Chemistry of Metals and Alloys

Chem. Met. Alloys 1 (2008) 38-42
Ivan Franko National University of Lviv
www.chemetal-journal.org

Crystal structure of δ-Tm_2S_3

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Received December 21, 2007; accepted February 17, 2008; available on-line March 31, 2008

The crystal structure of the δ-modification of thulium sesquisulfide, δ-Tm_2S_3, has been determined by X-ray analysis of a single crystal (automatic diffractometer Xcalibur3^{TM} CCD, 1425 unique reflections, R1 = 0.0425, wR2 = 0.0834). The compound crystallizes in the δ-Ho_2S_3 structure type: space group $P2_1/m$, mP30, with lattice parameters a = 10.0626(14), b = 3.9675(5), c = 17.396(2) Å, β = 98.655(11)°. The coordination numbers of the Tm atoms are 6 (distorted octahedron) and 7 (mono-capped trigonal prism), whereas the S atoms have coordination numbers 4 and 5 (trigonal and tetragonal pyramids).

Rare-earth alloys and compounds / Crystal structure / X-ray diffraction

Introduction

The search for novel inorganic compounds is necessary for the development of new materials, and the accurate and precise determination of their crystal structures is the basic requirement for a better understanding of their physical properties. The rare-earth metal chalcogenides have attracted large attention because of their interesting and useful physical properties, such as optical, thermoelectric, magnetic and superconducting. Extensive reviews on rare-earth metal chalcogenides can be found in [1,2].

During our systematic investigation of the ternary Tm-Ni-S system with the purpose to synthesize new phases we obtained as by-product several single crystals of Tm_2S_3, suitable for X-ray diffraction studies. The preliminary investigation of the crystal structure showed the isotypism with monoclinic Ho_2S_3 [3]. The existence of a monoclinic δ-modification of Tm_2S_3 was firstly reported in [4], and further confirmed in [5], but only the cell parameters were determined and isotypism with Ho_2S_3 stated. On the contrary, complete structure refinements have been performed on the isotypic compounds Y_2S_3, Er_2S_3 and Yb_2S_3, even if the latter was refined in the subgroup $P2_1$.

Like the other rare-earth sesquisulfides, Tm_2S_3 is known to adopt several structural modifications, several of them forming at high pressures. Table 1 summarizes the seven modifications of thulium sesquisulfide known up to date. Only for three of them the conditions of formation are more or less well established at the present time.

The aim of this work was the complete determination of the crystal structure of the δ-modification of Tm_2S_3 from good quality single-crystal X-ray diffraction data.

Experimental

Needle-shaped single crystals were extracted from a hot-sintered sample of composition $Tm_{25}Ni_{25}S_{50}$ that had been melted under an argon atmosphere (Ti-getter) in an arc furnace with a water-cooled copper hearth. The single crystal suitable for X-ray analysis was at a preliminary step investigated by the Laue and Weissenberg methods (RKV-86 and RGNS-2 chambers, MoKα-radiation), then transferred to an automatic single-crystal diffractometer (Xcalibur3^{TM} CCD, MoKα-radiation, graphite monochromator, ω-scans). The data collection and reduction were performed using CrysAlis CCD [13] and CrysAlis RED [14] programs. The structure was solved and refined with programs from the SHELXL-97 [15] package. The program Structure Tidy [16] was applied to standardize the raw crystallographic data. Additional information about the experimental conditions and some structural parameters can be found in Table 2.

Table 1 Literature data on thulium sesquisulfides.

Phase, conditions of formation	Pearson symbol, space group, prototype	Lattice parameters, Å			Reference
		a	*b*	*c*	
Tm_2S_3	*hR*30, $R\bar{3}c$, Al_2O_3	6.768(2)		18.236(3)	[6]
Tm_2S_3	*hP*30, $P6_3cm$, Yb_2S_3	6.777		18.32	[7]
Tm_2S_3 (θ)	*cI*80, $Ia\bar{3}$, Mn_2O_3	12.489(4)			[8]
Tm_2S_3 (γ)	*cI*28, $I\bar{4}3d$, Th_3P_4	8.223(1)			[9]
1900 K, 1.2 GPa					
Tm_2S_3	*oP*20, *Pnma*, U_2S_3	10.479(5)	3.805(3)	10.353(5)	10
1073 K, 2.0 GPa					
Tm_2S_3 (δ)	*mP*30, $P2_1/m$, Ho_2S_3	10.039	3.960 $\beta = 98.78°$	17.363	[4]
		10.037(2)	3.954(1) $\beta = 98.68(2)$	17.350(4)	[9]
Tm_2S_3 (F) 1873 K, 1.0 GPa	*mP*20, $P2_1/m$, Tm_2S_3	11.110(5)	3.874(3) $\beta = 108.88°$	10.872(5)	[11]
1123 K, NaCl-flux		11.162(4)	3.9024(8) $\beta = 108.87°$	10.897(3)	[12]

Table 2 Experimental and crystallographic data for δ-Tm_2S_3.

