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Samarium Tantalum Oxysulfide, Sm$_2$Ta$_3$S$_2$O$_8$

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Abstract

The title compound is isostructural with La$_2$Ta$_3$S$_2$O$_8$. The Sm atoms are in tricapped trigonal prismatic sites enclosed by two S and seven O atoms. The Ta atoms are octahedrally coordinated, one to six O atoms and the other to two *trans*-O and four S atoms. The structure comprises alternate layers of Sm tricapped trigonal prisms and Ta octahedra. The Ta(1)$\cdots$Ta(1) distances in the octahedral layers are 3.314 (4), 3.775 (1) and 4.236 (4) Å.

Comment

The present work constitutes part of our study of the structure and physical properties of the lanthanide–transition metal oxychalcogenide compounds. A family

of RCrS$_2$O (R = La to Sm) quaternary oxysulfides is known (Dugue, Vovan & Villers, 1990a,b) and Dugue, Vovan & Laruelle (1985) reported the structure of La$_5$V$_3$S$_6$O$_7$, which contains both V^{5+} and V^{3+} sites. The series of compounds Ln$_2$Ta$_3$Se$_2$O$_8$ (Ln = La, Ce, Pr, Nd) were synthesized by Brennan, Aleandri & Ibers (1991) and the isostructural compounds La$_2$Ta$_3$S$_2$O$_8$ and La$_2$Nb$_3$S$_2$O$_8$, which contain mixed-valency Ta atoms, were subsequently characterized (Brennan & Ibers, 1992). We present here the crystal structure of Sm$_2$Ta$_3$S$_2$O$_8$.

Each Sm atom is coordinated to two S and seven O atoms in arrangement whereby the two S and one of the O atoms can be described as being face-capped trigonal prismatic. The Sm—S distances are 2.95 (1) and 2.99 (1) Å and the Sm—O distances are in the range 2.39 (1)–2.53 (2) Å. The Sm tricapped trigonal prisms are face shared through the O(1), O(2) and O(4) atoms, forming chains in the c-axis direction. The Sm$\cdots$Sm distance is 3.775 (1) Å. The prisms are corner shared through the S atoms in the a direction, forming layers of Sm tricapped trigonal prisms.

Fig. 1 shows the layer of Ta octahedra. Ta(1) is octahedrally coordinated to four S and two O atoms. The Ta(1)—O distance is 1.98 (3) Å and the Ta(1)—S distances are 2.386 (8) and 2.728 (7) Å; these distances are 1.978 (9), 2.462 (3) and 2.692 (3) Å, respectively, in La$_2$Ta$_3$S$_2$O$_8$. The Ta(1) octahedra form chains in the c-axis direction *via* edge-shared S atoms, with three Ta(1)$\cdots$Ta(1) distances of 3.314 (4), 3.775 (1) and 4.236 (4) Å. Ta(2) is octahedrally coordinated to six O atoms with Ta—O distances ranging from 1.85 (2) to 2.33 (2) Å [1.820 (2)–2.299 (8) Å in La$_2$Ta$_3$S$_2$O$_8$]. The Ta(2)O$_6$ octahedra are edge shared in the a direction through O(1) atoms, and corner shared through O(3) atoms in the c direction, forming double chains of octahedral Ta(2) dimers. The edge-shared Ta(2)$\cdots$Ta(2) distance is 3.286 (2) Å, compared with 3.292 (2) Å in
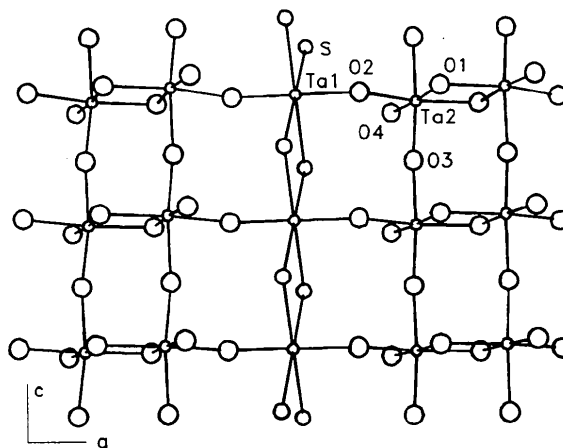

Fig. 1. A layer of Ta octahedra viewed along the b-axis direction.

