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Preparation and Crystal Structure Model of a New Strontium Tantalum Sulfide: $Sr_{17}Ta_{10}S_{42}$

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A new strontium tantalum sulfide, $Sr_{17}Ta_{10}S_{42}$, has been prepared by sulfurization of a mixture of $SrCO_3$ and Ta_2O_5. The electron and powder X-ray diffraction patterns of the compound were indexed on the basis of a rhombohedral cell with hexagonal setting lattice constants of $a = 18.1525(4)$ and $c = 18.6574(4)$ Å. A structure model described in space group $R3$ with additional local symmetry operations is proposed based on the Rietveld analysis of the powder X-ray diffraction intensities.

Introduction

Six compounds have been reported so far in the Ba–Ta–S system (*1–9*). The compounds show surprising variation of compositions and crystal structures. The structures of $BaTaS_3$ (*1–3*), $Ba_3Ta_2S_8$ (*5*), $Ba_{16.5}Ta_9S_{39}$ (*7*), Ba_2TaS_5 (*8*), and $Ba_9Ta_4S_{20}$ (*4, 9*) are related, and the structure of $BaTa_2S_5$ (*6*) has not yet been determined. On the other hand, only one paper has been published so far on the Sr–Ta–S system, Novoselova and Aslanov (*10*), and the detailed data have not yet been reported.

During our search for ternary sulfides in the Sr–Ta–S system, the existence of a new compound of a composition close to $Sr_{17}Ta_{10}S_{42}$ has been revealed.

The present paper describes the preparation and crystal structure model of the new compound.

Experimental

(1) Preparation

The starting materials, $SrCO_3$ (purity 99.9%) and Ta_2O_5 (99.9%), were mixed in the proportion $Sr/(Sr + Ta) = 0.63$. After mixing, they were heated in a furnace at 700°C for 48 hr in an atmosphere of CS_2 carried by N_2 gas.

(2) Analysis

A chemical analysis was performed for Sr, Ta, and S as follows: After calcination at 900°C, the specimen was decomposed under pressure with $HF–H_2SO_4$. The insoluble part containing Sr was removed by filtration, and Ta was determined in the cupferron complex gravimetry after separation through an ion exchange resin from the solution. Sr was determined by the use of both $SrSO_4$ gravimetry for the insoluble part and an ICP–AES (inductively coupled plasma–atomic emission spectroscopy) method for the soluble part. To determine the sulfur content, the specimen was fused with NaOH and Na_2O_2 and then extracted in water. The sulfur content was calculated through the $BaSO_4$ precipitation process.

(3) Diffraction Data and Density

The X-ray and electron diffraction of the specimen was measured to obtain informa-

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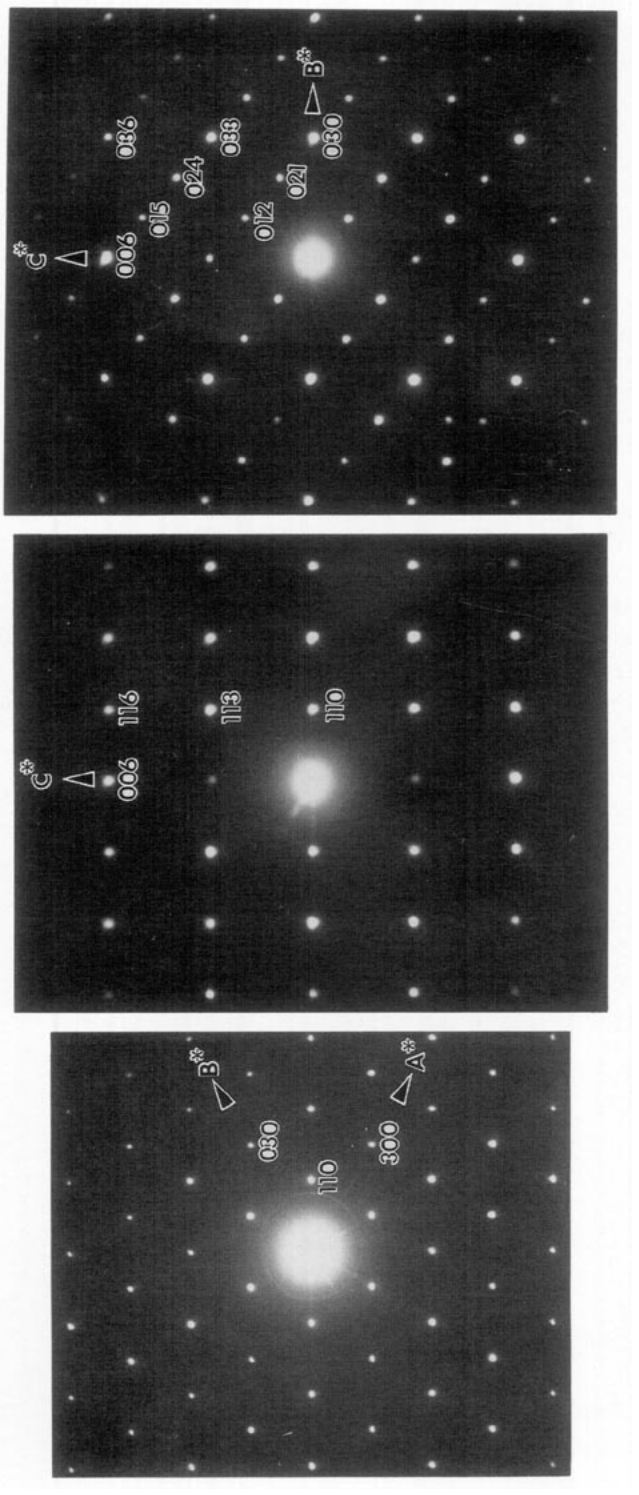

