nine-coordinate and is identical to that of the analogous uranium compound (Serezkin *et al.*, 1974).

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The Structure of Ba_4PtO_6 from Time-of-Flight Powder Neutron Diffraction Data

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Abstract. Tetrabarium platinum(IV) hexaoxide, $M_r = 840{\cdot}45$, rhombohedral, $R\bar{3}c$, $a = 10{\cdot}2101\ (2)$, $c = 12{\cdot}6172\ (3)$ Å (hexagonal setting), $V = 1139{\cdot}08\ (5)$ Å^3, $Z = 6$, $D_x = 4{\cdot}42$ g cm^{-3}. Rietveld refinement using time-of-flight powder neutron diffraction data [TOF 40 000–120 000 μs, $T = 298$ K, $F(000) = 391{\cdot}98$ fm, 240 contributing reflections] resulted in $R_p = 5{\cdot}09$, $R_{wp} = 5{\cdot}79$ ($R_{\rm exp} = 5{\cdot}83$), $\chi^2 = 0{\cdot}99$. The structure of a new phase of Ba_4PtO_6, isostructural with Sr_4PtO_6 and rhombohedral Ca_4PtO_6, has been determined.

Introduction. In a study of the Ba—Pt—O phase diagram Schneider & McDaniel (1969) reported the existence of three phases, one which was unidentified, and the other two were Ba_4PtO_6 and a solid solution centred on $Ba_3Pt_2O_7$. Compositions in the solid solution have since been studied by other workers; the structure of $Ba_3Pt_2O_7$ has been determined (Haradem, Chamberland, Katz & Gleizes, 1977) and the composition $BaPtO_3$ has been examined (Gallagher, Johnson, Vogel, Wertheim & Schnettler, 1977).

The phase Ba_4PtO_6 was found to be hexagonal by Schneider & McDaniel, $a = 10{\cdot}064$, $c = 12{\cdot}663$ Å, and stable over the temperature range 1320–1490 K. The authors suggested that this phase could not be isostructural with the previously reported compound Sr_4PtO_6 which is rhombohedral, $R\bar{3}c$, $a = 9{\cdot}74$, $c = 11{\cdot}90$ Å (Randall & Katz, 1959), even though the unit cells were similar, as the available powder data could not be indexed on a rhombohedral unit cell. In the present work, powder neutron diffraction has been used to determine the structure of Ba_4PtO_6.

Experimental. A sample of Ba_4PtO_6 was prepared by the reaction of $BaCO_3$ and PtO_2. About 5 g of starting materials were mixed, ground and pressed into 13 mm diameter pellets. The pellets were placed in an alumina crucible lined with platinum foil and the sample was heated at 1370 K for 3 days. The sample was then quenched by tipping the crucible contents on to a thick aluminium plate. The pellets which had been in contact with the platinum foil had reacted with it, forming a brown material. All the brown material was carefully separated from the bulk of the sample, which was olive-green. The sample was then transferred to a desiccator to avoid sample hydrolysis. Our quenching procedure avoids the possibility of hydrolysis due to sample icing.

Powder X-ray data collected on the green material implied the presence of a single rhombohedral phase, $a = 10{\cdot}225\ (7)$, $c = 12{\cdot}642\ (8)$ Å, analogous to Sr_4PtO_6, rather than the hexagonal phase reported by Schneider & McDaniel (1969). Powder neutron data were then collected at the High Resolution Powder Diffractometer (HRPD) at ISIS

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Table 1. *Neutron diffraction data collection and analysis*

Diffractometer	HRPD, Rutherford–Appleton Laboratory
Data range	30 000–130 000 μs collected; 40 000–120 000 μs analysed in steps of 4·043 μs with 240 contributing reflections
Sample can	Flat plate aluminium can with thin vanadium windows
Scattering lengths (fm)	Ba 5·250 Pt 9·500 O 5·805 (Koester & Yelon, 1982)
Refinement	Rietveld technique; program *VDELSQ* (David, Akporiaye, Ibberson & Wilson, 1988)
Background	Four-term Chebychev polynomial
Function minimized	$\sum_i w_i[y_i(\mathrm{obs})-y_i(\mathrm{calc})]^2$ $w_i = 1/\sigma_i^2$
Peak shape	Voigt convoluted with a double exponential (David, Akporiaye, Ibberson & Wilson, 1988)

Table 2. *Coordinates and equivalent isotropic temperature factors for* Ba_4PtO_6

