

the plane of the three O atoms. Clearly, spatial accommodation of the sodium-halide pair is much more important than the precise direction of bonds within the NaO_3A groups. The Na atom has a marked anisotropy of thermal motion in the direction of the sodium-halide bond which may be related to the rather large thermal vibration of the halide ion. The oxygen thermal motion is markedly anisotropic normal to the plane of the Al-O, Ge-O bond plane, as expected.

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Structure of Tin Hafnium Sulfide and Lead Hafnium Sulfide

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Abstract. SnHfS_3 , $M_r = 393.36$, orthorhombic, *Pnma*, $a = 9.139$ (1), $b = 3.694$ (1), $c = 13.875$ (4) Å, $V = 468.4$ (2) Å³, $Z = 4$, $D_x = 5.578$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 284.1$ cm⁻¹, $F(000) = 680$, $T = 298$ K, $R_F = 0.036$ for 1301 observed reflections with $I \geq 2.5\sigma(I)$. PbHfS_3 , $M_r = 481.88$, orthorhombic, *Pnma*, $a = 8.988$ (2), $b = 3.739$ (1), $c = 13.924$ (2) Å, $V = 467.9$ (2) Å³, $Z = 4$, $D_x = 6.840$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 593.0$ cm⁻¹, $F(000) = 808$, $T = 298$ K, $R_F = 0.036$ for 1343 observed reflections with $I \geq 2.5\sigma(I)$. The compounds are isostructural with PbZrS_3 with modified NH_4CdCl_3 structure. There are columns running along the *b* axis of double edge-sharing octahedra $(\text{Hf}_2\text{S}_6)_\omega$; these columns are linked by Sn or Pb with coordinations typical for Sn^{2+} and Pb^{2+} with lone-pair *s*² electrons.

Introduction. Structures of the ternary sulfides *ABS*₃ (*A* = Pb; *B* = Zr, Hf) have been studied using powder methods by Sterzel & Horn (1970), Yamaoka & Okai

(1970) and Lelieveld & IJdo (1978). The latter authors concluded from a neutron powder diffraction refinement of PbZrS_3 that the compound, and probably also PbHfS_3 , is isostructural with PbSnS_3 and Sn_2S_3 . The structures are strongly related to the NH_4CdCl_3 structure (*Strukturbericht*, type E 24). In a study of the ternary sulfides with the assumed composition *ABS*₃ (*A* = Sn, Pb; *B* = Nb, Ta) we found that single crystals could be obtained by vapour transport using chlorine as transport agent. We found this method also suitable for compounds PbHfS_3 and SnHfS_3 , the latter being a new compound. Structure determinations using single crystals are reported.

Experimental. Powder samples of SnHfS_3 and PbHfS_3 were obtained by heating the elements in evacuated quartz ampoules. An intimate mixture of the elements was first slowly heated to about 673 K for two days during which the binary sulfides are probably formed. The ampoules were then heated at 1023 K for ten days. In this way the reaction of the metals with quartz from the wall was avoided. PbHfS_3 was then heated for three

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days at 1123 K. X-ray powder data of the samples showed that the compounds were probably isostructural. Single crystals were grown by vapour transport in a temperature gradient of 1043 to 983 K. To about 300 mg of the compounds about 10 mg $(\text{NH}_4)_2\text{PbCl}_6$ was added. This compound decomposes at high temperature into PbCl_2 , NH_4Cl and Cl_2 . Cl_2 probably acts as transport agent. The crystals grow as bundles of red needles at the low-temperature side of the quartz ampoules; the needle axes correspond to the b axes of the orthorhombic unit cells.

Suitable red needle-shaped crystals were glued on the top of glass fibres and mounted on an Enraf-Nonius CAD-4F diffractometer, with graphite monochromator. Unit-cell dimensions and their standard deviations were determined from the setting angles of 18 reflections in the range $27 < \theta < 30^\circ$ in four alternate settings (de Boer & Duisenberg, 1984). All reflections were measured in one quadrant of the Ewald sphere up to $\theta = 40^\circ$. Three check reflections were measured every 2 h of X-ray exposure time; these exhibit no significant decay during data collection. A $360^\circ \psi$ scan for the close to axial reflection (040) showed an intensity variation up to 30% for SnHfS_3 and up to 32% for PbHfS_3 about the mean value. The intensity data were corrected for the scale variation, Lorentz and polarization effects and for absorption using a Gaussian integration method (Spek, 1983). Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance of the three reference reflections: $\sigma^2(I) = \sigma_{\text{cs}}^2(I) + (PI)^2$ where P is the instability constant (McCandlish, Stout & Andrews, 1975). The space group was derived from the observed systematic absences.

