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## Redetermination of Tristrontium Uranate(VI). A Rietveld Refinement of Neutron Powder Diffraction Data

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**Abstract.** Sr<sub>3</sub>UO<sub>6</sub>,  $M_r = 596.89$ , monoclinic,  $P2_1/n$ . At room temperature,  $a = 6.0126$  (2),  $b = 6.2138$  (2),  $c = 8.6139$  (3) Å,  $\beta = 90.239$  (2)°,  $V = 321.82$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 6.160$  (1) Mg m<sup>-3</sup>,  $\mu R = 0.12$ ,  $\lambda = 2.57155$  (3) Å,  $R_{wp} = 3.19\%$ . The structure has been refined by Rietveld analysis of neutron powder diffraction data for 147 reflections. The structure is of a monoclinic GdFeO<sub>3</sub>-type perovskite. The octahedra are in complete order.

**Introduction.** Since strontium is an important fission product in nuclear technology the compounds and phase relations in the system Sr–U–O are a common subject of research. The crystal structures of  $\beta$ -SrUO<sub>4</sub>, Sr<sub>2</sub>UO<sub>5</sub> and Sr<sub>3</sub>UO<sub>6</sub> have been reported (Loopstra & Rietveld, 1969) and recently the structure of Sr<sub>3</sub>U<sub>11</sub>O<sub>36</sub> was determined (Cordfunke, van Vlaanderen, Onink & IJdo, 1991). Sr<sub>3</sub>UO<sub>6</sub> is reported by Loopstra & Rietveld (1969) to adopt a monoclinic deformed perovskite-like structure with

space group  $P2_1$ . In relation to other substituted perovskites, this space group seems improbable (van Duivenboden & IJdo, 1986) and a redetermination of the structure is reported here.

**Experimental.** Sr<sub>3</sub>UO<sub>6</sub> was prepared from a stoichiometric mixture of SrO and U<sub>3</sub>O<sub>8</sub> which was kept in a gold crucible at 1250 K in oxygen for a week, with repeated grindings and then annealed for one week at 1073 K. X-ray powder diffraction patterns were obtained with a Guinier camera; no other phases were observed. Systematic absences suggest the space group  $P2_1/n$ . Since no single crystals were available, Rietveld's (1969) method was used for refinement of the neutron powder diffraction data. Experimental details were given earlier in the paper describing the structure determination of Sr<sub>2</sub>CaUO<sub>6</sub> (Groen & IJdo, 1987). This structure was used as a trial model and refinement used the program *DBW3.2S* version 8802, with correction for multiplicities of Laue group

$P2/m$  (Young & Wiles, 1982). 34 parameters were included in the refinement: a scale factor, three half-width parameters defining the Gaussian-like shape of the reflections, the counter zero errors, six background parameters, unit-cell parameters, atomic positional parameters, isotropic thermal parameters and an asymmetry parameter. Coherent scattering lengths were: Sr 7.02, U 8.42 and O 5.805 fm (Koester, Rauch, Herkens & Schroeder, 1981).  $\Delta/\sigma < 0.3$  in the final cycle. Maximum absorption correction is 5%;  $\mu R = 0.12$  (Weber, 1967). Refinement led to  $R_{wp} = 3.19$ ,  $R_{exp} = 2.13\%$ ,  $S = 1.50$ ,  $D-wD = 1.17$ . The largest correlation-matrix element for structural parameters was 0.45.

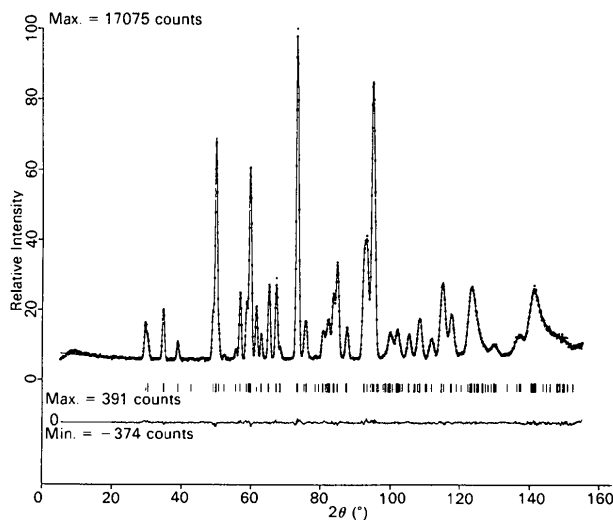


Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile of  $Sr_3UO_6$  at room temperature; positions of nuclear lines and  $I_{obs} - I_{calc}$  are indicated.

