

OW4B	0.1143 (10)	0.1233 (10)	0.8006 (6)	0.047 (4)
OW5	0.5790 (4)	0.1825 (4)	0.9109 (3)	0.038 (2)
OW6	-0.2401 (8)	0.2781 (8)	0.3934 (5)	0.086 (6)
OW7	0.6124 (20)	0.2489 (21)	1.0001 (14)	0.054 (14)
OW8	0.0485 (22)	-0.0258 (22)	0.9713 (14)	0.016 (13)

Table 2. Selected geometric parameters (Å)

Nd1—O4	2.478 (6)	S10—O13 ⁱⁱⁱ	1.482 (6)
Nd1—O52	2.477 (6)	S20—O22 ^{iv}	1.447 (8)
Nd1—O62	2.484 (5)	S20—O21 ^{iv}	1.445 (9)
Nd1—O3	2.487 (5)	S20—O23 ^v	1.467 (6)
Nd1—O6	2.495 (6)	S20—O23 ^{iv}	1.467 (6)
Nd1—O5	2.498 (6)	S30—O31 ⁱ	1.329 (13)
Nd1—O7	2.503 (6)	S30—O33 ⁱ	1.439 (6)
Nd1—O2	2.520 (6)	S30—O33 ^{vi}	1.439 (6)
Nd1—O42 ⁱ	2.520 (5)	S30—O32 ⁱ	1.605 (13)
Nd2—O1 ⁱⁱ	2.483 (6)	S40—O42 ^{vii}	1.449 (6)
Ce3—O33	2.273 (6)	S40—O41 ^{vii}	1.453 (6)
Ce3—O13	2.283 (6)	S40—O44 ^{vii}	1.486 (6)
Ce3—O23	2.282 (6)	S40—O43 ^{vii}	1.490 (6)
Ce3—O63	2.366 (5)	S50—O52 ^{viii}	1.441 (6)
Ce3—O53	2.390 (6)	S50—O51 ^{viii}	1.459 (6)
Ce3—O43	2.405 (5)	S50—O54 ^{ix}	1.485 (6)
Ce3—O54	2.454 (6)	S50—O53 ^{ix}	1.499 (6)
Ce3—O64	2.482 (6)	S60—O62 ^x	1.451 (6)
Ce3—O44	2.487 (6)	S60—O61 ^x	1.456 (6)
S10—O11	1.437 (8)	S60—O64 ^x	1.489 (6)
S10—O12	1.452 (9)	S60—O63 ^x	1.493 (6)
S10—O13	1.482 (6)		

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

Evaporation at room temperature of a solution of $\text{Nd}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in $2\text{M H}_2\text{SO}_4$ gave a mixture of yellow $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ crystals and hexagonal columnar greyish yellow crystals of the product. The latter kept indefinitely under the mother liquor but lost water in air. Data were collected and the unit cell refined on the SERC Enraf-Nonius FAST diffractometer at Cardiff University, using graphite-monochromated Mo radiation. Scattering factors, dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C). The structure was solved in space group $P1$ and extended to show all the metal and S atoms and 105 unique O atoms ($R = 0.11$). At this stage the relationship to the true hexagonal cell and the correct space group, $P6_3/m$, became apparent.

We thank the SERC for the provision of diffractometer facilities and Professor M. B. Hursthouse (Cardiff University) and his staff for collecting the data.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71417 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: L11068]

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Structure Determination of SnZrS_3

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Abstract

The structure of tin zirconium trisulfide is of the NH_4CdCl_3 type with double columns of edge-sharing Zr octahedra. These columns are linked together by Sn atoms. Sn is coordinated to three S atoms at 2×2.619 (2) and 2.765 (2) Å; a fourth S atom is at 3.065 (2) Å. The zirconium coordination is approximately octahedral with six S atoms at 2.524 (2), 2×2.545 (2), 2.582 (2) and 2×2.592 (2) Å. Powder diffraction data were also collected; the JCPDS File No. for tin zirconium sulfide is 44-1494.