$La_2Ta_3S_2O_8$. The chains of Ta(1) octahedra are linked to the double chains through corner sharing *via* the O(2) atoms in the *a* direction, forming layers of Ta octahedra.

Fig. 2 shows a view of the $Sm_2Ta_3S_2O_8$ unit cell along the *c*-axis direction. The structure comprises layers of Ta octahedra alternating with layers of Sm tricapped trigonal prisms through sharing O(1), O(2), O(3), O(4) and S atoms in the *b* direction. The Sm···Ta(2) distance is 3.448 (2) Å.
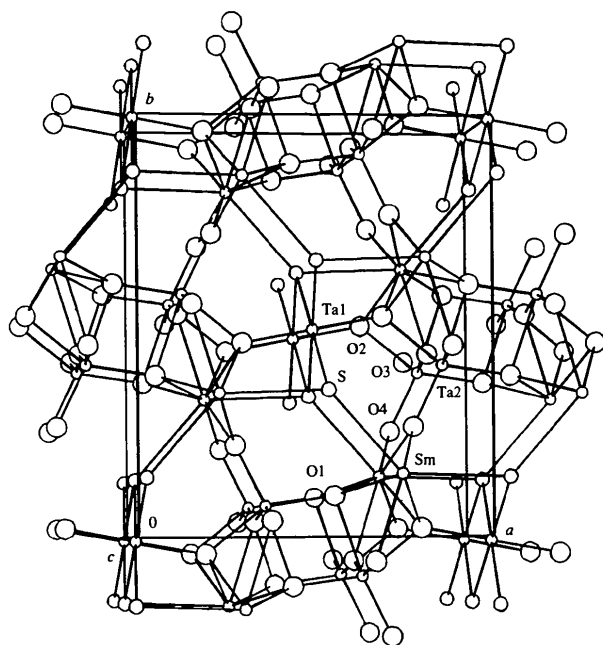

Fig. 2. A view of the $Sm_2Ta_3S_2O_8$ unit cell along the *c*-axis direction.

Experimental

The starting material was prepared from SmOCl, Ta (99.5%, Shanghai Chemical Corporation) and S (99.99%, Shanghai Chemical Corporation) powders in a 1:1:1 molar ratio in an evacuated and sealed quartz ampoule. The reaction mixture was progressively heated to 1223 K for 7 days. A pressed pellet of the product and about 30 mg of NH_4Cl were evacuated and sealed in a quartz ampoule, slowly heated to 1273 K, transported at a temperature gradient of 1273/1233 K for 5 days and then slowly cooled to 1093 K and air quenched. The crystals obtained were stable in air. EXAD analysis of a single crystal for use in X-ray analysis showed it to contain the elements Sm, Ta and S, and a semi-quantitive analysis gave a composition of $Sm_{2.0}Ta_{3.3}S_{2.1}$

Crystal data

$Sm_2Ta_3S_2O_8$
$M_r = 1035.76$
Orthorhombic
Pbam
$a = 9.845\,(2)$ Å
$b = 11.513\,(4)$ Å
$c = 3.775\,(1)$ Å

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10-25°$
$\mu = 51.84$ mm^{-1}
$T = 295$ K

$V = 427.9\,(2)$ Å^3
$Z = 2$
$D_x = 8.04$ Mg m^{-3}

Rectangular
$0.3 \times 0.07 \times 0.07$ mm
Black

Data collection

Rigaku AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scans (North, Phillips & Mathews, 1968)
  $T_{min} = 0.755$, $T_{max} = 0.996$
1580 measured reflections
1580 independent reflections

786 observed reflections
  $[I > 3\sigma(I)]$
$\theta_{max} = 40°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 7$
3 standard reflections
  monitored every 250 reflections
  intensity decay: none

Refinement

Refinement on F
$R = 0.058$
$wR = 0.076$
$S = 1.33$
786 reflections
36 parameters
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 4.54$ e Å^{-3}
$\Delta\rho_{min} = -5.78$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

		x	y	z	U_{eq}
Ta(1)†	4(e)	0	0	0.0613 (6)	0.0069 (6)
Ta(2)	4(g)	0.3648 (1)	0.0836 (1)	0	0.0030 (2)
Sm	4(h)	−0.2833 (2)	0.1572 (1)	1/2	0.0085 (3)
S	4(h)	0.016 (1)	0.149 (1)	1/2	0.016 (2)
O(1)	4(g)	−0.441 (2)	0.108 (2)	0	0.006 (4)
O(2)	4(g)	−0.197 (3)	0.031 (3)	0	0.016 (5)
O(3)	4(h)	−0.358 (3)	−0.048 (2)	1/2	0.013 (4)
O(4)	4(g)	−0.218 (2)	0.272 (2)	0	0.008 (4)

† Occupancy = 0.5.

