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Single crystals of F-Tm_2S_3 and T-Yb_2S_3*

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Abstract

The reaction of thulium and ytterbium with sulphur (2:3 molar ratios, 850 °C, 7 days) in sealed silica containers yields single-crystal sesquisulphides in the presence of some NaCl as a flux. Yellow needles of F-Tm_2S_3 (monoclinic, $P2_1/m$ (no. 11), $Z=4$, $a=1115.13(9)$ pm, $b=389.42(3)$ pm, $c=1089.06(9)$ pm, $\beta=108.811(7)°$, $R=0.049$, $R_w=0.037$) and orange beads of T-Yb_2S_3 (cubic, $Ia\bar{3}$ (no. 206), $Z=16$, $a=1246.83(3)$ pm, $R=0.015$, $R_w=0.014$) are the single-phase binary products.

There are four crystallographically independent Tm^{3+} in F-Tm_2S_3, two in distorted octahedral, one in monocapped and one in bicapped trigonal prismatic coordination of S^{2-}. Previously addressed as Tm_2S_3-II, it is the only sesquisulphide structure known so far that offers coordination numbers of six, seven *and* eight for M^{3+} simultaneously.

The crystal structure of T-Yb_2S_3 (bixbyite-type structure, well known for the sesquioxides of the "heavier" lanthanides as C type) exhibits two crystallographically independent Yb^{3+} in a more or less distorted octahedral neighbourhood of S^{2-}.

1. Introduction

The sesquisulphides of thulium and ytterbium exhibit a large variety of crystal structures. So far, six different types are known, but only a few of them are well established from single-crystal data [1]. The U-type structure of M_2S_3 (for $M \equiv Tm$, Yb, realized as high pressure modification III [2]) contains M^{3+} with coordination numbers (CN) = 7 and 7 + 1 (mono- and bicapped trigonal prisms) and appears to have the highest density of all sesquisulphides with the heaviest lanthanides. Not much lower in density, the C type, a defect–Th_3P_4 structure according to $M_{2.67}\square_{0.33}S_4$, exhibits M^{3+} in eightfold (trigonal–dodecahedral) coordination of S^{2-} [3, 4]. For $M \equiv Tm$, Yb, medium pressure–high temperature techniques are necessary to obtain II-type modifications of M_2S_3 [5, 6], where M^{3+} is six-, seven- *and* eight-coordinated. Moderate pressure is also required for the synthesis of D-Yb_2S_3 [6, 7], whereas D-Tm_2S_3 (CN = 6 and 7) represents the stable form at ambient conditions [8]. The E type (corundum structure, CN = 6) forms as high temperature modification for both thulium and ytterbium sesquisulphide [9, 10]. Finally, poor quality powders of the so-called T type (bixbyite or Tl_2O_3 structure) with M^{3+} in sixfold coordination of S^{2-} were obtained from low temperature reactions of the elements [11].

The oxidation of reduced chlorides (MCl_2) or chloride–hydrides ($MClH_x$) of the lanthanides with sulphur proved to be fruitful for the synthesis of lanthanide sesquisulphides, M_2S_3 [12–14]. Especially when single crystals or single-phase products are desired, the presence of an alkali chloride flux (*e.g.* NaCl) is very helpful. Moreover, the application of different fluxes (NaCl or CsCl) seems to favour special (single-phase) modifications of M_2S_3 during their synthesis from the elements [12]. So far, all reactions of this kind have been carried out in sealed tantalum containers [15]. Unfortunately, this reducing material turned out to be inconvenient for the synthesis of the sesquisulphides of thulium and ytterbium: Tm_5S_7 [16] (along with Tm_8S_{11} [17] and $Tm_{15}S_{22}$ [18]) and YbS [19] were the products richest in sulphur even when a slight excess of sulphur was used [14]. In order to obtain information on the influence of alkali chloride fluxes on the formation of Tm_2S_3 and Yb_2S_3, (non-reducing) silica tubing was tested. Although silica as a container material may cause problems owing to the formation of disilicate sulphides, $M_4S_3[Si_2O_7]$ ($M \equiv$ Nd–Er) [20], it could be applied successfully for the synthesis of Tm_2S_3 and Yb_2S_3 in the work presented here.

