

Synthesis and Crystal Structure of a New Pentanary Thiophosphate, $K_{0.5}Ag_{0.5}Nb_2PS_{10}$

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Single crystals of the new pentanary thiophosphate, $K_{0.5}Ag_{0.5}Nb_2PS_{10}$ has been prepared through reactions of the elements with halide fluxes. The structure of $K_{0.5}Ag_{0.5}Nb_2PS_{10}$ has been analyzed by single crystal X-ray diffraction technique. The structure of $K_{0.5}Ag_{0.5}Nb_2PS_{10}$ is made up of one-dimensional $\infty^1[Nb_2PS_{10}]$ chains along the [001] direction and these chains are separated from one another by Ag^+ and disordered K^+ ions. This chain is basically built up from bicapped trigonal prismatic $[Nb_2S_{12}]$ units and tetrahedral $[PS_4]$ groups. The $[Nb_2S_{12}]$ units are connected together to form the linear chain, $\infty^1[Nb_2S_9]$ by sharing the S-S prism edge. Short (2.885(2) Å or 2.888(2) Å) and long (3.743(1) Å) Nb-Nb distances are alternating along the chain, and the S_2^{2-} and S^{2-} anionic species are observed. The distorted octahedral coordination around the Ag^+ ion can be described as [2+4] bonding interaction.

Key Words : Thiophosphate, Crystal structure

Introduction

Due to the low-dimensional structural varieties and interesting anisotropic properties,¹ group 5 transition metal thiophosphates form an interesting class of materials. Especially, these low-dimensional compounds have potential applications as cathode materials for high energy density secondary batteries.² Preparation of the alkali metal thiophosphates is crucial to understand the nature of the intercalation and to analyze their electronic structure. This gives us motivation to insert alkali metals in Nb_2PS_{10} . However, no stable alkali metal intercalated product in Nb-P-S system has been obtained and structurally characterized. This is probably due to the fact that the crystallinity of the host structure is not maintained during the electrochemical insertion procedure. We have applied halide flux method to detour this problem. This technique exploits metal halides as a flux and as a reactant. The resultant products usually include various monovalent cations and this technique enabled us to find the first niobium thiophosphates containing alkali metals, KNb_2PS_{10} .³ Here we describe the synthesis and characterization of a new pentanary thiophosphate, $K_{0.5}Ag_{0.5}Nb_2PS_{10}$.

Experimental Section

Synthesis. The compounds $K_{0.5}Ag_{0.5}Nb_2PS_{10}$ was prepared by the reaction of elemental Nb, P, and S with the use of the reactive halide flux technique. Stoichiometric combinations of the pure elements, Nb powder (CERAC 99.8%), P powder (CERAC 99.5%), and S powder (Aldrich 99.999%) were mixed in quartz tubes with the addition of eutectic mixture of KI/AgI. The mass ratio of reactants and fluxes was 1 : 3. The tubes were evacuated (10^{-2} Torr), sealed, and heated gradually to 1073 K, where they were kept for 72 hrs. The tubes were cooled to room temperature at the rate of 5

K/hr. The excess halide fluxes were removed with distilled water and dark red needle-shaped crystals were obtained. 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, Ag, Nb, P, and S. No other element was detected.

X-ray Crystallography. The crystal structures of $K_{0.5}Ag_{0.5}Nb_2PS_{10}$ was determined by single-crystal X-ray diffraction methods. Preliminary examination and data collection were performed on an MXC³ diffractometer (Mac science) equipped with graphite-monochromatized $MoK\alpha$ 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 24 reflections in the range $20.0^\circ < 2\theta(MoK\alpha) < 28^\circ$ that had been automatically centered. The intensities of some standard reflections measured every 100 reflections and showed no significant deviations during the data collection. Intensity data for the title compound were collected at room temperature with the ω - 2θ scan technique. Additional crystallographic details are described in Table 1.

The space group $P\bar{1}$ was assumed because the distribution of normalized structure factor ($\langle E^2-1 \rangle$) indicates the centrosymmetric space group. The satisfactory refinement confirmed the choice of this space group. The initial positions for all atoms were obtained by using direct methods of the SHELXS-86 program.⁴ The structures were refined by full-matrix least-squares techniques with the use of the SHELXL-97 program.⁵

The very large anisotropic displacement parameters (ADP) for K atoms implied that this site should be disordered. The occupation factor for the K atom was refined to 0.48 and thus it was fixed to 0.5. With the composition established the data for the compound were corrected for absorption with the use of the analytical method of Tompa and de Meulenaer.⁶

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

Formula mass, amu	610.88
Space group	$P\bar{1}$
a , Å	7.017(3)
b , Å	7.119(3)
c , Å	12.926(4)
α , deg.	89.56(3)
β , deg.	76.26(3)
γ , deg.	89.39(3)
V , Å ³	634.2(4)
Z	2
T, K	293(2)
Radiation	graphite monochromated MoK α (λ (K α)=0.7107 Å)
No. of unique data with $F_o^2 > 0$	2651
No. of unique data with $F_o^2 > 2\sigma(F_o^2)$	2060
wR2 ($F_o^2 > 0$)	0.1288
R (on F_o for $F_o^2 > 2\sigma(F_o^2)$)	0.0564
Goodness-of-fit on F^2	1.084
Minimum and Maximum	min. = -1.120
Residual electron density ($e/\text{Å}^3$)	max. = 3.495

