Use of Molten Alkali-Metal Polythiophosphate Fluxes for Synthesis at Intermediate Temperatures. Isolation and Structural Characterization of $ABiP_2S_7$ (A = K, Rb)

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Recent advances in the development of alkali-metal polychalcogenide fluxes as reaction media at intermediate temperatures ($200 < T < 500$ °C) produced a variety of new ternary and quaternary chalcogenides.[1] This method is particularly useful in stabilizing structural fragments which are not stable at higher temperatures such as long S_x^{2-} (x = 4, 5, 6) units.[2] During our studies with polychalcogenides, we noticed that another set of main group structural units, namely the various thiophosphates $[P_xS_y]^{n-}$ were also rather uncommon in their occurrence in solid-state compounds. With the exception of the important MPS_3 class of compounds,[3] which contains the ethane-like $[P_2S_6]^{4-}$ ligand, $[P_xS_y]^{n-}$ containing solids are relatively few.[4-6] Group 5 transition-metal thiophosphates have been reported and reviewed by Evain et al.[7] These compounds exhibit structural diversity due to a variety of anionic P/S ligands and tendency for low dimensionality. Transition-metal thiophosphates are of potential importance as low-dimensional cathode materials for secondary lithium batteries.[8] Metal thiophosphates are typically synthesized by direct combination of the elements at high temperature (500-800 °C). It has been noted that complicated Lewis acid-base equilibria exist among $[P_2S_6]^{4-}$, $[P_2S_6]^{2-}$, $[P_2S_7]^{4-}$, and $[PS_4]^{3-}$ ligands at high temperatures.[9] To date, very little effort has been invested in the synthesis of *quaternary* metal thiophosphate compounds at intermediate temperatures. Thus, we are interested to develop a general methodology by which new thiophosphate (or chalcophosphate) compounds can be consistently obtained in a similar fashion that we have observed in polychalcogenides. Here we report the use of novel low-melting (300-400 °C) alkali-metal *polythiophosphate* fluxes to synthesize new quaternary metal thiophosphates. This temperature window should allow access to new, metastable compounds that may not be thermodynamically stable at higher temperatures. The recently reported $RbVP_2S_7$ was prepared at 550 °C and is a notable example.[10] We have applied this new molten salt flux to group 15 (Bi and Sb) metals and application to other p-block elements and transition metals seems very promising.[11] Using these fluxes, we prepared the new compounds $KBiP_2S_7$ and $RbBiP_2S_7$ which feature a new layered structure type containing the pyrothiophosphate building block. Their structural characterization and optical properties are reported.

The formation of molten alkali-metal thiophosphate fluxes results from the fusion of alkali-metal sulfide, phosphorous pentasulfide, and elemental sulfur (see eq 1).

$$(x/2)A_2S + (y/4)P_4S_{10} + zS \xrightarrow[A = K, Rb, Cs]{T > 300\ °C} A_x[P_yS_{x+y+z}] \quad (1)$$

We view the $A_x[PS_y]$ fluxes as a significant variation over the A_2S_x fluxes in that they provide not just P atoms but excess $[P_xS_y]^{n-}$ anions which act as mineralizers. In other words, the acid/base characteristics of the $A_x[PS_y]$ fluxes are very different from those of the A_2S_x fluxes in that they tend to be more basic.[1] The chemical properties of these melts can be controlled by the ratios of their constituent elements. The relatively good solubility properties of $A_n[P_xS_y]$ salts in water and organic solvents allow for easy isolation of products.

$KBiP_2S_7$ was synthesized from a mixture of $Bi/P_4S_{10}/K_2S/S$ (1:1.5:2:4) at 400 °C.[12] The structure[13] of $ABiP_2S_7$ is layered and shown in Figure 1a. It represents a complex new structure type. The corrugated layers are separated by eight-coordinate K+ ions (K-S mean = 3.34(6) Å). Another view of $KBiP_2S_7$ is shown in Figure 1b. The layers are assembled from Bi^{3+} and $[P_2S_7]^{4-}$ units forming irregular eight-membered Bi-S-P rings. The P(2)-S_4 tetrahedron of the pyrothiophosphate ligand $[P_2S_7]^{4-}$ coordinates in a bidentate fashion to Bi and acts as a bridge to a second Bi to form the top side of the eight-membered ring. The Bi atoms are connected at the bottom of the ring by the P(2)-S_4 tetrahedron of a second P_2S_7 group that acts as a tridentate to both Bi atoms. The bridging mode of the $[P_2S_7]^{4-}$ fragment is rather complicated and