Comment

A number of ternary chalcogenides ABX_3 ($X = \text{S}, \text{Se}$) occur in the NH_4CdCl_3 structure type characterized by double columns of edge-sharing octahedra of B, linked together by A. This is found for PbZrS_3 (Lelieveld & IJdo, 1978), SnHfS_3 and PbHfS_3 (Wiegiers, Meetsma, Haange & de Boer, 1989), where Zr and Hf are in octahedra of S atoms, for the mixed-valence compound Sn_2S_3 (Mootz & Puhl, 1967; Jumas, Ribes, Philippott & Maurin, 1972; Yamaoka & Okai, 1970), and for the selenides LaCrSe_3 (Huy-Dung, Etienne & Laruelle, 1971)

and EuZrSe_3 (Mar & Ibers, 1992), where Cr and Zr are in octahedra of Se atoms. They are differentiated by the coordination number of the large A cation which can vary from $CN = 3$ for Sn to $CN = 9$ for La in LaCrSe_3 ; Eu in EuCrSe_3 has $CN = 8$. In this paper the structure determination of SnZrS_3 is described. The crystals were obtained during our study of the misfit layer compounds $(MX)_nTX_2$ ($M = \text{Sn, Pb, Sb, Bi, rare-earth metals}$; $T = \text{Ti, V, Cr, Nb, Ta}$; $X = \text{S, Se}$; $1.08 < n < 1.23$) (Wiegers & Meerschaut, 1992).

The structure of SnZrS_3 consists of columns of double edge-sharing octahedra of Zr linked together by Sn atoms. These columns run along the b axis (Fig. 1). Among the compounds with such edge-sharing octahedra of the B element, SnZrS_3 and SnHfS_3 have the A element (Sn) with $CN = 3$, the Sn—S bonds making angles close to 90° . The Sn—S bond lengths (Table 2) are close to those of isostructural SnHfS_3 , viz. 2×2.613 (2) and 2.758 (2) Å (Wiegers *et al.*, 1989). With the larger distances to S taken into account, the coordination of Sn is a distorted bicapped trigonal prism with Sn in a very asymmetric position. A much less distorted version of this coordination is found in the LaCrSe_3 structure, in which nine La—Se bonds define a tricapped trigonal prism (Huy-Dung *et al.*, 1971). $CN = 8$ of the A metal is found for Eu in EuZrSe_3 (Mar & Ibers, 1992). Pb in PbZrS_3 (Lelieveld & IJdo, 1978) and PbHfS_3 (Wiegers *et al.*, 1989) is coordinated like Sn but with a smaller difference between the longer and the shorter Pb—S bonds. The asymmetric coordination of Sn and Pb is typical for Sn^{2+} and Pb^{2+} with a lone pair of s electrons ($5s$ for Sn^{2+} and $6s$ for Pb^{2+}). The Zr—S distances are in agreement with Zr^{4+} , so the compound may be formulated as $\text{Sn}^{\text{II}}\text{Zr}^{\text{IV}}\text{S}_3$. Sn_2S_3 , isostructural with SnZrS_3 , is a mixed-valence compound, $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}\text{S}_3$ (Mootz & Puhl, 1967; Jumas *et al.*, 1972; Yamaoka & Okai, 1970).

