

Insertion of Alkali Metals into Open Framework, TaPS₆ by Using Alkali Metal Halide Fluxes: Single Crystal Structures of K_{0.18}TaPS₆, K_{0.28}TaPS₆, and Rb_{0.09}TaPS₆

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Three new quaternary tantalum thiophosphates, K_{0.18}TaPS₆, K_{0.28}TaPS₆, and Rb_{0.09}TaPS₆ have been synthesized by using reactive alkali metal halide fluxes and structurally characterized by single crystal X-ray diffraction techniques. The crystal structures of K_{0.18}TaPS₆, K_{0.28}TaPS₆, and Rb_{0.09}TaPS₆ contain 3-dimensional open framework anions, [TaPS₆]^{x-} (x = 0.09, 0.18, 0.28) with the empty channel which disordered alkali metal cations, K⁺ and Rb⁺ are located in. Crystal data: K_{0.18}TaPS₆, tetragonal, space group *I4₁/acd* (no. 142), a=15.874(3) Å, c=13.146(4) Å, V=3312.7(12) Å³, K, Z=16, R1=0.0545. Crystal data: K_{0.28}TaPS₆, tetragonal, space group *I4₁/acd* (no. 142), a=15.880(2) Å, c=13.134(3) Å, V=3312.1(10) Å³, Z=16, R1=0.0562. Crystal data: Rb_{0.09}TaPS₆, tetragonal, space group *I4₁/acd* (no. 142), a=15.893(3) Å, c=13.163(4) Å, V=3324.7(15) Å³, Z=16, R1=0.0432.

Key Words : Metal halide fluxes, Chalcogenides, Insertion into open framework

Introduction

Many layered chalcogenide phases such as MQ₂ (M = Ti, Zr, Hf, V, Nb, Ta, Mo, W; Q = S, Se) and MPQ₃ (M = Mg, V, Mn, Fe, Co, Ni, Zn, Cd, In; Q = S, Se) are known to readily intercalate alkali metal cations.^{1,2} These 2-dimensional layered intercalation phases are intensively studied and considered as an important class of solid state materials because of their potential applications in solid electrolytes, sensors, electrochromic displays and batteries.³ In intercalation reactions, the charge transfer from the ionic guest species into the crystalline host lattice is an important phenomenon. Generally, the concentration of cationic guest species is fixed by the chemical composition or can be altered by reduction of the host lattice through electrochemical procedure.⁴

Given the many utility of semiconducting properties and natural fragility of low-dimensional structures such as 2-dimensional layers (upon the insertion/desertion of guest), it is important and useful to expand to new metal chalcogenide phases with rigid 3-dimensional open framework structures. However, to the best our knowledge, such an example has not been reported yet. This is probably due to the fact that the host structure is not retained during the insertion procedure by using traditional synthetic methods. Therefore, new synthetic conditions may be necessary to stabilize compounds with framework structures that cannot be prepared by conventional techniques. To extend this work and obtain solids with alkali metal cations in the 3-dimensional framework lattice, we carried out a synthetic approach using the reactive halide fluxes, Li_xM_yCl_z (M = K, Rb) in molten form as a reaction media to incorporate the alkali metal cations into the structures. We have already demonstrated that the alkali metal halide eutectic mixture

methods represent another direction for the synthesis of novel alkali metal-incorporated chalcogenides.⁵ Examples include several quaternary thiophosphates such as ANb₂PS₁₀ (A=K, Rb, Cs) and ATiPS₅ (A=K, Rb) [5c,d]. Here, we report synthesis and structures of K_{0.18}TaPS₆, K_{0.28}TaPS₆, and Rb_{0.09}TaPS₆ that exhibit the charge transfer of guest atoms and substantial structural modification of the host framework, TaPS₆.⁶

Experimental Section

Alkali metal halide flux synthesis. The title compounds were prepared by the reactions of a 1 : 1 : 6 ratios of the elements Ta powder (Cerac 99.9%), P powder (Cerac 99.5%), and S powder (Aldrich 99.999%) in a eutectic mixture of KCl/LiCl or RbBr/NaBr.