All atomic thermal parameters were refined anisotropically. The final cycle of refinement performed on F_o^2 with 2651 unique reflections afforded residuals $wR2 = 0.1288$ and conventional R index based on the reflections having $F_o^2 > 2\sigma(F_o^2)$ is 0.0564. A difference Fourier synthesis calculated with phase based on the final parameters shows no peak heights greater than 3.495 $e/\text{Å}^3$ or lower than -1.120 $e/\text{Å}^3$.

Results and Discussion

The structure of $K_{0.5}Ag_{0.5}Nb_2PS_{10}$ is similar to that of the previously reported KNb_2PS_{10} ,³ $RbNb_2PS_{10}$,⁷ $AgNb_2PS_{10}$, $NaNb_2PS_{10}$ ⁸ and it is closely related to those of the other group 5 metal thiophosphates.⁹⁻¹² It consists of the one-dimensional $\infty^1[Nb_2PS_{10}]$ chains along the [001] direction (Fig. 1), and they are stabilized by K^+ and Ag^+ ions. A projection of the structure of $K_{0.5}Ag_{0.5}Nb_2PS_{10}$ along the c axis is shown in Figure 2. Like most of the group 5 metal thiophosphates, the chain found in $K_{0.5}Ag_{0.5}Nb_2PS_{10}$ has the typical biprismatic $[Nb_2S_{12}]$ units and $[PS_4]$ units. Both Nb1 and Nb2 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 (Fig. 3). This unit is different from those found in ANb_2PS_{10} ($A=K, Rb$)^{3,7} in the arrangement of the $(S-S)^{2-}$ ligands. While the ligands occupy the same sites, an inversion symmetry is found in the title compound, whereas a 2-fold rotation symmetry is found in ANb_2PS_{10} .^{3,7} 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. These chains are linked together by tetrahedral $[PS_4]$ groups.

In the arrangement of Nb atoms, Nb \cdots Nb interactions alternate in the sequence of one short (Nb1-Nb1, 2.885(2) Å

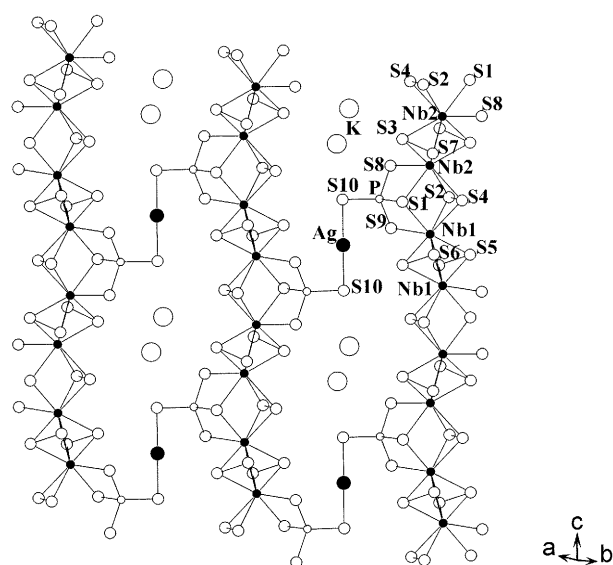


Figure 1. A view of $K_{0.5}Ag_{0.5}Nb_2PS_{10}$ showing an individual layer and coordination around Nb, P, and Ag atoms. The labeling scheme is shown. Large, medium, and small open circles are K, S, and P atoms respectively; large and small filled circles represent Ag and Nb atoms respectively. The K site is occupied by statistically disordered (50%) K atoms.

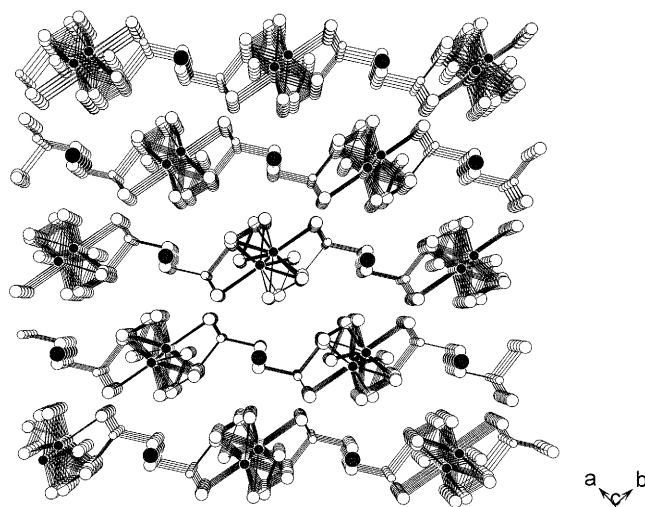


Figure 2. A view of the $K_{0.5}Ag_{0.5}Nb_2PS_{10}$ down the chain axis (c -axis) showing the low-dimensional nature of the compound.

or Nb2-Nb2, 2.888(2) Å) and one long (Nb1-Nb2, 3.743(1) Å). The short distance is typical of Nb⁴⁺-Nb⁴⁺ bonds¹³ and the long Nb1-Nb2 distance shows that there is no significant intermetallic bonding interaction and such an arrangement is consistent with the highly resistive nature of the compound.

