$V = 292.5$ Å^3
$Z = 2$
$D_x = 3.899$ Mg m^{-3}

Cube
$0.12 \times 0.12 \times 0.12$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
$T_{\min} = 0.949$, $T_{\max} = 0.999$
1355 measured reflections
1293 independent reflections
1279 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0093$
$\theta_{\max} = 34.20°$
$h = -11 \rightarrow 0$
$k = -6 \rightarrow 0$
$l = -15 \rightarrow 15$
3 intensity and 2 orientation control reflections; orientation control every 200 reflections
intensity control every 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0241$
$wR(F^2) = 0.0661$
$S = 1.023$
1293 reflections
53 parameters
$w = 1/[\sigma^2(F_o^2) + (0.060P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.764$ e Å^{-3}
$\Delta\rho_{\min} = -3.28$ e Å^{-3}

Extinction correction: $F_c^* = |F_c|k[1 + (0.001\chi \times F_c^2\lambda^3/\sin 2\theta)]^{-1/4}$
Extinction coefficient: $\chi = 0.111\,(5)$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)
Absolute configuration: $\chi = 0.00\,(2)$ (Flack, 1983)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Nb	0	0.3846 (1)	0.9958 (1)	0.006 (1)
Cs	1/2	0.9717 (1)	0.1047 (1)	0.020 (1)
O(1)	0.1787 (3)	0.4455 (8)	0.1480 (2)	0.015 (1)
O(2)	0.1893 (4)	0.4386 (9)	0.8612 (3)	0.020 (1)
O(3)	1/2	0.4646 (13)	0.8496 (4)	0.019 (1)
O(4)	1/2	0.0602 (11)	0.4956 (6)	0.026 (1)
B	0.3363 (4)	0.4877 (9)	0.7839 (4)	0.013 (1)

Table 2. *Selected geometric parameters* (Å, °)

[NbO$_6$] octahedron			
Nb—O(2)	1.948 (3)	O(4$^{\rm i}$)—Nb—O(4$^{\rm v}$)	179.9 (3)
Nb—O(2$^{\rm ii}$)	1.948 (3)	O(2)—Nb—O(1$^{\rm iii}$)	89.5 (1)
Nb—O(1$^{\rm iii}$)	2.016 (3)	O(2$^{\rm ii}$)—Nb—O(1$^{\rm iv}$)	89.5 (1)
Nb—O(1$^{\rm iv}$)	2.016 (2)	O(2$^{\rm ii}$)—Nb—O(4$^{\rm v}$)	83.6 (1)
Nb—O(4$^{\rm i}$)	1.775 (5)	O(2)—Nb—O(4$^{\rm v}$)	83.6 (1)
Nb—O(4$^{\rm v}$)	2.217 (5)	O(2$^{\rm ii}$)—Nb—O(2)	94.1 (2)
[BO$_3$] triangle			
B—O(1$^{\rm v}$)	1.353 (4)	O(2)—B—O(1$^{\rm v}$)	120.2 (3)
B—O(2)	1.353 (4)	O(1$^{\rm v}$)—B—O(3)	122.4 (3)
B—O(3)	1.392 (4)	B—O(3)—B$^{\rm viii}$	124.7 (4)
Cs coordination			
Cs—O(1$^{\rm vi}$)	3.101 (3)	Cs—O(3$^{\rm xi}$)	3.167 (4)
Cs—O(1$^{\rm vii}$)	3.101 (3)	Cs—O(3$^{\rm xii}$)	3.202 (5)
Cs—O(1)	3.232 (3)		
Cs—O(1$^{\rm viii}$)	3.232 (3)		
Cs—O(2$^{\rm ix}$)	3.308 (3)	Cs—B$^{\rm ix}$	3.580 (4)
Cs—O(2$^{\rm x}$)	3.308 (3)	Cs—B$^{\rm x}$	3.580 (4)

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Structure solution: *SHELXS86* (Sheldrick, 1990). Structure refinement: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: SH1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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SrTa$_4$O$_{11}$: a Rietveld Refinement Using Neutron Powder Diffraction Data

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Abstract

Rietveld refinement using neutron powder diffraction data for the low-temperature form of strontium tantalum oxide, SrTa$_4$O$_{11}$, resulted in $R_{wp} = 3.10\%$. The structure is of the CaTa$_4$O$_{11}$ type and consists of layers of Ta(2)O$_7$

pentagonal bipyramids sharing edges, as found in U_3O_8. Between the layers lie Sr atoms with distorted cubic coordination geometry and Ta(1) atoms with distorted octahedral coordination geometry.

Comment

The study of the crystal structure of $Sr_3U_{11}O_{36}$ (Cordfuncke, van Vlaanderen, Onink & IJdo, 1991) focused our attention on other structures related to U_3O_8, such as $CaTa_4O_{11}$ and $SrTa_4O_{11}$. We report here the crystal structure of $SrTa_4O_{11}$.

