The Crystal Structure of a New Ternary Metal-Rich Sulfide $Ta_{6.08}Nb_{4.92}S_4$

XIAOQIANG YAO AND HUGO F. FRANZEN

Ames Laboratory–DOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011

The metal-rich sulfide $Ta_{6.08}Nb_{4.92}S_4$ has been prepared by high temperature techniques and characterized by means of X-ray diffraction experiments. It crystallizes in the orthorhombic space group *Pnma* with four formula units in the cell: $a = 3121.00$ (54) pm, $b = 335.07$ (7) pm, and $c = 959.18$ (19) pm. Its structure is similar to that of niobium-rich sulfides, rather than to that of tantalum-rich sulfides. The metal coordinations are capped distorted cubic prisms and the coordinations of sulfur are capped trigonal prisms. © 1990 Academic Press, Inc.

Introduction

Although tantalum and niobium are in the same group in the periodic table, the metal clusters in the binary metal-rich sulfides of tantalum and niobium are totally different. The metal clusters in the tantalum-rich sulfides are unique arrangements of face-sharing pentagonal antiprismatic tantalum columns centered by tantalum (*1–3*). The metal clusters in the niobium-rich sulfides are capped cubes and capped pentagonal prisms (*4, 5*). Ta_2S has been chemically modified by the addition of first-row transition metals. Two kinds of ternary metal-rich sulfides $M_xTa_{6-x}S$ (M = V, Cr; $x \simeq 1$) (*6*) and $M'_2Ta_9S_6$ (M' = Fe, Co, Ni) (*7*) were found.

In this study Ta_2S was modified by the addition of niobium. A new ternary metal-rich sulfide, $Ta_{6.08}Nb_{4.92}S_4$ (*Pnma*, 3121.00 (54), 335.07 (7), 959.18 (19) pm, obtained from indexing of powder pattern), was found.

Experimental Details

A. Samples Preparation and Characterization

Cold pressed samples of Ta_2S prepared from the elements as previously described (*1*) and equimolar amounts of niobium (Alpha Products: Ta M3N8; Nb M2N8; S from Fisher Scientific Co.; lab grade) were arc-melted three times on a water-cooled copper plate with a thoriated nonconsumable tungsten electrode in an argon atmosphere. The sample was subsequently annealed for 10 hr at 1700 K in an inductively heated tungsten crucible. The resultant partially melted sample contained some small needle-like gray crystals in addition to the bulk sample.

An X-ray powder pattern was obtained with a vacuum Guinier camera FR552 (Enraf Nonius, Delft, The Netherlands) using $CuK\alpha_1$ radiation and silicon as an internal standard. The pattern was very diffuse. If this melted sample was inductively an-

nealed again at a slightly lower temperature (1600 K) for 5 hr, the powder pattern could be indexed as two phases, Ta$_{6.1}$Nb$_{4.9}$S$_4$ [3121.00 (54), 335.07 (7), 959.18 (19) pm, *Pnma*] and NbS$_2$ (8), according to the 2θ angles calculated with program POWDER (using data from the structure solution for Ta$_{6.08}$Nb$_{4.92}$S$_4$). The main product was Ta$_{6.08}$ Nb$_{4.92}$S$_4$ in this sample. In the diffuse pattern (only annealed at 1700 K) some reflections of Ta$_{6.08}$Nb$_{4.92}$S$_4$ were also found, and the cell constants were determined to be 3118.90 (1.24), 335.01 (13), and 960.21 (62) pm, respectively. Powder diffraction data for this new compound are presented in Table I. Intensities were calculated using the computer program POWDER. Positional parameters were used from the refined structure.

A crystal from this sample was examined by electron-dispersive analysis by X-rays (EDAX) in a scanning electron microscope, and the composition of this crystal was obtained as follows: S, 27.75 at.%; Nb, 32.24 at.%, and Ta, 40.01 at.% (Ta$_{5.77}$Nb$_{4.65}$S$_4$).

