

The structure of  $\text{Ba}_2\text{Ce}_{3/4}\text{SbO}_6$  may be described as a perovskite structure with ordering of nearly regular  $\text{CeO}_6$  and  $\text{SbO}_6$  octahedra. Owing to the formula there are two empty octahedra, at 000 and  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  in the Ce sublattice. Each  $\text{CeO}_6$  octahedron shares corners with six  $\text{SbO}_6$  octahedra. The  $\text{Sb1O}_6$  octahedron shares corners with five  $\text{CeO}_6$  octahedra and the  $\text{Sb2O}_6$  octahedron shares corners with six  $\text{CeO}_6$  octahedra. There is no tilting of the octahedra as was reported for  $\text{BaCeO}_3$  (Jacobson, Tofield & Fender, 1972) and  $\text{Ba}_2\text{SrUO}_6$  (Groen & IJdo, 1987).

The Ba atoms are shifted from their ideal positions at  $\frac{1}{4}\frac{1}{4}\frac{1}{8}$  in the direction of the vacancy, leading to short Ba—O4 and Ba—O5 distances (Table 2). The coordination of Ba to O atoms is 12 as in a regular cubic perovskite.

The Ce—O distances are in good agreement with similar distances reported for  $\text{BaCeO}_3$  (Jacobson, Tofield & Fender, 1972). The Sb—O distances are in agreement with those found in  $\text{SbO}_6$  octahedra in  $\text{Sr}_2\text{Sb}_2\text{O}_7$  (Groen & IJdo, 1988). The model of Treiber & Kemmler-Sack (1980a) has been confirmed using a reduced unit cell.

Treiber & Kemmler-Sack (1980b) reported that  $\text{Ba}_2\text{Zr}_{3/4}\text{SbO}_6$  has the same structure as  $\text{Ba}_2\text{Ce}_{3/4}\text{SbO}_6$ . From their X-ray diffraction data it can be derived that  $\text{Ba}_2\text{Zr}_{3/4}\text{SbO}_6$  has an *I*-centred tetragonal lattice with about the same lattice parameters and intensity distribution as the title compound. In conclusion, we have for  $\text{Ba}_2\text{Zr}_{3/4}\text{SbO}_6$ :  $a = 8.2625$  (5),  $c = 16.605$  (5) Å, *I4/mmm*,  $Z = 8$ .

Betz, Schittenhelm & Kemmler-Sack (1982) report for low-temperature  $\text{Ba}_2\text{Ca}_{1/4}\text{Y}_{1/2}\text{UO}_6$  an ortho-

rhombic face-centred structure with  $a=b=2a_p\sqrt{2}$  and  $c=4a_p$  with the same structure as  $\text{Ba}_2\text{Ce}_{3/4}\text{SbO}_6$ . Using the program *LINES2.0* (de Graaff, 1990), their X-ray data could be refined tetragonally with  $a = 8.667$  (6),  $c = 17.36$  (1) Å with all reflections  $h+k+l=2n$ , so it is likely that this compound has the same structure as the title compound.

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## $\text{Pb}_3\text{U}_{11}\text{O}_{36}$ , a Rietveld Refinement of Neutron Powder Diffraction Data

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**Abstract.** Trilead undecauranate,  $\text{Pb}_3\text{U}_{11}\text{O}_{36}$ ,  $M_r = 3815.88$ , orthorhombic, *Pmmn*. At  $T = 295$  K,  $a = 28.459$  (1),  $b = 8.3790$  (3),  $c = 6.7650$  (3) Å,  $V = 1613.2$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 7.854$  Mg m<sup>-3</sup>,  $\mu R = 0.11$ ,  $\lambda = 2.5700$  (1) Å,  $R_p = 2.94$ ,  $R_{wp} = 3.99\%$ . The structure has been refined by Rietveld analysis of neutron powder diffraction data for 427 reflections. The structure is closely related to  $\alpha\text{-U}_3\text{O}_8$ .

