

Notes

Synthesis and Structure of a New Mixed-metal Disulfide Thiophosphate, $\text{Nb}_{0.44}\text{Ta}_{0.56}\text{PS}_6$

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Group 5 transition metal thiophosphates are known for their low-dimensional structural varieties and interesting anisotropic properties.¹ Especially, tantalum disulfide thiophosphate, TaPS_6 and its derivatives have porous framework structures and have been extensively investigated for potential applications as cathode materials of high energy density secondary batteries.²⁻⁶ To the best of our knowledge, however, the niobium analogue of this phase, NbPS_6 has not been discovered yet. As a result of efforts to find new phases in this family, we were able to prepare a new phase with disordered metals with the halide flux method. Here, we report the synthesis and structure of a new mixed-metal disulfide thiophosphate, $\text{Nb}_{0.44}\text{Ta}_{0.56}\text{PS}_6$.

Crystallographic data for $\text{Nb}_{0.44}\text{Ta}_{0.56}\text{PS}_6$ are given in Table

Table 1. Crystal Data and Structure Refinement for $\text{Nb}_{0.44}\text{Ta}_{0.56}\text{PS}_6$

Empirical formula	$\text{Nb}_{0.44}\text{P S}_6 \text{Ta}_{0.56}$
Formula weight	365.16
Temperature	290(1) K
Wavelength	0.71073 Å (MoK α)
Crystal system	tetragonal
Space group	$I4_1acd$
Unit cell dimensions	$a = 15.944(1) \text{ \AA}$ $c = 13.1857(7) \text{ \AA}$
Volume	$3352.1(3) \text{ \AA}^3$
Z	16
Density (calculated)	2.894 Mg/m^3
Absorption coefficient	9.512 mm^{-1}
Crystal size	$0.35 \times 0.18 \times 0.12 \text{ mm}^3$
Theta range for data collection	3.25 to 27.48°
Index ranges	$-20 \leq h \leq 20, -20 \leq k \leq 19,$ $-15 \leq l \leq 17$
Reflections collected / unique	14798 / 967 [R(int) = 0.0870]
Completeness to theta = 27.49°	99.9 %
Data / restraints / parameters	967 / 0 / 39
Goodness-of-fit on F^2	1.190
Final R index [I > 2sigma(I)]	R1 = 0.0569
Weighted R index (all data)	wR2 = 0.1121
Largest diff. peak and hole	1.857 and -1.467 e/\AA^3

1. Selected interatomic distances and angles are given in Tables 3. The title compound is isostructural with the previously reported TaPS_6 ² and its structure is closely related to those of the quaternary alkali metal thiophosphates such as $\text{K}_{0.38}\text{TaPS}_6$,⁴ $\text{A}_2\text{Nb}_2\text{P}_2\text{S}_{12}$ (A = K, Rb),⁵ $\text{K}_{0.18}\text{TaPS}_6$, $\text{K}_{0.28}\text{TaPS}_6$, and $\text{Rb}_{0.09}\text{TaPS}_6$.⁶ As shown in other group 5 transition metal thiophosphates,⁷ the structure of the title compound is made up of the bicapped trigonal bipyramidal $[\text{M}_2\text{S}_5]$ unit (M = Nb, Ta) and the tetrahedral $[\text{PS}_4]$ group. This structural motif has already been encountered in other group 5 metal (V, Nb, Ta) thiophosphates such as $\text{RbNb}_2\text{PS}_{10}$.⁸ In the title structure, the metal(A) site is occupied

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$).

Atom	Wyckoff Notation	x	y	z	U(eq) [*]
Nb	4e	739(1)	1761(1)	1250	18(1)
Ta	4e	739(1)	1761(1)	1250	18(1)
P	2b	694(2)	0	2500	22(1)
S1	4e	13(2)	319(2)	1255(3)	29(1)
S2	4e	465(2)	2939(2)	2497(2)	23(1)
S3	4e	1469(2)	1067(2)	-190(2)	29(1)

^{*}U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor. The site occupation factor (SOF) of the K site is refined to 0.34

Table 3. Selected Bond Lengths [Å] and Angles [deg] for $\text{Nb}_{0.44}\text{Ta}_{0.56}\text{PS}_6$