After the structure and composition of Ta$_{6.08}$Nb$_{4.92}$S$_4$ were determined, an attempt was made to synthesize the title compound starting with the elements. A mixture of Ta, Nb, and S ($n_{Ta} = n_{Nb} = n_S \simeq 6:5:4$) was heated at 700 K in a previously out-gassed quartz tube until the yellow color of sulfur disappeared. The temperature was increased to 1050 K and the sample was held at this temperature for 3 days. The mixture was arc-melted and then inductively annealed at 1500 K for 11 hr. The total mass loss after these processes was less than 0.5%. From comparison of the powder pattern of the final product with that of the standard one of Ta$_{6.08}$Nb$_{4.92}$S$_4$ calculated using program POWDER, it is certain that almost all of the sample is Ta$_{6.08}$Nb$_{4.92}$S$_4$.

B. Single-Crystal Data Collection

Some single crystals were selected from the gray product only annealed at 1700 K and examined by single-crystal X-ray diffraction. From the rotation and Weissenberg patterns it was found that there were

TABLE I

POWER DIFFRACTION DATA OF Ta$_{0.68}$Nb$_{4.92}$S$_4$ (CuKα$_1$ RADIATION)

h k l	2θ$_c$	2θ$_0$	I$_c$	I$_0$^{a}	h k l	2θ$_c$	2θ$_0$	I$_c$	I$_0$	h k l	2θ$_c$	2θ$_0$	I$_c$	I$_0$
2 0 0	5.66	5.58	36.7	MS	10 0 3	40.35	40.37	4.2	W	9 1 5	61.75	61.75	2.2	VW
1 0 1	9.64	9.57	9.2	W	10 1 1	40.57	40.61	6.9	MW	14 1 4	63.31	63.35	1.7	VW
2 0 1	10.82	10.74	13.4	M	6 0 4	41.43	41.40	7.5	W	9 2 2	64.72	64.80	6.3	W
3 0 1	12.54	12.48	27.0	MS	5 1 3	41.60	41.60	3.8	VW	6 2 3	65.33	65.37	1.3	VW
4 0 1	14.62	14.60	1.8	VW	11 0 3	42.56	42.45	8.4	W	4 1 6	65.76	65.78	3.8	VW
6 0 2	25.24	25.27	0.7	VW	15 0 1	44.52	44.54	3.2	VW	19 1 2	66.23	66.21	10.3	M
1 0 3	28.03	27.87	0.2	VW	12 0 3	44.89	44.89	13.9	M	8 2 3	67.46	67.46	16.6	M
3 1 1	29.49	29.46	1.0	W	16 0 0	46.52	46.52	3.4	W	16 1 4	67.91	67.91	7.7	W
4 1 1	30.46	30.42	0.6	VW	4 1 4	48.05	48.06	1.6	VW	7 1 6	68.26	68.28	7.6	W
5 1 1	31.68	31.66	5.7	MW	4 0 5	48.85	48.85	2.0	W	9 2 3	68.74	68.74	10.5	M
9 0 2	31.82	31.80	18.4	M	14 0 3	49.82	49.89	0.4	VW	8 1 6	69.38	69.48	8.0	W
1 1 2	32.70	32.68	10.0	M	17 0 1	50.58	50.58	2.9	W	14 1 5	70.54	70.54	5.8	W
2 1 2	33.08	33.05	19.9	MS	15 0 3	52.42	52.40	0.9	VW	17 0 5	71.00	70.95	2.3	VW
10 0 2	34.25	34.23	9.3	M	18 0 1	53.67	53.66	5.1	W	7 2 4	71.86	71.80	1.7	VW
12 0 0	34.45	34.39	0.3	VW	0 2 0	54.74	54.73	29.0	S	15 2 1	73.12	73.11	2.0	VW
7 1 1	34.74	34.74	12.7	M	19 0 1	56.81	56.82	4.5	w	12 2 3	73.39	73.39	8.6	W
8 0 3	36.30	36.29	39.9	S	1 0 6	57.69	57.68	2.8	W	1 2 5	75.30	75.30	6.9	W
8 1 1	36.54	36.53	13.7	M	3 0 6	58.35	58.32	4.9	W	14 2 3	77.14	77.13	0.3	VW
9 0 3	38.26	38.23	22.7	M	20 0 0	59.15	59.17	6.0	W	17 2 1	77.74	77.82	2.3	VW
9 1 1	38.49	38.48	12.2	M	20 0 1	60.01	60.02	2.5	W	22 1 3	79.12	79.07	2.1	VW
1 1 3	39.01	38.98	48.9	S	6 0 6	60.54	60.55	1.9	VW					
10 1 0	39.42	39.38	100.0	VVS	13 1 4	61.18	61.15	1.6	VW					