FIG. 1. Electron diffraction patterns of $Sr_{17}Ta_{10}S_{42}$. Indexes (H, K, and L) are based on the trigonal cell (A = 18.1525 and C = 18.6574 Å), and the incident beams are parallel to [0 0 1] (left), [−1 1 0] (center), and [1 0 0] (right) directions. The spots with indexes HKL ($H - K = 3n$) are main spots of the basic structure (hexagonal unit cell: $a = A/\sqrt{3}$, $c = C/3$), while the spots with indexes HKL ($H - K \neq 3n$) are superspots.

tion on the crystal structure. The powder X-ray diffraction data were collected with a stepscan procedure on a Rigaku RAD-2B type diffractometer using counter-side monochromatized Cu$K\alpha$ radiation. Electron diffraction patterns were taken from the crushed particles using 100 kV electron microscope (Hitachi H500 type). Density of the specimen was obtained by measuring buoyancy in carbon tetrachloride at 25°C.

Results and Discussion

A single phase of an unknown compound was obtained when starting cation ratio was Sr/(Sr + Ta) = 0.63. The specimen was contaminated by SrS at any composition richer in Sr than this composition, and contaminated by another ternary sulfide of the Sr–Ta–S system (*11*) if richer in Ta. The compound is dark brown in color and an insulator. It is decomposed slowly by water, evolving into hydrogen sulfide gas. The chemical analysis, repeated four time, yielded the results: 31.7–31.8 wt% for Sr, 38.8–38.9 wt% for Ta, 28.8–29.1 wt% for S. The composition of the compound is estimated to be $Sr_{17}Ta_{10}S_{42}$.

The product was found to be hexagonal with superspots by powder X-ray and electron diffractometry as shown in Figs. 1 and 2. The main reflections were indexed from a hexagonal cell (a = 10.48 and c = 6.22 Å) considered to be compatible with the $L_6B_2C_2S_{14}$-type structure such as $La_6Cu_2Si_2S_{14}$ (*12–19*).

Weak reflections indicating the supercell could be indexed by means of a unit cell ($A = B = a\sqrt{3}$ and $C = 3c$) with the systematic reflection condition $-H + K + L = 3n$. The additional systematic extinction of $L = 6n + 3$ for $00L$ reflections was observed in an electron microscope by tilting the crystal. Taking into account the cell dimension and the symmetry, it is considered that the model shown in Fig. 3 is the most probable one among possible models of order of tantalum vacancies in the $L_6B_2C_2S_{14}$-type structure. The model is rhombohedral and can be described in space group $R3$.