Compound	Tm_2S_3 (δ-form)
Structure type	δ-Ho_2S_3
Space group	$P2_1/m$
Z, Pearson symbol	6, *mP*30
Lattice parameters, Å	$a = 10.0626(14)$ $b = 3.9675(5)$ $c = 17.396(2)$, $\beta = 98.655(11)°$
Volume V, $Å^3$	686.60(16)
Crystal size, mm	$0.27 \times 0.07 \times 0.03$
Crystal color	semitransparent metallic light grey
Absorption coefficient, mm^{-1}	39.670
Absorption correction	analytical, $T_{min} = 0.051$, $T_{max} = 0.305$
Theta range for data collection	4.09 to 25.30°
Limiting indices	$-12 \le h \le 12$, $-4 \le k \le 3$, $-20 \le l \le 20$
Reflections collected / unique	3791 / 1425 [R(int) = 0.0358]
Completeness to theta	97.9%
Refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	1425 / 0 / 92
Goodness-of-fit on F^2	1.243
Final R indices [I>2sigma(I)]	R1 = 0.0425, wR2 = 0.0834
R indices (all data)	R1 = 0.0445, wR2 = 0.0841
Extinction coefficient	0.00024(7)
Largest diff. peak and hole	2.676 and -1.775 e $Å^{-3}$

Results and discussion

The structure solution of Tm_2S_3 by direct methods in space group $P2_1/m$ confirmed the Ho_2S_3 structure type [3]. The atomic parameters were refined in the anisotropic approximation down to R = 0.0425 and the final values are listed in Table 3. Refinements of the occupancies of the cation sites indicated no deviation from full occupation by Tm. The cell parameters are in good agreement with those reported in the literature and the presence of Ni in the structure could be excluded. Fig. 1 shows a clinographic projection of the unit cell content of δ-Tm_2S_3 with indication of atomic connections Tm-S.

A look at the interatomic distances in Table 4 confirms the iono-covalent character of the chemical bonding in Tm_2S_3. Some distances, e.g. the shortest distances Tm6-S9 in the [TmS_6] octahedron (2.594(5) Å) are slightly shorter than the sum of ionic radii of Tm^{3-} and S^{2-} (2.79 Å).

Table 3 Atomic positional and displacement parameters for δ-Tm_2S_3 (all atoms in Wyckoff site 2*e*: *x ¼ z* with site occupation number *G* = 1).

Atom	*x*	*z*	Displacement parameters[a], $Å^2 \times 10^3$				
			U_{eq}	U_{11}	U_{22}	U_{33}	U_{13}
Tm1	0.1248(1)	0.9299(1)	7(1)	9(1)	7(1)	5(1)	1(1)
Tm2	0.1867(1)	0.2203(1)	8(1)	10(1)	8(1)	5(1)	-1(1)
Tm3	0.1891(1)	0.5207(1)	7(1)	8(1)	6(1)	6(1)	0(1)
Tm4	0.4872(1)	0.8989(1)	9(1)	11(1)	7(1)	8(1)	3(1)
Tm5	0.5490(1)	0.6153(1)	7(1)	9(1)	7(1)	5(1)	0(1)
Tm6	0.8295(1)	0.2813(1)	8(1)	12(1)	7(1)	4(1)	0(1)
S1	0.0083(5)	0.7678(3)	6(1)	6(2)	9(2)	4(2)	0(2)
S2	0.0526(5)	0.0751(3)	7(1)	8(2)	11(3)	3(2)	2(2)
S3	0.2680(5)	0.3729(3)	8(1)	10(2)	11(2)	2(2)	0(2)
S4	0.3200(5)	0.6826(3)	8(1)	10(2)	3(2)	13(3)	4(2)
S5	0.3668(5)	0.0312(3)	8(1)	10(2)	4(2)	7(3)	0(2)
S6	0.6157(5)	0.4673(3)	5(1)	6(2)	4(2)	5(2)	-1(2)
S7	0.6375(5)	0.7825(3)	9(1)	10(2)	10(2)	4(2)	-3(2)
S8	0.7101(5)	0.1315(3)	8(1)	10(2)	6(2)	8(3)	0(2)
S9	0.9516(5)	0.4237(3)	10(1)	9(2)	11(3)	10(3)	0(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2\mathbf{a}^{*2}U_{11} + ... + 2hk\mathbf{a}^*\mathbf{b}^*U_{12}]$, $U_{12} = U_{23} = 0$.

Table 4 Interatomic distances (δ, Å) and coordination numbers (C.N.) for δ-Tm_2S_3.

