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Tm₂S₃-V, a Corundum-Type Modification of Thulium Sesquisulfide

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Abstract. Tm₂S₃-V, $M_r = 434.07$, rhombohedral, $R\bar{3}c$, hexagonal axes $a = 6.768$ (2), $c = 18.236$ (3) Å, $V = 723.40$ Å³, $Z = 6$, $D_x = 5.98$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 380.2$ cm⁻¹, $F(000) = 1116$, $T = 295$ K. The structure was refined to $R = 0.041$, $wR = 0.017$ for 290 absorption corrected reflections. Tm₂S₃-V crystallizes with the corundum ($D5_1$, $hR10$)-type structure.

Experimental. Tm₂S₃ synthesized by direct reaction of Tm metal and sulfur inevitably contained small amounts of thulium oxide sulfide, Tm₂O₂S. Pure Tm₂S₃ could be prepared by sulfidation of Tm₂O₃ (99.99%; Research Chemicals) in a stream of dry hydrogen sulfide using a tube made from glassy carbon (Sigradur G; RF heating) (Range, Lange & Drexler, 1984). After reaction at temperatures between 1675 and 1875 K, a yellow substance was obtained which proved to be Tm₂S₃-I with the monoclinic *D*-type structure (Prewitt & Sleight, 1968). At 1925 K a transformation to a nearly white powder was observed. Its Guinier pattern showed a striking similarity with that of Lu₂S₃ with corundum-type structure (Range & Leeb, 1975). Single crystals of the new modification could be obtained by melting a sample at 2000 K and subsequent cooling in a stream of H₂S. Gandolfi patterns showed the identity of crystals and bulk material.

A clear crystal fragment (approx. $0.04 \times 0.04 \times 0.02$ mm) was used for data collection on an Enraf-Nonius CAD-4 diffractometer (Mo $K\alpha$, $\lambda = 0.71073$ Å, graphite monochromator in incident beam). Lattice parameters were refined from 2θ values of 25 reflections in the range $14 \leq \theta \leq 24^\circ$. Intensities measured for $2 \leq \theta \leq 30^\circ$; ω - 2θ scan technique, scan width $(1.0 + 0.35 \tan \theta)^\circ$. Three standard reflections showed only small random variations and indicated no loss of intensity throughout data collection. An experimental correction for absorption was

applied, based on ψ scans; transmission factors varied between 78 and 100%. Merging of the 1352 collected intensities $[(\sin \theta_{\max})/\lambda = 0.70 \text{ \AA}^{-1}; -9 \leq h \leq 9, 0 \leq k \leq 9, -25 \leq l \leq 25]$ gave 290 unique reflections ($R_{\text{int}} = 0.037$), which were used for all calculations (program system *SDP3.1*; Enraf-Nonius, 1988).

The structure was solved by routine direct methods. In the least-squares refinement $|F|$ magnitudes were used to refine positional parameters, occupation factors (s.o.f.'s), anisotropic temperature factors, and an extinction parameter. Convergence was obtained after a few cycles with s.o.f.'s for Tm and S corresponding to the stoichiometry Tm₂S₃ within one standard deviation. Consequently, the s.o.f.'s were fixed again at 100% before performing the final anisotropic refinement. Final $R = 0.041$, $wR = 0.017$ (including all reflections). $w^{-1} = \sigma^2(F)$, $(\Delta/\sigma)_{\max} < 0.001$ in final refinement cycle, 10 variables, $S = 0.67$. Max. features in the final difference Fourier synthesis $+1.1, -1.2 \text{ e \AA}^{-3}$. Atomic scattering factors and f', f'' values set by *SDP* program. Bond distances and angles were calculated using the program *SADIAN* (Baur & Wenninger, 1969). Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1, derived bond distances in Table 2.†

Tm₂S₃-V crystallizes with the corundum ($D5_1$, $hR10$)-type structure. The Tm atoms are not exactly at the centers of the trigonal antiprisms formed by sulfur, but are displaced along the threefold axis towards opposite trigonal faces of two face-shared antiprisms in such a way that three Tm—S bonds are shorter (2.660 Å) than the other three (2.743 Å), thereby increasing the Tm—Tm distance. The obvious

† Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52358 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Tm	0	0	0.35007 (1)	76.4 (4)
S	0.3026 (2)	0	$\frac{1}{4}$	97.5 (4)

Table 2. Interatomic distances (\AA)

Tm—S	2.660 (1) ($\times 3$)	S—Tm	2.660 (1) ($\times 2$)
—S	2.743 (1) ($\times 3$)	—Tm	2.743 (1) ($\times 2$)
—Tm	3.650 (1)	—S	3.547 (2) ($\times 2$)
—Tm	3.995 (1) ($\times 3$)	—S	3.683 (1) ($\times 2$)
		—S	3.852 (1) ($\times 4$)
		—S	4.100 (2) ($\times 4$)

reason is the electrostatic repulsion between Tm atoms. Owing to the face sharing of TmS₆ octahedra in Tm₂S₃-V, however, the closest Tm-Tm approach (3.65 \AA) is still shorter than in the other Tm₂S₃ modifications. The volume increase connected with the I \rightarrow V transformation is 6.2%.

Related literature. For the P,T phase diagram of Tm₂S₃ see Range *et al.* (1984). The only other sul-

fides with corundum-type structure are Lu₂S₃ and Yb₂S₃ (Flahaut, Domange & Pardo, 1964; Range & Leeb, 1975), a high-pressure modification of In₂S₃ (Range & Zabel, 1978), and, not yet confirmed, the so-called γ -Al₂S₃ (Flahaut, 1952).

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Diammonium Trimolybdate(VI), (NH₄)₂Mo₃O₁₀

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Abstract. (NH₄)₂Mo₃O₁₀, $M_r = 483.89$, orthorhombic, $Pnma$, $a = 13.182$ (2), $b = 7.589$ (2), $c = 9.286$ (2) \AA , $V = 928.95$ \AA^3 , $Z = 4$, $D_x = 3.450$ Mg m^{-3} , $\lambda(\text{Cu } K\alpha) = 1.5418$ \AA , $\mu = 34.67$ mm^{-1} , $F(000) = 912$, $T = 296$ K. The structure was refined to $R = 0.043$, $wR = 0.031$ for 848 absorption-corrected reflections. Distorted MoO₆ octahedra [Mo(1)—O = 1.72–2.24 \AA , Mo(2)—O = 1.71–2.32 \AA] are face- and edge-shared to form Mo₃O₁₀²⁻ chains along [010]. The ammonium ions are situated between the chains with N(1) in eightfold [N(1)—O = 2.77–3.39 \AA] and N(2) in tenfold coordination [N(2)—O = 2.88–3.27 \AA].

Experimental. (NH₄)₂Mo₃O₁₀ was prepared by high-pressure-high-temperature decomposition of

ammonium heptamolybdate, (NH₄)₆Mo₇O₂₄·2H₂O. Experiments were carried out in a modified Belt-type high-pressure apparatus (Range & Leeb, 1975), using silver as crucible material. After quenching from 0.1 GPa and 723 K the new phase was obtained. Reaction time had to exceed half an hour. A light-red crystal fragment (approx. 5 \times 5 \times 60 μm) was used for data collection on an Enraf-Nonius CAD-4 diffractometer (Cu $K\alpha$, $\lambda = 1.5418$ \AA , graphite monochromator, $T = 296$ K). Lattice parameters were refined from 2θ values of 25 reflections in the range $5.8 \leq \theta \leq 29.8^\circ$. Intensities measured for $2 \leq \theta \leq 50^\circ$; ω - 2θ -scan technique, scan width $(0.8 + 0.14 \times \tan \theta)^\circ$. Three standard reflections indicated no loss of intensity throughout data collection. An experimental correction for absorption was applied based on ψ scans; transmission factors varied between 92.8 and 99.6%. Merging of the 3231 collected intensities

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