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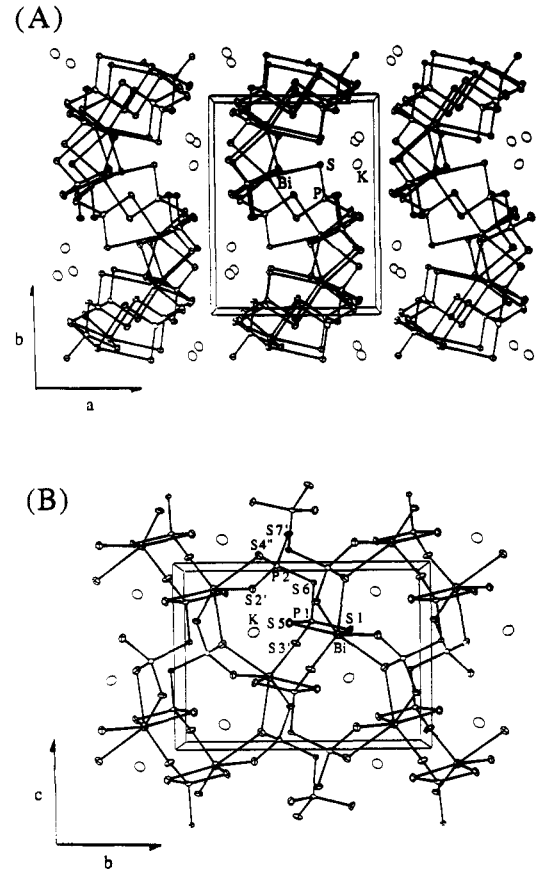
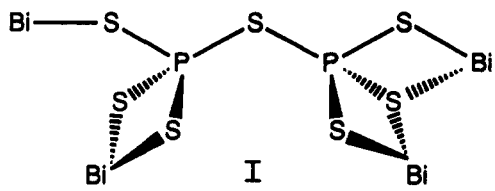


Figure 1. (A) ORTEP packing diagram of $KBiP_2S_7$ looking down the *c* axis with labeling. (B) ORTEP representation and labeling of the $KBiP_2S_7$ layer looking down the *a* axis. Selected distances are as follows: P(1)–S(1) 2.003(3), P(1)–S(3)′ 2.035(3), P(1)–S(5) 2.018(3), P(1)–S(6) 2.115(3), P(2)–S(2)′ 2.015(3), P(2)–S(4)″ 2.016(3), P(2)–S(6) 2.111(3), P(2)–S(7)′ 2.024(3) Å. Selected angles are as follows: P(1)–S(6)–P(2) 111.2(1), S(1)′–P(1)–S(6) 100.4(1), S(3)′–P(1)–S(5) 109.6(1), S(7)′–P(2)–S(6) 98.2(1), S(2)′–P(2)–(S4)″ 108.1(1).

it is illustrated in I. The rings are connected in two dimensions by P–S–Bi linkages to form the layer. The