Atoms		δ, Å	C.N.	Atoms		δ, Å	C.N.
Tm1	– 2S2	2.661(3)	7	S1	– 2Tm6	2.783(3)	5
	– S2	2.731(5)			– 2Tm2	2.819(4)	
	– S5	2.783(5)			– Tm1	2.887(5)	
	– S1	2.887(5)		S2	– 2Tm1	2.661(3)	4
	– 2S8	2.893(4)			– Tm2	2.679(5)	
Tm2	– S3	2.657(5)	6		– Tm1	2.731(5)	
	– 2S7	2.663(4)		S3	– Tm2	2.658(5)	4
	– S2	2.679(5)			– 2Tm5	2.694(4)	
	– 2S1	2.819(4)			– Tm3	2.803(5)	
Tm3	– 2S9	2.700(4)	7	S4	– 2Tm6	2.623(3)	4
	– S9	2.710(5)			– Tm5	2.737(5)	
	– 2S6	2.777(4)			– Tm3	2.925(6)	
	– S3	2.803(5)		S5	– 2Tm4	2.652(4)	4
	– S4	2.925(6)			– Tm4	2.756(5)	
Tm4	– 2S5	2.652(4)	6		– Tm1	2.783(5)	
	– S7	2.704(5)		S6	– Tm5	2.757(5)	5
	– S7	2.756(5)			– 2Tm3	2.777(4)	
	– 2S8	2.800(4)			– 2Tm5	2.834(4)	
Tm5	– 2S3	2.694(4)	7	S7	– 2Tm2	2.663(4)	4
	– S4	2.737(5)			– Tm4	2.704(5)	
	– S6	2.757(5)			– Tm5	2.911(5)	
	– 2S6	2.834(4)		S8	– Tm6	2.701(5)	5
	– S7	2.911(5)			– 2Tm4	2.800(4)	
Tm6	– S9	2.594(5)	6		– 2Tm1	2.893(4)	
	– 2S4	2.623(3)		S9	– Tm6	2.594(6)	4
	– S8	2.701(5)			– 2Tm3	2.700(4)	
	– 2S1	2.783(3)			– Tm3	2.710(5)	

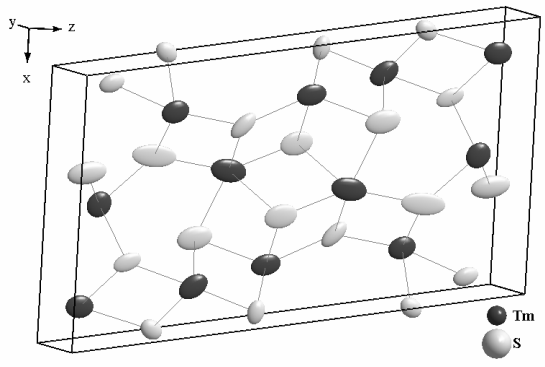

Fig. 1 Clinographic projection of the unit cell of δ-Tm_2S_3 with displacement ellipsoids and atomic connections of Tm and S atoms between layers with y = 1/4 and y = 3/4.

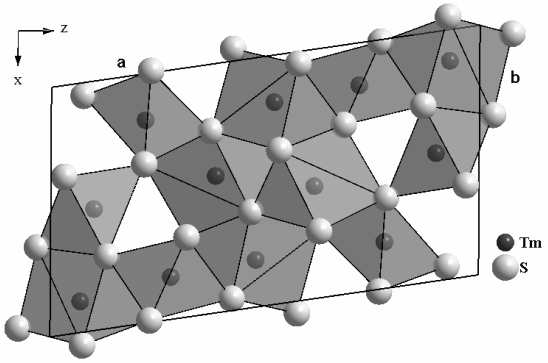

Fig. 2 Stacking of distorted octahedrons [TmS_6] (a) and mono-capped trigonal prisms [TmS_7] (b) in δ-Tm_2S_3.

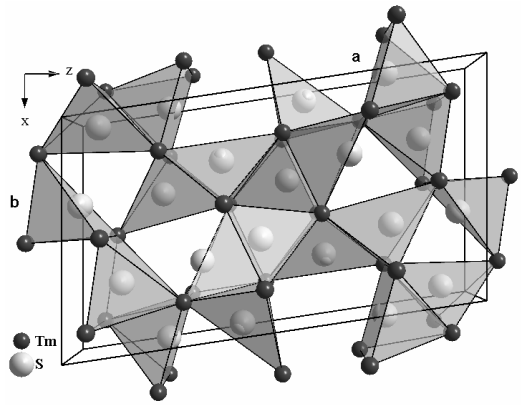

Fig. 3 Stacking of tetragonal pyramids [STm_5] (a) and trigonal pyramids [STm_4] (b) in δ-Tm_2S_3. The sulfur atoms are situated in the bases of the pyramids.

For half of the thulium atoms the coordination number is 6. The interatomic distances within the considerably distorted octahedra range from 2.59 to 2.82 Å. The remaining thulium atoms have coordination number 7, with Tm-S distances between ~2.7 and 2.9 Å. The coordination polyhedra can for all three crystallographically independent sites be assimilated to a mono-capped trigonal prism [TmS_7]. The trigonal prisms, as well as the octahedra, share edges to form infinite columns in the direction of the unique axis of the monoclinic structure. Fig. 2 shows the stacking of these polyhedra, which share atoms to form a 3D-framework. Fig. 3 shows the same structure, but focusing this time on the environment of the sulfur atoms. Three of the sulfur atom sites are surrounded by five cations forming tetragonal pyramids [STm_5], while for the other sulfur atoms the coordination number is 4 and the coordination polyhedra are distorted tetrahedra [STm_4].

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Proceeding of the IX International Conference on Crystal Chemistry of Intermetallic Compounds, Lviv, September 20-24, 2005.