

Synthesis and Structure of a New Layered Thiophosphate, $K_{0.34}Cu_{0.5}Nb_2PS_{10}$

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Group 5 transition metal thiophosphates are known for their low-dimensional structural varieties and interesting anisotropic properties.¹ Especially, these low-dimensional compounds have been investigated for potential applications as cathode materials of high energy density secondary lithium batteries.² Consequently, numerous attempts to prepare alkali metal thiophosphates to understand the nature of the intercalation and to analyze their behavior during charge and discharge processes have been tried. To the best of our knowledge, however, no stable product including alkali metals in this system has survived after intercalation/deintercalation processes. This is probably due to the fact that the crystallinity of the host structure cannot be maintained during the diffusion process of alkali metals. We have applied halide flux method to bypass this problem. This technique exploits metal halides both as fluxes and as reactants. The resultant products usually include various alkali metal cations and this technique enabled us to find various chalcogenides³⁻⁹ including the first alkali metal niobium thiophosphates, KNb_2PS_{10} .³ During an effort to expand the range of compounds by substituting monovalent cations such as Cu^+ or Ag^+ , we were able to prepare single crystals of a new derivatives in this thiophosphate system. Here we report the synthesis and characterization of a new layered pentanary thiophosphate, $K_{0.34}Cu_{0.5}Nb_2PS_{10}$.

Crystallographic data and selected interatomic distances and angles for $K_{0.34}Cu_{0.5}Nb_2PS_{10}$ are given in Tables 1 to 3. A view down the b-axis (Figure 1) clearly shows the layered nature of the structure. Figure 2 shows that an individual layer is composed of one-dimensional $\infty^1[Nb_2PS_{10}]$ chains along the [010] direction. This anionic chain is closely related to those of the previously reported group 5 metal thiophosphates, KNb_2PS_{10} ,³ $RbNb_2PS_{10}$,⁴ $AgNb_2PS_{10}$,⁵ $AuNb_4P_2S_{20}$,⁶ $CsNb_2PS_{10}$,⁷ and $NaNb_2PS_{10}$.⁵ Like most of the known niobium thiophosphates, the chains found in $K_{0.34}Cu_{0.5}Nb_2PS_{10}$ are composed of the typical biprismatic $[Nb_2S_{12}]$ and tetrahedral $[PS_4]$ units. The Nb atoms are surrounded by 8 S atoms in a bicapped trigonal prismatic fashion. Two prisms are sharing a rectangular face to form the $[Nb_2S_{12}]$ unit. These units are bound through the S-S prism edges and through one of the capping sulfur atoms to make infinite $\infty^1[Nb_2S_9]$ chains. One of the S atoms at the prism edge and two other capping S atoms are bound to the P atom and an additional S atom is attached to the P atom to complete the infinite $\infty^1[Nb_2PS_{10}]$ chains. These anionic

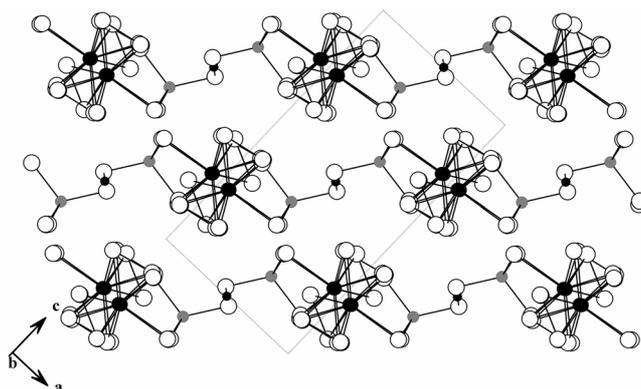


Figure 1. A view of $K_{0.34}Cu_{0.5}Nb_2PS_{10}$ down the b-axis (needle axis) showing the stacking of the layers. Large and small filled circles are Nb and Cu atoms respectively; Small gray circles are P atoms; open circles represent S atoms. K atoms are omitted for clarity.

chains are linked through S-Cu-S bridge to form the two-dimensional layer. These layers then stack on top of each other to complete the three-dimensional structure with an undulating van der Waals gap shown in Figure 1.

The Nb-S distances, ranging from 2.491(2) to 2.621(2) Å are in agreement with those of the related phases.⁴ The P-S distances are also in good agreement with the P-S bonding distances found in other thiophosphates.¹⁰⁻¹³ Atoms S(5) is bonded to Cu atoms and connects the chains and this is responsible for the short P-S(5) distances (1.999(2) Å) and its large atomic displacement parameters. The S(5)-Cu-S(5) linkage is linear and this is typical of coinage metals with coordination number 2.¹⁴

In the arrangement of Nb atoms, Nb(1)⋯Nb(2) interactions alternate in the sequence of one short (2.903(1) Å) and one long (3.728(1) Å). The short distance is close to that of the typical $Nb^{4+}-Nb^{4+}$ bond⁹ and the long Nb⋯Nb distance shows that there is no significant intermetallic bonding interaction and such an arrangement is consistent with the high resistivity of the compound.