2. Experimental details

Thulium and ytterbium (both powders, 99.99%, Johnson–Matthey) were reacted with sulphur (pellets,

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99.9995%, Johnson–Matthey) in the presence of NaCl (suprapur, E. Merck; dried in an HCl gas stream at 300 °C before used) at 850 °C for 7 days. The use of 2:3 molar ratios of the elements, low heating rates (10 °C h^{-1}) and evacuated, sealed silica tubing secured the M_2S_3 stochiometry of the desired products. Since both sesquisulphides are insensitive to water, the flux (NaCl) may be rinsed off from the well-crystallized crude products with water, leaving pure Tm_2S_3 and Yb_2S_3 behind. Suitable single crystals were easy to select: yellow needles of F-Tm_2S_3 (Table 1) and orange beads of T-Yb_2S_3 (Table 2) emerged as the binary single-phase products. Their quality was checked by X-ray film techniques and complete intensity data sets were recorded with a four-circle diffractometer for both compounds. The structure refinement of F-Tm_2S_3 basically confirmed the previous results for (high pressure–high temperature) Tm_2S_3-II [5] with much higher accuracy. For the first time, suitable crystals of T-Yb_2S_3 [11] were investigated and the bixbyite structure was verified from X-ray single-crystal data. More details of the data collections, the structure refinements and the

TABLE 1. F-Tm_2S_3: crystallographic data and their determination

Lattice constants (pm, deg), *molar volume* V_m (cm^3 mol^{-1})
Guinier powder data [21]:
$a = 1115.13(9)$, $b = 389.42(3)$, $c = 1089.06(9)$
$\beta = 108.811(7)$, $V_m = 67.397(9)$
Four-circle diffractometer single-crystal data:
$a = 1116.2(4)$, $b = 390.24(8)$, $c = 1089.7(3)$
$\beta = 108.87(2)$, $V_m = 67.62(3)$

Crystal system: monoclinic, *space group*: $P2_1/m$ (no. 11), $Z = 4$

Data collection: four-circle diffractometer Siemens–Stoe AED 2, Mo Kα radiation, graphite monochromator, $\lambda = 71.07$ pm, ω scan, scan width and speed: variable ("learnt profile" [22]), $2° \leqslant \Theta \leqslant 33°$, $F(000) = 744$, $\mu = 396.31$ cm^{-1}

Data corrections: background, polarization and Lorentz factors; absorption: Ψ scan for 20 reflections; extinction: $g = 51(1) \times 10^{-5}$

Data statistics: 4049 reflections measured, of which 1908 were symmetrically independent ($R_{int} = 0.051$), 1844 with $|F_o| \geqslant 2\ \sigma(F_o)$

Structure determination and refinement: programmes SHELX-76 [23] and SHELXS-86 [24], scattering factors from Cromer and Mann [25], direct methods (Tm) and successive difference Fourier syntheses (S), full-matrix least-squares refinement, $R = 0.049$, $R_w = 0.037$ ($w = k\sigma(F_o)^{-2}$, $k = 0.375$)

Atomic positions:		*x/a*	*y/b*	*z/c*
Tm1	(2*e*)	0.00124(4)	1/4	0.17956(5)
Tm2	(2*e*)	0.19595(5)	1/4	0.55098(6)
Tm3	(2*e*)	0.33348(4)	1/4	0.94500(5)
Tm4	(2*e*)	0.58753(4)	1/4	0.66129(5)
S1	(2*e*)	0.1121(2)	1/4	0.9786(3)
S2	(2*e*)	0.2524(2)	1/4	0.3026(3)
S3	(2*e*)	0.5550(2)	1/4	0.8931(3)
S4	(2*e*)	0.5919(2)	1/4	0.4170(3)
S5	(2*e*)	0.7697(2)	1/4	0.2311(3)
S6	(2*e*)	0.9627(2)	1/4	0.6211(3)