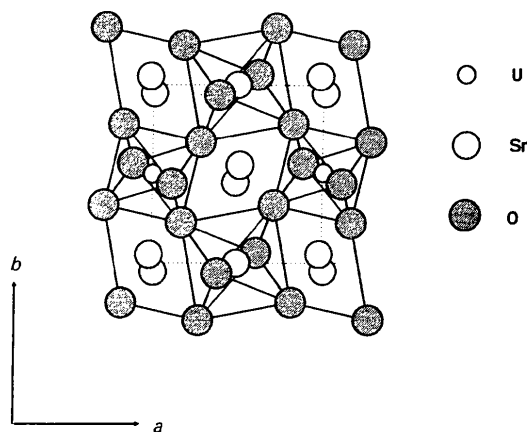


Fig. 2. Section of the structure of  $Sr_3UO_6$  projected along the  $c$  axis.

Table 1. Fractional atomic coordinates and thermal parameters ( $\text{\AA}^2$ ) for  $Sr_3UO_6$  at room temperature

	$x$	$y$	$z$	$B$
Sr1	0.5128 (4)	0.5490 (2)	0.2440 (5)	1.05 (5)
Sr2	0.5	0	0	0.28 (7)
U	0	0.5	0	0.74 (9)
O1	0.1731 (6)	0.2242 (5)	0.9283 (4)	1.32 (9)
O2	0.2823 (5)	0.6759 (5)	0.9484 (4)	1.02 (8)
O3	0.3857 (4)	0.9415 (3)	0.2728 (4)	1.23 (8)

Table 2. Atomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in  $Sr_3UO_6$  at room temperature

Sr1O <sub>8</sub> bicapped prism			
Sr1—O1	2.514 (5)	Sr1—O2	2.937 (4)
—O1	2.789 (5)	—O2	2.498 (4)
—O1	3.230 (5)	—O3	2.568 (2)
—O2	3.000 (5)	—O3	2.491 (3)
Sr2O <sub>6</sub> octahedron			
Sr2—O1	2.485 (3)	O1—Sr2—O2	90.3 (1)
—O2	2.441 (3)	O1—Sr2—O3	95.5 (1)
—O3	2.478 (3)	O2—Sr2—O3	95.7 (1)
UO <sub>6</sub> octahedron			
U—O1	2.100 (3)	O1—U—O2	92.3 (1)
U—O2	2.069 (3)	O1—U—O3	91.6 (1)
U—O3	2.103 (3)	O2—U—O3	91.5 (1)

**Discussion.** Atomic parameters are given in Table 1 and selected atomic distances and angles in Table 2. The agreement between the observed and calculated profile is shown in Fig. 1.\* The projection of the structure along the  $c$  axis is shown in Fig. 2. The structure can be described as a perovskite with nearly regular  $Sr_2O_6$  and  $UO_6$  octahedra. Each  $UO_6$  octahedron shares corners with six  $Sr_2O_6$  octahedra and *vice versa*. The Sr1 atoms are in bicapped trigonal prisms between the octahedra. All octahedra are rotated around a fourfold axis parallel to  $[001]$  and a twofold axis parallel to  $[110]$  of the aristotype (Megaw, 1973). As a result of these rotations, the coordination of Sr1 is changed from 12 in the aristotype to 8 in the present structure. The new neutron diffraction experiments have removed many of the anomalies in the structure of  $Sr_3UO_6$  deduced previously (Loopstra & Rietveld, 1969); in particular, the bond lengths and bond angles presented in Table 2 show that the  $UO_6$  octahedra are more regular than the earlier work suggested. As a result, the  $UO_6$  octahedra are very similar in size to those found in  $Ca_3UO_6$  (van Duivenboden & IJdo, 1986) and in  $Sr_2CaUO_6$  and  $Ba_2SrUO_6$  (Groen & IJdo, 1987).