Synthesis of K_{0.18}TaPS₆: The mass ratio of reactants and fluxes was 1.0 : 4.0 for K_{0.18}TaPS₆. The reagent were mixed, sealed in an evacuated silica tube (~10⁻³ torr), and heated at 680, where they were kept for 3 days. The tubes were cooled to at a rate of 6/hr to 300 followed by rapid cooling to room temperature. The solid products were washed with water to remove excess halide fluxes. Product recovery gave black shiny polyhedral crystals of K_{0.18}TaPS₆. Electron microprobe analysis of the crystals gave an average composition of K_{0.15}Ta₁P_{0.98}S_{5.48}. The structural details of the compound were determined by single-crystal X-ray diffraction study. The product slowly decayed in air but is stable in water.

Synthesis of K_{0.28}TaPS₆: The reagent were mixed, sealed in an evacuated silica tube (~10⁻³ torr), and heated at 880 °C, where they were kept for 4 day. The tubes were cooled to at a rate of 6 °C/hr to 300 °C followed by rapid cooling to room temperature. The solid products were washed with water to remove excess halide fluxes. Product recovery gave black

shiny polyhedral crystals of $K_{0.18}TaPS_6$. Electron microprobe analysis of the crystals gave an average composition of $K_{0.22}Ta_1P_{0.92}S_{5.46}$. The structural details of the compound were determined by single-crystal X-ray diffraction study. The product slowly decayed in air but is stable in water.

Synthesis of $Rb_{0.09}TaPS_6$: The mass ratio of reactants and fluxes was 1.0:2.0 for $Rb_{0.09}TaPS_6$. The reagent were mixed, sealed in an evacuated silica tube ($\sim 10^{-3}$ torr), and heated at 700 °C, where they were kept for 7 days. The tubes were cooled to at a rate of 4 °C/hr to room temperature. The solid products were washed with water to remove excess halide fluxes. Product recovery gave black shiny polyhedral crystals of $K_{0.18}TaPS_6$. Electron microprobe analysis of the crystals indicated the presence of Rb, Nb, P, and S. The structural details of the compound were determined by single-crystal X-ray diffraction study. The product slowly decayed in air but is stable in water. For all compounds, no other elements such as halogen atoms and other alkali metals were detected.

Characterization. Elemental analysis on the products was performed with a Hitachi S-2400/Microspec X600 scanning electron microprobe (SEM) equipped with a micro analyzer wavelength dispersive X-ray spectroscopy (WDS) system detector. The samples were analyzed using a 20 kV accelerating voltage and an accumulation time of 30s.

Crystal Structures.

Crystallography of $K_{0.18}TaPS_6$: Of 975 reflections collected in the 2θ range 3.0° - 55.0° using an ω - 2θ scans on an MXC Science MXC³ diffractometer, 877 were unique reflections ($R_{int} = 0.0073$). An analytical absorption correction

using the analytical method ($T_{min} = 0.292$, $T_{max} = 0.356$) was applied.⁷ The structure was solved and refined against F^2 using SHELXS and SHELXL97,^{8,9} 45 variables, $wR2 = 0.1220$ (the 877 unique reflections having $F_o^2 > 0$), $R1 = 0.0545$ (the 822 reflections having $F_o^2 > 2\sigma(F_o^2)$), $GOF = 1.391$, and max/min residual electron density $2.247/-2.418$ eÅ⁻³.

Crystallography of $K_{0.28}TaPS_6$: Of 1120 reflections collected in the 2θ range 3.0° - 55.0° using an ω - 2θ scans on an MXC Science MXC³ diffractometer, 959 were unique reflections ($R_{int} = 0.000$). An analytical absorption correction using the analytical method ($T_{min} = 0.460$, $T_{max} = 0.513$) was applied.⁷ The structure was solved and refined against F^2 using SHELXS and SHELXL97,^{8,9} 44 variables, $wR2 = 0.1003$ (the 959 unique reflections having $F_o^2 > 0$), $R1 = 0.0562$ (the 748 reflections having $F_o^2 > 2\sigma(F_o^2)$), $GOF = 1.374$, and max/min residual electron density $1.465/-2.595$ eÅ⁻³.