^{a} V, very; W, weak; M, medium; S, strong.

two kinds of crystals in the sample, $Ta_{6-x}Nb_xS$ (C $2/c$, 1412.14 (1.68), 528.49 (41), 1483.31 (1.82) pm, $\beta = 117.97°$ (5)) and $Ta_{6.08}Nb_{4.92}S_4$.

Intensity data for $Ta_{6.08}Nb_{4.92}S_4$ crystal (0.5 × 0.02 × 0.01 mm) were collected using a RIGAKU AFC6R single-crystal diffractometer and monochromated Mo$K\alpha$ radiation, employing the ω–scan technique up to 60° (2θ). From the total 3473 reflections ($\pm h$, k, l), 929 independent reflections with $F^2 > 3\sigma(F_0^2)$ were obtained and used for structure analysis. The observed intensities were corrected for Lorentz polarization and absorption effects. No remarkable decay was observed during the data collection.

Structure of $Ta_{6.08}Nb_{4.92}S_4$

A. Space Group Determination

From preliminary Weissenberg and rotation photographs the conditions limiting the possible reflections were observed to be as follows: hkl, no conditions; $0kl$, $k + l = 2n$; $h0l$, no conditions; $hk0$, $h = 2n$; $h00$, $h = 2n$; $00l$, $l = 2n$. These conditions indicate two possible space groups, $Pna2_1$ and $Pnma$, differing by a center of symmetry.

B. Structure Determination

This structure was determined using program TEXSAN. First the empirical absorption correction was applied with an absorption coefficient ($\mu(MoK\alpha)$) of 748.02 cm^{-1}. The averaging of all F_0 values of $Ta_{6.08}Nb_{4.92}S_4$ according to $Pnma$ symmetry gave an internal factor $R = 0.164$. Application of the direct method resulted in an electron map containing several strong peaks per asymmetric unit on the $y = 1/4$ section. These peaks were assigned as Ta and the refinement was initiated. After the refinement had converged for this trial structure, a difference Fourier map was calculated. From the difference Fourier map, some

strong peaks were found and they were assigned as Ta. The above processes were then repeated. Finally, 11 metal positions and four sulfur positions were found. The distances and coordination were chemically reasonable, e.g., by comparison with $Nb_{21}S_8$ (4) and $Nb_{14}S_5$ (5).

The occupancies of the Ta positions were then refined. From the occupancies obtained a rough combination of Nb and Ta at each position was assumed and the occupancies for the metal positions were refined by fixing the total occupancy at each position as 1. After this refinement had converged the isotropic temperature factors were refined with a secondary extinction correction applied (second extinction coefficient = $1.22405 × 10^{-7}$).

F_0 values of $Ta_{6.08}Nb_{4.92}S_4$ were corrected for absorption effects with the program DIFABS (9) in the mode that utilizes θ-dependent systematic deviations $|F_0| - |F_c|$. After this correction, the R and R_w dropped from 0.066 and 0.099 to 0.056 and 0.063, respectively, in isotropic refinement. The F_c values which entered into the calculations were obtained from refinement of the positional and isotropic thermal parameters in $Pnma$.

The anisotropic refinement was carried out, but it was not successful since some anisotropic thermal parameters were nonpositive definite. The refinement of the structure is complicated by the fact that the temperature factor at each position correlates with the occupancy of tantalum and niobium at that position.