M - S3	2.486(2)	M - S1 ⁱ	2.575(2)
M - S3 ⁱ	2.486(2)	M - M ⁱⁱⁱ	3.3321(14)
M - S2	2.534(3)	P - S1	2.033(4)
M - S2 ^t	2.534(3)	P - S1 ^{iv}	2.033(4)
M - S2 ⁱⁱ	2.572(3)	P - S3 ^v	2.038(4)
M - S2 ⁱⁱⁱ	2.572(3)	P - S3 ⁱ	2.038(4)
M - S1	2.575(2)	S2 - S2 ⁱⁱⁱ	2.039(5)
S1 - P - S1 ^{iv}	115.4(3)	S1 - P - S3 ⁱ	101.89(10)
S1 - P - S3 ^v	114.29(12)	S1 ^{iv} - P - S3 ⁱ	114.29(12)
S1 ^{iv} - P - S3 ^v	101.89(10)	S3 ^v - P - S3 ⁱ	109.4(2)

Symmetry codes: (i) $-\bar{y}-1/4, -x+1/4, -z-1/4$; (ii) $\bar{y}-1/4, x-1/4, -z+1/4$; (iii) $-x, -\bar{y}+1/2, z$; (iv) $x, -\bar{y}, -z+1/2$; (v) $-\bar{y}+1/4, x-1/4, z-1/4$.

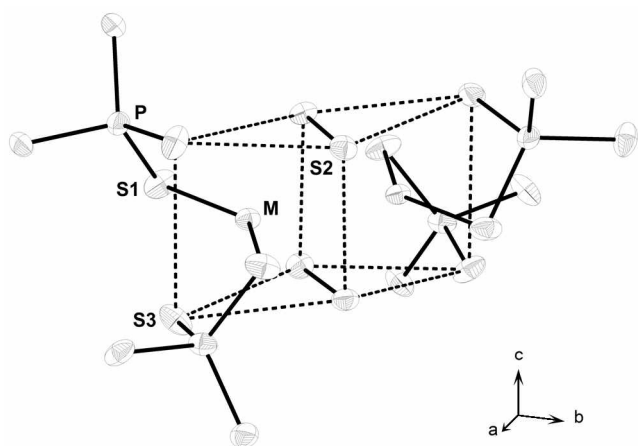


Figure 1. A perspective view of the bicapped trigonal bipyrametric $[M_2S_{12}]$ unit ($M = \text{Nb}$ or Ta) and its neighboring tetrahedral $[PS_4]$ groups. The M-S bonds have been omitted for clarity, except for the capping S atoms. Displacement ellipsoids are drawn at the 60% probability level.

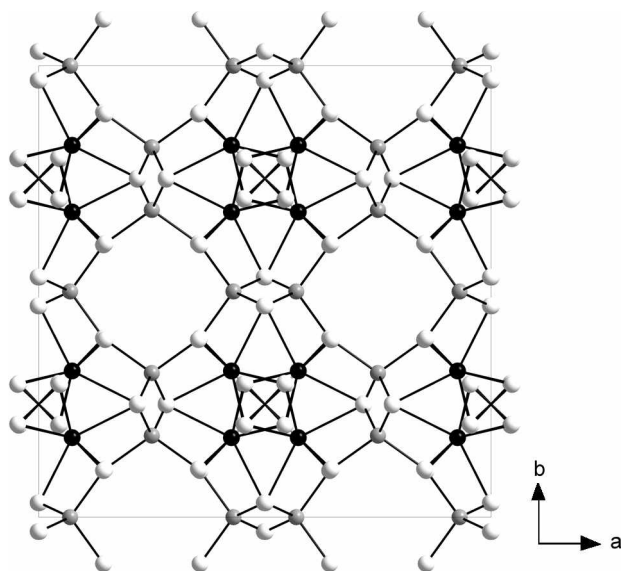


Figure 2. View of $\text{Nb}_{0.44}\text{Ta}_{0.56}\text{PS}_6$ along the c axis, showing the channels along the 4_1 and 4_3 axes. Black, gray, and white circles represent M ($M = \text{Nb}$ or Ta), P and S atoms, respectively.

by statistically disordered Nb (0.44(1)%) and Ta (0.56(1)%) atoms. The metal atom is surrounded by eight S atoms in a bicapped trigonal prismatic arrangement. Two prisms share a rectangular face to form the $[M_2S_{12}]$ unit. This unit shows twofold rotation symmetry. The rotation axis bisects the $(S-S)^{2-}$ side of the rectangular faces shared by each trigonal prism. Each one of the bicapped S atoms and unshared edge S atoms in this unit are bound to the P atom (Figure 1). Additional two S atoms from the neighboring $[M_2S_{12}]$ unit are connected to complete the $[PS_4^{3-}]$ tetrahedral coordination. Each $[M_2S_{12}]$ unit connects four P atoms to build up left- and right-handed helices extended along the 4_1 and 4_3 screw axis.² The helices interwind to each other to form infinite channels along the direction of the c axes (Figure 2).