Crystallography of $Rb_{0.09}TaPS_6$. Of 964 reflections collected in the 2θ range 3.0° - 55.0° using an ω - 2θ scans on an MXC Science MXC³ diffractometer, 872 were unique reflections ($R_{int} = 0.000$). An analytical absorption correction using the analytical method ($T_{min} = 0.392$, $T_{max} = 0.444$) was applied.⁷ The structure was solved and refined against F^2 using SHELXS and SHELXL97,^{8,9} 45 variables, $wR2 = 0.0836$ (the 872 unique reflections having $F_o^2 > 0$), $R1 = 0.0432$ (the 652 reflections having $F_o^2 > 2\sigma(F_o^2)$), $GOF = 1.200$, and max/min residual electron density $1.600/-1.245$ eÅ⁻³. For all the cases, search for additional potential symmetry with the use of the MISSYM and ADDSYM algorithm in the PLATON program package could not found

Table 1. Crystallographic details for A_xTaPS_6 (A = K, Rb; x = 0.09, 0.18, 0.28)

	$K_{0.18}PS_6Ta$	$K_{0.28}PS_6Ta$	$Rb_{0.09}PS_6Ta$
empirical formula	$K_{0.18}PS_6Ta$	$K_{0.28}PS_6Ta$	$Rb_{0.09}PS_6Ta$
formula weight	411.36	415.27	412.01
crystal system	tetragonal	tetragonal	tetragonal
space group	$I4_1/acd$ (no. 142)	$I4_1/acd$ (no. 142)	$I4_1/acd$ (no. 142)
a, Å	15.874(3)	15.880(2)	15.893(3)
c, Å	13.146(4)	13.134(3)	13.163(4)
V, Å ³	3312.7(12)	3312.1(10)	3324.7(15)
Z	16	16	16
T, K	293(2)	293(2)	293(2)
λ , Å	0.71073	0.71073	0.71073 A
ρ_{calc} , g/cm ³	3.283	3.317	3.292
μ , cm ⁻¹	149.43	150.00	153.47
F(000)	2983	3016	2997
Crystal size, mm ³	$0.7 \times 0.1 \times 0.1$	$0.35 \times 0.1 \times 0.1$	$0.34 \times 0.06 \times 0.06$
measured reflections	907	959	872
independent reflections	877	959	872
2θ range, deg	5.14-54.98	5.14-54.98	5.12-55.0
GOF on F_o^2	1.391	1.374	1.200
R1 [$I > 2\sigma(I)$]	0.0545	0.0562	0.0432
wR2 (all data) ^a	0.1220	0.1003	0.0836
A, B ^d	0.0147, 403.29	0.0045, 243.96	0.0234, 69.29
extinction coefficient	0.00014(2)	n/a	0.00015(2)

$$wR2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]; P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3 \text{ (all data)}$$

the other symmetry in this structure.¹⁰

Results and Discussion

The structures of the compounds are determined by single-crystal X-ray diffraction. Crystallographic details, fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table 1 and 2, respectively. Selected bond distances for all the compounds are listed in Table 3. For $K_{0.18}TaPS_6$, one crystallographically distinct tantalum atom is coordinated by eight sulfur atoms in a distorted bicapped prismatic arrangement with distances ranging from 2.491(4) to 2.564(4) Å. Two Ta_8 bicapped prisms share a common face to form a Ta_2S_{12} dimeric core. Four sulfur atoms sharing rectangular prism faces are in pairs with two disulfide ions, $(S-S)^{2-}$. Each one of the bicapped sulfur atoms and unshared edge sulfur atoms in Ta_2S_{12} unit are bound to phosphorous atoms. Additional two sulfur atoms from neighboring Ta_2S_{12} unit are connected to phosphorous atoms to complete PS_4 tetrahedral coordination. Each Ta_2S_{12} bicapped biprism connects four phosphorous atoms to build up left- and right-handed helices extended along the 4_1 -screw axis, Figure 1. The left- and right-handed helices interwind to each other forming 8-ring channel in the [001] direction counting the number of PS_4 and Ta_2S_{12} units, Figure 2. The free diameter of the channel is about 4.69 Å. Partially filled and heavily disordered alkali metal cations are found in the channel. A similar structural motif of $TaPS_6$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) of A_xTaPS_6 ($A = K, Rb$; $x = 0.09, 0.18, 0.28$). $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(eq)$
$K_{0.18}TaPS_6$				
K	2500	660(2)	0	43(19)
Ta	734(1)	3234(1)	1250	18(1)
P	4303(4)	0	2500	20(1)
S(1)	4535(3)	2946(3)	2494(3)	23(1)
S(2)	3534(3)	3944(3)	190(3)	27(1)
S(3)	-5(3)	325(2)	1256(4)	26(1)
$K_{0.28}TaPS_6$				
K	2500	663(15)	0	95(17)
Ta	727(1)	3227(1)	1250	17(1)
P	4305(3)	0	2500	19(1)
S(1)	4536(2)	2945(2)	2487(3)	21(1)
S(2)	3535(2)	3948(2)	192(3)	23(1)
S(3)	-1(2)	322(2)	1258(2)	24(1)
$Rb_{0.09}TaPS_6$				
Rb	-2500	648(12)	0	50(10)
Ta	743(1)	1757(1)	1250	19(1)
P	2500	1800(3)	0	23(1)
S(1)	8(2)	318(2)	1250(4)	28(1)
S(2)	444(2)	2965(2)	3(2)	24(1)
S(3)	1449(2)	1032(2)	2685(2)	29(1)

