Structure Modification on Quaternary Rare Earth Thiophosphates: NaYbP$_2$S$_6$, NaSmP$_2$S$_6$, and KSmP$_2$S$_7$

Eun-Young Goh, Eun-Jeong Kim, and Sung-Jin Kim[1]

Department of Chemistry, Ewha Womans University, 120-750 Seoul, Korea

Three rare earth quaternary compounds, NaYbP$_2$S$_6$, NaSmP$_2$S$_6$, and KSmP$_2$S$_7$, are synthesized using alkali metal halide or polychalcogenides flux. NaYbP$_2$S$_6$ was prepared from the stoichiometric reaction of Yb/S/P/NaCl flux at 700°C, and NaSmP$_2$S$_6$ and KSmP$_2$S$_7$ were prepared from Sm/S/P/Na$_2$S (K$_2$S$_x$) flux at 750°C. The structures were determined by the single-crystal X-ray diffraction technique. The air-sensitive dark-red crystals of NaYbP$_2$S$_6$ crystallize in the triclinic space group P-1 with $a = 6.8241(10)$ Å, $b = 7.0371(10)$ Å, $c = 9.107(2)$ Å, $\alpha = 87.17(2)°$, $\beta = 87.62(2)°$, $\gamma = 88.30(2)°$, and $Z = 2$. The yellow plate crystals of NaSmP$_2$S$_6$ crystallize in the monoclinic space group $P2_1/a$ with $a = 11.0717(10)$ Å, $b = 7.2999(1)$ Å, $c = 11.579(3)$ Å, $\beta = 111.30(2)°$, and $Z = 4$. The pale yellow plate crystals of KSmP$_2$S$_7$ crystallize in the monoclinic space group $P2_1/a$ with $a = 8.981(2)$ Å, $b = 12.254(2)$ Å, $c = 9.609(1)$ Å, $\beta = 90.27(2)°$, and $Z = 4$. NaYbP$_2$S$_6$ and NaSmP$_2$S$_6$ are derivatives of the M^IM^{III}P$_2$S$_6$ family. NaYbP$_2$S$_6$ has a flat mono-layered structure, and there are weak interactions between neighboring layers. In NaSmP$_2$S$_6$, two MPS$_3$-type layers are condensed together. The ordering features of sodium and rare earth metal cations in two-dimensional layers are different: Na and Yb atoms are arranged in pairing fashion in NaYbP$_2$S$_6$, while Na and Sm atoms are arranged in a triangular pattern in NaSmP$_2$S$_6$. The structure of KSmP$_2$S$_7$ is similar to that of ABiP$_2$S$_7$ (A = K, Rb), where corrugated layers are formed from Sm^{3+} and [P$_2$S$_7$]$^{4-}$ units. The optically measured band gaps of NaYbP$_2$S$_6$ and NaSmP$_2$S$_6$ are 1.85 eV and 2.54 eV, respectively.

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Key Words: rare earth quaternary; layered structure; NaYbP$_2$S$_6$; NaSmP$_2$S$_6$; KSmP$_2$S$_7$; M^IM^{III}P$_2$S$_6$ family; MPS$_3$ type; polychalcogenides; band gap.

INTRODUCTION

MPS$_3$-type (M = transition metals) transition metal chalcophosphates (1) have been extensively studied because of their interesting structural properties as well as their

potential importance as cathode materials for secondary batteries (2), nonlinear optics (3), and ion-exchange applications (4). The structure of MPS$_3$-type compounds can be described as layered CdCl$_2$ type, where two-thirds of the octahedral sites in alternatively filled anionic layers are occupied by metal ions and the remaining one-third of these are occupied by P$_2$ pairs. The same prototype of MPS$_3$, but with heterocharged metal compounds MM'(P$_2$s$_6$), have stimulated investigation on the ordering feature (coloring problem) of two mixed metals and one-dimensional antiferromagnetism was found to result from such ordering (5). The choice of reaction condition such as basity of flux drives modification of [P$_n$Q$_m$]$^{x-}$ groups (Q = S, Se) other than (P$_2$S$_6$)$^{4-}$; thus, various frameworks other than the MM'(P$_2$S$_6$) family can be produced (6).

Many quaternary transition metal chalcophosphates have been prepared in the past few decades (7, 8), but there has been very limited exploration of the chemistry in the field of rare earth metal chalcophosphates. Examples of known rare earth phosphates include the following: from Brockner and Becker, Eu$_2$P$_2$S$_6$ (9), from Dorhout *et al.*, K(RE)P$_2$Se$_6$ (RE = Y, La, Ce, Pr, Gd) (10), from Chondroudis and Kanatzidis, A_2(RE)P$_2$Se$_7$ (A = Rb, Cs; RE = Ce, Gd) (11), K$_4$Eu(PSe$_4$)$_2$ (12), and Rb$_9$Ce(PSe$_4$)$_4$ (13), and from Jobic *et al.*, K$_3$CeP$_2$S$_8$ (14).

Attempts to synthesize new rare earth metal chalcophosphates resulted in three new phases, NaYbP$_2$S$_6$, NaSmP$_2$S$_6$, and KSmP$_2$S$_7$. In this report, we present the synthesis and structural characterization of these new quaternary thiophosphates.

EXPERIMENTAL SECTION

NaYbP$_2$S$_6$ was prepared from a mixture of Yb chips (2.36 mmol, Aldrich 99.99%), P powder (4.95 mmol, Aldrich 99.99%), and S powder (14.6 mmol, Aldrich 99.999%) in a molar ratio of 1:2.1:6.2 with an excess of NaCl (233 mmol). NaSmP$_2$S$_6$ was prepared from a mixture of Na$_2$S (1.41 mmol, Kojundo 99%), Sm chips (2.17 mmol, Aldrich 99.9%), P powder (4.67 mmol), and S powder

TABLE 1
Crystallographic Data for $NaYbP_2S_6$, $NaSmP_2S_6$, and $KSmP_2S_7$

Empirical formula	$NaYbP_2S_6$	$NaSmP_2S_6$	$KSmP_2S_7$
Formula weight (g mol^{-1})	450.33	427.64	475.81
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/a$	$P2_1/a$
Unit cell dimensions (Å)	$a = 6.8241(10)$	$a = 11.0717(10)$	$a = 8.981(2)$
	$b = 7.0371(10)$	$b = 7.2994(11)$	$b = 12.254(2)$
	$c = 9.107(2)$	$c = 11.579(3)$	$c = 9.6094(10)$
	$\alpha = 87.17(2)°$	$\beta = 111.30(2)°$	$\beta = 90.27(2)°$
	$\beta = 87.62(2)°$		
	$\gamma = 88.30(2)°$		
Volume (Å^3)	436.3(2)	871.9(3)	1057.6(3)
Z	2	4	4
Density (calculated) (g cm^{-3})	3.428	3.26	2.988
Θ range for data collection (deg)	2.24–24.97	1.89–24.95	2.12–24.96
Absorption coefficient (mm^{-1})	6.241	2.125	7.562
Reflection collected	3102 [$R_{int} = 0.0192$]	1726 [$R_{int} = 0.0730$]	2092 [$R_{int} = 0.0269$]
Data/restraints/parameters	1533/0/92	1529/0/92	1854/0/101
Goodness of fit on F^2	1.054	1.093	0.889
R_1 ($F_o > 3\sigma(F_o)$)	1.47%	4.37%	2.42%
WR_2 ($F_o > 0$)	4.17%	12.83%	7.33%