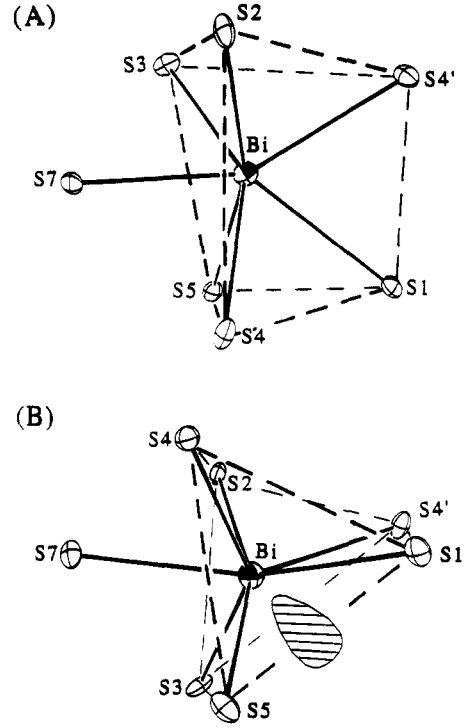


Figure 2. (A) ORTEP representation and labeling of the Bi–S coordination site. The polyhedron is outlined with dotted lines for clarity. Selected distances are as follows: Bi–S(1) 3.047(2), Bi–S(2) 2.867(2), Bi–S(3) 2.761(2), Bi–S(4) 2.930(2), Bi–S(4)′ 2.971(2), Bi–S(5) 2.906(2), Bi–S(7) 2.820(2). Selected angles are as follows: S(1)–Bi–S(2) 125.46(5), S(1)–Bi–S(3) 138.29(5), S(4)′–Bi–S(5) 130.43(6), S(4)–Bi–S(4)′ 113.69(5), S(1)–Bi–S(4) 71.58(6), S(1)–Bi–S(4)′ 70.16(5), S(3)–Bi–S(7) 74.76(6), S(4)–Bi–S(7) 70.04(6), S(3)–Bi–S(5) 93.25(6), S(4)–Bi–S(5) 78.63(5). (B) ORTEP representation and labeling of the BiS_7 polyhedron viewed from the top of the capped trigonal prism. The probable location of the Bi^{3+} lone pair is shown.

layers stack with their eight-membered rings in registry so that they form channels running down the *a* axis.

Bi is coordinated by seven S atoms to form a distorted capped trigonal prism (see Figure 2a). The distances range from 2.761(2) to 3.047(2) Å which compare well with those found in $BiPS_4$.[4c] The coordination geometry is distorted because of the stereochemically active $6s^2$ lone pair of Bi^{3+}. The S(7) atom caps one of the three rectangular faces of the trigonal prism. The lone pair presumably caps one of the other two faces. Inspection of the angles of the face, defined by S(2), S(4), S(1), S(4)′ (see Figure 2b), reveal S(1)–Bi–S(2) and S(4)–Bi–S(4)′ angles of 125.46(5)° and 113.69(5)°, respectively. The S(1)–Bi–S(3) and S(4)′–Bi–(5) angles of the second face, defined by S(3), S(4)′, S(5), S(1), are larger at 138.29(5)° and 130.43(6)°, respectively, and are probably due to the repulsive effect of the lone pair and the atoms. Each capped trigonal prism shares three edges and one corner with the terminal sulfides of four $[P_2S_7]^{4-}$ ligands.

$ABiP_2S_7$ is structurally quite different from $RbVP_2S_7$, which also possesses a layered structure. The major differences are in the coordination number and geometry of the M^{3+} atom, and bonding modes of the $[P_2S_7]^{4-}$ fragment. Furthermore, the sheets of $ABiP_2S_7$ are cor-

(12) $KBiP_2S_7$ was synthesized from a mixture of 0.031 g (0.15 mmol) of Bi, 0.050 g (0.225 mmol) of P_4S_{10}, 0.033 g (0.30 mmol) of K_2S, and 0.019 g (0.60 mmol) of S. This mixture was sealed under vacuum in a Pyrex tube and heated to 400 °C for 4 days followed by cooling to 110 °C at 4 °C/h. The excess yellow-colored $K_xP_yS_z$ matrix was removed from the red crystals (68% yield) with dimethylformamide (DMF). The crystals are air and water stable. Single crystals of the isostructural Rb analogue were also synthesized under the same conditions, except at 420 °C (57% yield). The compound was found to be isostructural to $KBiP_2S_7$ by powder X-ray diffraction. Quantitative microprobe analysis on red crystals gave $Rb_{1.0}Bi_{1.3}P_{1.9}S_{7.4}$ (average of three data acquisitions).

(13) Crystal data for $KBiP_2S_7$ at 20 °C (Mo Kα radiation): a = 9.500(3) Å, b = 12.303(4) Å, c = 9.097(3) Å, β = 90.59(3)°, V = 1063.1(6) Å^3, Z = 4, D_{calcd} = 3.339 g/cm^3, space group $P2_1/c$ (no. 14), $2\theta_{max}$ = 50°, total data collected, 2192; unique data (averaged), 2060; data with $F_o^2 > 3\sigma(F_o^2)$, 1672. The structure was solved using SHELXS-86 (direct methods).[14] An empirical absorption correction based on ψ scans was applied to the data, followed by a (DIFABS)[15] correction to the isotropically refined data. Complete anisotropic refinement (100 variables) resulted in a final R/R_w = 2.8/3.1%.