Table 3. Selected bond distances [\AA] for A_xTaPS_6 ($A = K, Rb$; $x = 0.09, 0.18, 0.28$)

$K_{0.18}TaPS_6$			
Ta-S(2)#4	2.491(4)	Ta-S(2)#5	2.491(4)
Ta-S(1)#6	2.533(4)	Ta-S(1)#7	2.533(4)
Ta-S(1)#2	2.561(4)	Ta-S(1)#8	2.561(4)
Ta-S(3)#9	2.564(4)	Ta-S(3)#1	2.564(4)
Ta-Ta#9	3.2967(19)		
P-S(3)#10	2.037(6)	P-S(3)#11	2.037(6)
P-S(2)#12	2.040(6)	P-S(2)#3	2.040(6)
S(1)-S(1)#13	2.045(8)		
$K_{0.28}TaPS_6$			
Ta-S(2)#4	2.504(3)	Ta-S(2)#5	2.504(3)
Ta-S(1)#6	2.528(3)	Ta-S(1)#7	2.528(3)
Ta-S(1)#3	2.556(3)	Ta-S(1)#8	2.556(3)
Ta-S(3)#1	2.577(3)	Ta-S(3)#9	2.577(3)
Ta-Ta#9	3.2670(17)		
P-S(3)#10	2.034(4)	P-S(3)#11	2.034(4)
P-S(2)#12	2.048(5)	P-S(2)#2	2.048(5)
S(1)-S(1)#13	2.040(6)		
$Rb_{0.09}TaPS_6$			
Ta-S(3)	2.480(3)	Ta-S(3)#3	2.480(3)
Ta-S(2)#2	2.539(3)	Ta-S(2)#1	2.539(3)
Ta-S(1)	2.568(3)	Ta-S(1)#3	2.568(3)
Ta-S(2)	2.571(3)	Ta-S(2)#3	2.571(3)
Ta-Ta#2	3.3406(14)		
P-S(3)#3	2.041(5)	P-S(3)#4	2.041(5)
P-S(1)#3	2.043(6)	P-S(1)#4	2.043(6)
S(2)-S(2)#2	2.044(6)		

Symmetry transformations for $K_{0.18}TaPS_6$:

- | | |
|-----------------------------------|-----------------------------------|
| #1 $-y + 1/4, -x + 1/4, -z + 1/4$ | #2 $y - 1/4, x - 1/4, z - 1/4$ |
| #3 $-y + 3/4, x - 1/4, -z + 1/4$ | #4 $y - 1/4, -x + 3/4, z + 1/4$ |
| #5 $-x + 1/2, y, -z$ | #6 $-y + 1/4, -x + 3/4, z - 1/4$ |
| #7 $-x + 1/2, -y + 1/2, -z + 1/2$ | #8 $x - 1/2, y, -z + 1/2$ |
| #9 $-x + 0, -y + 1/2, z + 0$ | #10 $x + 1/2, y, -z + 1/2$ |
| #11 $x + 1/2, -y, z$ | #12 $-y + 3/4, -x + 1/4, z + 1/4$ |
| #13 $-x + 1, -y + 1/2, z + 0$ | |

Symmetry transformations for $K_{0.28}TaPS_6$:

- | | |
|-----------------------------------|-----------------------------------|
| #1 $-y + 1/4, -x + 1/4, -z + 1/4$ | #2 $-y + 3/4, x - 1/4, -z + 1/4$ |
| #3 $y - 1/4, x - 1/4, z - 1/4$ | #4 $y - 1/4, -x + 3/4, z + 1/4$ |
| #5 $-x + 1/2, y, -z$ | #6 $-y + 1/4, -x + 3/4, z - 1/4$ |
| #7 $-x + 1/2, -y + 1/2, -z + 1/2$ | #8 $x - 1/2, y, -z + 1/2$ |
| #9 $-x + 0, -y + 1/2, z + 0$ | #10 $x + 1/2, y, -z + 1/2$ |
| #11 $x + 1/2, -y, z$ | #12 $-y + 3/4, -x + 1/4, z + 1/4$ |
| #13 $-x + 1, -y + 1/2, z + 0$ | |