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

		x	y	z	B_{eq}(Å^2)
Ba(1)	6(*a*)	0·00000	0·00000	0·25000	1·11
Ba(2)	18(*e*)	0·36904 (20)	0·00000	0·25000	0·84
Pt	6(*b*)	0·00000	0·00000	0·00000	0·33
O	36(*f*)	0·17742 (12)	0·02178 (13)	0·09530 (8)	0·61

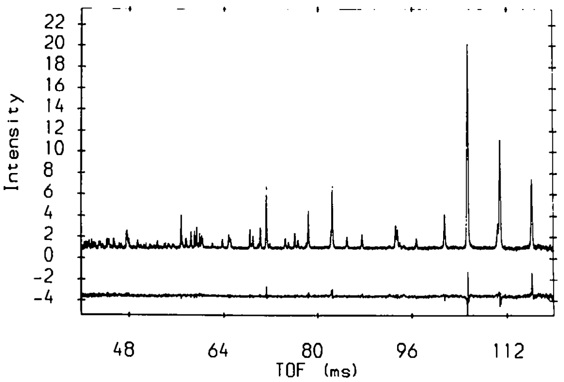

Fig. 1. The observed (dots), calculated (line) and difference profiles from the time-of-flight powder neutron diffraction study of Ba_4PtO_6.

(Rutherford–Appleton Laboratory); details of the data collection and structure refinement are given in Table 1.*

Discussion. The initial structural model was obtained from the single-crystal structure of Sr_4PtO_6, space group $R\bar{3}c$ (Randall & Katz, 1959). All coordinates

Table 3. *Selected bond lengths* (Å) *and angles* (°) *for* Ba_4PtO_6

Ba(1)—O	(6×)	2·596 (1)	Ba(2)—O	(2×)	2·834 (2)
Ba(2)—O	(2×)	2·722 (1)	Ba(2)—O	(2×)	2·850 (2)
Ba(2)—O	(2×)	2·783 (1)	Pt—O	(6×)	2·091 (1)
O—Pt—O	(6×)	90·24 (4)	O—Ba(1)—O	(3×)	98·16 (6)
O—Pt—O	(6×)	89·76 (4)	O—Ba(1)—O	(3×)	133·87 (4)
O—Pt—O	(3×)	180·00	O—Ba(1)—O	(3×)	149·47 (6)
O—Ba(1)—O	(6×)	69·23 (4)			

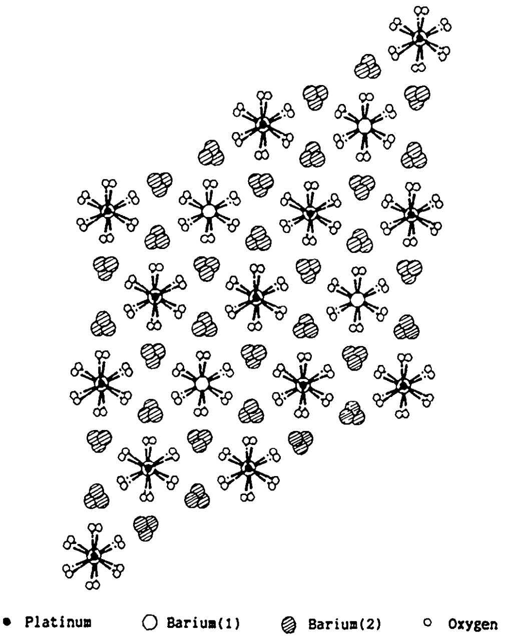

Fig. 2. A view of the structure of Ba_4PtO_6 down [001]. Note that platinum is shown at (0,0,0) and (2/3,1/3,5/6); the Pt at (1/3,2/3,2/3) is obscured by Ba(1) at (1/3,2/3,11/12).

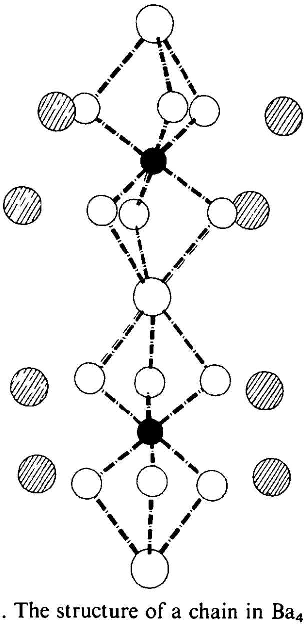

Fig. 3. The structure of a chain in Ba_4PtO_6.

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* A list of anisotropic thermal parameters has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51943 (1 p.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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_4PtO_6 and the rhombohedral form of Ca_4PtO_6 (McDaniel, 1972). It is also related to the newly discovered compound Sr_3CuPtO_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_4PtO_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}, λ(Mo $K\alpha$) = 0·7107 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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