**Introduction.** In the system Pb–U–O, several compounds have been reported but only the crystal structures of  $\text{Pb}_3\text{UO}_6$  (Sterns, 1967) and  $\text{PbUO}_4$  (Cremers, Eller, Larson & Rozenzweig, 1986) have been determined. In the system PbO–UO<sub>3</sub>, Polunina, Kovba & Ippolitova (1973) report the existence of  $\text{Pb}_{11}\text{U}_5\text{O}_{26}$  and  $\text{Pb}_3\text{U}_{11}\text{O}_{36}$  in addition to the compounds already mentioned. In the present paper the

Table 1. X-ray data of  $\text{Pb}_3\text{U}_{11}\text{O}_{36}$ 

<i>d</i> (exp.)	<i>d</i> (calc.)	<i>I</i> (obs.)	<i>h</i>	<i>k</i>	<i>l</i>
8.000	8.038	2	1	1	0
4.733	4.744	1	6	0	0
4.597	4.603	4	3	1	1
4.1909	4.1894	95	0	2	0
3.8785	3.8839	2	6	0	1
3.4850	3.4849	100	7	0	1
3.3823	3.3826	45	0	0	2
3.1459	3.1488	1	8	0	1
3.0614	3.0631	1	2	1	2
2.9498	2.9475	2	8	1	1
2.8712	2.8701	1	4	1	2
2.8505	2.8482	1	6	2	1
2.6812	2.6792	65	7	2	1
2.6323	2.6318	28	0	2	2
2.3209	2.3220	1	11	1	1
2.1199	2.1224	4	3	1	3
2.0937	2.0947	20	0	4	0
2.0325	2.0329	15	14	0	0
1.9714	1.9720	16	7	0	3
1.8289	1.8290	15	14	2	0
1.7953	1.7954	25	7	4	1
1.7822	1.7842	15	7	2	3
	1.7809	0	4	2	2
1.7415	1.7424	10	14	0	2
1.6084	1.6088	10	14	2	2

Table 2. Fractional coordinates and thermal parameters ( $\text{\AA}^2$ ) for  $\text{Pb}_3\text{U}_{11}\text{O}_{36}$  at 295 K

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	
Pb1	2( <i>b</i> )	0.75	0.25	0.774 (4)	1.90 (25)
Pb2	4( <i>f</i> )	0.6015 (5)	0.25	0.706 (2)	1.90
U1	2( <i>a</i> )	0.25	0.25	0.337 (3)	0.08 (8)
U2	4( <i>f</i> )	0.3859 (5)	0.25	0.237 (2)	0.08
U3	4( <i>f</i> )	0.4656 (4)	0.25	0.780 (2)	0.08
U4	4( <i>f</i> )	0.3186 (5)	0.25	0.777 (2)	0.08
U5	4( <i>f</i> )	0.6782 (5)	0.25	0.233 (2)	0.08
U6	4( <i>f</i> )	0.5279 (4)	0.25	0.240 (2)	0.08
O1	4( <i>e</i> )	0.25	0.469 (3)	0.322 (3)	0.84 (7)
O2	8( <i>g</i> )	0.3837 (4)	0.465 (2)	0.249 (2)	0.84
O3	8( <i>g</i> )	0.5323 (5)	0.522 (2)	0.222 (2)	0.84
O4	8( <i>g</i> )	0.6802 (6)	0.516 (2)	0.219 (2)	0.84
O5	4( <i>f</i> )	0.3118 (8)	0.25	0.082 (3)	0.84
O6	4( <i>f</i> )	0.4615 (7)	0.25	0.144 (3)	0.84
O7	4( <i>f</i> )	0.5984 (7)	0.25	0.281 (3)	0.84
O8	2( <i>b</i> )	0.75	0.25	0.121 (4)	0.84
O9	2( <i>a</i> )	0.25	0.25	0.685 (4)	0.84
O10	4( <i>f</i> )	0.3904 (7)	0.25	0.901 (3)	0.84
O11	4( <i>f</i> )	0.5434 (8)	0.25	0.932 (3)	0.84
O12	4( <i>f</i> )	0.6629 (7)	0.25	0.960 (3)	0.84
O13	4( <i>f</i> )	0.3270 (9)	0.25	0.464 (3)	0.84
O14	4( <i>f</i> )	0.4224 (8)	0.25	0.537 (3)	0.84
O15	4( <i>f</i> )	0.5228 (6)	0.25	0.513 (3)	0.84
O16	4( <i>f</i> )	0.6804 (7)	0.25	0.494 (3)	0.84

crystal structure of  $\text{Pb}_3\text{U}_{11}\text{O}_{36}$  as determined by neutron powder diffraction is discussed. The compound has the same structure as  $\text{Sr}_3\text{U}_{11}\text{O}_{36}$  (Cordfunke, van Vlaanderen, Onink & IJdo, 1991) and is closely related to  $\alpha\text{-U}_3\text{O}_8$ .

