Synthesis and Thermoelectric Properties of the New Ternary Bismuth Sulfides KBi$_{6.33}$S$_{10}$ and K$_2$Bi$_8$S$_{13}$

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KBi$_{6.33}$S$_{10}$ and K$_2$Bi$_8$S$_{13}$ were synthesized by the direct combination of K$_2$S/Bi$_2$S$_3$ at high temperature (> 700 °C). The reaction of K$_2$S/3Bi$_2$S$_3$ at 800 °C revealed the presence of a new ternary sulfide KBi$_{6.33}$S$_{10}$ (I, 92% yield). The shiny, silver polycrystalline material crystallizes in the orthorhombic space group Pnma (No. 62) with a = 24.05(1) Å, b = 4.100-(2) Å, c = 19.44(1) Å, V = 1917(3) Å$^3$, Z = 4, and d$_c$ = 5.828 g/cm$^3$. Data with F$^2 > 3$α(F$^2$), 862; no. of variables 108, 2R$_{max}$ 50°. The final R/R$_w$ = 4.3/4.7%. The structure consists of blocks of Bi$_2$Te$_3$- and CdI$_2$-type units that are connected to form a three-dimensional network with K$^+$ ions located in the channels that run along the b axis. The same reaction but with a different reactant ratio at 750 °C gave the new ternary sulfide K$_2$Bi$_8$S$_{13}$ (II, 94% yield). This compound crystallizes in the monoclinic space group P2$_1$/m (No. 11) with a = 16.818(2) Å, b = 4.074(5) Å, c = 17.801(3) Å, β = 90.48(1)°, V = 1220(2) Å$^3$, Z = 2, and d$_c$ = 5.900 g/cm$^3$. Data with F$^2 > 3$α(F$^2$), 1924; no. of variables 131, 2R$_{max}$ 50°. The final R/R$_w$ = 7.3/8.2%. The structure of the shiny rodlike crystals is closely related to that of I. As in I, it also consists of Bi$_2$Te$_3$- and CdI$_2$-type fragments that connect to form K$^+$-filled channels. The two potassium atoms and one bismuth atom are disordered over three sites. Electrical conductivity on I show semiconducting behavior with 10$^2$ S/cm at 300 K. Compound II possesses an electrical conductivity of 10$^2$ S/cm at 300 K. The optical bandgaps of I and II (0.06–0.24 eV) were estimated by infrared diffuse reflectance measurements. Thermal analysis and thermal conductivity data for I and II are reported. The thermal conductivity of KBi$_{6.33}$S$_{10}$ is found to be substantially lower than that of Bi$_2$Te$_3$.

Introduction

Group 15 chalcogenide compounds have received considerable attention, due to their potential application as nonlinear optical materials,1 photoelectrics,2 and thermoelectrics.3 The most common application that is unique to group 15 chalcogenides is in the area of thermoelectric cooling materials. The most investigated systems over the past 30 years are various solid solutions of M$_2$Q$_3$ (M = As, Sb, Bi; Q = S, Se, Te) compounds.5 These materials possess high electrical conductivity and thermoelectric power and low thermal conductivity and are excellent materials for thermoelectric applications near room temperature.5 With these properties in mind, it is surprising that very little exploratory synthesis of new ternary bismuth chalcogenide phases has been reported. Bi is very attractive for study because of its inert 6s$^2$ lone pair of electrons which may or may not be manifested structurally in a given compound. Whether the lone pair is stereochemically active or not affects the lattice structure, the electronic structure, and thus the properties of the resulting compounds. Exploration of the solid-state chemistry of Bi is therefore warranted. This issue is related to the larger question of stereochemical activity of a lone pair in compounds with heavy main-group elements in a $s^2$ configuration.

Outside of the well-known NaCl-type ABiQ$_2$ (A = Li, Na, K; Q = S, Se) compounds, the only other phases that have been fully characterized structurally are RbBiQ$_2$ (Q = S, Se),7 CsBi$_3$S$_5$,8 RbBi$_3$S$_5$,9 Tl$_4$Bi$_2$S$_5$,10 α-(j-

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2 ACS PRF Summer Research Fellow. Aquinas College, Grand Rapids, Michigan.