The occupancy of tantalum and niobium at each metallic position was, therefore, changed arbitrarily to make as many anisotropic temperature factors positive as possible. $R = 0.051$ and $R_w = 0.068$ were finally obtained from the anisotropic refinement with the nonpositive-definite anisotropic temperature factors at the $S1$, $S3$, and $S4$ positions. Information concerning the refinement is in Table II. The final composi-

TABLE II

CRYSTAL DATA FOR $Ta_{6.08}Nb_{4.92}S_4$

Empirical formula	$Ta_{6.08}Nb_{4.92}S_4$
Formula weight	Orthorhombic
Diffractometer	Rigaku AFC6
Space group	*Pnma* (62)
Lattice parameters:	
a, Å	31.210 (5)
b, Å	3.3507 (6)
c, Å	9.592 (2)
V, Å^3	1001 (3)
Z value	4
D_{calcd}	11.14 g/cm^3
F_{000}	2828
μ (MoKα)	748.02 cm^{-1}
Radiation	MoKα (λ = 0.71069 Å), Graphite-monochromated
Temperature	23°C
$2\theta_{max}$	60.2°
No. observations ($I > 3\sigma(I)$)	933
No. variables	92
Residuals: R, R_w	0.051, 0.068
Goodness of fit indicator	1.71
Maximum shift in final cycle	0.01
Largest peak in final diff. map	4.74 e^-/Å^3

TABLE III

POSITIONAL, THERMAL PARAMETERS AND OCCUPANCIES FOR $Ta_{6.08}Nb_{4.92}S_4$

Atom	Occupancy	x	y	z	B_{eq} (Å^2)
$M1$	76% Ta + 24% Nb	0.2177 (1)	1/4	0.5355 (2)	0.27 (7)
$M2$	76% Ta + 24% Nb	0.3268 (1)	1/4	0.8482 (2)	0.24 (7)
$M3$	72% Ta + 28% Nb	0.4247 (1)	1/4	0.7579 (2)	0.32 (7)
$M4$	70% Ta + 30% Nb	0.0254 (1)	1/4	0.0853 (2)	0.26 (7)
$M5$	66% Ta + 34% Nb	0.2357 (1)	1/4	0.2166 (2)	0.27 (7)
$M6$	54% Ta + 46% Nb	0.3401 (1)	1/4	0.1834 (2)	0.31 (8)
$M7$	50% Ta + 50% Nb	0.4207 (1)	1/4	0.4183 (2)	0.30 (8)
$M8$	48% Ta + 52% Nb	0.2150 (1)	1/4	0.8917 (2)	0.32 (8)
$M9$	46% Ta + 54% Nb	0.1350 (1)	1/4	0.1206 (2)	0.28 (8)
$M10$	44% Ta + 56% Nb	0.1102 (1)	1/4	0.4761 (2)	0.30 (9)
$M11$	6% Ta + 94% Nb	0.0233 (1)	1/4	0.7255 (3)	0.4 (1)
$S1$		0.4200 (4)	1/4	0.153 (1)	0.6 (4)
$S2$		0.3044 (4)	1/4	0.580 (1)	0.6 (4)
$S3$		0.1367 (3)	1/4	0.865 (1)	0.3 (3)
$S4$		0.0296 (3)	1/4	0.380 (1)	0.6 (4)

structure factors are available upon request from the authors.