Coefficients of the "anisotropic" thermal displacement factors: $\exp[-2\pi^2(a^{*2}h^2U_{11} + \ldots + b^*c^*kl2U_{23} + \ldots)]$, U_{ij} (pm^2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tm1	101(2)	138(2)	109(2)	0	20(2)	0
Tm2	200(2)	263(3)	218(3)	0	34(2)	0
Tm3	100(2)	124(2)	132(2)	0	22(2)	0
Tm4	99(2)	120(2)	104(2)	0	26(2)	0
S1	128(10)	94(10)	213(15)	0	40(10)	0
S2	55(8)	140(10)	153(13)	0	53(8)	0
S3	60(9)	254(13)	103(12)	0	3(9)	0
S4	156(10)	161(11)	71(12)	0	13(10)	0
S5	122(9)	152(11)	145(14)	0	40(9)	0
S6	126(9)	118(10)	136(13)	0	43(9)	0

TABLE 2. T-Yb_2S_3: crystallographic data and their determination

Lattice constant (pm), *molar volume* V_m ($cm^3\ mol^{-1}$)
Guinier powder data [21]:
$a = 1246.83(3)$, $V_m = 72.953(5)$
Four-circle diffractometer single-crystal data:
$a = 1246.86(6)$, $V_m = 72.96(1)$

Crystal system: cubic, *space group*: $Ia\bar{3}$ (no. 206), $Z = 16$

Data collection: four-circle diffractometer Siemens–Stoe AED 2, Mo Kα radiation, graphite monochromator, $\lambda = 71.07$ pm, ω scan, scan width and speed: variable ("learnt profile" [22]), $2° \leqslant \Theta \leqslant 30°$, $F(000) = 3008$, $\mu = 393.20\ cm^{-1}$

Data corrections: background, polarization and Lorentz factors; absorption: Ψ scan for 10 reflections and spherical correction ($\mu r = 9.0$)

Data statistics: 4607 reflections measured, of which 374 were symmetrically independent ($R_{int} = 0.062$), 359 with $|F_o| \geqslant 2\sigma(F_o)$

Structure determination and refinement: programme SHELX-76 [23] and SHELXS-86 [24], scattering factors from Cromer and Mann [25], direct methods (Yb) and successive difference Fourier syntheses (S), full-matrix least-squares refinement, $R = 0.015$, $R_w = 0.014$ ($w = k\sigma(F_o)^{-2}$, $k = 0.819$)

Atomic positions:		*x/a*	*y/b*	*z/c*
Yb1	(8*b*)	1/4	1/4	1/4
Yb2	(24*d*)	0.95544(3)	0	1/4
S	(48*e*)	0.3984(2)	0.1607(2)	0.3796(2)

Coefficients of the "anisotropic" thermal displacement factors: $\exp[-2\pi^2(a^{*2}h^2U_{11} + \ldots + b^*c^*kl2U_{23} + \ldots)]$, U_{ij} (pm^2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Yb1	252(2)	U_{11}	U_{11}	1(2)	U_{23}	U_{23}
Yb2	180(2)	175(2)	173(2)	−1(1)	0	0
S	361(10)	342(9)	358(10)	7(8)	13(7)	−2(8)

final atomic positions and anisotropic thermal displacement factors are summarized in Table 1 for F-Tm_2S_3 and Table 2 for T-Yb_2S_3.

Analogous reaction conditions (850 °C, 7 days) without flux yield approximately 1:1 mixtures of the F- and D-type sulphides for Tm_2S_3 and the E- and T-type sulphides for Yb_2S_3, judging from Guinier patterns. Upon firing these mixtures to 1000 °C for 5 days in sealed, evacuated silica tubes, D-Tm_2S_3 and E-Yb_2S_3 are the single-phase products. Neither sulphide disilicates ($M_4S_3[Si_2O_7]$ [20]) nor oxysulphides (M_2O_2S [26] or M_2OS_2 [27]) with M ≡ Tm, Yb could be detected among the products. However, too large amounts of NaCl flux seem to favour the formation of ternary $NaMS_2$-type sulphides [28] (with α-$NaFeO_2$-type structure) according to

$$12M + 18S + 6NaCl = 4M_2S_3 + Na_3MCl_6 + 3NaMS_2$$
$$(M \equiv Tm, Yb)$$

(along with ternary chlorides, Na_3MCl_6 [29]) in both cases. These become even the main products in the presence of equimolar amounts of NaCl (with respect to M). More than 50% excess turns them into the only sulphidic product according to

$$4M + 6S + 6NaCl = Na_3MCl_6 + 3NaMS_2$$
$$(M \equiv Tm, Yb)$$

They form transparent platelets with trigonal (or hexagonal) cross-section. Single crystals of $NaTmS_2$ look pale bluish-green, $NaYbS_2$ is golden-yellow and both were of suitable quality for X-ray structure refinements [30].