(13.0 mmol) in a molar ratio of 1.3:2:4.3:12. $KSmP_2S_7$ was prepared from a mixture of K_2S_x (1.41 mmol synthesized by stoichiometric reaction in liquid ammonia), Sm chips (2.17 mmol), P powder (4.67 mmol), and S powder (13.0 mmol) in a molar ratio of 1.3:2:4.3:12. The reacting mixture was double-sealed in an evacuated quartz tube and heated at 700°C for 2 weeks for $NaYbP_2S_6$ and at 750°C for 5 days for $NaSmP_2S_6$ and $KSmP_2S_7$. To obtain single crystals with suitable size for the structure determination, the mixtures are heated with a temperature gradient of 50°C and slowly cooled to room temperature.

The reactions led to the formation of dark-red square plate crystals for $NaYbP_2S_6$ and yellow plates for $NaSmP_2S_6$ and $KSmP_2S_7$. $NaYbP_2S_6$ was air and moisture sensitive. However, $NaSmP_2S_6$ and $KSmP_2S_7$ were stable. From the reaction products of $NaSmP_2S_6$ and $KSmP_2S_7$, many crystals with small amounts of yellow-white powder and unreacted Na_2S (K_2S_x in $KSmP_2S_7$) were observed at the hot end and unreacted P and S powder were observed at the cold end. No evidence of side products of ternary or quaternary phases other than $NaYbP_2S_6$, $NaSmP_2S_6$, and $KSmP_2S_7$ were detected. The chemical compositions of the crystals were confirmed by using SEM (Philips XL20) and EDX (PV9900).

Preliminary examination and data collection were performed with Mo $K\alpha_1$ radiation ($\lambda = 0.71073$ Å) on an Enraf Nonius diffractometer (CAD4) equipped with an incident beam monochromator graphite crystal. The unit cell parameters and orientation matrix for data collection were ob-

tained from the least-squares refinement, using the setting angles of 25 reflections in the range of $18° < 2\theta(MoK) < 25°$. The observed Laue symmetry and systematic extinctions ($h00$ and $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$, and $k = 4n + 1$) were indicative of the space group P2$_1$/a for $NaSmP_2S_6$, and $KSmP_2S_7$. The observed Laue symmetry and systematic extinctions for the data of $NaYbP_2S_6$ crystal were indicative of the space group P-1.

Intensity data were collected with the ω–2θ scan technique. The intensities of three standard reflections, measured every hour, showed no significant deviations during the data collection. The initial positions of all atoms were

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Factors $U_{(eq)}$ (Å^2) for $NaYbP_2S_6$

Atoms	x	y	z	$U_{(eq)}$[a]
Na	0.4683(3)	0.3977(3)	0.2677(3)	0.035(1)
Yb	0.0273(1)	0.8814(1)	0.2559(1)	0.013(1)
P1	0.0659(2)	0.6087(2)	0.5645(1)	0.011(1)
P2	0.3500(2)	0.9640(2)	0.9731(1)	0.011(1)
S1	0.6530(2)	0.0268(2)	0.2489(1)	0.016(1)
S2	0.8762(2)	0.5191(2)	0.2402(1)	0.016(1)
S3	0.1464(2)	0.1807(2)	0.4405(1)	0.014(1)
S4	0.2977(2)	0.7041(2)	0.4410(1)	0.014(1)
S5	0.1671(2)	0.1665(2)	0.0575(1)	0.016(1)
S6	0.2971(2)	0.7084(2)	0.0707(1)	0.016(1)

[a] $U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3
Atomic Coordinates and Equivalent Isotropic Displacement Factors $U_{(eq)}$ (Å^2) for NaSmP$_2$S$_6$

Atoms	x	y	z	$U_{(eq)}$[a]
Na	0.3791(5)	0.3910(5)	0.6397(4)	0.032(1)
Sm	0.4094(1)	0.1099(1)	0.1539(1)	0.012(1)
P1	0.7507(2)	0.1145(3)	0.3073(2)	0.011(1)
P2	0.2495(2)	0.1036(2)	0.8232(2)	0.010(1)
S1	0.6615(2)	0.0068(3)	0.4121(2)	0.017(1)
S2	0.1857(2)	0.9803(3)	0.9491(2)	0.014(1)
S3	0.4356(2)	0.1877(3)	0.907(1)	0.013(1)
S4	0.4349(2)	0.2996(3)	0.3809(2)	0.015(1)
S5	0.3667(2)	0.7971(3)	0.2840(2)	0.015(1)
S6	0.1453(2)	0.1853(3)	0.1930(2)	0.014(1)

[a] $U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4
Atomic Coordinates and Equivalent Isotropic Displacement Factors $U_{(eq)}$ (Å^2) for KSmP$_2$S$_7$

Atoms	x	y	z	$U_{(eq)}$[a]
K	0.1320(2)	0.1933(2)	0.6069(2)	0.031(1)
Sm	0.1078(1)	0.8573(1)	0.8566(1)	0.013(1)
P1	0.9776(2)	0.6010(1)	0.7232(2)	0.012(1)
P2	0.1984(2)	0.9635(1)	0.1848(2)	0.012(1)
S1	0.9267(2)	0.6688(1)	0.9096(2)	0.015(1)
S2	0.9294(2)	0.9748(2)	0.6641(2)	0.018(1)
S3	0.1459(2)	0.8056(1)	0.1479(2)	0.017(1)
S4	0.1808(2)	0.0589(1)	0.0136(2)	0.015(1)
S5	0.1124(2)	0.7072(1)	0.6264(2)	0.018(1)
S6	0.2892(2)	0.9446(2)	0.6281(2)	0.019(1)
S7	0.0772(2)	0.4458(1)	0.7515(2)	0.015(1)

[a] $U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

obtained by direct methods from the SHELXS-86 program (15). The structure was refined by full-matrix least-squares techniques with the use of the SHELXL-93 program (16).

Crystallographic data for NaYbP$_2$S$_6$, NaSmP$_2$S$_6$, and KSmP$_2$S$_7$ are given in Table 1. Tables 2–4 list positional parameters and equivalent isotropic thermal parameters for NaYbP$_2$S$_6$, NaSmP$_2$S$_6$, and KSmP$_2$S$_7$, respectively.