**Experimental.**  $\text{Pb}_3\text{U}_{11}\text{O}_{36}$  was prepared by heating an appropriate mixture of  $\text{PbUO}_4$  and  $\alpha\text{-U}_3\text{O}_8$  at 1063 K in an alumina crucible for two weeks in air, with repeated grindings. The X-ray powder diffraction pattern (Table 1) was obtained with a Philips PW1050 diffractometer. The presence of the repetition of a similar structural motif is evident from the intensity distribution of a small set of strong and a large set of weak reflections. The former set is given by  $h (=7p)kl$ ,  $p+l=2n$ ,  $k=2n$ . Electron diffraction patterns (Siemens Elmico 102; 100 kV) confirm this result and only show systematic absences  $hk0$ ,  $h+k=2n+1$ , indicating space group  $Pm\bar{m}n$  (No. 59). Since no single crystals were available, Rietveld's method (Rietveld, 1969) was used for the refinement of neutron powder diffraction data. The neutron powder profile was recorded at the Petten High-Flux Reactor;  $5 < 2\theta < 154^\circ$  in steps of  $0.1^\circ$ ; neutrons at 295 K from the (111) planes of a Cu crystal; pyrolytic graphite with a total thickness of 120 mm as a second-order filter; Soller slits, horizontal divergence  $0.5^\circ$ , placed between the reactor and the monochromator and in front of the four  $^3\text{He}$  counters; sample holder ( $\varnothing$  14.46 mm) consisting of a vanadium tube, closed with Cu plugs with 'O' rings. No precautions were taken to avoid preferred orientation. Maximum absorption correction was 5%;  $\mu R = 0.11$  (Weber, 1967). Weights and e.s.d.'s were calculated by the program *DBW3.2S* version 8802 which was used in the refinement (Wiles,

Sakthivel & Young, 1988). The parameters of  $\text{Sr}_3\text{U}_{11}\text{O}_{36}$  (Cordfunke, van Vlaanderen, Onink & IJdo, 1991) were used as a starting model.

The coherent scattering lengths used were: Pb 9.401, U 8.42 and O 5.805 fm. 65 parameters were included in the refinement: one scale factor, six background parameters, three half-width parameters defining the Gaussian line shape of the reflections, the counter-zero error, an asymmetry parameter, the unit-cell parameters, the atomic positions and three thermal parameters.  $\Delta/\sigma < 0.3$  in the final cycle. The final *R* values obtained were  $R_p = 2.94$ ,  $R_{wp} = 3.99$ ;  $R_{\text{exp}} = 2.43\%$ ;  $S = 1.64$ ;  $D - wD = 0.93$ .

**Discussion.** Atomic parameters are given in Table 2 and selected atomic distances in Table 3. The agreement between the observed and calculated profile of the data is shown in Fig. 1.\* Fig. 2 gives a section of the structure at  $y = 0.25$ . The space group  $Pm\bar{m}n$  allows a sufficient description of the structure. The space group  $Pc\bar{m}n$  as proposed by Polunina, Kovba & Ippolitova (1973) is not in agreement with the electron diffraction data and the structure presented here. The metal atoms in the structure of  $\text{Pb}_3\text{U}_{11}\text{O}_{36}$  are partly in pentagonal bipyramidal coordination, and partly in octahedral coordination (U4, U5 and U6). The structure consists of layers built from folded chains of pentagonal bipyramidal groups sharing two opposite edges, with octahedra in

\* Primary diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55741 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1002]

between. The layers are connected by vertex sharing to give a three-dimensional structure and are related by inversion centres.