3. Results and discussion

Attempts to oxidize thulium or ytterbium with sulphur in sealed tantalum containers (850 °C, 7 days) never result in the formation of the corresponding sesquisulphide, even if an excess of sulphur compared with the required 2:3 molar ratio is used [14]. Tm_5S_7 [16] (along with Tm_8S_{11} [17] and $Tm_{15}S_{22}$ [18]) and YbS [19] are the products richest in sulphur. Upon exchange of the reducing tantalum containers for silica, analogous conditions readily result in the formation of Tm_2S_3 and Yb_2S_3. These, however, are not available as crystallographically uniform phases but as mixtures of at least two different modifications (D and F type for Tm_2S_3, E and T type for Yb_2S_3). In the presence of (small amounts of) NaCl as a flux the same reactions yield yellow needles of F-Tm_2S_3 and orange beads of T-Yb_2S_3 as uniform sesquisulphide products.

TABLE 3. Important internuclear distances, M^{3+}–S^{2-} (pm), and effective coordination numbers, ECoN(M^{3+}), in F-Tm_2S_3 and T-Yb_2S_3

F-Tm_2S_3			
Tm1–S1	263.7 (2×)	Tm2–S6	288.0 (2×)
S2	268.7	S6′	293.8
S5	281.4	S2	296.8
S1′	284.0	S4	299.6 (2×)
S6	284.7 (2×)	S5	299.7 (2×)
$\bar{d}$(Tm1–S)	275.8 (CN = 7)	$\bar{d}$(Tm2–S)	295.7 (CN = 8)
ECoN(Tm1)	6.66	ECoN(Tm2)	7.92
Tm3–S1	261.0	Tm4–S2	258.4 (2×)
S3	265.2 (2×)	S3	266.4
S3′	270.6	S4	267.7
S5	271.5 (2×)	S4′	272.4 (2×)
$\bar{d}$(Tm3–S)	267.5 (CN = 6)	$\bar{d}$(Tm4–S)	266.0 (CN = 6)
ECoN(Tm3)	5.95	ECoN(Tm4)	5.89
T-Yb_2S_3			
Yb1–S	269.7 (6×)	Yb2–S	266.0 (2×)
		S′	267.1 (2×)
		S″	278.8 (2×)
$\bar{d}$(Yb1–S)	269.7 (CN = 6)	$\bar{d}$(Yb2–S)	270.6 (CN = 6)
ECoN(Yb1)	6.00	ECoN(Yb2)	5.90

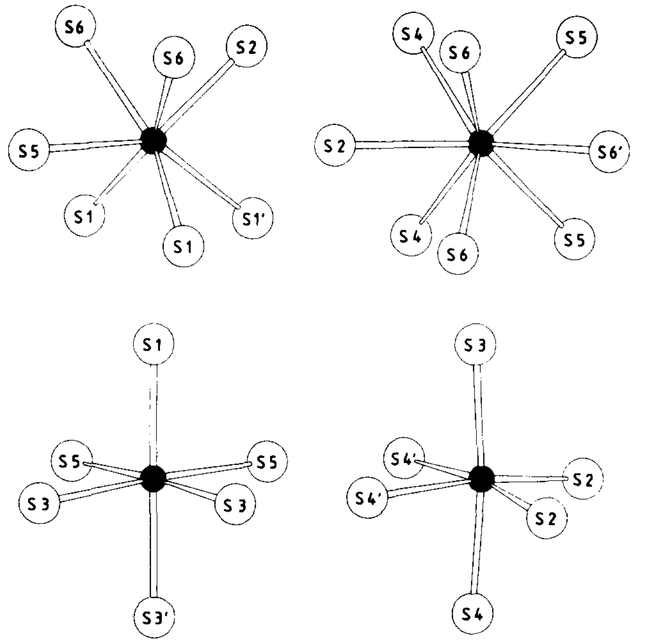

Fig. 1. Polyhedra of coordination in F-Tm_2S_3: [(Tm1)S_7] (left, above), [(Tm2)S_8] (right, above), [(Tm3)S_6] (left, below) and [(Tm4)S_6] (right, below).