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rugated. The stereochemically active lone pair of Bi^{3+} also influences the structure of the layers by distorting the BiS_7 polyhedron. The potential multiple denticity of the $[P_2S_7]^{4-}$ ligand suggests that a large number of new solid-state structures may be possible with various main-group and transition metals. The $[P_2S_7]^{4-}$ ligand has been observed in $Ag_7(PS_4)(P_2S_7)$,[5b] $RbVP_2S_7$,[11] $Ag_4P_2S_7$,[16] $Hg_2P_2S_7$,[17] and $As_2P_2S_7$.[18]

The optical properties of $KBiP_2S_7$ and $RbBiP_2S_7$ suggest that they are medium bandgap semiconductors.[19] The optical absorption spectrum of $KBiP_2S_7$ is shown in Figure 3 and exhibits a steep absorption edge from which the bandgap, E_g, can be estimated at 2.25 eV. Two absorptions at 2.67 and 3.47 eV are readily resolved and are tentatively assigned to electronic S → Bi charge-transfer transitions. The bandgap of $RbBiP_2S_7$ is also 2.25 eV. The far-IR spectrum of the compound shows the characteristic absorbances of the $[P_2S_7]^{4-}$ ligand.[20]

In conclusion, the synthesis of new quaternary thiophosphate compounds with alkali metal polythiophosphate molten salts is an interesting and promising synthetic method that is potentially broadly applicable to most metal systems. A number of other new A/M/P/Q (A = K, Rb, Cs; M = Bi, Sb; Q = S, Se) compounds have been synthesized with this method and have been structurally characterized.[24] The relatively low melting temperatures of the $A_x[PS_y]$ fluxes not only should favor metastable structures but more importantly provide a reliable method for stabilization of $[P_xS_y]^{n-}$ units. The various flux characteristics favoring formation of a particular $[P_xS_y]^{n-}$ anion are under investigation.

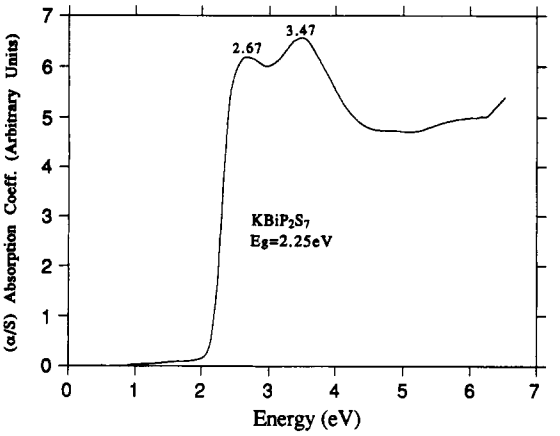

Figure 3. Optical absorption spectrum of $KBiP_2S_7$.

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Supplementary Material Available: Listings of powder diffraction patterns, positional parameters, B and U values, and intermolecular bond distances and angles for $KBiP_2S_7$ (20 pages); list of observed and calculated structure factors for $KBiP_2S_7$ (12 pages). Ordering information is given on any current masthead page.

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(19) (a) Absorption data were calculated from the reflectance data using the Kubelka-Munk function $\alpha/S = (1 - R)^2/2R$, where R is the reflectance at a given wavelength, α is the absorption coefficient, and S is the scattering coefficient. The scattering coefficient has been shown to be practically wavelength independent for particles larger than 5 μm which is smaller than the particle size of the samples used here. $BaSO_4$ powder was used as reference (100% reflectance). (b) Wendlandt, W. W.; Hecht, H. G. Reflectance Spectroscopy; Interscience Publishers: New York, 1966. (c) Kotüm, G. Reflectance Spectroscopy; Springer Verlag: New York, 1969. (d) Tandon, S. P.; Gupta, J. P. *Phys. Status Solidi* **1970**, *38*, 363–367.

(20) The solid state far-IR spectrum of $KBiP_2S_7$ in a CsI matrix shows absorbances at 600 (s), 583 (s), 576 (ssh), 564 (msh), 557 (msh), 526 (wsh), 464 (vs), 412 (w) cm^{-1}.[21] The very strong absorbance at 464 cm^{-1} represents the characteristic P–S–P stretching vibration while the remaining absorbances are due to $-PS_3$ stretching vibrations by analogy to $Ag_4P_2S_7$.[9,22] A second set of absorbances at 300 (vw), 270 (wsh), 250 (msh), 247 (m), 238 (msh), 227 (wsh), 208 (wsh), 203 (wsh), 192 (vw), 174 (vw), 169 (vw), 157 (vw), and 149 (vw) cm^{-1} are assigned to Bi–S stretching vibrations and P–S deformation modes.[9,22,23]

(21) Abbreviations: s = strong, m = medium, w = weak, sh = shoulder, v = very.

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