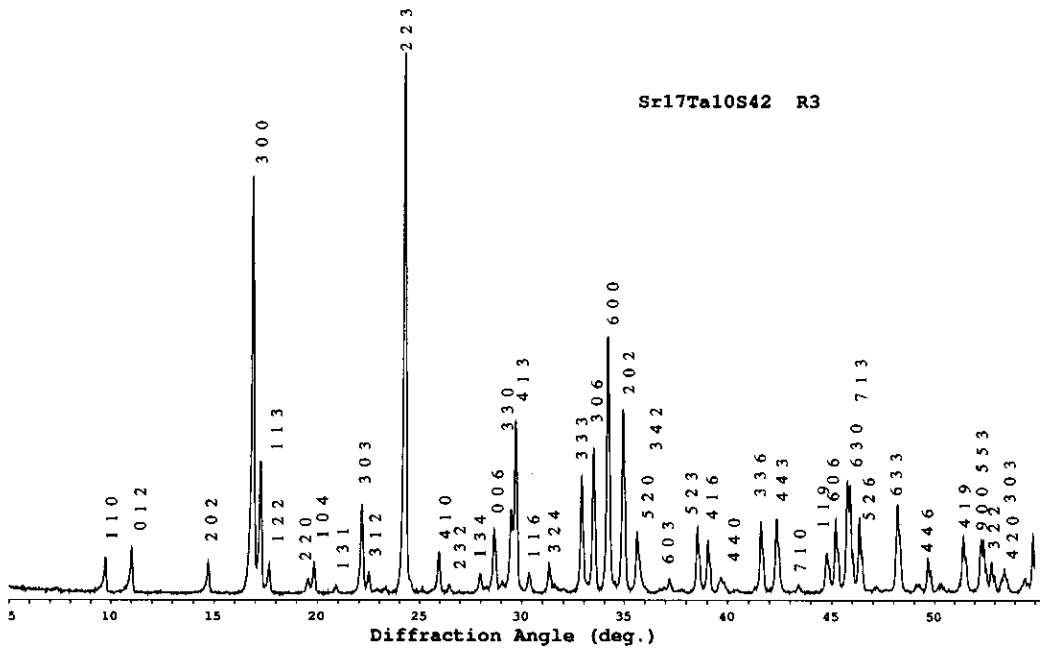

FIG. 2. Powder X-ray diffraction pattern (Cu$K\alpha$) of $Sr_{17}Ta_{10}S_{42}$. Indexes are the same as those of Fig. 1.