Table 2. *Selected geometric parameters* (Å, °)

Ta(1)···Ta(1^i)	3.314 (4)	Ta(2)—O(1^{ix})	1.93 (2)
Ta(1)···Ta(1^{ii})	3.775 (1)	Ta(2)—O(3^{vi})	1.933 (6)
Ta(2)···Ta(2^{iii})	3.286 (2)	Ta(2)—O(3^{vii})	1.933 (6)
Sm···Sm^{iv}	3.775 (1)	Ta(2)—O(2^{vi})	2.11 (3)
Sm···Sm^v	3.775 (1)	Ta(2)—O(1^{vi})	2.33 (2)
Ta(2)···Sm^{vi}	3.448 (2)	Sm—O(4)	2.39 (1)
Ta(2)···Sm^{vii}	3.448 (2)	Sm—O(4^v)	2.39 (1)
Ta(1)—O(2)	1.98 (3)	Sm—O(3)	2.47 (3)
Ta(1)—O(2^{vi})	1.98 (3)	Sm—O(1)	2.51 (1)
Ta(1)—S	2.386 (8)	Sm—O(1^v)	2.51 (1)
Ta(1)—S^{vi}	2.386 (8)	Sm—O(2)	2.53 (2)
Ta(1)—S^{vi}	2.728 (7)	Sm—O(2^v)	2.53 (2)
Ta(1)—S^{iv}	2.728 (7)	Sm—S	2.95 (1)
Ta(1)—S^{vii}	2.728 (7)	Sm—S^x	2.99 (1)
Ta(2)—O(4^{viii})	1.85 (2)		
O(2)—Ta(1)—O(2^{vi})	166.6 (2)	O(1)—Sm—O(2^v)	129.7 (6)
O(2)—Ta(1)—S^{iv}	81.7 (5)	O(1^v)—Sm—O(2)	129.7 (6)
O(2^{vi})—Ta(1)—S^{vii}	81.7 (5)	O(1)—Sm—S^x	76.0 (4)
O(2)—Ta(1)—S^{vii}	87.9 (5)	O(1^v)—Sm—S^x	76.0 (4)
O(2^{vi})—Ta(1)—S^{iv}	87.9 (5)	O(1)—Sm—S	127.8 (3)
O(2)—Ta(1)—S	91.1 (5)	O(1^v)—Sm—S	127.8 (3)
O(2^{vi})—Ta(1)—S^{vi}	91.1 (5)	O(2^v)—Sm—O(2)	96.3 (8)
O(2)—Ta(1)—S^{vi}	98.2 (5)	O(2)—Sm—S	69.2 (5)
O(2^{vi})—Ta(1)—S	98.2 (5)	O(2^v)—Sm—S	69.2 (5)
S^{iv}—Ta(1)—S^{vii}	78.1 (3)	O(2)—Sm—S^x	130.9 (4)
S—Ta(1)—S^{vi}	92.1 (3)	O(2^v)—Sm—S^x	130.9 (4)
S^{vi}—Ta(1)—S^{vii}	94.9 (3)	O(3)—Sm—O(1)	66.5 (5)