Initial atomic parameters were taken from Lelieveld & IJdo (1978). Refinement on F by full-matrix least-squares techniques with anisotropic thermal parameters converged at $R_F = 0.036$ ($wR = 0.028$) for SnHfS_3 and $R_F = 0.037$ ($wR = 0.045$) for PbHfS_3 , respectively. The crystals exhibited some secondary extinction for which the F values were corrected by refinement of an empirical isotropic extinction parameter (Zachariasen, 1967). The final difference Fourier map did not show any significant residual features. Crystal data and experimental details of the structure determination are compiled in Table 1.* Final fractional atomic coordinates and equivalent isotropic thermal parameters for the atoms are given in Table 2. Bond distances and angles are listed in Table 3. Scattering factors were taken from Cromer & Mann

Table 1. Details of the structure determination

| | SnHfS_3 | PbHfS_3 |
|---|--|--------------------------------------|
| Data collection | | |
| Crystal dimensions (mm) | 0.007 × 0.042 × 0.42 | 0.02 × 0.03 × 0.60 |
| θ range: min., max. ($^\circ$) | 1.47, 40.0 | 1.46, 40.0 |
| $\omega/2\theta$ scan ($^\circ$) | $\Delta\omega = 0.90 + 0.35\tan\theta$ | $1.20 + 0.35\tan\theta$ |
| Data set | $h: 0-16; k: -0-6;$ $l: -25-25$ | $h: -16-16; k: -0-6;$ $l: -25-25$ |
| Crystal-to-receiving-aperture distance (mm) | 173 | 173 |
| Horizontal, vertical aperture (mm) | 4.0, 4.5 | 4.0, 4.5 |
| Reference reflections, r.m.s. deviation (%) | 202, 0.63 | 0.66 |
| | 202, 0.63 | 0.69 |
| | 211, 0.66 | 0.80 |
| Instability constant P | 0.005 | 0.015 |
| Drift correction | 1.00-1.00 | 0.992-1.000 |
| Min. and max. absorption correction factor | 1.23-3.07 | 2.18-5.32 |
| X-ray exposure time (h) | 66.5 | 83.1 |
| Total data | 3365 | 6446 |
| Unique data | 1610 | 1611 |
| Observed data $ I \geq 2.5\sigma(I)$ | 1301 | 1343 |
| $R_i = \sum(I - \bar{I})/\sum I$ | 0.034 | 0.111 |
| $R_j = \sum\sigma(I)/\sum I$ | 0.054 | 0.056 |
| Number of equivalent reflections | 3266 | 6440 |
| Refinement | | |
| Number of reflections | 1301 | 1343 |
| Number of refined parameters | 32 | 32 |
| Isotropic secondary-extinction coefficient, g | 0.0075 (6) × 10 ⁻⁴ | 0.0137 (8) × 10 ⁻⁴ |
| Final agreement factors | | |
| R_F | 0.036 | 0.037 |
| wR | 0.028 | 0.045 |
| Weighting scheme | 1/ $\sigma^2(F)$ | 1 |
| S | 2.058 | 3.930 |
| Residual electron density in final difference Fourier map ($\text{e } \text{\AA}^{-3}$) | -4.5, 6.1 | -4.8, 5.8 |
| Max. (shift/ σ) final cycle | 2.3×10^{-3} | 6.2×10^{-6} |
| Average (shift/ σ) final cycle | 1.7×10^{-4} | 8.2×10^{-7} |

Table 2. Final fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

| | x | y | z | $U_{\text{eq}}^*(\text{\AA}^2)$ |
|-------|-------------|---------------|-------------|---------------------------------|
| Sn(1) | 0.53676 (7) | $\frac{1}{4}$ | 0.82850 (5) | 0.0161 (2) |
| Hf(1) | 0.16246 (4) | $\frac{1}{4}$ | 0.05048 (3) | 0.0095 (1) |
| S(1) | 0.2724 (2) | $\frac{1}{4}$ | 0.2155 (2) | 0.0125 (5) |
| S(2) | 0.1697 (2) | $\frac{1}{4}$ | 0.4930 (2) | 0.0098 (4) |
| S(3) | 0.0146 (2) | $\frac{1}{4}$ | 0.8931 (2) | 0.0085 (5) |
| Pb(1) | 0.51515 (6) | $\frac{1}{4}$ | 0.82589 (4) | 0.0175 (1) |
| Hf(1) | 0.16611 (6) | $\frac{1}{4}$ | 0.05057 (4) | 0.0100 (1) |
| S(1) | 0.2731 (4) | $\frac{1}{4}$ | 0.2154 (2) | 0.0130 (6) |
| S(2) | 0.1683 (3) | $\frac{1}{4}$ | 0.4902 (2) | 0.0104 (6) |
| S(3) | 0.0130 (3) | $\frac{1}{4}$ | 0.8948 (2) | 0.0092 (6) |

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

(1968). Anomalous-dispersion factors were taken from Cromer & Liberman (1970). All calculations carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages XTAL (Hall & Stewart, 1987), and EUCLID (Spek, 1982; calculation of geometric data).