Results and Discussion

tion $Ta_{6.08}Nb_{4.92}S_4$ was obtained from the refinement. The atomic positions, occupancies, and isotropic temperature factors at each position are given in Table III. The failure of anisotropic refinement may have arisen from the quality of the crystal. The powder pattern of the sample from which the crystals were selected was diffuse, i.e., the sample was not well crystallized. Listing of observed and calculated

Figure 1 is the structure of $Ta_{6.08}Nb_{4.92}S_4$. The coordination of the sulfur and metal atoms in this compound is similar to that found in a broad class of transition metal compounds in which atoms are located in mirror planes perpendicular to short (about 3.5 Å) axes. Some examples of compounds belonging to this class are $Nb_{21}S_8$ *(4)*,
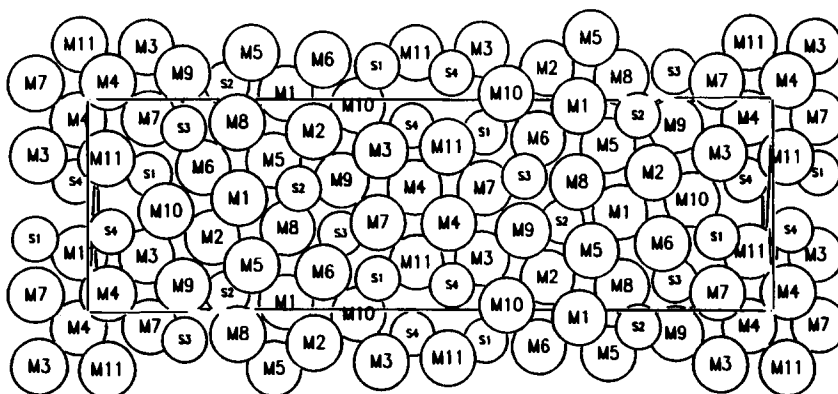

FIG. 1. The crystal structure of $Ta_{6.08}Nb_{4.92}S_4$ viewed along the *b* axis.

$Nb_{14}S_5$ (5), Ti_2S (10), Nb_7P_4 (11), Nb_5P_3 (12), Fe_2P (13), and Co_2P (14). The metallic coordinates are capped, distorted cubic prisms. The coordination of sulfur is a capped trigonal prism. The distorted cubic prisms of M1, M2, and M4 contain only metal atoms. The capping atoms of the distorted cubic prism for M1 are M5, M8, M10, and S2. For other metal positions the distorted cubic prisms are partially substituted by sulfur, so there is more distortion for this kind of distorted cubic prism, e.g., two S4 occupy two corners of the distorted cubic prism for M3.

It is easy to recognize that the coordination of S2 is a bicapped trigonal prism. The coordinations of S1 and S3 are trigonal prisms that are bisected by the mirror plane vertically other than horizontally. The coordination of S4 is interesting and is shown in Fig. 2. The coordination of S4 may be thought of as a trigonal prism on which two of the six corners are missing. This is similar to that of sulfur in Ta_2S (1). The coordination of S4 is the typical case of the lower coordinated sulfur atoms in metal-rich compounds; i.e., there apparently are some structurally significant nonbonding orbitals on S giving rise to an incomplete trigonal prism. It can be seen that these van der Waals interactions lead to a void region surrounded by these atoms.

The shortest metal–metal distance in this compound is 282 pm. There is no doubt that
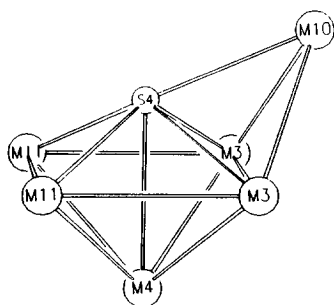

FIG. 2. The coordination of S4 atom.