There is no bonding interaction, only van der Waals forces, between the layers. Instead, the K^+ cations reside in the van der Waals gap. They are surrounded by nine S atoms if we arbitrarily choose a cutoff of 3.8 Å for the $K\cdots S$. The nonstoichiometry of metal ions in this thiophosphate family is not without precedent. $Ag_{0.87}Nb_2PS_{10}$ has been prepared

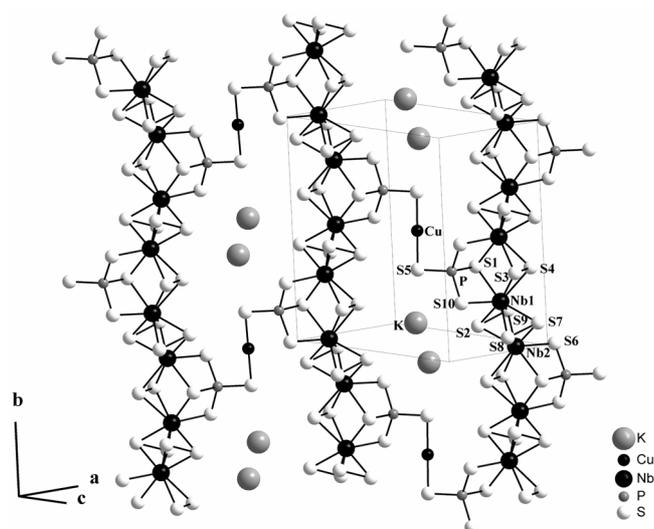


Figure 2. A view of $K_{0.34}Cu_{0.5}Nb_2PS_{10}$ showing an individual layer and coordination around Nb, Cu, and P atoms. Atoms are as marked as in Fig. 1. The K site is occupied by statistically disordered K atoms (SOF = 0.34).

and structurally characterized in our laboratory.¹⁵ Although it is isostructural with stoichiometric $AgNb_2PS_{10}$, our X-ray studies clearly favors the nonstoichiometric model. Considering the cationic vacancies, we concluded that balance of the compound can be represented by $[K^+]_{0.34} [Cu^+]_{0.5} [Nb^{4.08+}]_2 [PS_4^{3-}] [S_2^{2-}]_3$ and this is responsible for the relatively long Nb-Nb bond distance.

Experimental Section

Synthesis. $K_{0.34}Cu_{0.5}Nb_2PS_{10}$ was prepared by the reaction of elements Cu, Nb, P, and S by the reactive halide-flux technique. A combination of Cu powder (Aldrich 99.9%), Nb powder (CERAC 99.8%), P powder (CERAC 99.5%), and S powder (Aldrich 99.999%) were mixed in a fused silica tube in a molar ratio of Cu:Nb:P:S = 1:2:1:10 and then KCl was added in a weight ratio of $CuNb_2PS_{10}:KCl = 1:1$. The tube was evacuated (10^{-2} Torr), sealed, and heated gradually (50 K/h) to 973 K, where it was kept for 96 h. The tube was cooled to room temperature at the rate of 4 K/h. The excess halide was removed with distilled water. Black needle-shaped crystals up to 1.1 mm in length were found. The crystals are stable in air and water. Analysis of this compound with the microprobe of an EDAX-equipped AMRAY 1200C scanning electron microscope indicated the presence of K, Cu, Nb, P, and S. No other element was detected.

X-ray Crystallography. The crystal structures of $K_{0.34}Cu_{0.5}Nb_2PS_{10}$ 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 $MoK\alpha$ radiation ($\lambda = 0.7107$). Cell constants and an orientation matrix for data collection were obtained from the least-squares analysis, using the setting angles of 7096 reflections in the range

Table 1. Crystal Data and Structure Refinement for $K_{0.34}Cu_{0.5}Nb_2PS_{10}$

Empirical formula	$K_{0.34}Cu_{0.5}Nb_2PS_{10}$
Formula weight	582.65
Temperature	295(2) K
Wavelength	0.71073 Å (MoK α)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 7.1829(5)$ Å $b = 12.9234(8)$ Å $\beta = 90.255(2)^\circ$ $c = 13.5346(9)$ Å
Volume	$1256.36(15)$ Å ³
Z	4
Density (calculated)	3.080 Mg/m ³
Absorption coefficient	4.503 mm ⁻¹
Crystal size	0.60 × 0.03 × 0.03 mm ³
Theta range for data collection	3.0 to 27.45°
Index ranges	$-9 \leq h \leq 9, -15 \leq k \leq 16, -16 \leq l \leq 17$
Reflections collected / unique	11300 / 2830 [R(int) = 0.0536]
Data / restraints / parameters	2830 / 0 / 134
Goodness-of-fit on F ²	1.086
Final R index [I > 2sigma(I)]	R1 = 0.046
Weighted R index (all data)	wR2 = 0.099
Largest diff. peak and hole	2.164 and -1.145 e/Å ³