\* Primary diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55742 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0289]

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## Ba<sub>2</sub>Ce<sub>3/4</sub>SbO<sub>6</sub>, a Rietveld Refinement of Neutron Powder Diffraction Data

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**Abstract.** Dibarium cerium antimonate, Ba<sub>2</sub>Ce<sub>3/4</sub>SbO<sub>6</sub>,  $M_r = 597.52$ , tetragonal,  $I4/mmm$ . At room temperature,  $a = 8.4562$  (1),  $c = 17.0002$  (4) Å,  $V = 1215.64$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 6.5297$  (1) Mg m<sup>-3</sup>,  $\mu_R = 0.15$ ,  $\lambda = 2.5717$  (1) Å,  $R_{wp} = 2.85\%$ . The structure has been refined using Rietveld analysis of neutron powder diffraction data recorded for 106 reflections. The structure is a perovskite with complete order of CeO<sub>6</sub> and SbO<sub>6</sub> octahedra. Ordered vacancies in the cerium sublattice give rise to a superstructure.

**Introduction.** In a research project concerned with investigation of uranium perovskites, the structures of  $A_2BUO_6$ ,  $A = Ba, Sr, Ca$  and  $B = Sr$  and  $Ca$ , were determined (Groen & IJdo, 1987; IJdo, 1993). Also, perovskites with vacancies on the  $B$  site are known (Rausser & Kemmler-Sack, 1980); some examples are Ba<sub>2</sub>Sm<sub>2/3</sub>UO<sub>6</sub>, Ba<sub>2</sub>Ce<sub>3/4</sub>SbO<sub>6</sub> and Ba<sub>2</sub>Zr<sub>3/4</sub>SbO<sub>6</sub>. Ordering of the vacancies is indicated by the occurrence of superstructures, but details of these structures are unavailable at present. Because Sb<sup>v</sup> and U<sup>v</sup> in oxides sometimes give rise to isomorphous compounds (Cordfunke & IJdo, 1988), the study of the structure of Ba<sub>2</sub>Ce<sub>3/4</sub>SbO<sub>6</sub> is attractive in relation to the perovskite phases in nuclear fuel elements. This paper deals with the crystal structure of Ba<sub>2</sub>Ce<sub>3/4</sub>SbO<sub>6</sub>.

Treiber & Kemmler-Sack (1980a) reported an ochre-coloured compound with a tetragonal superstructure of the perovskite type [ $a = 11.954$  Å  $\approx 2a_p\sqrt{2}$ ,  $c = 17.000$  Å  $\approx 4a_p$ ,  $P4/mmm$ , where  $a_p$  is the lattice parameter of a simple cubic perovskite  $ABO_3$ ]. A model structure was given suggested by X-ray powder diffraction data; however, the positions of the O atoms could not be determined accurately.

**Experimental.** AR starting materials BaO<sub>2</sub>, CeO<sub>2</sub> and Sb<sub>2</sub>O<sub>3</sub> were thoroughly mixed in an agate mortar in the appropriate ratios. The mixture was heated in an alumina crucible in air at 973 K for 1 d, at 1273 K for 1 d, and at 1523 K for 7 d with repeated grinding. In addition, the compound was annealed at 1273 K for 1 d and cooled in air to room temperature.

X-ray diffraction patterns were obtained at room temperature with a Philips 1050 diffractometer by step scanning in the range  $5 < 2\theta < 90^\circ$ , with  $\Delta(2\theta) = 0.05^\circ$ ,  $t = 3$  s per step. All calculations were made with the program *DBW3.2S* version 8804 (Young & Wiles, 1982). Electron diffraction data were collected with a Siemens Elmiskop 102 electron microscope: double tilt; lift cartridge; 100 kV. The electron diffraction patterns showed a tetragonal unit cell with  $a \approx 2a_p$  and  $c \approx 4a_p$  with systematic absences for  $h + k + l = 2n + 1$ , indicating the space group  $I4/mmm$  or a lower one. Refinement of the X-ray powder diffrac-