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Bismuth Sulfide, Bi₂S₃. An amount of 2.090 g (10.0 mmol) of Bi and 0.496 g (15.5 mmol) of S were ground thoroughly with a mortar and pestle. The mixture was transferred to a 6 mL Pyrex tube and was subsequently flame-sealed in vacuum (∼10⁻³ Torr). The reaction was heated to 500 °C for 24 h in a computer-controlled furnace, then isothermed at 500 °C for 4 days, followed by cooling to 100 °C at a rate of 4 °C/h, then to 50 °C in 1 h. The product was ground into a fine powder and stored in the glovebox.

K₄Bi₆S₁₀. An amount of 0.020 g (0.181 mmol) of K₂S and 0.308 g (0.599 mmol) of Bi₂S₃ were mixed together with a spatula in a glass vial. Several drops of acetone were placed in a quartz tube (9 mm diameter, 6 mL volume), and it was heated with a flame to create a carbon film on the inside surface of the tube. The mixture was transferred to the carbon-coated quartz tube and was subsequently flame-sealed under diffusion pump vacuum (∼10⁻⁵ Torr). The reaction was heated to 800 °C over a 5 h period in a computer-controlled furnace and then isothermed at 800 °C for 6 days, followed by cooling to 550 °C at a rate of 10 °C/h, then to 50 °C in 10 h. The product was washed with degassed water (50 mL), methanol (20 mL) and ether (20 mL) to remove any trace amounts of K₂S. An amount of 0.301 g (92% yield, based on Bi₂S₃) of shiny silver polycrystalline material of needle morphology was obtained. Standardless semi-quantitative microprobe analysis gave K₂Bi₆S₁₀ (average of six acquisitions).

K₂Bi₃S₁₃ (II). The reaction of 0.040 g (0.363 mmol) of K₂S and 0.746 g (1.45 mmol) of Bi₂S₃ was prepared as above using a carbon quoted tube. The mixture was heated to 750 °C over a 40 h period and then isothermed for 6 days, followed by cooling to 550 °C at 10 °C/h, then to 50 °C in 10 h. The product was isolated as above to give 0.739 g (94% yield) of shiny silver needle crystals and bundles. Microprobe analysis gave K₂Bi₃S₁₃ (average of six acquisitions).

The homogeneity of I and II was confirmed by comparing the observed and calculated X-ray powder diffraction patterns. The d(hkl) spacings observed for the bulk materials were compared and found to be in good agreement with the d(hkl) spacings calculated from the single-crystal data.²² The results are listed in the supporting information.

Physical Measurements

Infrared Spectroscopy. Infrared diffuse reflectance spectra of I and II were recorded as a solid. The sample was ground into a powder prior to data acquisition. The spectra were recorded in the mid-IR region (4000–400 cm⁻¹, 4 cm⁻¹ resolution) with the use of a Nicolet 740 FT-IR spectrometer equipped with a diffuse reflectance attachment.

Electron Microscopy. Quantitative microprobe analysis of the compounds was performed with a J EOL J SM-35C scanning electron microscope (SEM) equipped with a Tracor Northern X-ray dispersive spectroscopy (EDS) detector. Data were acquired using an accelerated voltage of 20 kV and a 1 mm accumulation time.

UV/Vis/Near-IR Spectroscopy. Optical diffuse reflectance measurements were made at room temperature with a Shimadzu UV-3100PC double-beam, double-monochromator spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. The measurement of diffuse reflectivity can be used to obtain


values for the bandgap in the range 0.5–6.0 eV, which agree rather well with values obtained by absorption measurements from single crystals of the same material.

**Differential Thermal Analysis.** Differential thermal analysis (DTA) measurements were made using a computer-controlled Shimadzu DTA-50 thermal analyzer. The ground single crystals (~20.0 mg total mass) were sealed in quartz ampules under vacuum. An quartz ampule containing alumina of equal mass was sealed and placed on the reference side of the detector. The samples were heated to the desired temperature at 10 °C/min and then isothermed for 10 min followed by cooling at 10 °C/min to 100 °C and finally by rapid cooling to room temperature. The reported DTA temperatures are peak temperatures. The DTA samples were examined by powder X-ray diffraction after the experiments.