$6.0^\circ < 2\theta(MoK\alpha) < 55.0^\circ$. Intensity data for the title compound were collected at 295(2) K with the ω scan technique. Additional crystallographic details are described in Table 1. The observed Laue symmetry and the systematic extinction ($h0l: k + l = 2n + 1, 0k0: k = 2n + 1$) were indicative of the monoclinic space group $P2_1/c$. The initial positions for all atoms were obtained by using direct methods of the SHELXS-86 program.¹⁶ The structure was refined by full-matrix least-

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

Atom	Wyckoff Notation	x	y	z	U(eq) [*]
K ^{**}	4e	953(9)	851(6)	4651(5)	58(3)
Cu	2b	5000	5000	5000	89(1)
Nb(1)	4e	9285(1)	1761(1)	7496(1)	13(1)
Nb(2)	4e	641(1)	9645(1)	7471(1)	15(1)
P	4e	6104(2)	3243(1)	6426(1)	18(1)
S(1)	4e	8967(2)	3217(1)	6168(1)	16(1)
S(2)	4e	9066(2)	543(1)	6067(1)	21(1)
S(3)	4e	8879(2)	3181(1)	8798(1)	20(1)
S(4)	4e	1465(2)	3181(1)	8155(1)	20(1)
S(5)	4e	4561(3)	3311(1)	5195(1)	29(1)
S(6)	4e	4197(2)	9547(1)	7723(1)	23(1)
S(7)	4e	787(2)	837(1)	8916(1)	20(1)
S(8)	4e	8174(2)	329(1)	8586(1)	20(1)
S(9)	4e	1697(2)	1072(1)	6339(1)	22(1)
S(10)	4e	5718(2)	1918(1)	7217(1)	23(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 $K_{0.34}Cu_{0.5}Nb_2PS_{10}$

Nb(1)-S(2)	2.4979(17)	Nb(2)-S(4)	2.5638(17)
Nb(1)-S(8)	2.4994(17)	Nb(2)-S(6)	2.5788(18)
Nb(1)-S(7)	2.5028(17)	Nb(2)-S(3)	2.5802(17)
Nb(1)-S(9)	2.5048(18)	Nb(2)-S(1)	2.6213(16)
Nb(1)-S(3)	2.5620(17)	Cu-S(5)	2.2213(18)
Nb(1)-S(4)	2.5698(17)	P-S(5)	1.999(2)
Nb(1)-S(10)	2.5959(18)	P-S(10)	2.040(2)
Nb(1)-S(1)	2.6122(16)	P-S(6)	2.052(2)
Nb(1)-Nb(2)	2.9026(8)	P-S(1)	2.088(2)
Nb(2)-S(7)	2.4912(17)	S(2)-S(9)	2.041(2)
Nb(2)-S(2)	2.4938(17)	S(3)-S(4)	2.055(2)
Nb(2)-S(8)	2.4938(18)	S(7)-S(8)	2.037(2)
Nb(2)-S(9)	2.5176(17)		
S(5)-P-S(1)	113.47(11)	S(5)-Cu-S(5)	180.00(10)
S(5)-P-S(6)	111.84(10)		
S(10)-P-S(6)	112.35(11)		
S(5)-P-S(1)	113.82(11)		
S(10)-P-S(1)	102.16(10)		
S(6)-P-S(1)	102.33(10)		

squares techniques with the use of the SHELXL-97 program.¹⁷

Refinement went smoothly ($wR2 = 0.137$, $R1 = 0.076$) but the anisotropic displacement parameters (ADPs) of the K atom were large compared with those of the other atoms. Because nonstoichiometry in metal chalcogenides is sometimes observed and the distance between K atoms is too short (2.42(2) Å) if the full occupancy is assumed, the occupancies of each metal atom was checked by refining the site occupation factors (SOFs) and ADPs of K and Cu atoms while those of the other atoms were fixed. With the non-stoichiometric model, the SOF of K was reduced significantly from 1 to 0.34 and the residuals ($wR2 = 0.108$, and $R1 = 0.055$) were also improved. With the composition established the data for the compound were corrected for absorption with the use of the numerical methods.¹⁸ All ADPs were refined anisotropically. The final cycle of refinement per-

formed on F_o^2 with 2803 unique reflections afforded residuals $wR2 = 0.099$ and conventional $R1$ index based on the reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.046. A difference Fourier synthesis calculated with phase based on the final parameters shows that the highest residual electron density (2.164 e/Å³) is 0.01 Å from the K site and the deepest hole (-1.145e/Å³) is 0.77 Å from the K site. No additional symmetry, as tested by PLATON¹⁹ was detected in this structure.

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