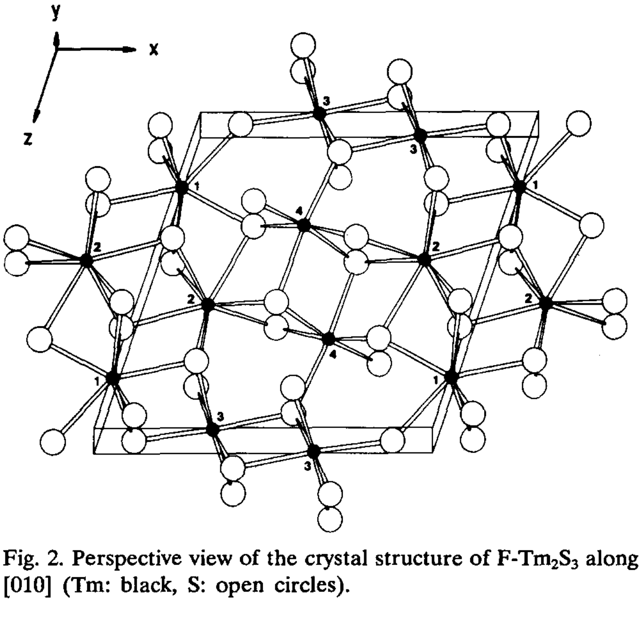

Fig. 2. Perspective view of the crystal structure of F-Tm_2S_3 along [010] (Tm: black, S: open circles).

The crystal structure of *F-Tm_2S_3* contains four crystallographically independent Tm^{3+} (see Table 1). Two of them are in distorted octahedral (Tm3 and Tm4), one in monocapped (Tm1) and one in bicapped trigonal prismatic coordination of S^{2-} (Tm2). Figure 1 shows the four different polyhedra of coordination, while Table 3 gives the corresponding internuclear distances. A view of the crystal structure of F-Tm_2S_3 along [010] is shown in Fig. 2. All atoms (thulium and sulphur) are located in mirror planes parallel to (010) with $y/b = \pm 1/4$ and the site symmetry .*m*). (≡(2*e*) in $P2_1/m$). It is the only sesquisulphide structure known so far that offers coordination numbers of six, seven *and* eight for M^{3+} simultaneously. Table 4 gives an idea of the interconnection of the different polyhedra of coordination (Fig. 1) via S^{2-} by their motifs of (mutual) adjunction [31] (and coordination numbers, *i.e.* four and five) relative to the Tm^{3+} cations. The mean distances $\bar{d}(Tm^{3+}–S^{2-})$ of the "octahedrally" coordinated cations (266 pm for Tm4, 268 pm for Tm3) are not very different from those in D-Tm_2S_3 (Tm3: 268, Tm4: 271, Tm5: 272 pm, all CN = 6) [8], E-Tm_2S_3 (Tm_2S_3-V: 270 pm, CN = 6) [9] or $NaTmS_2$ (272 pm, CN = 6) [30]. The same is true for seven-coordinated $(Tm1)^{3+}$ ($\bar{d}$ = 276 pm) when compared with the cations in D-Tm_2S_3 (Tm1: 276, Tm6: 277, Tm2: 278 pm, all CN = 7) [8] or U-Tm_2S_3 (Tm_2S_3-III: 273 pm for Tm1, 280 pm for Tm2, both CN = 7) [2] in similar sevenfold sulphide coordination. The eightfold coordination of $(Tm2)^{3+}$ looks peculiar: all distances $(Tm2)^{3+}$–S^{2-} (from 288 to 300 pm, mean: 296 pm) are not too different, so that this "regular" coordination (ECoN(Tm2) = 7.9; see ref. 32 for the definition of effective coordination number (ECoN) and Table 3) is hard to compare with $(Tm2)^{3+}$ in U-Tm_2S_3 (Tm_2S_3-III) with CN = 7 + 1 and mean distances of 280 (for CN = 7) and 286 pm (for CN = 8) [2]. Even a comparison with eight-coordinated Tm^{3+} in C-Tm_2S_3 (Tm_2S_3-IV: $\bar{d}$ = 285 pm, CN = 8) [3] remains unsatisfying. A coordination number of eight appears to be too high