Band Gap Measurements

Optical diffuse reflectance measurements were performed at room temperature with a double-beam and double-monochromator spectrophotometer (Shimadzu UV,
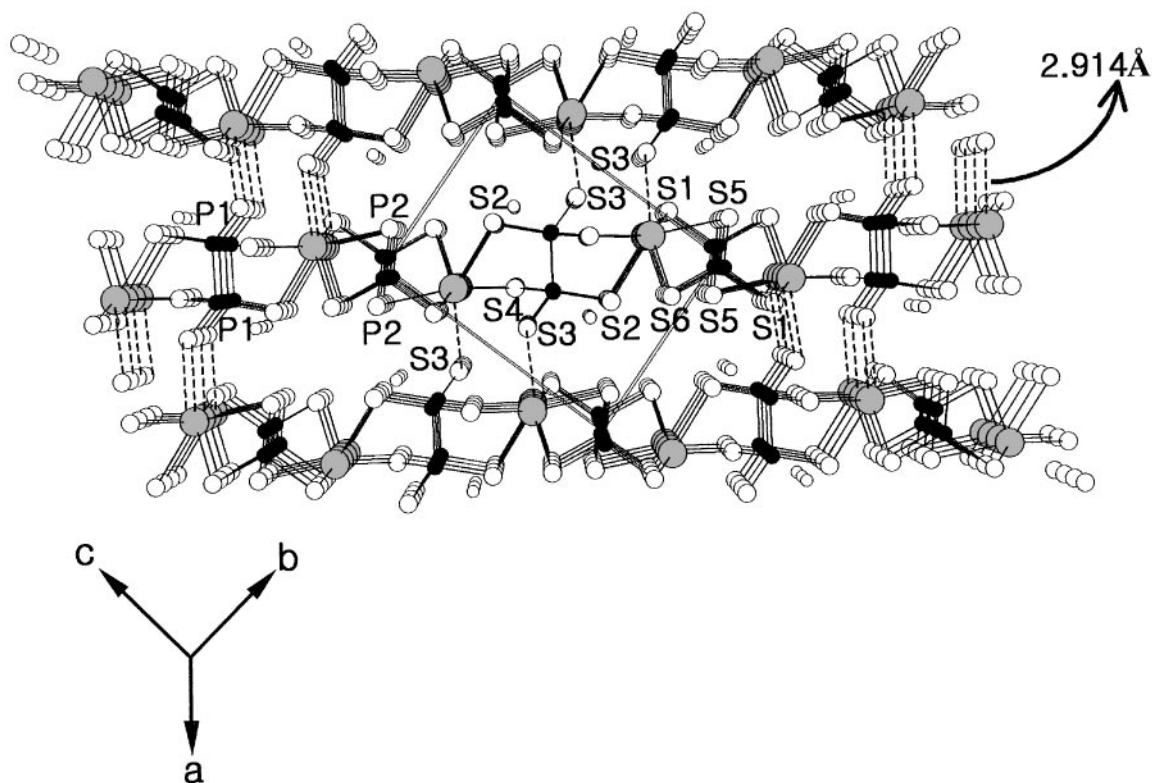

FIG. 1. Crystal structure of NaYbP$_2$S$_6$ projected along the *a*-axis. Large and small open circles are S and Na atoms, respectively, and shaded large and small filled circles are Yb and P atoms, respectively. The unit cell boundaries are shown. The dotted lines illustrate weak interlayer interactions between Yb atoms and S(3) atoms.

FIG. 2. (a) $[Yb_2(P_2S_6)_4]^{10-}$ units showing two crystallographically different $[P_2S_6]^{4-}$ units. (b) One layer of $NaYbP_2S_6$ projected along the b-axis.

3101PC). $BaSO_4$ was used as a 100% reflectance standard. Samples were prepared by grinding them to a fine powder and spreading them on a compacted surface of the standard material preloaded into a sample holder. The reflectance vs wavelength data were converted to absorption data through the Kubelka–Munk function (17).

Tables of crystallographic details, anisotropic thermal parameters, complete bond distances and angles, and lists of observed and calculated structure factors for $NaYbP_2S_6$, $NaSmP_2S_6$, and $KSmP_2S_7$ are available from the author.

RESULTS AND DISCUSSION

Description of Structure

$NaYbP_2S_6$ has a two-dimensional layered structure as shown in Fig. 1. Between two sulfur layers, P_2 dimers and Yb atoms are alternatively filled along the [011] direction and coordinated by six and five sulfur atoms, respectively. The P_2 dimers are centered between the sulfur layers; however, Yb atoms are zigzag up and down along the center of the layers. The layers are stacked perpendicularly to the plane direction and are separated by van der Waals gaps. A similar single-layer structure was found in KYP_2Se_6, but the local structure in the layer of $NaYbP_2S_6$ is different from that of KYP_2Se_6. In KYP_2Se_6, Y atoms are aligned through the center of layers in the b direction, and ethane-like $[P_2Se_6]^{4-}$ units are pushed away with Se atoms pointing into the van der Waals gap. The layers of $NaYbP_2S_6$ are composed of Yb dimers $[Yb_2(P_2S_6)_4]^{10-}$ as illustrated in Fig. 2a. In $[Yb_2(P_2S_6)_4]^{10-}$ units, there are two crystallographically different $[P_2S_6]^{4-}$ units, type I and type II, where the two P–P bonds are almost perpendicular to each other. Two Yb atoms in the dimer are connected by three sulfur atoms from the first thiophosphate units (type I) in an edge-sharing arrangement by S(5), S(6) and single coordination by S(1), while the second ligand (type II) connects two neighboring Yb_2 dimers to form chains along the c-axis by bidentate bonding with S(2) and S(4). The neighboring chains are further bridged by a P(2)–P(2) bond of a type I phosphate unit forming large holes containing Na atoms