The P-S distances in the tetrahedral PS_4 group (1.993(4)-2.083(4) Å) agree well with those found in other related thiophosphates.⁹⁻¹¹ The S10 is the only terminal atom in the compound and this is responsible for the short P-S10 distance (1.993(4) Å) and the large ADP of the S10 atom.³ The infinite chains composed of $[Nb_2S_9]$ chains and $[PS_4]$ units are joined together to form two dimensional layer through the S-Ag-S bridge. The alkali metals reside between

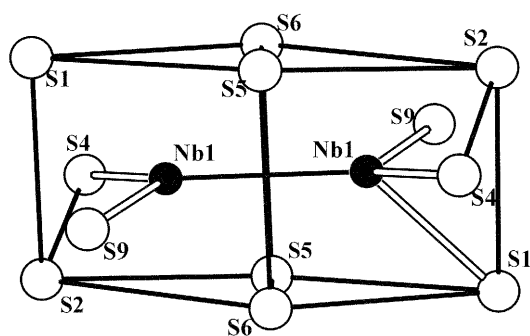


Figure 3. A perspective view of the $[Nb_2S_{12}]$ unit with inversion symmetry. Small filled circles are Nb atoms and large open circles are S atoms. Nb-S bonds are omitted except for the capping S atoms for clarity.

Table 2. Selected Bond Lengths [\AA] and Angles [deg] for $K_{0.5}Ag_{0.5}Nb_2PS_{10}$

Ag-S10	2.470(3)	Ag-S10#3	2.470(3)
Ag-S6#1	3.048(3)	Ag-S6#4	3.048(3)
Ag-S9	3.246(4)	Ag-S9#3	3.246(4)
Nb1-S1	2.623(3)	Nb2-S1	2.621(3)
Nb1-S2	2.574(3)	Nb2-S2	2.587(3)
Nb1-S4	2.570(3)	Nb2-S3	2.496(3)
Nb1-S5	2.499(3)	Nb2-S3#5	2.488(3)
Nb1-S5#2	2.496(3)	Nb2-S4	2.562(3)
Nb1-S6	2.495(3)	Nb2-S7	2.518(3)
Nb1-S6#2	2.492(3)	Nb2-S7#5	2.501(3)
Nb1-S9	2.588(3)	Nb2-S8	2.595(3)
Nb1-Nb1#2	2.885(2)	Nb2-Nb2#5	2.888(2)
P-S1#3	2.083(4)	P-S8#3	2.046(4)
P-S9#3	2.045(4)	P-S10	1.993(4)
S2-S4	2.048(4)	S5-S6	2.037(4)
S3-S7	2.038(5)		
S8#3-P-S1#3	102.31(17)	S9#3-P-S1#3	102.57(17)
S10-P-S1#3	114.2(2)	S9#3-P-S8#3	112.15(19)
S10-P-S8#3	111.9(2)	S10-P-S9#3	112.90(19)
S9-Ag-S9	180.0	S8-Ag-S9	85.60(10)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z$ #2 $-x+1, -y+2, -z$ #3 $-x+2, -y+1, -z$ #4 $x+1, y, z$ #5 $-x+1, -y+2, -z+1$

layers and are surrounded by eight S atoms if we arbitrarily choose a cutoff of 3.6 \AA for the $K \cdots S$. Thus, the classical charge balance of the compound can be represented by $[K^+]_{0.5}[Ag^+]_{0.5}[Nb^{4+}]_2[P^{5+}][S_2^{2-}]_3[S^{2-}]_4$.

The Ag metal is octahedrally coordinated by six S atoms and the coordination around Ag atom can be described as [2+4] bonding interaction. Four S atoms are bound to the Ag atoms in the plane (Ag-S6, 3.048(3) \AA , Ag-S9, 3.246(4) \AA), whereas two trans S atoms are coordinated to the Ag atom (Ag-S10, 2.470(3) \AA). These values are comparable to the sum of the ionic radii of each element, 2.51 \AA for CN=2; 2.99 \AA for CN=6.¹⁴ According to the calculation, tetragonal contraction would be favored for the d^{10} configuration,¹⁵ and their prediction is compatible with our results. In addition, d^{10} metals exhibit large anisotropic displacement parameters. The reason for this large displacement motion could be explained by the second-order Jahn-Teller coupling between the filled e_g manifold and the empty s orbitals.

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