TABLE 4. Motifs of mutual adjunction for F-Tm_2S_3 and T-Yb_2S_3

F-Tm_2S_3							
	S1	S2	S3	S4	S5	S6	CN
Tm1	3/3	1/1	0/0	0/0	1/1	2/2	7
Tm2	0/0	1/1	0/0	2/2	2/2	3/3	8
Tm3	1/1	0/0	3/3	0/0	2/2	0/0	6
Tm4	0/0	2/2	1/1	3/3	0/0	0/0	6
CN	4	4	4	5	5	5	
T-Yb_2S_3							
	S	CN					
Yb1	6/1	6					
Yb2	6/3	6					
CN	4						

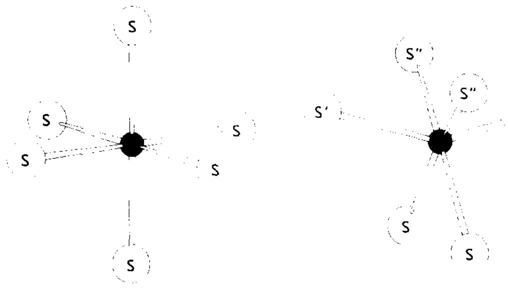

Fig. 3. Polyhedra of coordination in T-Yb_2S_3: $[(Yb1)S_6]$ (left) and $[(Yb2)S_6]$ (right).

for Tm^{3+} (see Table 1 for the larger thermal displacement factors of $(Tm2)^{3+}$ compared with the others). Curious enough to be realized for a binary lanthanide sulphide, the F-type structure is quite common for mixed sulphides such as $CeYb_3S_6$ [33] with Ce^{3+} in eight- and Yb^{3+} in six- and sevenfold coordination.

For the first time obtained as Tm_2S_3-II at 10 kbar and 1600 °C [5] and successfully quenched to ambient conditions, (metastable) single crystals were investigated. Owing to their fibrous growth, they often turned out to be severely twinned. Thus the previous structure determination lacked quality (all atomic positions were not very precise and the standard deviations of the atomic positions for $(Tm2)^{3+}$ did not differ from the others). No thermal displacement factors had been refined and, moreover, some conflicting values emerged for Tm^{3+}–S^{2-} distances in the tables and the figures [5]. Therefore a new structure refinement seemed to be useful, especially if one keeps in mind that a high pressure–high temperature form (Tm_2S_3-II) was obtained at ambient pressure (and lower temperatures) now, just driven by some NaCl flux present.

The crystal structure of *T-Yb_2S_3* exhibits two crystallographically independent Yb^{3+} in more (Yb2) or less (Yb1) distorted octahedral coordination of S^{2-}. Figure 3 shows the two different polyhedra of coordination, while Table 3 gives the corresponding internuclear distances. The polyhedron $[(Yb1)S_6]$ is best described as a trigonal antiprism (site symmetry: .$\bar{3}$. for Yb1) with six equidistant S^{2-} ligands around $(Yb1)^{3+}$ (d(Yb1–S) = 270 pm, 6×). The site symmetry of Yb2 (2..) forces the polyhedron $[(Yb2)S_2S'_2S''_2]$ to be far away from an ideal octahedron: four S^{2-} (two S and two S′) at rather short distances (d(Yb2–S) = 266 pm, 2×; d(Yb2–S′) = 267 pm, 2×) form a compressed disphenoid around $(Yb2)^{3+}$, while two additional S^{2-} (S″) at distances almost 5% larger (d(Yb2–S″) = 279 pm, 2×) complete for a coordination number of six ($\bar{d}$(Yb2–S) = 271 pm, CN = 6). This might be the reason for ECoN(Yb2) (= 5.9) being somewhat smaller than ECoN(Yb1) (= 6.0); see Table 3. Figure 3 illustrates that the $[(Yb2)S_6]$ polyhedron can also be derived from a (distorted) cube with two diametral ligands missing at one face. Therefore the crystal structure (see Fig. 4 for a projection on (001)), in fact the bixbyite- (or Tl_2O_3-) type structure, well known as C type for the oxide Yb_2O_3 [34], is usually described as a fluorite-like structure with one quarter of the anion sites left empty according to the formulation $(Yb1)[(Yb2)_3O_6\square_2]$ [35]. However, both mean distances ($\bar{d}$(Yb1–S) = 270, $\bar{d}$(Yb2–S) = 271 pm) in T-Yb_2S_3 are in good agreement with those for "octahedrally" coordinated Yb^{3+} in other sulphides such as E-Yb_2S_3 (270 pm, CN = 6) [10] or $NaYbS_2$ (271 pm, CN = 6) [30].