TABLE 5
Selected Bond Distances (Å) and Bond Angles (deg) for
$NaYbP_2S_6$

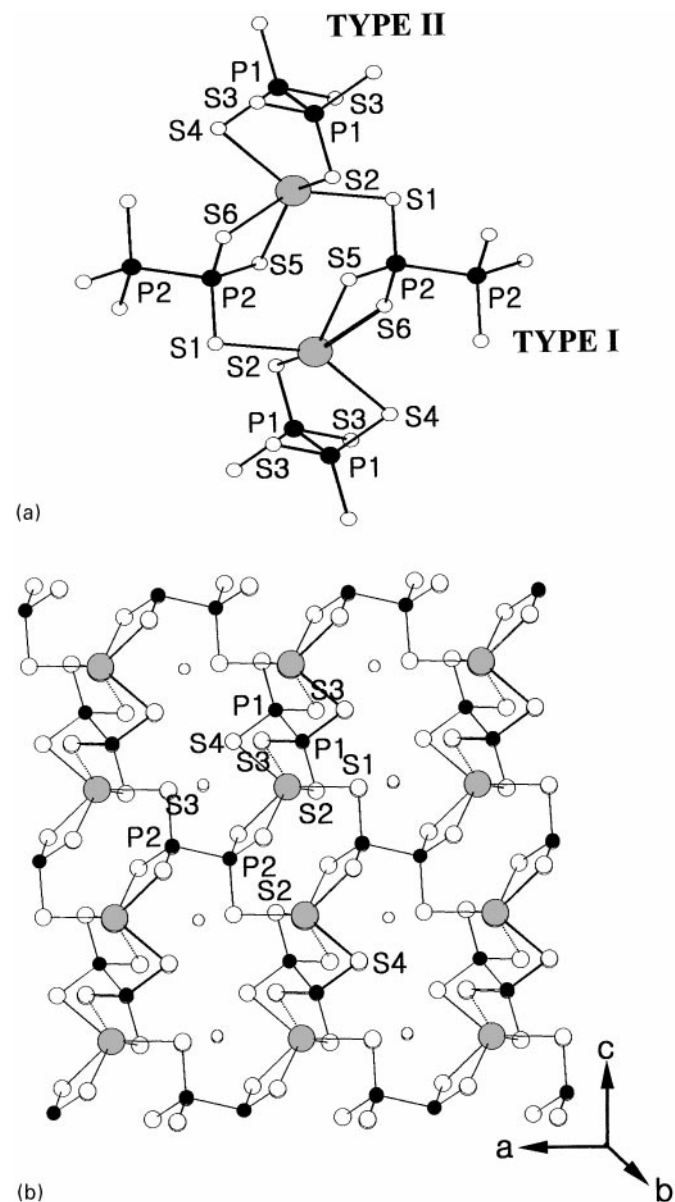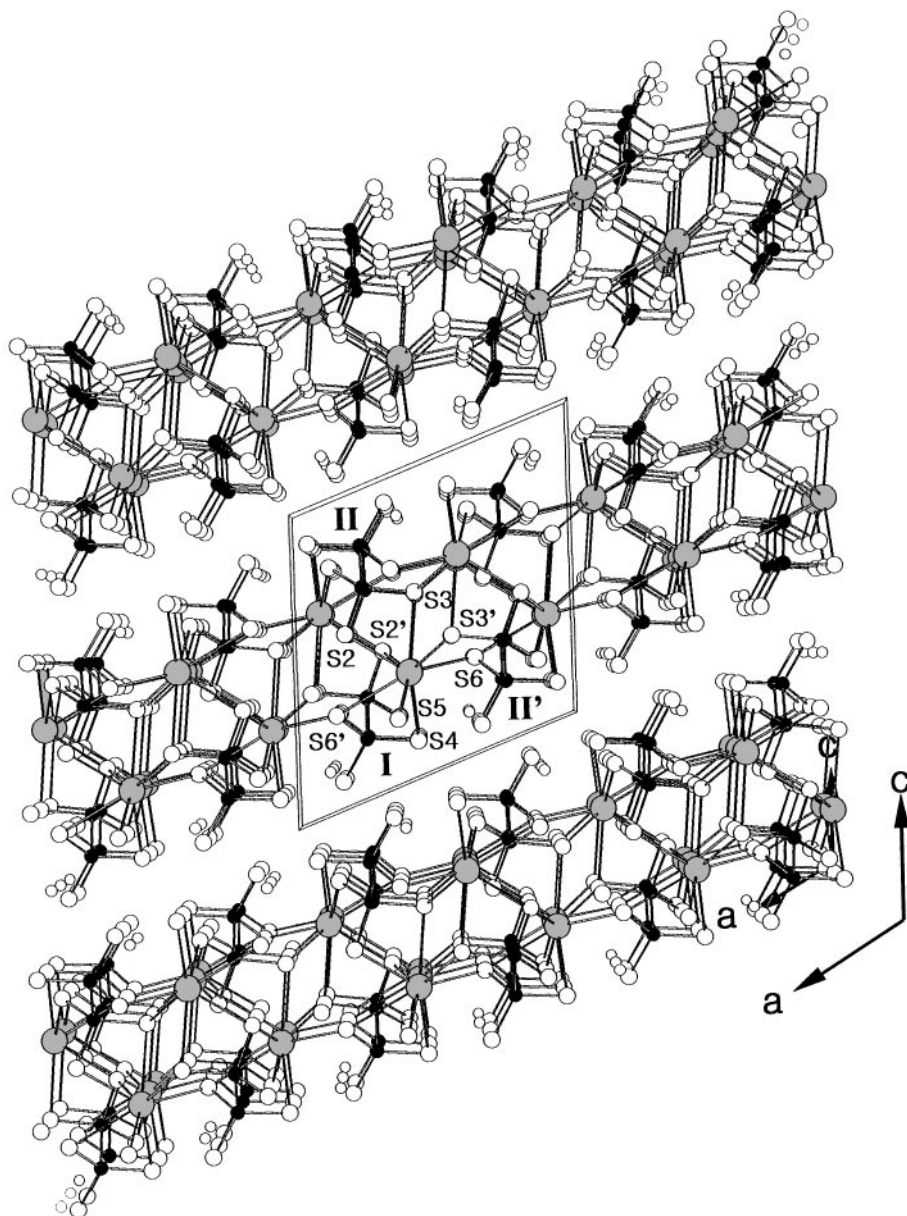|			
Yb–S1	2.725(1)	Yb–S2	2.790(1)
Yb–S5	2.795(1), 3.233(1)	Yb–S6	2.744(11)
Yb–S4	2.778(1)	Yb–S3	2.914(1), 2.980(1)
Na–S1	2.874(2)	Na–S5	3.374(2)
Na–S4	2.921(2), 3.193(3)	Na–S3	3.052(3)
Na–S2	2.932(2)	Na–S6	3.001(3)
P1–S2	2.002(2)	P2–S1	2.020(2)
P1–S3	2.041(2)	P2–S5	2.025(2)
P1–S4	2.015(2)	P2–S6	2.002(2)
P1–P1	2.209(2)	P2–P2	2.204(2)
S2–P1–S4	116.62(7)	S6–P2–S5	110.82(7)
S2–P1–S3	117.80(7)	S1–P2–S5	111.13(7)
S4–P1–S3	107.30(6)	S6–P2–S1	114.75(7)
S1–Yb–S6	138.49(3)	S2–Yb–S5	136.82(3), 68.97(3)
S1–Yb–S4	142.94(3)	S1–Yb–S3	91.91(3), 73.90(3)
S6–Yb–S4	75.25(3)	S6–Yb–S3	120.21(3), 138.58(3)
S1–Yb–S2	88.39(3)	S4–Yb–S3	75.34(3), 69.04(3)
S6–Yb–S2	77.73(3)	S2–Yb–S3	147.77(3), 79.01(3)
S4–Yb–S2	85.20(3)	S5–Yb–S3	75.38(3), 142.12(3)
S1–Yb–S5	92.26(3), 67.49(3)	S3–Yb–S5	139.76(3), 129.59(3)
S6–Yb–S5	73.53(3), 71.04(4)	S3–Yb–S3	70.18(3)
S4–Yb–S6	116.86(4), 140.90(3)	S5–Yb–S5	71.54(4)

FIG. 3. Crystal structure of $NaSmP_2S_6$ projected along the b-axis. Large and small open circles are S and Na atoms, respectively. Shaded large and small filled circles are Sm and P atoms, respectively. The unit cell boundaries and atomic labels are shown.