**Charge-Transport Measurements.** DC electrical conductivity and thermopower measurements were made on single crystals and polycrystalline compacts of the compounds. Conductivity measurements were performed in the usual four-probe geometry with 60- and 25-μm gold wires used for the current voltage electrodes, respectively. Measurements of the pellet cross-sectional area and voltage probe separation were made with a calibrated binnocular microscope. Conductivity data were obtained with the computer-automated system described elsewhere. Thermoelectric power measurements were made by using a slow ac technique with 60-mm gold wires serving to support and conduct heat to the sample, as well as to measure the voltage across the sample resulting from the applied temperature gradient. In both measurements, the gold electrodes were held in place on the sample with a conductive gold paste.

Conductivity specimens were mounted on interchangeable sample holders, and thermopower specimens were mounted on a fixed sample holder/differential heater. Mounted samples were placed under vacuum (10−3 Torr) and heated to room temperature for 2–4 h to cure the gold contacts. For a variable-temperature run, data (conductivity or thermopower) were acquired during both sample cooling and warming to check reversibility. The temperature drift rate during an experiment was kept below 1 K/min. Typically, three to four separate variable-temperature runs were carried out for each sample to ensure reproducibility and stability. At a given temperature, reproducibility was within ±5%.

**Thermal Transport Measurements.** Thermal conductivity of polycrystalline samples was measured using a steady-state method. Samples were attached to the cold tip of a variable-temperature cryostat with the aid of Stycast epoxy. A small strain-gauge resistor serving as a heater was glued to the other end of the sample. Small crossbars made of flattened 0.25-mm diameter copper wire were attached with a tiny amount of Stycast at two positions along the length of a cylindrical sample. The samples were grown as cylindrical polycrystalline ingots from a recrystallization from the melt. Crossbar copper wires serving to support and conduct heat to the sample, as well as to measure the voltage across the sample resulting from the applied temperature gradient. In both measurements, the gold electrodes were held in place on the sample with a conductive gold paste.

Conductivity specimens were mounted on interchangeable sample holders, and thermopower specimens were mounted on a fixed sample holder/differential heater. Mounted samples were placed under vacuum (10−3 Torr) and heated to room temperature for 2–4 h to cure the gold contacts. For a variable-temperature run, data (conductivity or thermopower) were acquired during both sample cooling and warming to check reversibility. The temperature drift rate during an experiment was kept below 1 K/min. Typically, three to four separate variable-temperature runs were carried out for each sample to ensure reproducibility and stability. At a given temperature, reproducibility was within ±5%.

**Crystallographic Studies.** Both compounds were examined by X-ray powder diffraction for the purpose of phase purity and identification. Accurate d_\text{hkl} spacings (Å) were obtained from the powder patterns recorded on a Rigaku Rotaflex powder diffractometer with Ni-filtered Cu Kα radiation operating at 45 kV and 100 mA. The data were collected at a rate of 1.0°/min.

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**Table 1. Summary of Crystallographic Data and Structure Analysis for K\textsubscript{1}Bi\textsubscript{8}S\textsubscript{13} and K\textsubscript{4}Bi\textsubscript{1}S\textsubscript{3}**

<table>
<thead>
<tr>
<th></th>
<th>K\textsubscript{4}Bi\textsubscript{1}S\textsubscript{3}</th>
<th>K\textsubscript{1}Bi\textsubscript{8}S\textsubscript{13}</th>
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</thead>
<tbody>
<tr>
<td>formula</td>
<td>K\textsubscript{4}Bi\textsubscript{1}S\textsubscript{3}</td>
<td>K\textsubscript{1}Bi\textsubscript{8}S\textsubscript{13}</td>
</tr>
<tr>
<td>F W</td>
<td>1682.54</td>
<td>2166.82</td>
</tr>
<tr>
<td>a, Å</td>
<td>24.05(1)</td>
<td>16.818(2)</td>
</tr>
<tr>
<td>b, Å</td>
<td>4.100(2)</td>
<td>4.074(5)</td>
</tr>
<tr>
<td>c, Å</td>
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<td>17.80(3)</td>
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<td>a, deg</td>
<td>90.00(2)</td>
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</tr>
<tr>
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<td>90.48(1)</td>
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<td>γ, deg</td>
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<td>90.00</td>
</tr>
<tr>
<td>Z; V, Å\textsuperscript{3}</td>
<td>4; 1917</td>
<td>2; 1220</td>
</tr>
<tr>
<td>λ</td>
<td>0.71073 (Mo Kα)</td>
<td>0.71073 (Mo Kα)</td>
</tr>
<tr>
<td>space group</td>
<td>Pnma (No. 62)</td>
<td>P2\textsubscript{1}a\textsubscript{1}m (No. 11)</td>
</tr>
<tr>
<td>D\textsubscript{calc}, g/cm\textsuperscript{3}</td>
<td>5.828</td>
<td>5.890</td>
</tr>
<tr>
<td>μc, cm\textsuperscript{−1}</td>
<td>590 (Mo Kα)</td>
<td>588 (Mo Kα)</td>
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<td>2θ\text{max}, deg</td>
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<td>50</td>
</tr>
<tr>
<td>temp, °C</td>
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<td>23</td>
</tr>
<tr>
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<td>7.382</td>
</tr>
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<td>3888</td>
</tr>
<tr>
<td>total unique data</td>
<td>1944</td>
<td></td>
</tr>
<tr>
<td>data with F\textsubscript{2} &gt; 3σ(F\textsubscript{2})</td>
<td>862</td>
<td>1924 (averaged)</td>
</tr>
<tr>
<td>no. of variables</td>
<td>108</td>
<td>131</td>
</tr>
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</table>