Symmetry transformations for $Rb_{0.09}TaPS_6$:

- | | |
|-----------------------------------|---------------------------------|
| #1 $y - 1/4, x + 1/4, -z + 1/4$ | #2 $-x + 0, -y + 1/2, z +$ |
| #3 $-y + 1/4, -x + 1/4, -z + 1/4$ | #4 $y + 1/4, -x + 1/4, z - 1/4$ |

framework is also observed in $K_{0.28}TaPS_6$, and $Rb_{0.09}TaPS_6$.

The crystal structures of A_xTaPS_6 ($A = K, Rb$; $x = 0.09, 0.18, 0.28$) are closely related to that of a known ternary compound, $TaPS_6$, which contains the same framework structure with empty channels. However, the structural differences between A_xTaPS_6 ($A = K, Rb$; $x = 0.09, 0.18, 0.28$) and $TaPS_6$ are found in intermetallic distances. Ta-Ta interatomic distances in A_xTaPS_6 ($A = K, Rb$; $x = 0.09, 0.18, 0.28$) are shorter than one found in $TaPS_6$ ($d_{Ta-Ta} = 3.365(1)$ Å for $TaPS_6$, 3.341(1) Å for $Rb_{0.09}TaPS_6$, 3.297(2) Å for $K_{0.18}TaPS_6$, and 3.266(2) Å for $K_{0.28}TaPS_6$) and show

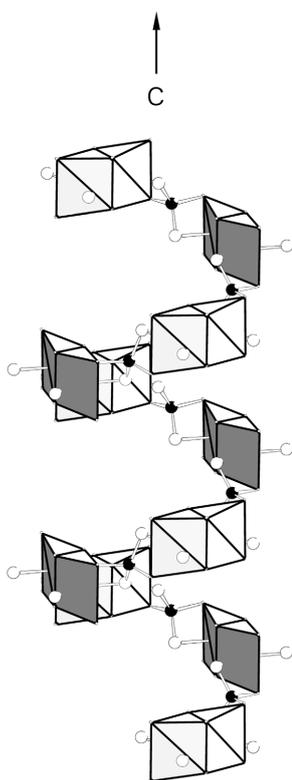


Figure 1. View of a right-handed helix. Ta_2S_{12} bicapped biprismatic units are shown light shaded polyhedra and P and S atoms as filled and open circles, respectively.

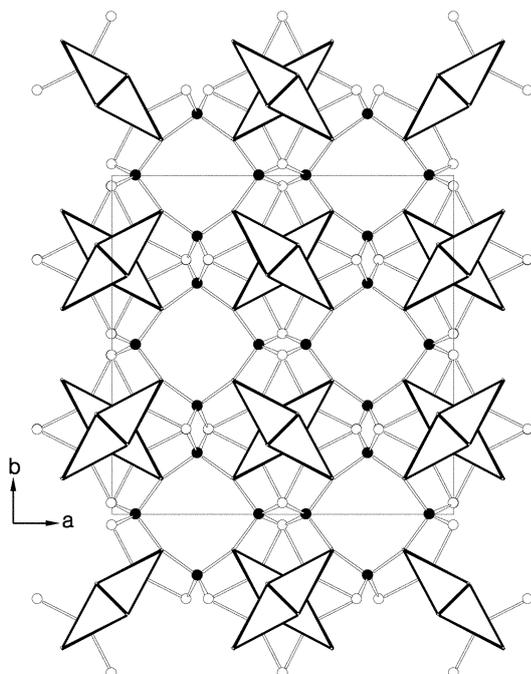


Figure 2. View of A_xTaPS_6 in the [001] direction showing the channels. The Ta_2S_{12} bicapped biprismatic units are shown light shaded polyhedra and P and S atoms as filled and open circles, respectively.

