

BRIEF COMMUNICATION

Sm₂Ta₂Cl₂O₇: A New Samarium ChlorotantalateGuocong Guo, Manfang Wang, Jiutong Chen, Jinshun Huang,¹ and Qianer Zhang

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The starting material was prepared by heating amounts of SmOCl/Ta₂O₅/Ta/Se in an evacuated quartz tube. Sm₂Ta₂Cl₂O₇ single crystals were obtained by chemical transport reactions using NH₄Cl as transport agent. It crystallizes in the monoclinic space group *C2/m* with $a = 15.290(4)$ Å, $b = 3.903(2)$ Å, $c = 6.862(2)$ Å, and $\beta = 113.92(2)^\circ$. The structure was refined to a final *R* value of 2.8% using 1123 reflections. The structure shows a three-dimensional arrangement and is built up from layers of Ta octahedral dimers alternating with layers of Sm face-capped trigonal prismatic dimers. © 1994 Academic Press, Inc.

INTRODUCTION

Many transition metal oxychlorides of the rare earths have been prepared. A series of *Ln*WO₄Cl compounds (*Ln* = Ce, Pr, Nd) was first described by Kharchenko *et al.* in the 1960s (1). Brixner *et al.* found the rare earth oxochloroniobates LaNb₂O₆Cl (2) and Pr₃NbO₄Cl₆ (3). A group of rare earth oxochlorotantalates of the formula *Ln*₃TaO₅XCl₃ (*X* = O, OH, F) was synthesized by Schaffrath and Gruehn (4, 5). Attempts to synthesize the samarium transitional oxyselenide compounds were unsuccessful and yielded the new compound Sm₂Ta₂Cl₂O₇. In the present paper we report on the preparation and structure of the new compound Sm₂Ta₂Cl₂O₇.

EXPERIMENTAL

A. Preparation. The starting material was prepared by heating appropriate amounts of SmOCl, Ta₂O₅ (99.95% purity, Shanghai Chemical Corp.), Ta (99.5% purity, Shanghai Chemical Corp.), and Se (99.999%, Shanghai

Chemical Corp.) in an evacuated and sealed quartz ampoule (o.d. about 1.1 cm, length about 13 cm). SmOCl was made by dissolving Sm₂O₃ (99.9% purity, Shanghai Chemical Corp.) in HCl, allowing the solution to dry, and firing the product at 900°C in air for 6–10 hr. The reaction was carried out at 950°C for 7 days. A pressed pellet of sintered polycrystalline powder and about 30 mg NH₄Cl were sealed into a quartz ampoule (o.d. about 1.1 cm, length about 13 cm) and slowly heated to 1000°C, exposed to a temperature gradient of 1000/960°C for 13 days with the sample at the hot end, slowly cooled to 820°C at the rate of 11°C per hour, and then air quenched. The obtained crystals are stable in air. EDAX analysis of a single crystal for the X-ray diffraction analysis showed that it contained Sm, Ta, and Cl and no Se. Preparation by direct stoichiometric combination according to the equation



will be carried out by the same technique.

B. Structure determination. A crystal with approximate dimensions 0.1 × 0.05 × 0.05 mm was selected for the X-ray study. The diffraction data were collected on

TABLE 1
Positional Parameters and *B*(eq)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq)
Ta	0.53456(2)	1/2	-0.20046(4)	0.255(8)
Sm	0.69345(2)	0	0.16486(6)	0.37(1)
Cl	0.6782(1)	0	0.5653(3)	0.64(4)
O1	0.8244(4)	0	0.0698(9)	0.5(1)
O2	0.5825(4)	1/2	0.1544(9)	0.4(1)
O3	0.5460(4)	0	-0.162(1)	0.7(1)
O4	1/2	-1/2	-1/2	0.7(2)

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TABLE 2
Anisotropic Thermal Parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta	0.0032(1)	0.0035(1)	0.0031(1)	0	0.00138(8)	0
Sm	0.0047(1)	0.0051(1)	0.0042(1)	0	0.0016(1)	0
Cl	0.0075(6)	0.0100(7)	0.0068(6)	0	0.0029(5)	0
O1	0.009(2)	0.008(2)	0.004(2)	0	0.004(2)	0
O2	0.008(2)	0.006(2)	0.003(2)	0	0.003(2)	0
O3	0.007(2)	0.007(2)	0.010(2)	0	0.002(2)	0
O4	0.009(3)	0.016(4)	0.003(3)	0	0.004(2)	0

TABLE 3
Interatomic Distances (Å)