TABLE IV

INTERATOMIC DISTANCE (pm) FOR $Ta_{6.08}Nb_{4.92}S_4$

Atom	Neighbor		Distance	Atom	Neighbor		Distance
M1	S2		274 (1)	M8	S3		246 (1)
	M5	2×	281.8 (2)		S2	2×	253.5 (8)
	M2	2×	282.1 (2)		M5	2×	282.7 (2)
	M6	2×	284.0 (2)		M1	2×	302.0 (2)
	M8	2×	302.0 (3)		M6	2×	312.4 (2)
	M5		311.0 (3)		M5		318.3 (2)
M2	S2		267 (1)	M9	S3		245.0 (9)
	M1	2×	282.1 (2)		S2	2×	255.6 (9)
	M10	2×	286.1 (3)		M3	2×	283.1 (2)
	M5	2×	286.4 (2)		M2	2×	299.9 (2)
	M9	2×	299.9 (2)		M7	2×	309.8 (2)
	M3		317.7 (3)		M5		327.6 (2)
	M6		324.2 (3)	M10	S1	2×	256.5 (8)
M3	S4	2×	249.2 (8)		S4		268 (1)
	M4	2×	282.4 (2)		M2	2×	286.1 (2)
	M9	2×	283.1 (3)		M3	2×	289.4 (2)
	M10	2×	289.4 (3)		M6	2×	302.8 (2)
	M11		308.0 (4)	M11	S1	2×	253.4 (9)
	M2		317.7 (2)		S4	2×	256.0 (8)
	M7		326.0 (3)		M4	2×	289.9 (3)
M4	M3	2×	282.4 (2)		M7	2×	304.7 (3)
	M4	2×	282.8 (3)		M3		308.0 (4)
	S4		283 (1)	S1	M6		251 (1)
	M7	2×	286.4 (3)		M11	2×	253.4 (8)
	M11	2×	289.9 (3)		M7		254 (1)
	M7		326.7 (3)		M10	2×	256.5 (8)
M5	S2	2×	247.1 (8)	S2	M5	2×	247.1 (8)
	M1	2×	281.8 (2)		M8	2×	253.5 (8)
	M8	2×	282.7 (2)		M9	2×	255.6 (9)
	M2	2×	286.4 (2)		M2		267 (1)
	M1		311.0 (2)		M1		274 (1)
	M8		318.3 (3)	S3	M9		245.0 (9)
	M6		327.3 (3)		M8		246 (1)
	M9		327.6 (3)		M7	2×	250.6 (7)
M6	S1		251 (1)		M6	2×	252.5 (7)
	S3	2×	252.5 (7)	S4	M3	2×	249.2 (8)
	M1	2×	284.0 (2)		M11	2×	256.0 (8)
	M10	2×	302.8 (3)		M10		268 (1)
	M8	2×	312.4 (3)		M4		283 (1)
	M2		324.2 (2)				
	M5		327.3 (3)				
M7	S3	2×	250.6 (8)				
	S1		254 (1)				
	M4	2×	286.4 (2)				
	M11	2×	304.7 (4)				
	M9	2×	309.8 (3)				
	M3		326.0 (2)				
	M4		326.7 (3)				

there are numerous strong metal–metal interactions in this solid. Table IV gives the interatomic distances for $Ta_{6.08}Nb_{4.92}S_4$. If only distances less than 330 pm (for S–S

only distance less than 300 pm) are considered, the metallic coordination number ranges from 9 to 12 and that for sulfur from 6 to 8. This structure provides support for the idea that the average coordination number of sulfur (CN (ave)) decreases with decreasing metal–sulfur ratio. CN (ave) is 8 for $M_xTa_{6-x}S$ (M = V, Cr; $x \simeq 1$), (6), 7 for Ta_6S (2), 6.5 for $Ta_{6.08}Nb_{4.92}S_4$, 4.67 for Ta_2S (1), and 4.50 for $M_2Ta_9S_6$ (M = Fe, Co, Ni) (7), respectively.

In the structures of the tantalum-rich and niobium-rich sulfides there are pentagonal antiprisms or prisms. In the structure of ternary (TaNb)-rich sulfide there are neither pentagonal prisms nor antiprisms. It is surprising that although the molar ratio of tantalum to niobium in this compound is larger than 1, the structure of this compound is more similar to that in the niobium-rich sulfides than to that in the tantalum-rich sulfides; e.g., there is a short axis about 350 pm and the metallic coordinations are distorted cubic prisms. Attempts were made to synthesize $Ta_{11}S_4$ and $Nb_{11}S_4$, but they failed and the products were Ta_6S (3) and Ta_2S (1) in the case of $Ta_{11}S_4$, and $Nb_{21}S_8$ (4) in the case of $Nb_{11}S4$.

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