(Fig. 2b). Similar holes composed of $M_2(P_2Se_6)_4$ dimers are found in the more complicated $Cs_8M_4(P_2Se_6)_5$ ($M =$ Sb, Bi) structure (18), where metal dimers are connected to form a staircase layered framework. However, Y atoms in KYP_2Se_6 have eightfold coordination in an intricate Se network; therefore, the Se layer does not have holes for K atoms.

In Table 5, selected bond distances and bond angles in $NaYbP_2S_6$ are listed. The first five short Yb–S distances range from 2.725(1) Å to 2.795(1) Å, and these compare well with the sum of ionic radii of Yb^{3+} and S^{2-} (2.708 Å) (19).

Yb atoms are surrounded by five sulfur atoms with distorted square pyramidal geometry. The fivefold coordination of Yb in $NaYbP_2S_6$ is the smallest coordination number compared with those of other known rare earth metal thiophosphates. Generally rare earth metals have coordination numbers between 6 and 9 in the similar compounds. In addition to five Yb–S bonds, there are weak interlayer interactions between Yb and S(3) at 2.914(1) Å as illustrated in dotted lines in Fig. 1. If we consider these weak interactions as bonding interactions, this structure can be described as a three-dimensional structure and the coord-

Sm–S5	2.868(2)	Sm–S6	2.899(2), 3.165(2)
Sm–S4	2.892(2)	Sm–S3	3.007(2), 3.031(2)
Sm–S2	2.896(2), 2.988(2)	Na–S1	2.949(5), 2.966(4)
Na–S5	3.963(5), 3.225(5)	Na–S6	2.969(5)
Na–S4	3.123(5), 3.340(5)	Na–S3	3.281(5)
P1–S1	1.984(3)	P2–S5	2.008(3)
P1–S4	2.005(3)	P2–S3	2.028(3)
P1–S6	2.032(3)	P2–S2	2.044(3)
P1–P2	2.195(3)		
S5–Sm–S4	83.35(6)	S5–Sm–S2	85.13(6), 145.96(6)
S4–Sm–S2	132.30(6), 80.41(6)	S5–Sm–S6	129.78(6), 74.11(6)
S4–Sm–S6	79.99(6), 65.01(6)	S2–Sm–S6	138.60(6), 67.31(6)
S2–Sm–S2	84.04(3)	S6–Sm–S2	76.26(6), 71.93(5)
S5–Sm–S3	76.41(6), 137.33(6)	S4–Sm–S3	133.10(6), 139.15(6)
S2–Sm–S3	87.88(6), 135.12(6), 68.58(6)	S6–Sm–S3	81.40(6), 70.18(6), 142.62(5), 120.81(6)
S2–Sm–S3	66.09(5)	S3–Sm–S3	69.86(6)
S6–Sm–S6	135.64(3)	S1–P1–S4	121.3(1)
S1–P1–S6	112.8(1)	S4–P1–S6	107.9(1)
S1–P1–S2	104.9(1)	S4–P1–S2	105.4(1)
S6–P1–S2	102.5(1)	S5–P2–S3	113.2(1)
S5–P2–S2	116.12(1)	S3–P2–S2	110.3(1)

ination around Yb is a trigonal prism. In NaYbP$_2$S$_6$, Na$^+$ ions are not located in the center of the void between the layers; instead, they are filled in near the edge of the layer. The P–S distances in [P$_2$S$_6$]$^{2-}$ units are 2.002(2)–2.015(2) Å, and those are comparable to the P–S distances observed in other thiophosphate compounds (1e). The Na$^+$ atoms are in a distorted square pyramid coordination, similar to Yb atoms.

Figure 3 shows the structure of NaSmP$_2$S$_6$, where two layers of MPS$_3$ type are condensed; selected bond distance and angles are listed in Table 6. The structure of NaSmP$_2$S$_6$ is similar to that of KLaP$_2$Se$_6$, but the coordination number around Sm metal is different due to the smaller radius of the Sm atom. The lanthanide metals have ninefold coordination. In KLaP$_2$Se$_6$, the nine La–Se distances are in the range 3.107(1)–3.378(1) Å. In the NaSmP$_2$S$_6$ structure, Sm metals lie within eightfold coordination in the range 2.868(2)–3.165(2) Å and S(1) atoms pointing out toward interlayer gaps are 3.3513 Å from the Sm atom. The sum of ionic radii of Sm^{3+} and S^{2-} is 2.92 Å (19); therefore, the distance Sm–S(1) at 3.3513 Å, is considered too long to be a bonding interaction. The Na atoms in NaSmP$_2$S$_6$ are coordinated to seven sulfur atoms with bicapped trigonal prismatic geometry. Na atoms are nested in holes that penetrate the layers with an average Na–S distance of 3.102(5) Å. Sm atoms also have a bicapped trigonal prismatic coordination as shown in Fig. 4a, where the bottom face is slightly distorted from the square plane. The two largest Sm–S distances between Sm atoms and capping S(3')
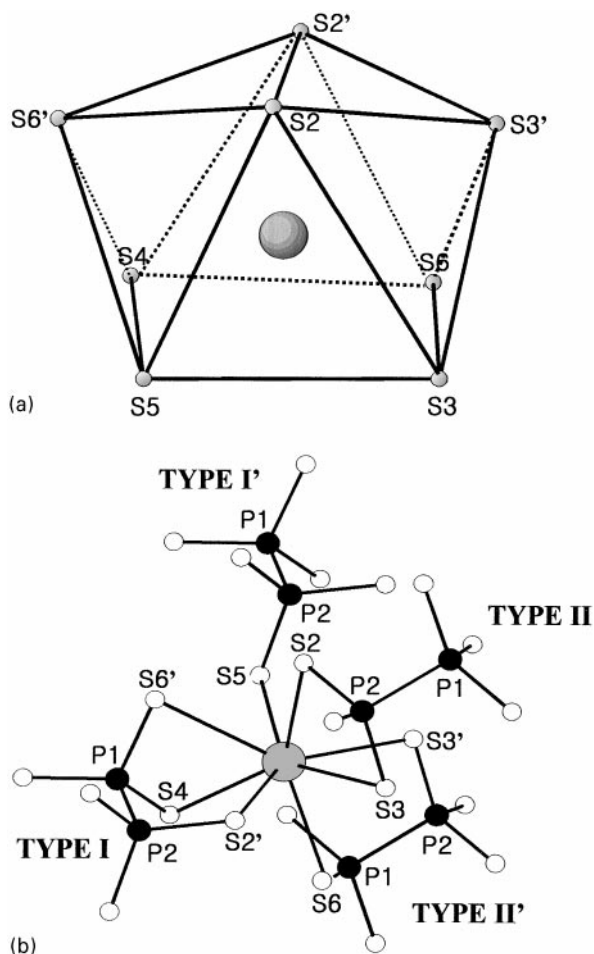