Results and Discussion

**Synthesis, Spectroscopy, and Thermal Analysis**

The synthesis of pure K\textsubscript{4}Bi\textsubscript{1}S\textsubscript{3} can be accomplished by reacting K\textsubscript{2}S and Bi\textsubscript{2}S\textsubscript{3} (1.0:3.3) at 800 °C. Pure K\textsubscript{1}Bi\textsubscript{8}S\textsubscript{13} can be obtained with a ratio of 1.0:4.0 at 750 °C. The known ternary phase, α-KBi\textsubscript{2}S\textsubscript{2}, was obtained as a pure phase by reacting K\textsubscript{2}S and Bi\textsubscript{2}S\textsubscript{3} (1:1) at 725 °C. Surprisingly, instead of α-KBi\textsubscript{2}S\textsubscript{2}, β-KBi\textsubscript{2}S\textsubscript{2} was observed as the major product in the reaction of K\textsubscript{2}S and Bi\textsubscript{2}S\textsubscript{3} (1:2) at 725 °C along with K\textsubscript{4}Bi\textsubscript{1}S\textsubscript{3} as a minor product. β-KBi\textsubscript{2}S\textsubscript{2} is isostrostructure to Bi\textsubscript{3}S\textsubscript{4} in which Cd\textsubscript{6}C\textsubscript{2} \textsuperscript{−} layers (perpendicular to the c axis) alternate with Rb\textsuperscript{+} ions. Three (Bi\textsubscript{2}S\textsubscript{2}) \textsuperscript{−} layers are found in the unit cell of this compound. The coordination sphere of Bi is nearly perfect octahedral. Increasing the amount of Bi\textsubscript{2}S\textsubscript{3} to 1:3 resulted in the formation of K\textsubscript{1}Bi\textsubscript{8}S\textsubscript{13}. The results of several direct combination reactions are shown in Table 4.

K\textsubscript{1}Bi\textsubscript{8}S\textsubscript{13}, K\textsubscript{2}Bi\textsubscript{2}S\textsubscript{2}, and β-KBi\textsubscript{2}S\textsubscript{2} belong to the (A\textsubscript{2}O\textsubscript{3})\textsuperscript{−} (Bi\textsubscript{2}O\textsubscript{3})\textsubscript{m} (A = alkali metal; Q = S, Se) general family of compounds with n = 1 and m = 6.33, 4, and 1, respectively. The synthesis of new ternary bismuth chalcogenides with various n and m values may be possible, e.g., ABi\textsubscript{2}O\textsubscript{3} (n = 1, m = 5).

The optical properties of K\textsubscript{1}Bi\textsubscript{8}S\textsubscript{13} were assessed by studying the UV–visible–near-IR reflectance spectra of the materials. The compounds absorbed all light in the range 0.5–6.2 eV. The spectra confirm that the bandgaps, E\textsubscript{g}, of these two compounds are less than 0.5 eV (the detection limit of the instrument). Diffuse reflectance infrared spectroscopy was used to probe the small bandgap of the compounds. The absorption edges in both compounds were found to be virtually identical in the range of 0.06–0.25 eV (see Figure 1). The narrow bandgaps for K\textsubscript{1}Bi\textsubscript{8}S\textsubscript{13} and K\textsubscript{2}Bi\textsubscript{2}S\textsubscript{2} could result from...
CdI₂-type fragmentsthat connect to form tunnels filled with structure made up of Bi₂Te₃-type (NaCl-type) blocksand KBi₆.33S₁₀.