Atoms	Distance	Atoms	Distance
Ta–O4	1.9034(5)	Sm–O1	2.344(5)
Ta–O2	1.940(5)	Sm–O3	2.452(6)
Ta–O3	1.968(1) (2x)	Sm–O1	2.474(3) (2x)
Ta–O1	1.971(6)	Sm–O2	2.567(4) (2x)
Ta–O2	2.240(5)	Sm–Cl	2.850(2)
Ta–Sm	3.3251(8) (2x)	Sm–Cl	2.854(2) (2x)
		Sm–Sm	3.8846(9) (2x)

a Rigaku AFC5R X-ray diffractometer, using a graphite monochromator, MoK α radiation ($\lambda = 0.71069$ Å), and an ω - 2θ scan mode. A total of 1320 reflections were measured in the range $2^\circ < 2\theta < 80^\circ$ and corrected for Lp factors, the decay factor, and empirical absorptions; only the unique 1123 reflections with $I \geq 3\sigma(I)$ were used in the structure determination and refinement. The structure was solved by direct methods and the difference Fourier technique and refined by a full-matrix least-squares method for the coordinates and anisotropic thermal factors to the final values $R = 0.028$, $R_w = 0.038$ ($\omega = 1/\sigma^2(F)$), $S = 1.04$, and $(\Delta/\sigma)_{\max} = 0.01$. For Sm₂Ta₂Cl₂O₇ with $Z = 2$, the calculated density equals 7.50 g/cm³. The minimum and maximum values on the final difference Fourier map were -6.67 and 6.07 e/Å³, respectively. All calculations were performed on a VAX-11/785 computer using a TEXSAN program system.

DISCUSSION

The atomic coordinates, thermal parameters, interatomic distances, and bond angles are listed in Tables 1, 2, 3, and 4, respectively. The crystal structures of Sm₂Ta₂Cl₂O₇ are shown in Fig. 1. All atoms are in special positions. The Sm is coordinated to three chlorine and six oxygen atoms, with face-capped trigonal prismatic Cl, O1, and O3 atoms, with two Cl occupying the apical position (Fig. 2). The Sm–Cl distances are 2.850(2) and 2.854(2) Å. The Sm–O distances are in the range of 2.344 to 2.567 Å. The Ta is octahedrally coordinated to six oxygen atoms, with the Ta–O distances ranging from 1.9034 to 2.240 Å (Fig. 3). The Ta–Sm distance is 3.3251 Å.

The Ta–O octahedral are edge shared through the O2 atoms and corner shared through the O3 atoms in the b

TABLE 4
Bond Angles (°)

Atoms	Angle	Atoms	Angle	Atoms	Angle
O4–Ta–O2	107.8(2)	O3–Sm–O1	65.6(1)	Cl–Sm–Cl	71.21(5)
O4–Ta–O3	96.7(2)	O3–Sm–O2	67.8(1)	Cl–Sm–Cl	86.30(6)
O4–Ta–O1	105.4(2)	O3–Sm–Cl	118.5(1)	Sm–Cl–Sm	108.79(5)
O4–Ta–O2	177.3(1)	O3–Sm–Cl	136.80(3)	Sm–Cl–Sm	86.30(6)
O2–Ta–O3	90.9(2)	O1–Sm–O1	104.2(2)	Ta–O1–Sm	140.7(3)
O2–Ta–O1	146.9(2)	O1–Sm–O2	59.0(2)	Ta–O1–Sm	96.2(2)
O2–Ta–O2	74.9(2)	O1–Sm–O2	133.2(2)	Sm–O1–Sm	107.4(2)
O3–Ta–O3	165.3(4)	O1–Sm–Cl	126.6(1)	Sm–O1–Sm	104.2(2)
O3–Ta–O1	85.3(2)	O1–Sm–Cl	75.4(1)	Ta–O2–Ta	105.1(2)
O3–Ta–O2	83.2(2)	O1–Sm–Cl	145.8(1)	Ta–O2–Sm	129.7(1)
O1–Ta–O2	71.9(2)	O1–Sm–O2	133.2(2)	Ta–O2–Sm	87.2(1)
O1–Sm–O3	108.6(2)	O1–Sm–O2	59.0(2)	Sm–O2–Sm	99.0(2)
O1–Sm–O1	72.6(2)	O2–Sm–O2	99.0(2)	Ta–O3–Ta	165.3(4)
O1–Sm–O2	128.4(1)	O2–Sm–Cl	73.5(1)	Ta–O3–Sm	97.0(2)
O1–Sm–Cl	132.9(1)	O2–Sm–Cl	76.8(1)	Ta–O4–Ta	180(4)
O1–Sm–Cl	74.9(1)	O2–Sm–Cl	144.2(1)		