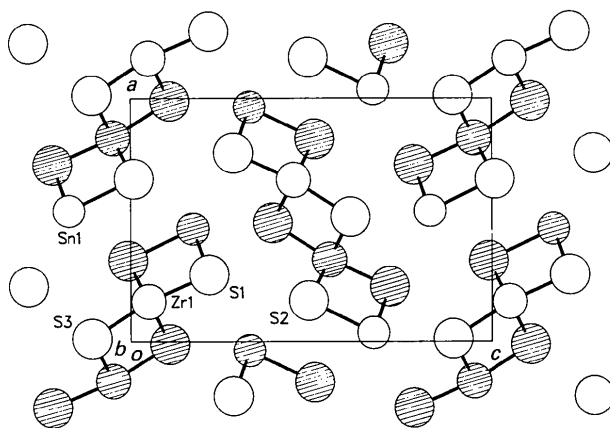


Fig. 1. Projection of the structure of SnZrS_3 along $[0\bar{1}0]$. Open and hatched circles are atoms at $y = \frac{1}{4}$ and $\frac{3}{4}$, respectively; bonds between atoms indicated by open and hatched circles occur in pairs.

Experimental

Crystal data

SnZrS_3
 $M_r = 306.133$
 Orthorhombic
Pnma
 $a = 9.188$ (1) Å
 $b = 3.717$ (1) Å
 $c = 13.839$ (1) Å
 $V = 472.63$ (14) Å³
 $Z = 4$
 $D_x = 4.302$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 20 reflections
 $\theta = 32.90$ – 34.33°
 $\mu = 8.566$ mm⁻¹
 $T = 295$ K
 Needle
 $1.6 \times 0.02 \times 0.02$ mm
 Red

Data collection

Enraf-Nonius CAD-4F
 single-crystal diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 3384 measured reflections
 1620 independent reflections
 1175 observed reflections
 $[I > 2.5\sigma(I)]$

$R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 40.00^\circ$
 $h = 0 \rightarrow 16$
 $k = 0 \rightarrow 6$
 $l = -25 \rightarrow 25$
 3 standard reflections
 frequency: 180 min
 intensity variation: 0.1%

Refinement

Refinement on F
 $R = 0.038$
 $wR = 0.031$
 $S = 2.190$
 1174 reflections
 31 parameters

Calculated weights
 $w = 1/[\sigma^2(F)]$
 $(\Delta/\sigma)_{\text{max}} = 0.024$
 $\Delta\rho_{\text{max}} = 1.91$ e Å⁻³
 $\Delta\rho_{\text{min}} = -2.87$ e Å⁻³
 Extinction correction: none

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Sn1	0.46328 (6)	$-\frac{1}{4}$	0.17150 (4)	0.0177 (1)
Zr1	0.16377 (7)	$\frac{1}{4}$	0.04954 (4)	0.0106 (2)
S1	0.27420 (19)	$\frac{1}{4}$	0.21656 (12)	0.0143 (4)
S2	0.33181 (18)	$-\frac{1}{4}$	-0.00820 (11)	0.0111 (3)
S3	0.01227 (17)	$\frac{1}{4}$	-0.10761 (11)	0.0095 (4)

Table 2. Geometric parameters (Å, °)

Sn1—S1	2.6193 (15)	Zr1—S2	2.5449 (14)
Sn1—S2	2.7647 (18)	Zr1—S3	2.5821 (18)
Sn1—S3 ⁱ	3.065 (2)	Zr1—S3 ⁱⁱ	2.5915 (14)
Zr1—S1	2.5243 (19)		
S1—Sn1—S2	85.66 (5)	S3—Zr1—S3 ⁱⁱ	85.68 (4)
S1—Sn1—S1 ⁱⁱⁱ	90.39 (4)	S3 ⁱⁱ —Zr1—S3 ^v	91.64 (4)
S1—Zr1—S2	92.50 (5)	Sn1—S1—Zr1	92.79 (5)
S1—Zr1—S3	171.08 (6)	Sn1—S1—Sn1 ^{iv}	90.39 (6)
S1—Zr1—S3 ⁱⁱ	88.10 (5)	Sn1—S2—Zr1	89.01 (4)
S2—Zr1—S3	93.59 (4)	Zr1—S2—Zr1 ⁱⁱⁱ	93.82 (6)
S2—Zr1—S2 ^{iv}	93.82 (4)	Zr1—S3—Zr1 ⁱⁱ	94.32 (4)
S2—Zr1—S3 ⁱⁱ	87.27 (4)	Zr1 ⁱⁱ —S3—Zr1 ^v	91.64 (5)
S2—Zr1—S3 ^v	178.73 (5)		
S2—Sn1—S1—Zr1	-1.57 (4)	S1—Zr1—S2—Sn1	-1.61 (4)
S1—Sn1—S2—Zr1	1.56 (4)	S3—Zr1—S2—Sn1	-175.09 (4)
S2—Zr1—S1—Sn1	1.70 (4)		