FIG. 4. (a) Bicapped trigonal prismatic environment around the Sm atom. (b) The full coordination sphere around Sm atom. Open circles, filled circles, and the shaded large circle are S, P, and Sm atoms, respectively.

and S(6') are 3.031(2) Å and 3.165(2) Å, respectively. Sm atoms are coordinated in a face-capping arrangement by the S(2'), S(4), and S(6') of type I [P$_2$S$_6$]$^{4-}$ units, and in a corner-sharing arrangement by the S(5) of the type I' [P$_2$S$_6$]$^{4-}$ unit. Finally, S(2) and S(3) from type II and S(3)' and S(6) from type II' units are coordinated to a Sm atom by an edge-sharing arrangement (Fig. 4b). The P–S distances in [P$_2$S$_6$]$^{2-}$ units are 1.984(3)–2.044(3) Å, and those are comparable to P–S distances observed in other thiophosphate compounds.

In the mixed metal MM'P$_2$S$_6$-type thiophosphates, the electronic factors determining the stability of the metal ordering were investigated by EHT calculations (5). Considering only the arrangement of two cations, M and M', in graphite-like configuration, there are three possible arrangements: triangular, zigzag, and pairing of like atoms (intermediate between triangular and zigzag patterns). In the triangular pattern, no like atoms are neighboring in the
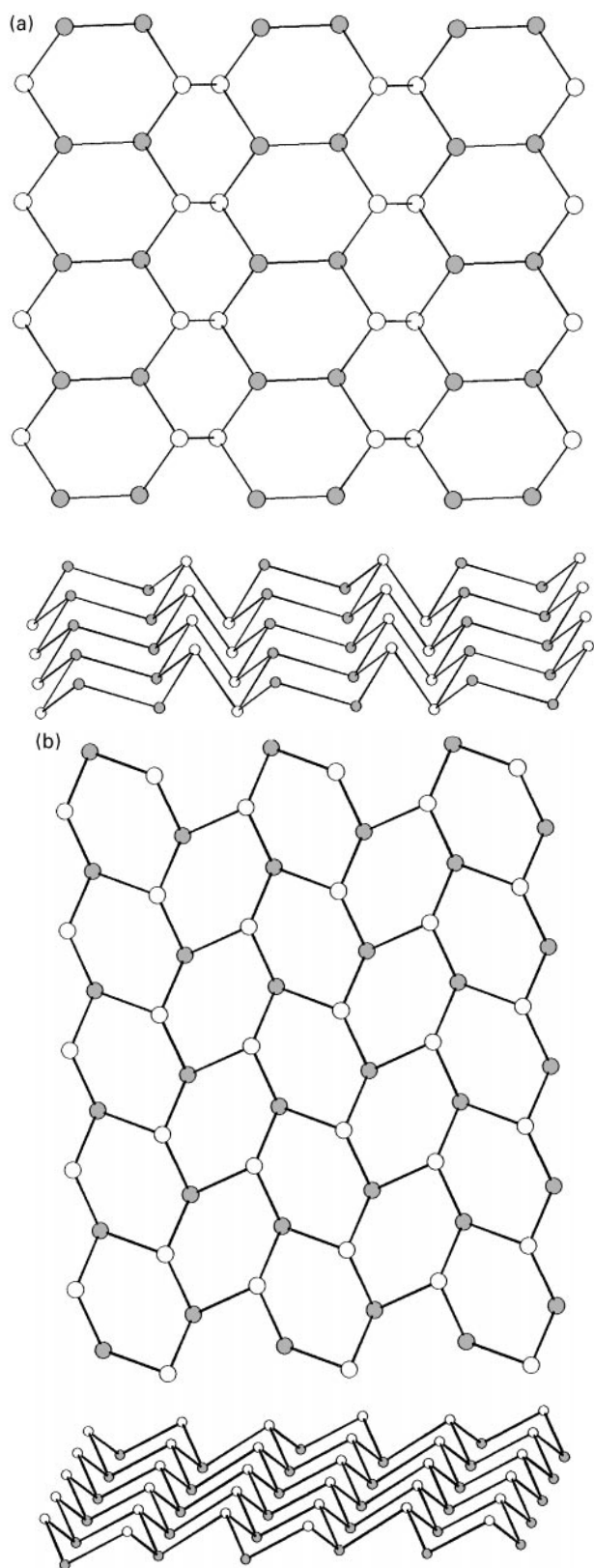
graphite-like net. However, in the zigzag pattern there are infinite linkages between like atoms. According to the previous studies, the compounds composed of cations with large differences in their radii tend to have zigzag chain arrangement, avoiding edge-sharing of heterometal-centered polyhedra, and the compounds composed of cations with similar sizes tend to have triangular arrangement, sharing edges of heterometal-centered polyhedra (5). The former two structure types are found experimentally in $AgCrP_2S_6$ and $AgInP_2S_6$, respectively, but the intermediate form has not been yet reported. Figure 5 shows a projected view of graphite-like nets of cations and a side view of the layer of $NaYbP_2S_6$ and $NaSmP_2S_6$. The monolayers of mixed cations in $NaYbP_2S_6$ and $NaSmP_2S_6$ have hexagonal configuration in common, even though they are severely distorted from the hexagonal plane into a chair form. $NaSmP_2S_6$ has a triangle arrangement and $NaYbP_2S_6$ has a pairing arrangement. The ionic radii of Na^+, Yb^{3+}, and Sm^{3+} are 0.99, 0.87, and 0.96 Å, respectively. Since the radii of Na^+ and Sm^{3+} ions are similar, $NaSmP_2S_6$ seems to prefer edge-sharing of heterometal-centered polyhedra. The sizes of two hexagons in $NaSmP_2S_6$ are the same, because they are composed of equal numbers of like cations. The relative size of alkali metal and rare earth metal can be estimated by the distance ratios of cation to sulfur d_{Na-S}/d_{RE-S}. The d_{Na-S}/d_{RE-S} in $NaSmP_2S_6$ and $NaYbP_2S_6$

FIG. 5. (a) Arrangement of cations in one layer of $NaYbP_2S_6$ and a side view of the layer. (b) Arrangement of cations in a single layer of doubly condensed $NaSmP_2S_6$ and a side view of the layer.