The diameter of the channel is about 4.7 Å. The M-S distances,

ranging from 2.486(2) to 2.575(2) Å are in agreement with those of the related phases.²⁻⁶ The P-S distances are also in good agreement with the P-S bonding distances found in other thiophosphates.⁷⁻⁸ The intermetallic M...M distance is 3.332(1) Å, which is similar to that of TaPS_6 (3.365(1) Å),² implies that there is no significant M...M interaction. This is much longer than those of the reduced group 5 metals found in the alkali metal group 5 metal disulfide thiophosphates such as $\text{Rb}_{0.46}\text{TaPS}_6$ (3.1011(5) Å).⁴ The short S2-S2 separation (2.039(5) Å) of the rectangular face is typical of $(S-S)^{2-}$ pair.⁹ Consequently, the classical charge balance of the title compound may be represented as $[M^{5+}][P^{5-}][S_2^{2-}]_4[S_2^{2-}]$ and this is consistent with the highly resistive and diamagnetic nature of the compound.

Experimental Section

Synthesis. The title compound, $\text{Nb}_{0.44}\text{Ta}_{0.56}\text{PS}_6$ was obtained from a reaction of Nb (CERAC 99.8%), Ta (CERAC 99.8%), P (CERAC 99.5%), and S (Aldrich 99.999%) in an elemental ratio of 1:1:1:6 in the presence of LiCl as a flux. The mass ratio of reactants and flux was 1:2. The starting materials were placed in a fused-silica tube. The tube was evacuated to 0.133 Pa, sealed, and heated to 873 K at a rate of 15 K/hr, where it was kept for 72 hrs. The tube was cooled at a rate of 5 K/hr to 373 K and the furnace was shut off. Air- and water-stable chunky black crystals were isolated after the flux was removed with water. Qualitative analysis of the crystals with an EDAX-equipped scanning electron microscope indicated the presence of Nb, Ta, P and S. No other element was detected.

X-ray Crystallography. The crystal structure of $\text{Nb}_{0.44}\text{Ta}_{0.56}\text{PS}_6$ was determined by single-crystal X-ray diffraction methods. Preliminary examination and data collection were performed on a Rigaku Rapid R-axis diffractometer equipped with graphite-monochromatized MoK_α radiation ($\lambda = 0.7107$ Å). Cell constants and an orientation matrix for data collection were obtained from the least-squares analysis, using the setting angles of 3442 reflections in the range $6.2^\circ < 2\theta(\text{MoK}_\alpha) < 55.0^\circ$. Intensity data for the title compound were collected at 290(1) K with the ω scan technique. Additional crystallographic details are described in Table 1. The observed Laue symmetry and the reflection conditions ($hkl: h+k+l = 2n, hk0: h, k = 2n, 0kl: k, l = 2n, 00l: l = 4n, hh0: h = 2n$) were indicative of the tetragonal space group $I4_1/acd$ (No. 142). The initial positions for all atoms were obtained by using direct methods of the SHELXS-86 program.¹⁰ The structure was refined by full-matrix least-squares techniques with the use of the SHELXL-97 program.¹⁰ The program *STRUCTURE TIDY* was used to standardize the cell parameters and the positional parameters.¹¹

The disordered nature of the metals in the title compound was checked by refining the anisotropic displacement parameters (ADPs). When the structure was refined with the use of the TaPS_6 and NbPS_6 models, the displacement parameters of the metal sites were very large and small, respectively. In both cases the reliability indices were high ($wR2 > 0.025$). With the mixed-metal model, the ADPs of the metal atom are comparable with those of the other atoms and the residuals was reduced

significantly ($wR2 = 0.112$).

With the composition established the data for the compound were corrected for absorption with the use of the numerical methods.¹² All ADPs were refined anisotropically. The final cycle of refinement performed on F_o^2 with 2803 unique reflections afforded residuals $wR2 = 0.112$ and conventional R1 index based on the reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.057. A difference Fourier synthesis calculated with phase based on the final parameters shows that the highest residual electron density ($1.86 e/\text{\AA}^3$) is 1.00 Å from the Ta site and the deepest hole ($-1.47 e/\text{\AA}^3$) is 0.86 Å from the Ta site. No unusual trends were found in the goodness of fit as a function of F_o , $\sin\theta/\lambda$ and Miller indices. Final values of the atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. No additional symmetry, as tested by *PLATON*¹³ was detected in this structure.

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