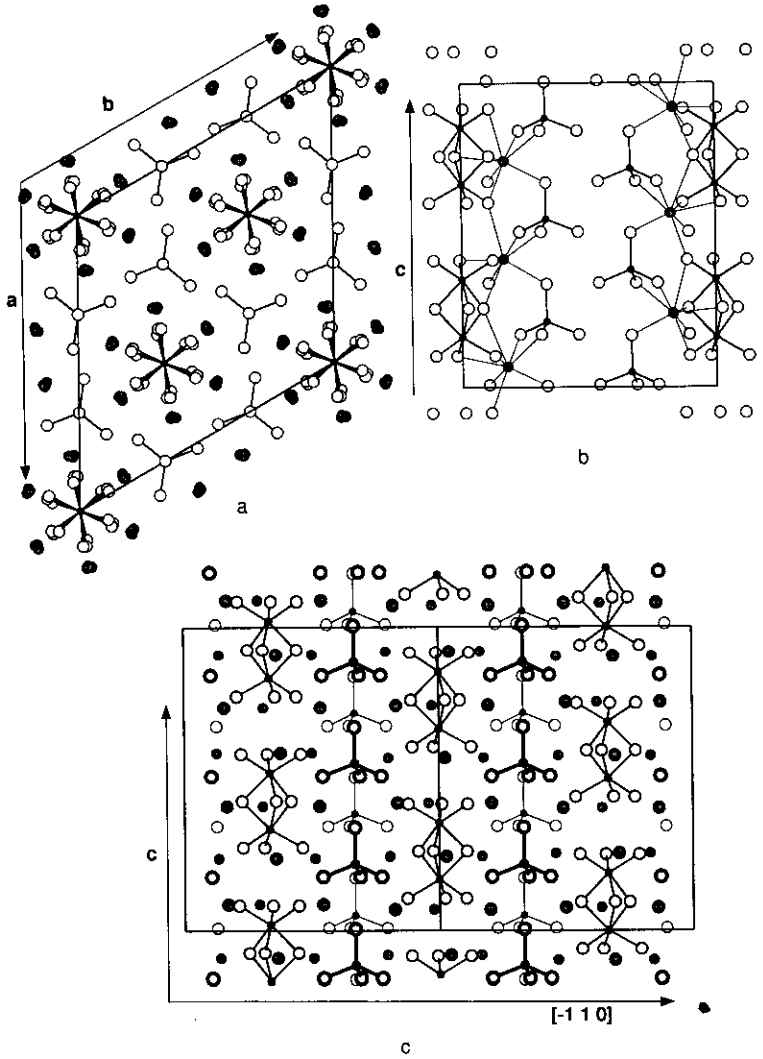

FIG. 3. (a) Projection of the structure model along the c-axis. (b) Bounded projection ($-0.17 < x < 0.17$ for most atoms, $-0.23 < x < 0.23$ for special S atoms) along the a-axis. (c) Bounded projection along [−1 −1 0]. Large open, medium hatched, and small solid circles represent S, Sr, and Ta atoms respectively.

In order to confirm the structure model, the total pattern fit program RIETAN (*20*) based on the Rietveld method (*21*) was used. The existence of Sr vacancies was assumed, because the superstructure model of Fig. 3 may be expressed as $Sr_{18}Ta_4Ta_6S_{42}$-type and the composition of the specimen is close to $Sr_{17}Ta_{10}S_{42}$. In the Rietveld analysis for structures which have large cell dimensions and rather low symmetry, it is considered difficult to achieve smooth convergence of parameters because of overlapping of reflection profiles in the powder X-ray diffraction data. A number of trials were performed using various starting values of parameters for the region from $d = 4.54$ to $d = 1.0$ Å.

The atomic parameters shown in Table I gave the smallest R-factor, that is R_{WP} =

TABLE I

CRYSTAL DATA AND THE STRUCTURE MODEL OF $Sr_{17}Ta_{10}S_{42}$

Crystal data (rhombohedral, space group R3(No.146))
a=18.1525(4)Å, c=18.6576(4)Å, V=5324.25Å^3,
Z=3 (according to the formula $Sr_{17}Ta_{10}S_{42}$)

Atomic parameters [coordinates of equivalent positions:
(0,0,0;2/3,1/3,1/3;1/3,2/3,2/3)+
x,y,z; -y,x-y,z; y-x,-x,z]

Atom[a]	x	y	z	Atom[a]	x	y	z
Sr1	-0.023 (2)	0.177 (2)	0.063 (3)	S1	0.015 (5)	-0.100 (6)	0.104 (4)
Sr2	0.023 (2)	-0.174 (2)	0.250 (2)	S2	-0.020 (6)	0.089 (5)	0.262 (5)
Sr3	-0.045 (2)	0.161 (2)	0.420 (3)	S3	0.008 (4)	-0.113 (5)	0.406 (4)
Sr4	0.033 (2)	-0.167 (3)	0.566 (2)	S4	-0.012 (5)	0.326 (6)	0.347 (3)
Sr5	-0.035 (2)	0.162 (3)	0.744 (3)	S5	0.099 (4)	0.300 (4)	0.165 (4)
Sr6	0.027 (2)	-0.174 (2)	0.907 (3)	S6	0.101 (5)	0.297 (4)	0.508 (4)
Ta1	0.0	0.0	0.1667	S7	0.100 (5)	0.306 (5)	0.837 (4)
Ta2	0.0	0.0	0.354 (3)	S8	-0.028 (4)	0.115 (4)	0.602 (4)
Ta3	0.001 (1)	0.331 (1)	0.217 (2)	S9	0.019 (6)	-0.095 (5)	0.756 (5)
Ta4	0.0	0.0	0.660 (3)	S10	-0.022 (5)	0.095 (6)	0.917 (4)
Ta5	0.0	0.0	0.853 (2)	S11	-0.002 (5)	-0.322 (4)	0.833 (3)
Ta6	0.001 (1)	-0.331 (1)	0.715 (2)	S12	-0.090 (5)	-0.317 (5)	0.684 (4)
				S13	-0.132 (3)	-0.335 (4)	0.015 (4)
				S14	-0.104 (4)	-0.331 (4)	0.332 (4)

Note. B(Sr) = 1.4(2), B(Ta) = 0.93(8), B(S) = 0.2(4) Å^2.
[a]Occupation numbers of Sr, Ta, and S are assumed to be 0.9444, 1.0, and 1.0, respectively.