TABLE 7
Selected Bond Distances (Å) and Bond Angles (deg) for
$KSmP_2S_7$

|			
Sm–S2	2.835(2)	Sm–S3	2.889(2)
Sm–S1	2.872(2), 2.924(2)	Sm–S6	2.942(2)
Sm–S5	2.877(2)	Sm–S4	2.966(2), 3.059(2)
K–S5	3.221(2), 3.359(3)	K–S2	3.285(3), 3.364(3)
K–S6	3.365(3)	K–S3	3.374(3), 3.440(2)
K–S7	3.428(2)		
P1–S6	1.999(2)	P2–S2	2.003(2)
P1–S5	2.009(2)	P2–S3	2.022(2)
P1–S1	2.029(2)	P2–S4	2.024(2)
P1–S7	2.119(2)	P2–S7	2.114(2)
S2–Sm–S1	101.87(5), 135.98(5)	S2–Sm–S5	80.38(5)
S1–Sm–S5	68.45(5), 92.66(5)	S2–Sm–S3	143.89(5)
S1–Sm–S3	73.53(5), 72.30(5)	S5–Sm–S3	127.08(5)
S1–Sm–S1	115.87(3)	S2–Sm–S6	68.97(5)
S1–Sm–S6	137.81(5), 67.93(5)	S5–Sm–S6	69.41(5)
S3–Sm–S6	137.69(5)	S2–Sm–S4	91.81(5), 67.56(5)
S1–Sm–S4	134.73(5), 7.79(5), 73.53(5), 142.82(5)	S5–Sm–S4	156.82(5), 122.93(5)
S3–Sm–S4	70.42(5), 77.02(5)	S6–Sm–S4	87.41(5), 130.94(5)
S4–Sm–S4	72.46(5)	S6–P1–S5	118.7(1)
S6–P1–S1	108.9(1)	S5–P1–S1	106.4(1)
S6–P1–S7	99.4(1)	S5–P1–S7	112.7(1)
S1–P1–S7	110.5(1)	S2–P2–S3	110.8(1)
S2–P2–S4	109.2(1)	S3–P2–S4	113.1(1)
S2–P2–S7	112.2(1)	S3–P2–S7	100.0(1)
S4–P2–S7	111.4(1)	P2–S7–P1	110.3(1)
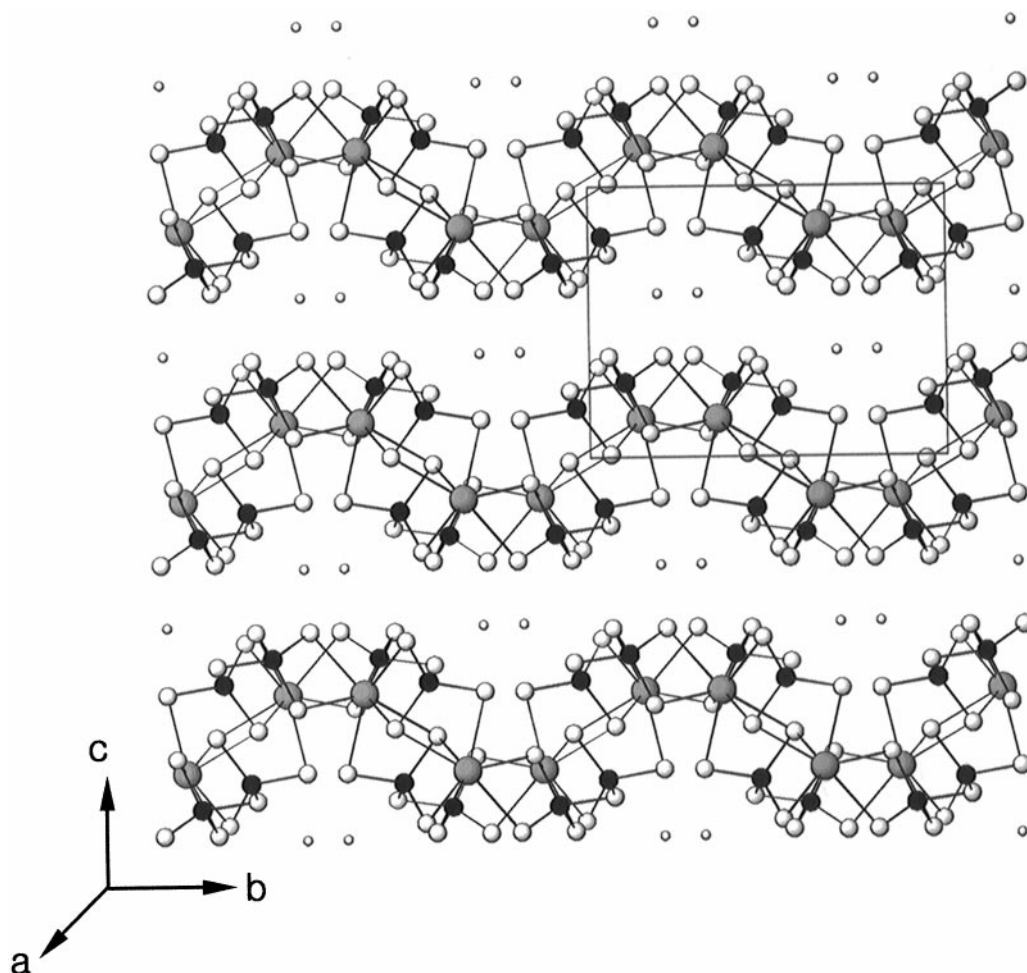
FIG. 6. Crystal structure of $KSmP_2S_7$ projected along the a-axis. Large and small open circles are S and K atoms, respectively, and shaded large and small filled circles are Sm and P atoms, respectively. The unit cell boundaries are shown.

are 1.022 and 1.056, respectively, which explains the preference of the edge-sharing of Na- and Sm-centered polyhedra in $NaSmP_2S_6$. In the pairing arrangement, two like atoms make pairs to form two different sizes of hexagons. The hexagons in $NaSmP_2S_6$ are also severely distorted into a chair form. Optically measured band gaps of $NaYbP_2S_6$ and $NaSmP_2S_6$ suggest that they are narrow and medium band gap semiconductors. The band gaps of $NaYbP_2S_6$ and $NaSmP_2S_6$ were 1.85 eV and 2.54 eV, respectively.