$SrTa_4O_{11}$ was prepared at low temperature by Bayer & Gruehn (1983, 1984). From X-ray diffraction patterns it was concluded that it is isostructural with $CaTa_4O_{11}$ (Jahnberg, 1970; Isobe, Marumo, Iwai & Kimura, 1975) but details of the structure were not known. $SrTa_4O_{11}$ changes into the tetragonal tungsten bronze modification in air at 1453 K (Bayer & Gruehn, 1983). The reverse transition was only observed in the presence of a transporting agent such as Cl_2 or a mineralizer such as molten B_2O_3 at 1373 K. This transition could not be achieved by means of a solid-state reaction.

The X-ray powder diagram for the sample of $SrTa_4O_{11}$ studied here is in agreement with the data of Bayer & Gruehn (1983). As no single crystals were available, the crystal structure was derived using Rietveld's (1969) method for refinement and neutron powder diffraction data collected on the powder diffractometer at the Petten High Flux Reactor (Netherlands Energy Research Foundation, ECN). The agreement between the observed and calculated profiles is shown in Fig. 1.

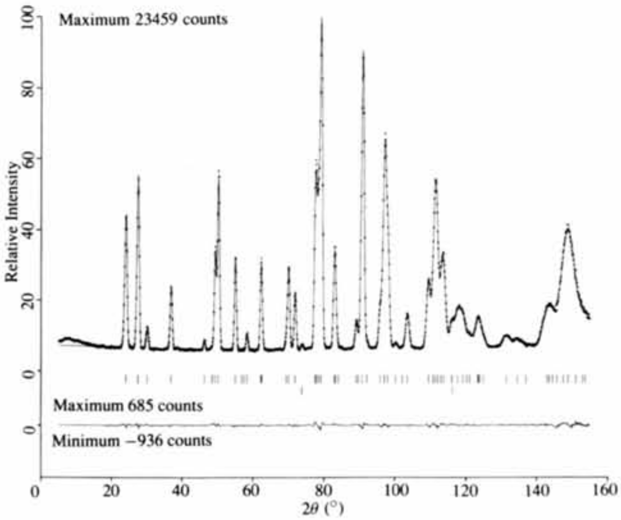

Fig. 1. Neutron powder diffraction pattern of the low-temperature form of $SrTa_4O_{11}$ at 295 K. The observed profile (dots) and calculated profile (full line) are shown. A difference curve (observed minus calculated) appears at the bottom of the figure. Tick marks for $SrTa_4O_{11}$ and V below the profile indicate the Bragg reflections included in the calculation.

The structure of $SrTa_4O_{11}$ consists of layers of pentagonal bipyramids sharing edges (Fig. 2), as in U_3O_8 (Loopstra, 1970). In U_3O_8 these layers are repeated in the perpendicular direction by sharing apex O atoms; without apex sharing the metal-to-oxygen ratio in the layers would be 3:11. In the structure of $SrTa_4O_{11}$ these layers are stacked on top of one another without apex sharing and every second layer is rotated by 180° such that octahedral sites are created by the apex O atoms. The Ta(2) atoms are in these flattened octahedra. The voids in which the Sr atoms are found are taller than for Ta(2); there are also two additional O atoms parallel to [001] giving a distorted cubic coordination geometry for Sr.

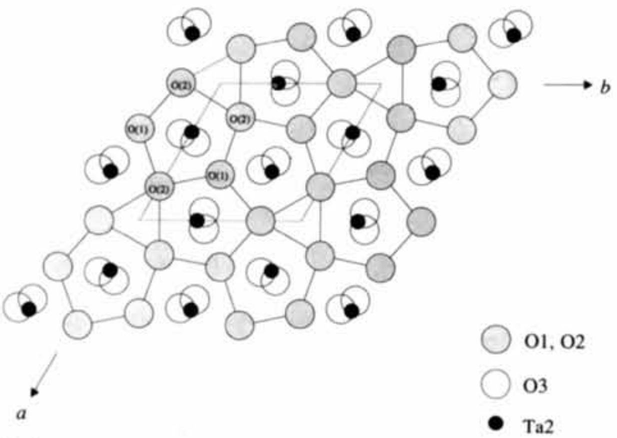

Fig. 2. A projection of the structure of $SrTa_4O_{11}$ on the *ab* plane showing edge sharing by the pentagonal bipyramids.

Jahnberg (1981) describes structural relationships within a series of related compounds of general formula $A_xM_{3n+1}O_{8n+3}$. The title compound, $LnTa_7O_{19}$ (Ln = La, Pr, Nd, Sm, Gd, Y) and U_3O_8 are members of this series.

Experimental

$SrTa_4O_{11}$ was prepared from AR $Sr(NO_3)_2$ and Ta_2O_5 by heating appropriate mixtures in a platinum crucible in air at 873 K overnight and then for three days at 1073 K with repeated grindings. The platinum crucible was placed in a quartz tube, evacuated and heated at 1300 K for two weeks, grinding once after one week (Bayer & Gruehn, 1984).