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

The compound was prepared by reaction of the elements in the appropriate ratio for SnZrS_3 . The mixture of elements was heated for 1 week at a temperature of 1073 K in an evacuated quartz tube. A grey-black powder was obtained. The powder pattern (Guinier-Hägg, Jungner Instruments, $\text{Cu K}\alpha_1$ radiation) was indexed using an orthorhombic unit cell with dimensions $a = 9.183$ (2), $b = 3.7195$ (5) and $c = 13.829$ (3) Å, which are close to those of SnHfS_3 (Wiegers *et al.*, 1989). Single crystals were grown by vapour transport using chlorine as the transport agent. Red needle-shaped crystals grew at the low side of the temperature gradient 923–823 K. The needle axis corresponds to the b axis of the orthorhombic unit cell.

Unit-cell parameters were determined from a least-squares treatment of the *SET4* setting angles (de Boer & Duisenberg, 1984) of 20 reflections with $32.90 < i < 34.33$. The unit cell was identified as orthorhombic, space group *Pnma*. Reduced-cell calculations did not indicate any higher metrical lattice symmetry (Spek, 1988).

Scattering factors were those given by Cromer & Mann (1968) and anomalous-dispersion factors taken from Cromer & Liberman (1970) were included in *F*. Calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program package *Xtal* (Hall & Stewart, 1990). Data collection: *CAD-4* (Enraf-Nonius, 1988). Cell refinement: *SET4*. Data reduction: *EUCLID* (Spek, 1982). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Geometric calculations: *PLATON* (Spek, 1990). Molecular graphics: *PLUTO92* (Meetsma, 1992; Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic thermal parameters, complete geometry and powder diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71388 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1082]

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Redetermination of the β - $\text{Ca}_2\text{P}_2\text{O}_7$ Structure

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Abstract

β Dicalcium diphosphate is composed of eclipsed P_2O_7 groups linked through Ca^{2+} cations. The $\text{P}-\text{O}_b$ bonds involving the bridging O atoms are longer [average 1.620 (5) Å] than the others [average 1.517 (5) Å]. As the 'O₄' tetrahedra are almost regular the displacement of the P atoms involves two sets of O—P—O angles: O—P—O \approx 112.7 (2) and O—P—O_b \approx 106.0 (2)°.

Comment

The structure was first studied by Webb (1966) in order to establish the geometry of the P_2O_7 groups and especially to determine accurately the P—O—P angle. During our studies of the Ca—V—P—O system by solid-state chemistry, we obtained single crystals of β - $\text{Ca}_2\text{P}_2\text{O}_7$. As the structure was established previously using multiple film techniques, we performed a new data collection with an automatic diffractometer in order to obtain the atomic parameters more accurately.

The redetermination of the structure confirms that it is composed of eclipsed P_2O_7 groups linked through Ca^{2+} cations (Fig. 1). The mean interatomic P—O distances are not significantly different from those previously observed within the range of 5σ , but are spread over a range of values narrower than in the first study, *e.g.* 0.01 Å for P—O distances involving the bridging O atoms and 0.05 Å for the other P—O distances instead of 0.05 and 0.08 Å, respectively. The ranges of angles are the same in the two studies. The Ca—O distances are the same as previously found within 3σ except for Ca(1)—O(4)