Discussion. The structures of SnHfS_3 and PbHfS_3 reported here, PbZrS_3 (Lelieveld & IJdo, 1978), PbSnS_3 (Jumas, Ribes, Philippot & Maurin, 1972), Sn_2S_3 (Mootz & Puhl, 1967) are strongly related to the NH_4CdCl_3 (E 24) structure with columns of double edge-sharing octahedra, $(\text{Cd}_2\text{Cl}_6)_\infty$, running along the b

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51683 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected data on the geometry; distances in Å, angles in °

Standard deviations in the last decimal place are given in parentheses. Bonds and angles occurring in pairs are indicated by *.

| | SnHfS ₃ | PbHfS ₃ |
|--------------|--------------------|--------------------|
| Hf-S(1) | 2.501 (2) | 2.488 (3) |
| Hf-S(2)* | 2.530 (2) | 2.533 (2) |
| Hf-S(3)* | 2.577 (2) | 2.582 (2) |
| Hf-S(3) | 2.567 (2) | 2.569 (3) |
| M-S(1)* | 2.613 (2) | 2.729 (3) |
| M-S(2) | 2.758 (2) | 2.907 (3) |
| M-S(3) | 3.082 (2) | 3.073 (3) |
| M-S(2)* | 3.490 (2) | 3.383 (3) |
| M-S(1)* | 3.722 (2) | 3.546 (3) |
| S(1)-M-S(1) | 89.97 (5) | 86.48 (7) |
| S(1)-M-S(2)* | 85.18 (6) | 81.68 (7) |
| S(1)-M-S(3)* | 79.08 (6) | 78.10 (7) |

Note: only angles between the shortest bonds are given.

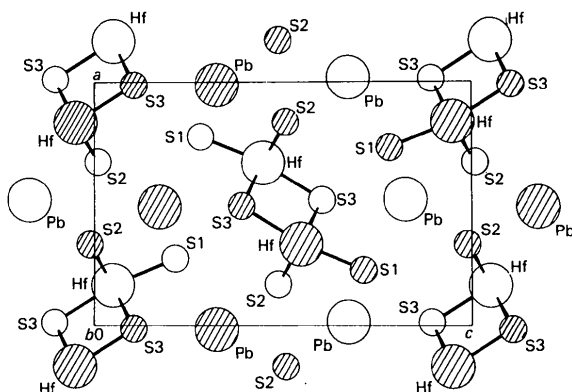


Fig. 1. Projection of the structure of SnHfS₃ and PbHfS₃ along [010]. Open and hatched circles are atoms at $\frac{1}{4}$ and $\frac{3}{4}$, respectively; bonds between atoms indicated by open and hatched circles occur in pairs.

axis. In SnHfS₃ and PbHfS₃ the columns of double edge-sharing octahedra (Hf₂S₆)_∞ are linked by Sn and Pb respectively (Fig. 1). The Hf-S distances are in the range 2.501 (2) to 2.577 (2) Å for SnHfS₃ and 2.488 (3) to 2.582 (2) Å for PbHfS₃. Sn and Pb atoms have three short bonds to S(1) and S(2): 2.613 (2) (2×) and 2.758 (2) Å, respectively, for SnHfS₃, 2.729 (3) (2×) and 2.907 (3) Å, respectively, for PbHfS₃. The bond angles, S-M-S, are close to 90°. If the somewhat longer Sn-S(3) [3.082 (2) Å] distance and the Pb-S(3) [3.073 (3) Å] distance are taken into account, the coordination is distorted square pyramidal. With S atoms at still larger distances, the coordination is a distorted dicapped trigonal prism with Sn and Pb in a very asymmetric position. This asymmetric coordination with three strong bonds with angles close to 90° is typical for Sn²⁺ and Pb²⁺ ions; the asymmetry is due to the presence of a lone pair of s electrons (5s for Sn²⁺, 6s for Pb²⁺). It is seen that the differences between the relatively small M-S distances (M = Sn, Pb) and

the large M-S distances are larger for SnHfS₃ than for PbHfS₃. This tendency is also visible in the structures of the low- and high-temperature forms of SnS (von Schnering & Wiedemeier, 1981; Wiedemeier & von Schnering, 1978) compared with PbS. The S(1), S(2) and S(3) atoms each have three close neighbours. S(1) has one close Hf and two close Pb neighbours; S(2) has two close Hf neighbours and one close Pb neighbour while S(3) has three close Hf neighbours. The coordination of the atoms in SnHfS₃ and PbHfS₃ is in agreement with ions Sn²⁺ (Pb²⁺) and Hf⁴⁺. Preliminary conductivity measurements showed the compounds to be semiconductors. Completely different structures are found for ternary sulfides 'SnMS₃' and 'PbMS₃' (M = Nb, Ta). Recent structure determinations (Meetsma, Wiegiers, Haange & de Boer, 1989; Wiegiers, Meetsma, Haange & de Boer, 1988) have shown that these compounds are misfit layer compounds consisting of two-atom-thick slabs of PbS and SnS with Pb and Sn in distorted square-pyramidal coordination and sandwiches NbS₂ and TaS₂ as also occur in NbS₂-2H and TaS₂-2H (Nb and Ta in trigonal-prismatic coordination with sulfur). The composition of these compounds, (SnS)_nMS₂, (PbS)_nMS₂, n = 1.13-1.17, is determined by the misfit between the SnS (PbS) and the NbS₂ (TaS₂) parts of the structure.

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