0.091, R_P = 0.065, R_I = 0.024, and R_F = 0.014. Although the good agreement seems to indicate that the structure model is reliable, there is a fear of excessive parameter shifts in the refinement because of the unfavorable data-to-parameter ratio. In addition, the observed extra rule of extinction for $00L$ indicates that there can be some local symmetry operations. As the crystallographic asymmetric unit contains two units of the same chemical composition, the two units near 0, 0, z were assumed to be linked by $-x$, $-y$, $z + \frac{1}{2}$. Accordingly the local twofold screw axes were assumed to exist at 0, 0, z, $\frac{2}{3}$, $\frac{1}{3}$, z, and $\frac{1}{3}$, $\frac{2}{3}$, z. The Rietveld analysis with the linear constraints expressing the local symmetry operations described above gave a good agreement to the calculated and observed d-spacings (Å) and intensities as shown in Fig. 4 and Table II, that is R_{WP} = 0.101, R_P = 0.073, R_I = 0.033, and R_F = 0.022. The atomic parameters with a significant decrease of the estimated standard deviations were obtained as shown in Table III, and the adopted local symmetry operations seem to have protected the refinement against excessive parameter shifts. The structure model shown in Fig. 3 were

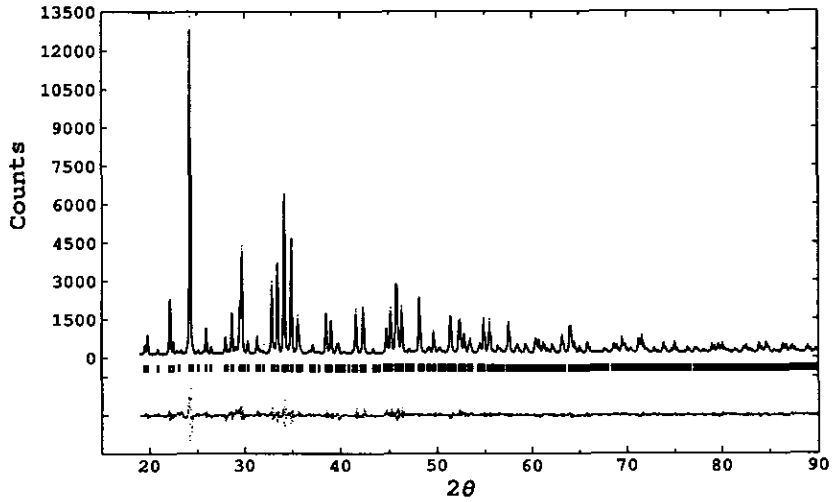

FIG. 4. Observed and calculated X-ray diffraction patterns. The vertical bars show the location of the reflections. The lower solid line represents the difference between the observed and calculated intensities.

actually illustrated from the parameters of Table III.

The density agreed well between experimental (4.31, 4.35, 4.31, 4.37 g cm^{-3}) and theoretical value (4.35 g cm^{-3}) calculated from $Z = 3$ and $V = 5324$ Å^3.

As shown in Fig. 3, four-tenths of Ta atoms are on the ternary axes which overlap with the presumed local twofold screw axes, inside octahedrons of S atoms, and columns of Ta_2S_9 are formed by face-sharing of two octahedrons. Six-tenths of Ta atoms are on the ternary axes, at the center of almost regular tetrahedrons of S atoms. Each Sr atom, with the presumed occupation number 0.9444, is located between rows of Ta_2S_9 columns and TaS_4 tetrahedra, and is coordinated by eight S atoms. Interatomic distances shown in Table IV were calculated from the atomic parameters of Table III. The TaS_6 and TaS_4 polyhedra show few distortions, with Ta–S bond lengths varying between 2.43–2.50 Å for octahedra and of about 2.3 Å for tetrahedra. Sr^{2+} are in a distorted dicapped regional prism and the Sr–S distances are between 2.7–3.9 Å.

Novoselova and Aslanov (*10*) reported the existence of $SrTaS_3$ (orthorhombic, $a = 10.48$, $b = 7.35$, and $c = 11.81$ Å). We, however, found the powder X-ray diffraction pattern of the specimen with starting cation ratio of Sr/Ta = 1.0 could be interpreted as that of the mixture of $Sr_{17}Ta_{10}S_{42}$ and another new ternary sulfide (*11*) of the Sr–Ta–S system.

