that of $RbAlSiO_4$ and consists of six-membered rings of tetrahedra, over which Al and Ti are statistically distributed. In any ring three tetrahedra face up and three face down (*UUUDDD*) in a manner described earlier as a 'tetrahedral framework with *Icmm* symmetry' (Hahn, Lohre & Chung, 1969). The infinite array of hexagonal rings can be considered to be derived from adjacent corner-shared strings of

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52052 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tetrahedra facing alternately up and down. The Cs ions are located within cavities formed by the rings of tetrahedra (Fig. 1), and their coordination detail can be seen in Fig. 2.

This is only the second compound reported to contain titanium(IV) ions tetrahedrally coordinated to oxygen ions. The first compound, reported in two forms, was Ba_2TiO_4–β-Ba_2TiO_4 (Bland, 1961; Wu & Brown, 1973) and α'-Ba_2TiO_4 (Günter & Jameson, 1984).

Al/Ti—O distances range from 1·751 (1) to 1·773 (2) Å with each O atom being involved in corner sharing between pairs of tetrahedra and in the Cs-ion coordination polyhedron. These Al/Ti—O distances are approximately midway between the Ti—O distances of α'-Ba_2TiO_4 [1·79 (2)–1·84 (2), mean 1·81 (2) Å] (Günter & Jameson, 1984) and β-Ba_2TiO_4 [1·766 (7)–1·836 (7), mean 1·808 (7) Å] (Wu & Brown, 1973) and the Al—O distances in $RbAlSiO_4$ [1·724 (4)–1·757 (4), mean 1·739 (4) Å] (Klaska & Jarchow, 1975). The structure of $RbAlSiO_4$ is reported in space group $Pc2_1n$; this would require that the y coordinate of one atom be fixed. That there are e.s.d.'s for all y coordinates is presumably an error (Klaska & Jarchow, 1975).

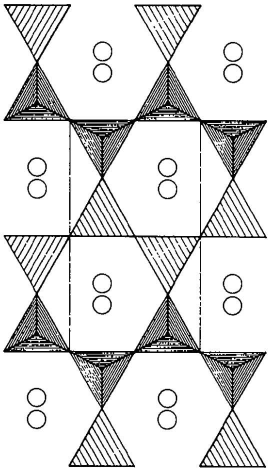

Fig. 1. An idealized [100] projection of the structure of $CsAlTiO_4$ with the Cs ions drawn as circles (*STRUPLO*: Fischer, 1984).

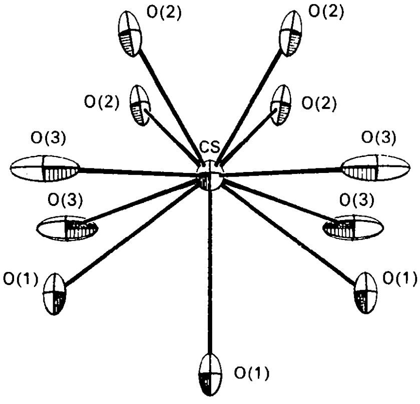

Fig. 2. The caesium-ion coordination in $CsAlTiO_4$ (all atoms drawn at the 50% limit) (*ORTEP*; Johnson, 1965).

Table 3. *Unit-cell dimensions of structures related to that of* $CsAlTiO_4$

	a (Å)	b (Å)	c (Å)		Vol. (Å^3)	Ref.
$RbLiSO_4$	5·288 (1)	9·105 (1) β 90·09 (2)°	8·731 (1)	$P2_1/n$	420·37	(1)
NH_4LiSO_4	5·280 (2)	9·140 (7)	8·786 (6)	$P2_1cn$	424·01	(2)
$RbAlLiSO_4$	9·226	5·337	8·741	$Pc2_1n$	430·40	(3)
$CsLiSO_4$	9·443	5·451	8·810	$Pc2_1n$	453·48	(4)
$CsAlSiO_4$	8·907 (2)	9·435 (1)	5·438 (1)	$Pna2_1$	457·0	(5)
$CsAlTiO_4$	8·978 (4)	5·740 (1)	9·969 (2)	$Imma$	513·74	(6)

Notes: each of these structures has an hexagonal ring of tetrahedra with three tetrahedra pointing up and three pointing down in the sequence *UUUDDD* around the ring. Tetrahedra (viewed perpendicular to the plane of the hexagonal ring) are eclipsed in each compound except the first where they are staggered.

References: (1) Tanisaki, Mashiyama, Hasebe, Shiroishi & Sawada (1980); (2) Dollase (1969); (3) Klaska & Jarchow (1975); (4) Hahn *et al.* (1969); (5) Gallagher, McCarthy & Smith (1977) (powder work); (6) this work.

The structure of $CsAlTiO_4$ has been reported here in the standard setting of space group *Imma* as it is apparent that no particular convention has been adopted for the series of related compounds arranged in Table 3 in order of increasing unit-cell volume.

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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 ($R_{\rm int} = 0{\cdot}042$).

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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