Table 4 lists the motifs of mutual adjunction [31] for the crystal structures of F-Tm_2S_3 and T-Yb_2S_3, showing that the S^{2-} anions have coordination numbers of four (S1–S3, distorted tetrahedra) and five (S4–S6, distorted tetragonal pyramids) for the F type and four (S, highly distorted tetrahedron, site symmetry: 1) for the T type. A comparison of the molar volumes (V_m) clearly reveals that F-Tm_2S_3 (CN = 6 (2×), 7 and 8, V_m = 67.4 cm^3 mol^{-1} or 66.6 cm^3 mol^{-1} for high pressure

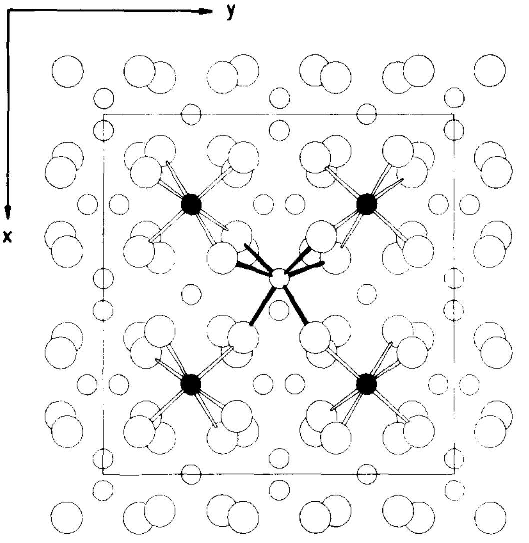

Fig. 4. Projection of the crystal structure of T-Yb_2S_3 on (001); all Yb1 (small black circles) and one Yb2 (small open circles) are depicted by open (Yb1) or bold bonds to their S ligands (large open circles).

Tm_2S_3-II [5]) has a higher density than D-Tm_2S_3 (CN = 6 (3×) and 7 (3×), $V_m = 68.5$ cm³ mol⁻¹) [8], the stable modification at ambient conditions. Therefore it is easy to understand that F-Tm_2S_3 ($\equiv Tm_2S_3$-II) should form under some pressure. However, the still larger densities of C-Tm_2S_3 (CN = 8, $V_m = 62.8$ cm^3 mol^{-1}) [3] and U-Tm_2S_3 (CN = 7 and 7 + 1, $V_m = 62.2$ cm^3 mol^{-1}) [2] show why highest pressure techniques must yield these modifications. Low temperature preparation from the elements (in the presence of NaCl) seems to favour the F- over D-Tm_2S_3 even without the application of high pressure. Higher temperatures, however, transform metastable F-Tm_2S_3 irreversibly into the D type.

On the other hand, a completely different picture emerges for the neighbouring ytterbium: with sulphur it reacts to T-Yb_2S_3 at low temperatures (and flux growth from NaCl melts provides single crystals). A molar volume of 73.0 cm^3 mol^{-1} places T-Yb_2S_3 at the lowest end of *all* lanthanide sesquisulphides when densities are considered. At higher temperatures the irreversible transformation of metastable T-Yb_2S_3 into the E type ($V_m = 72.0$ cm^3 mol^{-1}) [10] occurs, attesting to the thermodynamical stability of the corundum structure of Yb_2S_3 at ambient conditions.

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