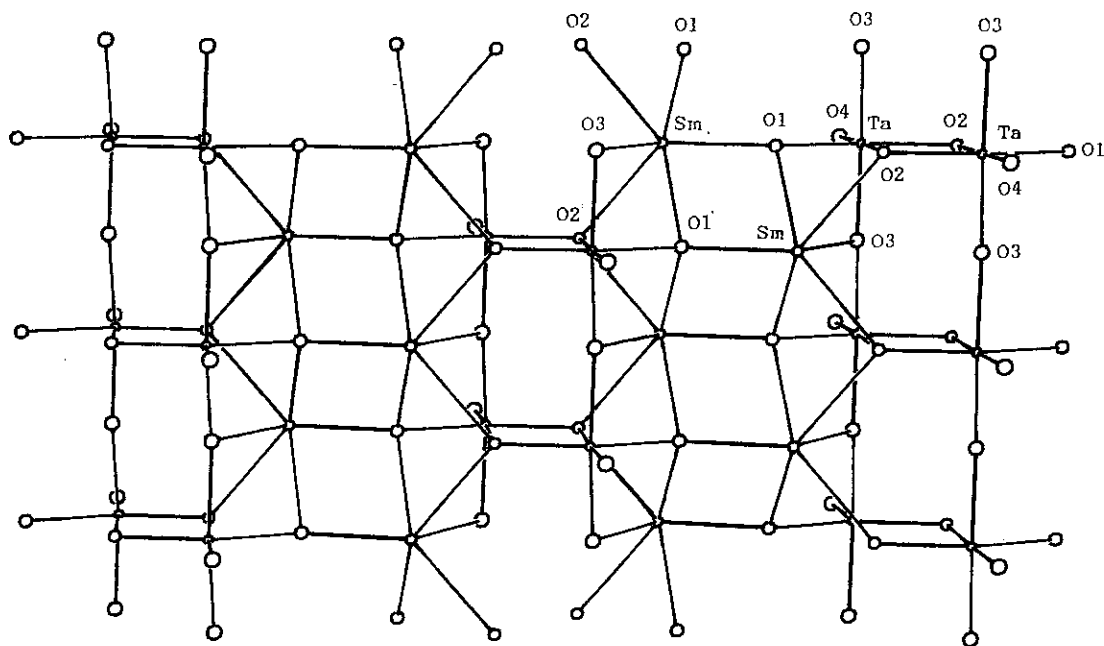


FIG. 1. A view along [001] showing the Ta octahedra dimer layers alternating with Sm face-capped trigonal prismatic dimer layers (Cl atoms omitted).

direction and corner shared through the O4 atoms in the c direction, forming the layers of Ta octahedral dimers. The edge-shared Ta-Ta distance is 3.323 Å. The Sm face-capped trigonal prism is linked by another one sharing two O1 atoms to form Sm face-capped trigonal prismatic

dimers, in which the Sm-Sm distance is 3.8846 Å. The Sm dimers are face shared through the O1, O2, and Cl atoms in the b direction and are edge shared through two Cl in the c direction, thus forming the layers of Sm face-capped trigonal prismatic dimers. The structure is built up from alternately stacked layers of Ta octahedral dimers and layers of Sm face-capped trigonal prismatic dimers through sharing atoms O1, O2, and O3 in the a direction.

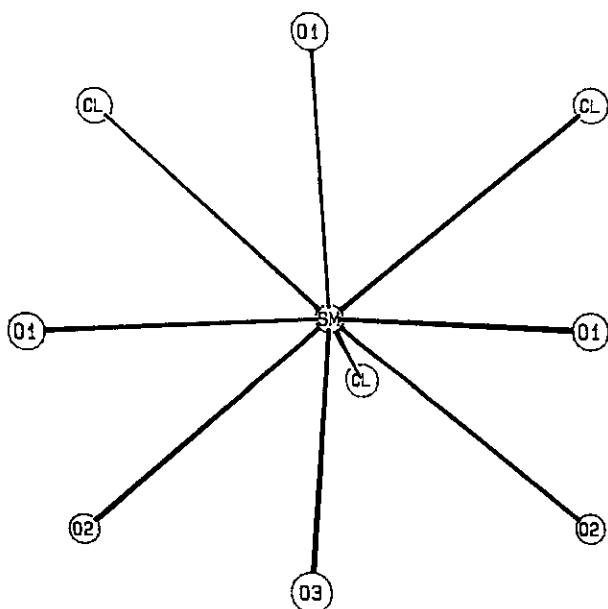


FIG. 2. Coordination sphere of SmO_6Cl_3 in $\text{Sm}_2\text{Ta}_2\text{Cl}_2\text{O}_7$.

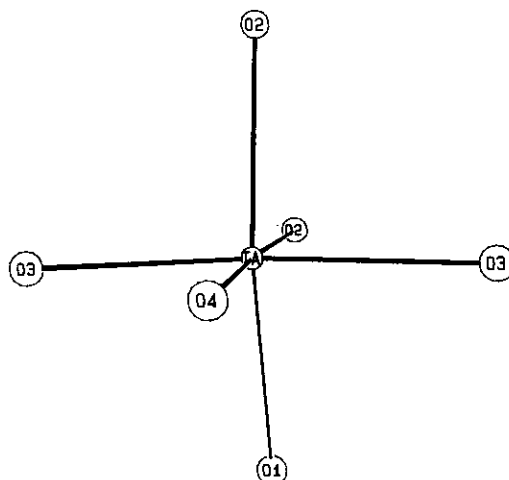


FIG. 3. Coordination of TaO_6 in $\text{Sm}_2\text{Ta}_2\text{Cl}_2\text{O}_7$.

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