Notes

Synthesis and Structure of a New Mixed-metal Disulfide Thiophosphate, $Nb_{0.44}Ta_{0.56}PS_6$

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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, $Nb_{0.44}Ta_{0.56}PS_6$.

Crystallographic data for $Nb_{0.44}Ta_{0.56}PS_6$ are given in Table 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 $K_{0.38}TaPS_6$,[4] $A_2Nb_2P_2S_{12}$ (A = K, Rb),[5] $K_{0.18}TaPS_6$, $K_{0.28}TaPS_6$, and $Rb_{0.09}TaPS_6$.[6] As shown in other group 5 transition metal thiophosphates,[7] the structure of the title compound is made up of the bicapped trigonal biprismatic $[M_2S_{12}]$ unit (M = Nb, Ta) and the tetrahedral $[PS_4]$ group. This structural motif has already been encountered in other group 5 metal (V, Nb, Ta) thiophosphates such as $RbNb_2PS_{10}$.[8] In the title structure, the metal(*M*) site is occupied

Table 1. Crystal Data and Structure Refinement for $Nb_{0.44}Ta_{0.56}PS_6$

Empirical formula	$Nb_{0.44}P\ S_6\ Ta_{0.56}$
Formula weight	365.16
Temperature	290(1) K
Wavelength	0.71073 Å (MoK_α)
Crystal system	tetragonal
Space group	$I4_1/acd$
Unit cell dimensions	a = 15.944 (1) Å
	c = 13.1857(7) Å
Volume	3352.1(3) $Å^3$
Z	16
Density (calculated)	2.894 Mg/m^3
Absorption coefficient	9.512 mm-1
Crystal size	0.35 × 0.18 × 0.12 mm^3
Theta range for data collection	3.25 to 27.48°.
Index ranges	$-20 \le h \le 20$, $-20 \le k \le 19$,
	$-15 \le l \le 17$
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/$Å^3$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$).

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 $Nb_{0.44}Ta_{0.56}PS_6$

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 − $S2^{i}$	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) $-y+1/4, -x+1/4, -z+1/4$; (ii) $y-1/4, x+1/4, -z+1/4$; (iii) $-x, -y+1/2, z$; (iv) $x, -y, -z+1/2$; (v) $-y+1/4, x-1/4, z+1/4$.

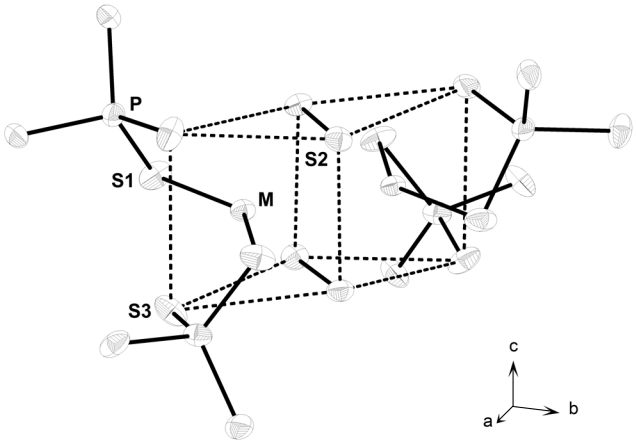

Figure 1. A perspective view of the bicapped trigonal biprismatic $[M_2S_{12}]$ unit (M = Nb or Ta) and its neighboring tetrahedral $[PS_4]$ groups. The M-S bonds have been omitted for clarity, except for the capping S atoms. Displacement ellipsoids are drawn at the 60% probability level.

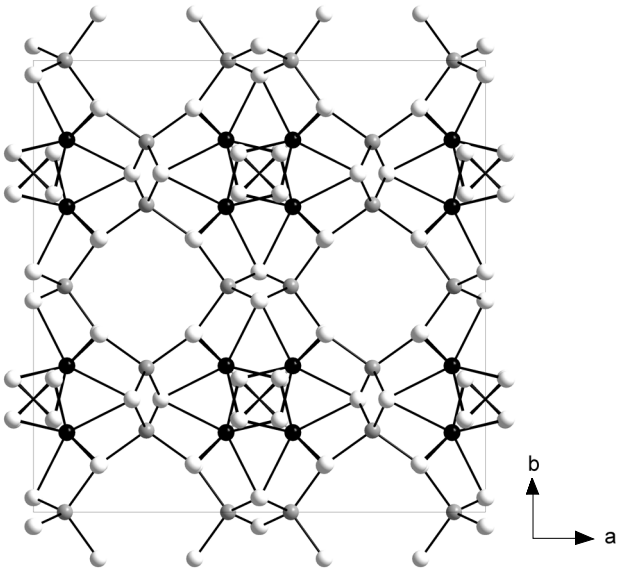

Figure 2. View of $Nb_{0.44}Ta_{0.56}PS_6$ along the c axis, showing the channels along the 4_1 and 4_3 axes. Black, gray, and white circles represent M (M=Nb or Ta), P and S atoms, respectively.

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 $(S\text{-}S)^{2-}$ 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 $Rb_{0.46}TaPS_6$, (3.1011(5) Å).[4] The short S2-S2 separation (2.039(5) Å) of the rectangular face is typical of $(S\text{-}S)^{2-}$ pair.[9] Consequently, the classical charge balance of the title compound may be represented as $[M^{5+}][P^{5+}][S^{2-}]_4[S_2^{2-}]$ and this is consistent with the highly resistive and diamagnetic nature of the compound.

Experimental Section

Synthesis. The title compound, $Nb_{0.44}Ta_{0.56}PS_6$ 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 $Nb_{0.44}Ta_{0.56}PS_6$ 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 (λ = 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 $6.2^\circ < 2\theta(MoK_\alpha) < 55.0^\circ$. 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/Å^3) is 1.00 Å from the Ta site and the deepest hole (-1.47e/Å^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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References

1. Rouxel, J. *J. Solid State Chem.* **1986**, *64*, 305.
2. (a) Fiechter, S.; Kuhs, W. F.; Nitsche, R. *Acta Cryst.* **1980**, *B36*, 2217. (b) Do, J. *M. S. Thesis*; Ajou University, 1995.
3. Evain, M.; Brec, R.; Whangbo, M. H. *J. Solid State Chem.* **1987**, *71*, 244.
4. Gutzmann, A.; Näther, C.; Bensch, W. *Solid State Sci.* **2004**, *6*, 1155.
5. Gieck, C.; Derstroff, V.; Block, T.; Felser, C.; Regelsky, G.; Jepsen, O.; Ksenofontov, V.; Gütlich, P.; Eckert, H.; Tremel, W. *Chem. Eur. J.* **2004**, *10*, 382.
6. Do, J.; Dong, Y.; Kim, J.; Hahn, S.; Yun, H. *Bull. Kor. Chem. Soc.* **2005**, *26*(8), 1260.
7. Yun, H.; Ryu, G.; Lee, S.; Hoffmann, R. *Inorg. Chem.* **2003**, *42*, 2253.
8. Kim, C.; Yun, H. *Acta Crystallogr.* **2002**, *C58*, i53.
9. (a) Kwak, J.; Kim, C.; Yun, H.; Do, J. *Bull. Kor. Chem. Soc.* **2007**, *28*(4), 701. (b) Kwak, J.; Yun, H. *Bull. Kor. Chem. Soc.* **2008**, *29*(1), 273.
10. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.
11 Gelato, L. M.; Parthé, E. *J. Appl. Cryst.* **1987**, *20*, 139.
12. Higashi, T. *NUMABS*; Rigaku Corporation: Japan, 2000.
13. Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7.