Separate linear chains of  $n$  bipyramidal pentagons with  $n$  octahedra in between lead to the composition  $M_nM'_nO_{5n}$  as in  $UVO_5$  (Chevalier & Gasperin, 1970). This structure element is present in Fig. 2. Folding once in a chain of  $n$  pentagons and introducing a link at two sites between successive chains as depicted in Fig. 2, reduces the number of octahedra to  $n-2$ . Folding in this way reduces the number of mirror planes to two leading to the composition  $M_nM'_{n-2}O_{5n-4}$  with  $n$  even. As may be seen from

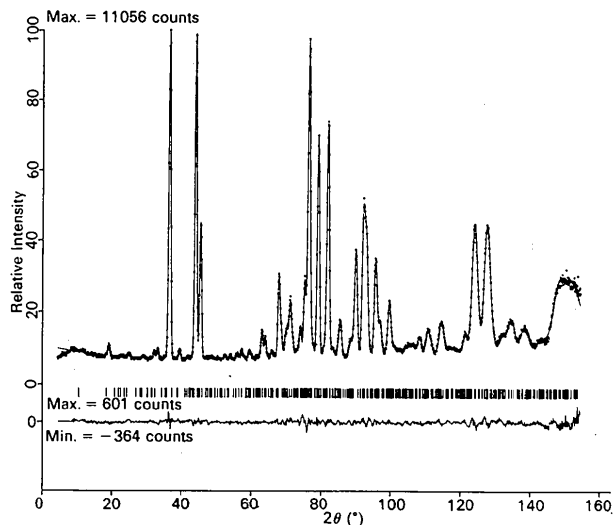


Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile of  $Pb_3U_{11}O_{36}$  at 295 K; a difference (observed - calculated) curve appears at the bottom of the plot. Tick marks below the profile indicate the positions of the Bragg reflections included in the calculation.

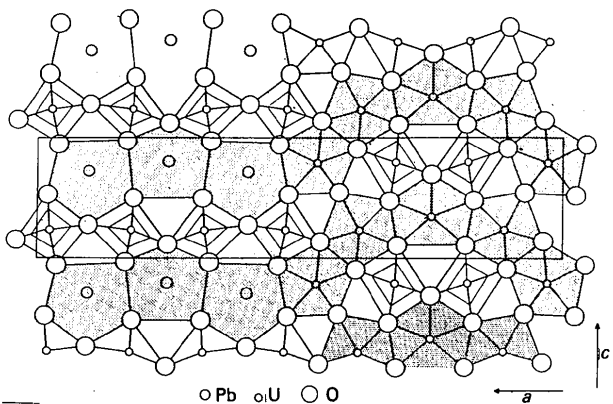


Fig. 2. Section of the structure of  $Pb_3U_{11}O_{36}$  at  $y = 0.25$ . The folded linear chain of eight pentagonal (bipyramidal) groups is indicated.

Table 3. Selected atomic distances (Å) for  $Pb_3U_{11}O_{36}$  at 295 K

Pentagonal bipyramids		Octahedra	
Pb1—O1	2.44 (2) × 2	U4—O4	1.96 (1) × 2
O8	2.35 (3)	O5	2.07 (3)
O12	2.78 (2) × 2	O9	2.05 (2)
O16	2.74 (3) × 2	O10	2.21 (2)
		O13	2.14 (2)
Pb2—O2	2.45 (2) × 2	U5—O4	2.23 (1) × 2
O7	2.88 (3)	O7	2.29 (2)
O11	2.25 (3)	O8	2.18 (2)
O12	2.45 (3)	O12	1.90 (3)
O15	2.59 (2)	O16	1.77 (2)
O16	2.66 (2)		
U1—O1	1.84 (2) × 2	U6—O3	2.29 (1) × 2
O5	2.46 (2) × 2	O6	2.00 (2)
O9	2.35 (3)	O7	2.03 (2)
O13	2.35 (2) × 2	O11	2.13 (2)
		O15	1.85 (2)
U2—O2	1.80 (1) × 2		
O5	2.36 (3)		
O6	2.24 (2)		
O10	2.28 (2)		
O13	2.27 (3)		
O14	2.28 (2)		
U3—O3	1.91 (1) × 2		
O6	2.46 (2)		
O10	2.29 (2)		
O11	2.44 (3)		
O14	2.06 (2)		
O15	2.44 (2)		

Fig. 2, the metal atoms lie on lines parallel to  $[100]$  and  $n-1$  centred subcells are present. In the limit, the structure of  $\alpha-U_3O_8$  (Loopstra, 1964) is a member of this series for  $n=4$ . The structure of  $Pb_3U_{11}O_{36}$  is the member for  $n=8$ . The structure of  $UNbO_{5+x}$ ,  $x=0.17$ , hitherto unknown, but with a subcell related to the compounds mentioned above (Kovba, Sirotkuna & Trunov, 1965) is a possible candidate for  $n=6$ , composition  $Nb_5U_5O_{26}$ .

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