Crystal data

$SrTa_4O_{11}$
$M_r = 987.42$
Hexagonal
$P6_322$
$a = 6.2543\ (1)$ Å
$c = 12.3320\ (3)$ Å
$V = 417.76\ (2)$ Å^3
$Z = 2$
$D_x = 7.850\ (1)$ Mg m^{-3}

Neutron radiation
$\lambda = 2.57167\ (7)$ Å
Cell parameters from 61 reflections
$2\theta = 5–155°$
$T = 295$ K
Powder sample
White

Data collection

Powder diffractometer at the Petten High Flux Reactor	61 measured reflections $2\theta_{\max} = 155°$

Refinement

$R_p = 0.0243$	61 reflections
$R_{wp} = 0.0310$	27 parameters
$S = 1.79$	$(\Delta/\sigma)_{\max} = 0.3$

Table 1. *Fractional atomic coordinates and isotropic displacement parameters* (Å^2)

	x	y	z	$U_{\rm iso}$
Sr	2/3	1/3	1/4	0.17 (8)
Ta1	1/3	2/3	1/4	0.20 (7)
Ta2	0.3570 (2)	0	0	0.14 (3)
O1	1/3	2/3	0.5347 (1)	0.22 (6)
O2	0.7532 (2)	0	0	0.53 (5)
O3	0.3701 (2)	0.4315 (2)	0.3454 (1)	0.47 (4)

Table 2. *Selected geometric parameters* (Å)

Sr—O1	× 2	2.655 (1)	Ta2—O2		2.478 (2)
Sr—O3	× 6	2.518 (1)	Ta2—O2	× 2	1.980 (1)
Ta1—O3	× 6	1.985 (1)	Ta2—O3	× 2	1.955 (1)
Ta2—O1	× 2	2.0598 (6)			

The neutron radiation was monochromated using the 111 reflection of a copper crystal and the λ/n contamination was reduced to less than 0.1% by means of a pyrolytic graphite filter. Data were collected in the range $5 < 2\theta < 155°$ in steps of 0.1°. Soller slits with a horizontal divergence of 30′ were placed between the reactor and the monochromator and in front of the four ^{3}He counters. No precautions to avoid preferred orientation were taken. An absorption correction according to Weber (1967) was applied ($\mu r = 0.17$).

The neutron diffraction pattern was analyzed using the program *DBW*3.2, version 8804 (Wiles & Young, 1981). The structure of $CaTa_4O_{11}$ (Jahnberg, 1970) was used as a trial model. Coherent scattering lengths of 7.02, 6.91 and 5.803 fm for Sr, Ta and O, respectively, were used (Sears, 1992). The 27 parameters in the refinement comprised a scale factor, three half-width parameters defining the Gaussian-like shape of the reflections, six background parameters, the counter zero error, the unit-cell parameters, the atomic positional parameters, isotropic displacement parameters, an asymmetry parameter and a scale factor for the vanadium holder. The largest correlation matrix element for the structural parameters was 0.49.

A list of raw powder diffraction data has been deposited with the IUCr (Reference: CR1170). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two New Scandium Phases: $ScSn_2$ and Sc_6Pb_5

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Abstract

The structures of two new phases in the scandium–tin and scandium–lead systems have been determined. The structure of $ScSn_2$ (Pearson symbol *tI*24) is an occupation variant of the $Zr_3Al_4Si_5$ and β-LiSn structures, closely related to the $ZrSi_2$ structure type. Sc_6Pb_5 (Pearson symbol *oI*44) is isotypic with Ti_6Ge_5 (or V_6Si_5). The shortest distances are Sn···Sn 2.954 (3) and Sc···Sn 3.030 (1) Å in $ScSn_2$, and Sc···Pb 2.858 (6), Sc···Sc and Pb···Pb 3.088 (1) Å in Sc_6Pb_5.

Comment

In the course of a recent investigation of the Sc–Sn and Sc–Pb phase diagrams (Palenzona & Manfrinetti, 1995) some new phases were identified. A complete structure determination has been undertaken for two, $ScSn_2$ and Sc_6Pb_5.

The structure of $ScSn_2$ can be compared with the structures of $Zr_3Al_4Si_5$ (Raman & Schubert, 1965) and β-LiSn (Blase & Cordier, 1990). All these phases belong to the same space group, with the same Wyckoff positions occupied and similar coordinates and lattice constants, so that they can be considered as occupation variants of the same structure. In $Zr_3Al_4Si_5$, all positions are statistically filled by two kinds of atoms (Al–Zr and Al–Si mixtures), while the other two compounds are ordered; the different stoichiometry in $ScSn_2$ is obtained by replacing the Li2 atoms [4(*b*)] in β-LiSn with Sn atoms.

The structure of $Zr_3Al_4Si_5$, together with the related structures of $ZrSi_2$ (Schachner, Nowotny & Kudielka, 1954), $HfGa_2$ and $ZrGa_2$ (Pötzschke & Schubert, 1962), have been described previously by Gladyshevskii (1971) and by Kripyakevich (1977). Likewise, $ScSn_2$ can

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