The formal valence of tantalum in $Sr_{17}Ta_{10}S_{42}$ must be 5+ on the basis of electrical neutrality. Flahaut and Laruelle (*12*) described the rules of substitution on each site of $L_6B_2C_2S_{14}$ as follows: L is always trivalent rare earth, the B atoms inside octahedral cavities have various nature (size, charge, and coordinance) and are often partially empty, the C atoms with tetrahedral coordination have very similar covalent tetrahedral radii of about 1.2 Å, and the anionic and cationic charges are exactly balanced. We were able to obtain a similar sulfide the first time with a divalent alkali earth ion and a 5*a* group transition metal ion, probably because the size of Sr^{2+} is similar to that of the light rare earth ion and the deficiency of cationic charge of Sr^{2+} in the L site can be compensated by the excess charge of Ta^{5+}

TABLE II

INDEXES, CALCULATED, AND OBSERVED VALUES OF d SPACINGS AND INTENSITIES FOR $Sr_{17}Ta_{10}S_{42}$ (a = 18.1525(4) Å, c = 18.6576(4) Å)

H	K	L	d_C	d_O	I_C	I_O	H	K	L	d_C	d_O	I_C	I_O
1	0	1	12.02	12.01	<1	1	5	2	6	1.957	1.957	1	16
1	1	0	9.08	9.08	8	7	2	5	6	1.957		14	
0	1	2	8.02	8.03	9	9	6	3	3	1.887	1.888	8	22
2	0	2	6.01	6.02	8	6	2	2	9	1.886		13	
3	0	0	5.24	5.23	77	77	1	0	10	1.853	1.853	1	3
1	1	3	5.13	5.13	24	24	5	4	4	1.848		1	
1	2	2	5.01	5.01	6	5	4	4	6	1.833	1.834	7	7
2	2	0	4.54	4.54	2	2	2	0	10	1.815	1.813	1	3
1	0	4	4.47	4.47	5	5	0	8	4	1.811		1	
1	3	1	4.25	4.25	1	1	2	1	10	1.780		1	
0	2	4	4.01	4.01	6	16	2	7	4	1.776	1.775	2	15
0	3	3	4.01		11		1	4	9	1.774		4	
3	1	2	3.95	3.95	4	4	4	1	9	1.774		8	
2	1	4	3.67	3.67	13	100	9	0	0	1.747	1.747	10	17
2	2	3	3.67		87		5	5	3	1.743		6	
4	1	0	3.43	3.43	8	8	7	1	6	1.730	1.731	3	7
2	3	2	3.36	3.36	1	1	1	7	6	1.730		4	
1	3	4	3.185	3.186	4	3	1	3	10	1.715		2	
0	0	6	3.110	3.110	13	13	8	1	4	1.712	1.712	3	7
3	3	0	3.025	3.026	14	15	3	3	9	1.710		2	
4	0	4	3.005	3.005	2	33	4	0	10	1.685	1.682	1	4
1	4	3	3.004		21		9	0	3	1.682		2	
4	1	3	3.004		10		6	3	6	1.671	1.671	4	13
1	1	6	2.942	2.943	4	4	3	6	6	1.671		8	
3	2	4	2.853	2.854	5	5	3	2	10	1.657	1.654	2	13
4	2	2	2.830	2.832	1	1	2	8	3	1.654		10	
3	3	3	2.721	2.722	22	23	4	7	0	1.630	1.630	2	3
3	0	6	2.674	2.675	29	29	0	5	10	1.605	1.600	2	13
6	0	0	2.620	2.620	52	54	2	5	9	1.600		7	
2	2	6	2.565	2.566	38	39	5	2	9	1.600		3	
5	2	0	2.517	2.517	12	15	2	4	10	1.580	1.577	2	5
2	4	4	2.506		3		7	4	3	1.577		1	
5	1	4	2.415	2.416	1	2	4	7	3	1.577		1	
2	5	3	2.333	2.334	7	14	5	1	10	1.557	1.556	3	5
5	2	3	2.333		6		0	0	12	1.555		1	
1	4	6	2.304	2.304	9	11	1	1	12	1.532	1.531	2	6
4	1	6	2.304		2		4	4	9	1.530		4	
1	3	7	2.274		1		9	0	6	1.523	1.523	4	5
4	4	0	2.269	2.273	2	5	4	3	10	1.513	1.513	1	5
4	3	4	2.261		2		6	6	0	1.513		3	
3	3	6	2.168	2.169	14	14	10	1	0	1.492	1.493	3	4
1	6	4	2.132	2.133	2	17	3	0	12	1.491		1	
4	4	3	2.132		14		2	2	12	1.471	1.470	2	8
7	1	0	2.082	2.083	2	1	9	2	4	1.470		1	
3	5	4	2.023	2.023	5	9	7	1	9	1.469		2	
1	1	9	2.021		5		1	7	9	1.469		2	
6	0	6	2.004	2.004	15	15	9	3	0	1.453	1.453	10	17
6	3	0	1.981	1.981	23	36	10	1	3	1.451		1	
6	2	4	1.975		3		1	10	3	1.451		6	
7	1	3	1.975		7		7	4	6	1.444	1.444	4	4
1	7	3	1.975		2		4	1	12	1.416	1.418	3	4