S—Ta(1)—S^{iv}	94.9 (3)	O(3)—Sm—O(1^v)	66.5 (5)
S—Ta(1)—S^{vii}	173.01 (6)	O(3)—Sm—O(2)	63.2 (6)
S^{iv}—Ta(1)—S^{vi}	173.01 (6)	O(3)—Sm—O(2^v)	63.2 (6)
O(1^{ix})—Ta(2)—O(1^{vi})	79.6 (7)	O(3)—Sm—S	105.4 (5)
O(1^{ix})—Ta(2)—O(3^{vi})	93.8 (6)	O(3)—Sm—S^x	121.2 (5)
O(1^{ix})—Ta(2)—O(3^{vii})	93.8 (6)	O(4)—Sm—O(1)	72.2 (5)
O(1^{ix})—Ta(2)—O(2^{vi})	150.1 (8)	O(4^v)—Sm—O(1^v)	72.2 (5)
O(2^{vi})—Ta(2)—O(1^{vi})	70.5 (8)	O(4)—Sm—O(1^v)	151.9 (6)
O(3^{vi})—Ta(2)—O(1^{vi})	79.0 (6)	O(4^v)—Sm—O(1)	151.9 (6)
O(3^{vii})—Ta(2)—O(1^{vi})	79.0 (6)	O(4)—Sm—O(2^v)	144.9 (6)
O(3^{vi})—Ta(2)—O(2^{vi})	80.8 (6)	O(4^v)—Sm—O(2)	144.9 (6)
O(3^{vii})—Ta(2)—O(2^{vi})	80.8 (6)	O(4)—Sm—O(2)	69.0 (6)
O(3^{vi})—Ta(2)—O(3^{vii})	155 (1)	O(4^v)—Sm—O(2^v)	69.0 (6)
O(4^{viii})—Ta(2)—O(1^{ix})	107.9 (8)	O(4)—Sm—O(3)	127.3 (4)
O(4^{viii})—Ta(2)—O(1^{vi})	172.5 (7)	O(4^v)—Sm—O(3)	127.3 (4)
O(4^{viii})—Ta(2)—O(2^{vi})	102.0 (9)	O(4^v)—Sm—O(4)	104.4 (7)
O(4^{viii})—Ta(2)—O(3^{vi})	100.1 (6)	O(4)—Sm—S	75.8 (4)
O(4^{viii})—Ta(2)—O(3^{vii})	100.1 (6)	O(4^v)—Sm—S	75.8 (4)
O(1^v)—Sm—O(1)	97.5 (6)	O(4)—Sm—S^x	76.2 (4)
O(1)—Sm—O(2)	61.3 (6)	O(4^v)—Sm—S^x	76.2 (4)
O(1^v)—Sm—O(2^v)	61.3 (6)	S—Sm—S^x	133.4 (1)

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

The Sm and Ta atoms were located by direct methods (*MITHRIL*; Gilmore, 1983) with Ta(1) situated near the 2(a) special position. However, refinements with Ta(1) at the 2(a) site led to very high B_{eq} and R values, indicating that Ta(1) cannot be located at that site. Refinement with Ta(1) at the 4(g) site (occupancy 0.5) led to the worse result of R = 0.15 and $\Delta\rho_{max}$ = 49.98 e Å^{-3}. Re-refinement with Ta(1) distributed statistically at the 4(e) position led to the better result of R = 0.06 and $\Delta\rho_{max}$ = 4.80 e Å^{-3}; thus Ta(1) was finally located at the 4(e) position. The remaining atoms were found in successive difference Fourier syntheses. The structure was refined by full-matrix least-squares methods with anisotropic displacement parameters for Sm, Ta and S atoms. All calculations were performed on a VAX 11/785 computer using *TEXSAN* software (Molecular Structure Corporation, 1987).

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Redétermination de la Structure du Sulfure de Cadmium et de Germanium, Cd$_4$GeS$_6$

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Abstract

The structure of tetracadmium germanium hexasulfide comprises GeS$_4$ and CdS$_4$ tetrahedra. The GeS$_4$ tetrahedra are regular but are not bonded. Each S-atom vertex of a GeS$_4$ tetrahedron is shared with two CdS$_4$ tetrahedra.

Commentaire

La structure de Cd$_4$GeS$_6$ a été résolue en 1970 par Susa & Steinfink (1971) avec un R conventionnel de 0,0715. Cependant, disposant d'un cristal de très bonne qualité, nous avons repris cette structure afin d'obtenir des valeurs plus précises des distances et des angles interatomiques; ceci dans le but d'attribuer avec précision les pics observés dans les spectres infrarouges de ce composé.

Chaque cation présente une coordinence soufrée tétraédrique classique (Tableau 2), tous les tétraèdres GeS$_4$ et CdS$_4$ sont liés les uns aux autres par des sommets. Dans la maille, il y a quatre atomes de Cd indépendants et les quatre tétraèdres correspondants sont liés entre eux par un atome de S commun, soit S(5) (Fig. 1), soit S(1). En revanche deux tétraèdres GeS$_4$ ne sont jamais liés entre eux. Chaque atome de S d'un tétraèdre GeS$_4$ est commun à deux tétraèdres CdS$_4$ (Fig. 2). Les tétraèdres GeS$_4$ et Cd(3)S$_4$ sont presque réguliers, les trois autres tétraèdres CdS$_4$ sont plus irréguliers (Tableau 2).

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