An attempt to prepare the K analogue of $NaSmP_2S_6$ or $NaYbP_2S_6$ resulted in $KSmP_2S_7$ with different structural-type and different $[P_nQ_m]^{x-}$ units. The structure of $KSmP_2S_7$ consists of corrugated layers as shown in Fig. 6; selected bond distance and angles are listed in Table 7. The layers are separated by an eight-coordinate potassium ion with an average K–S distance of 3.351(3) Å. The structure of $KSmP_2S_7$ is similar to that of $ABiP_2S_7$ (A = K, Rb) (20), but the coordination number around Sm atoms is larger

than that of the Bi atom. In $ABiP_2S_7$, seven Bi–S bond distances are in the range 2.761(2)–3.047(2) Å and Bi has stereochemically active $6s^2$ electrons. In the $KSmP_2S_7$ structure, Sm metals lie in eightfold coordination in the range 2.835(2)–3.059(2) Å, which is slightly shorter than the Sm–S distances in $NaSmP_2S_6$ (2.868(2)–3.165(2) Å). A projection of a single layer of $KSmP_2S_7$ is shown in Fig. 7, where an anionic building unit $[P_2S_7]^{4-}$ is highlighted. The layers of $KSmP_2S_7$ are composed of Sm^{3+} ions and $[P_2S_7]^{4-}$ units forming irregular eight-membered Sm–S–P rings. The eight-membered rings are stacked along the c-axis, providing space for K atoms. The $[P_2S_7]^{4-}$ unit consists of two tetrahedral $[PS_4]^{3-}$ units bridged by a sulfur atom. Even though we used the same ratio of reaction composition of $Na_2S/Sm/P/S$ and $K_2S/Sm/P/S$, different products of $KSmP_2S_7$ and $NaSmP_2S_6$ were obtained. Variations in the molar ratio of starting compositions of $K_2S/Sm/P/S$ do not stabilize any analogues of $NaSmP_2S_6$;

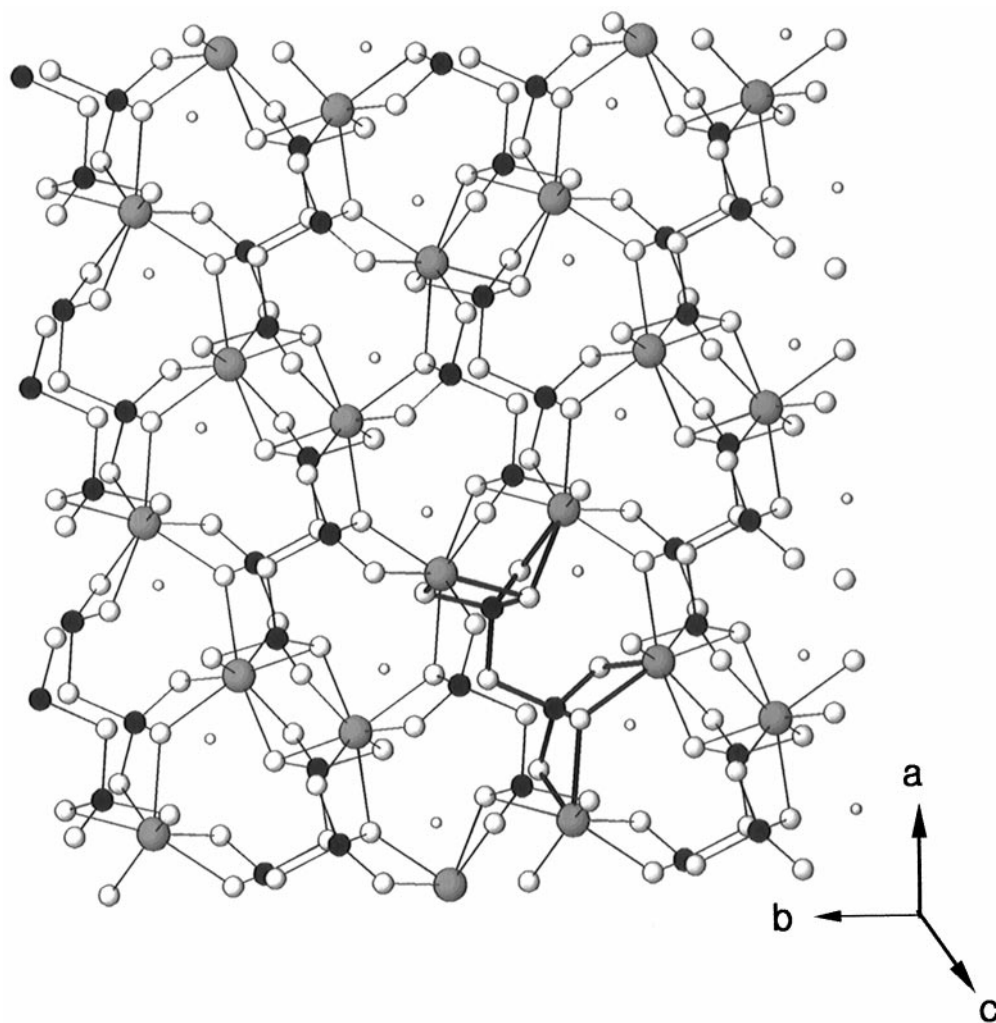**FIG. 7.** One layer of $KSmP_2S_7$ projected along the c-axis. One $[P_2S_7]^{4-}$ unit is highlighted.

therefore, the unique structure of $KSmP_2S_7$ seems to be due to the relatively large size of K atoms compared to Na atom in $NaSmP_2S_6$ and $NaYbP_2S_6$. The more basic character of K than Na is another possible factor that may stabilize the $[P_2S_7]^{4-}$ unit instead of the $[P_2S_6]^{4-}$ unit.

In the $[P_2S_7]^{4-}$ unit of $KSmP_2S_7$, the angle of the bridging P(2)–S(7)–P(1) bond, at $110.3(1)°$, is comparable to the bridging angles found in other compounds. The angles in a similar bridging P–S–P bond in $KBiP_2S_7$ (20), $Ag_4P_2S_7$ (21), and $Hg_2P_2S_7$ (22) are $111.2(1)°$, $113.4°$, and $108.63°$, respectively. The bond distances of P(1)–S(7) and P(2)–S(7) are $2.119(2)$ and $2.114(2)$ Å, respectively, which compare well to P–S distances of $2.115(3)$ Å and $2.111(3)$ Å in $KBiP_2S_7$.

In conclusion, we have synthesized new rare earth and alkali metal mixed thiophosphates. A slight increase of the size of the rare earth cation of Yb in $NaYbP_2S_6$ to Sm induces the condensation of MPS_3-type layers into double layers as found in $NaSmP_2S_6$. A further increase of the size

of the cation from Na to K forces a totally different structural modification from the $MM'P_2S_6$ type of $NaSmP_2S_6$ to a unique $KSmP_2S_7$ type with a different anionic ligand group. Many more phases with different thiophosphate ligand groups are anticipated by varying the combination of two cations.

ACKNOWLEDGMENTS

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