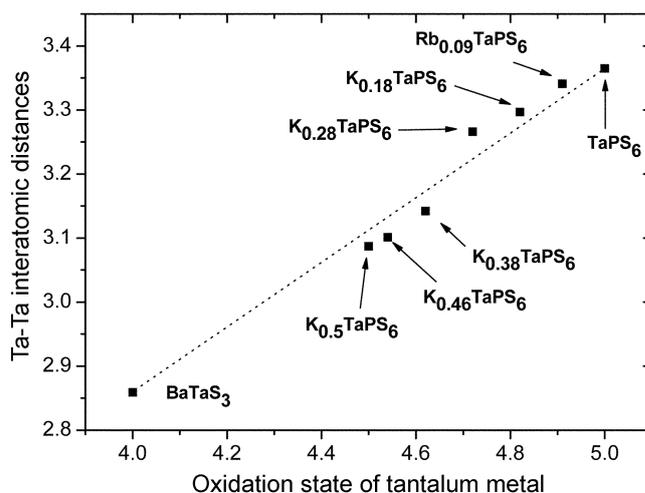


Figure 3. Plots of interatomic distances (Å) and oxidation states for TaPS_6 , $\text{Rb}_{0.09}\text{TaPS}_6$, $\text{K}_{0.18}\text{TaPS}_6$, $\text{K}_{0.28}\text{TaPS}_6$, $\text{K}_{0.38}\text{TaPS}_6$, $\text{K}_{0.46}\text{TaPS}_6$, $\text{K}_{0.5}\text{TaPS}_6$, and BaTaS_3 .

apparent trends. Substantial shortening of Ta-Ta interatomic distances by increasing the concentration of guest ions implies that the electrons released by K or Rb are transferred to pair-wise tantalum metal sites. The concentration of electrons transferred to pair-wise tantalum sites, i.e., reduction quantity of Ta^{5+} to $\text{Ta}^{(5-x)+}$ ($x = 0.09, 0.18, 0.28$), show a good linear relationship between pure Ta^{5+} and Ta^{4+} , Figure 3.

Very recently, two analogues, $\text{K}_{0.38}\text{TaPS}_6$ and $\text{Rb}_{0.46}\text{TaPS}_6$ are synthesized by alkali metal polychalcophosphate fluxes.¹¹ In the structures, Ta-Ta interatomic distances for $\text{K}_{0.38}\text{TaPS}_6$ and $\text{Rb}_{0.46}\text{TaPS}_6$ are 3.142(2) and 3.1011(5) Å, respectively that strongly support the linear relationships of Ta-Ta distances vs. oxidation state of tantalum metals (Figure 3).¹² Also, niobium analogues, $\text{ANb}_2\text{P}_2\text{S}_{12}$ ($A = \text{K, Rb, Cs}$) prepared by alkali metal polychalcophosphate flux methods demonstrate comparable Nb-Nb interatomic distances, 3.087(1) Å for $\text{KNb}_2\text{P}_2\text{S}_{12}$, 3.107(2) Å for $\text{RbNb}_2\text{P}_2\text{S}_{12}$, and 3.117(2) Å for $\text{CsNb}_2\text{P}_2\text{S}_{12}$ (Figure 3, effective ionic radii of Nb and Ta for CN = 8 are same to 0.88 Å).¹³ Note that though the size requirement of alkali metal cations may increase Nb-Nb interatomic distances, the increments are ignorable.

These compounds are also related to $\text{Ta}_4\text{P}_4\text{S}_{29}$, which can be formulated by $\text{Ta}_4\text{P}_4(\text{S}^{2-})_{16}(\text{S}_2^{2-})_4(\text{S}_5^0)$.¹⁴ In $\text{Ta}_4\text{P}_4\text{S}_{29}$, only right handed helices are developed along the c -axis which led to larger channel with free diameter, ~ 9 Å. Infinite sulfur chains are inserted and weakly bound to the channel.

According to previously reported tight-binding band electronic structure calculations on the TaPS_6 based on the crystal structure, the acceptor levels responsible for Li intercalation should be the empty or partially filled d -levels of the metal, and the σ^* antibonding levels of the ligands S_2^{2-} anions lie too high in energy to be good acceptor levels.¹⁵ Therefore, structural studies of A_xTaPS_6 ($A = \text{K, Rb}$; $x = 0.09, 0.18, 0.28$) revealing the reduction sites of tantalum metal for the insertion of K and Rb confirm the calculation

results.

Several other niobium analogues containing NbPS₆ frameworks have been synthesized by using a similar approach. These phases include higher concentration of alkali metals and will be described elsewhere.

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