in the B and C sites. The exact charge balance is obtained by Ta vacancies favorable to ordering in octahedral sites and a small amount of Sr vacancies.

From the results of the present study, it is concluded that there exists a previously unreported strontium tantalum sulfide whose composition is $Sr_{17}Ta_{10}S_{42}$, and which

TABLE III

ATOMIC PARAMETERS (LOCAL SYMMETRY IS ASSUMED)

Atom[a]	x	y	z	Atom[a]	x	y	z
Sr1	-0.024 (1)	0.177 (1)	0.0697 (9)	S1	0.022 (3)	-0.106 (3)	0.106 (2)
Sr2	0.028 (1)	-0.1677 (9)	0.243 (1)	S2	-0.025 (2)	0.084 (2)	0.260 (3)
Sr3	-0.0425 (8)	0.165 (1)	0.420 (1)	S3	0.010 (3)	-0.112 (3)	0.416 (2)
Sr4	0.024	-0.177	0.5697	S4	0.0	0.3333	0.339 (1)
Sr5	-0.028	0.1677	0.743	S5	0.1052 (6)	0.3125 (7)	0.1759 (7)
Sr6	0.0425	-0.165	0.920	S6	0.1052	0.3125	0.5093
Ta1	0.0	0.0	0.1667	S7	0.1052	0.3125	0.8426
Ta2	0.0	0.0	0.3537 (6)	S8	-0.022	0.106	0.606
Ta3	0.0	0.3333	0.2177 (5)	S9	0.025	-0.084	0.760
Ta4	0.0	0.0	0.6667	S10	-0.010	0.112	0.916
Ta5	0.0	0.0	0.8537	S11	0.0	-0.3333	0.839
Ta6	0.0	-0.3333	0.7177	S12	-0.1052	-0.3125	0.6759
				S13	-0.1052	-0.3125	0.0093
				S14	-0.1052	-0.3125	0.3426

Note. $B(Sr) = 1.3(1)$, $B(Ta) = 1.21(7)$, $B(S) = 1.4(2)$ Å^2.

[a]Occupation numbers of Sr, Ta, and S are assumed to be 0.9444, 1.0, and 1.0, respectively.

TABLE IV

SELECTED INTERATOMIC DISTANCES (Å) (CALCULATED FROM THE PARAMETERS OF TABLE III)

Ta1-S1	3×2.43 (5)	Sr2-S2	2.74 (5)
-S2	3×2.50 (5)	-S2	3.06 (4)
Ta2-S2	3×2.50 (5)	-S3	3.45 (4)
-S3	3×2.43 (4)	-S1	2.82 (4)
Ta3-S4	2.26 (2)	-S11	3.08 (2)
-S5	2.26 (1)	-S12	3.13 (3)
-S6	2.26 (1)	-S14	3.13 (2)
-S7	2.26 (1)	-S5	3.13 (2)
Sr1-S1	2.98 (7)	Sr3-S3	2.75 (4)
-S1	3.20 (4)	-S3	3.27 (7)
-S2	3.93 (5)	-S8	3.71 (4)
-S10	3.15 (4)	-S2	3.41 (5)
-S4	2.91 (2)	-S4	3.14 (2)
-S5	3.11 (2)	-S5	2.85 (3)
-S7	3.16 (3)	-S6	3.16 (2)
-S13	3.12 (2)	-S14	2.99 (2)

crystalizes in rhombohedral with lattice parameters of $a = 18.1525(4)$ and $c = 18.6576(4)$ Å.

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