XRD. Multiple heating/cooling cycles confirmed the existence of a narrow dopant level band just below the conduction band.

The thermal behavior of the two compounds was investigated with differential thermal analysis (DTA, see Figure 2). Both KBi₆.33S₁₀ and K₂Bi₈S₁₃ melt congruently at 710 and 713 °C as evidenced by powder XRD. Multiple heating/cooling cycles confirmed the thermal stability of these compounds.

**Description of Structures. Structure of KBi₆.33S₁₀.** This compound has a three-dimensional structure made up of Bi₂Te₂-type (NaCl-type) blocks and CdI₂-type fragments that connect to form tunnels filled with eight-coordinate K⁺ cations (K−S₈ave = 3.3(1) Å). Selected bond distances and angles for I are given in Tables 5 and 6. Figure 3 shows the packing diagram of the extended structure down the b axis. The [Bi₆.33S₁₀]⁻ framework is made of edge-sharing BiS₆ octahedra, as shown in Figure 4. In an architectural context, it can be thought of as an intimate composite of two different layered structure types interconnected to form a 3-D network. Structural features from the NaCl and CdI₂ frameworks are represented in this framework. The features derived from both these fundamental structure types found in the [Bi₆.33S₁₀]⁻ framework are highlighted in Figure 5. The NaCl-type rod-shaped fragments are linked by rod-shaped CdI₂-type blocks to form the channel framework. The two different fragments are joined via high coordinate Bi atoms (i.e., Bi(7)), in the same way it is found in mineral sulfosalts. Another interesting feature found in this structure is the wide dopant level band just below the conduction band.

**Figure 2.** Typical DTA diagram of K₂Bi₈S₁₃. KBi₆.33S₁₀ gives a similar diagram.

**Table 5. Selected Distances (Å) in KBi₆.33S₁₀ with Standard Deviations in Parentheses**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Standard Deviation (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(1)–S(2)</td>
<td>2.98(1)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(1)–S(2')</td>
<td>2.98(1)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(1)–S(3)</td>
<td>2.74(1)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(1)–S(3')</td>
<td>2.74(1)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(1)–S(5)</td>
<td>3.07(1)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(1)–S(6)</td>
<td>2.58(1)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(1)–S(6')</td>
<td>2.58(1)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(1)–S(mean)</td>
<td>2.8(2)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(2)–S(1)</td>
<td>3.04(1)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(2)–S(1')</td>
<td>3.04(1)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(2)–S(2)</td>
<td>3.28(2)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(2)–S(5)</td>
<td>2.70(1)</td>
<td>0.01(1)</td>
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<td>Bi(2)–S(5')</td>
<td>2.70(1)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(2)–S(8)</td>
<td>2.57(2)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(2)–S(mean)</td>
<td>2.9(3)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(3)–S(1)</td>
<td>2.86(2)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(3)–S(1')</td>
<td>2.86(2)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(3)–S(6')</td>
<td>2.86(2)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Bi(3)–S(mean)</td>
<td>2.9(3)</td>
<td>0.01(1)</td>
</tr>
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*The estimated standard deviations in the mean bond lengths and the mean bond angles are calculated by the equations \( a_{l} = \sqrt{(n(n-1)}^{1/2} \text{ and } a_{l} = \sqrt{(n(n-1)}^{1/2} \text{, where } l \text{ is the length (or angle) of the nth bond, } l \text{ the mean length (or angle), and } n \text{ the number of bonds.}

**References:**

compounds including CsBi₃S₅ (Bi₁,₂),³⁸ Tl₄Bi₂S₅,¹⁰ and
ingonsquare-pyramidalcoordination,isfoundinmany
sametypeofdistortedoctahedralcoordination,border-

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<table>
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<tr>
<td>S(2)–Bi(1)–S(2)</td>
<td>86.9(4)</td>
<td>S(2)–Bi(5)–S(2)</td>
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<td>S(2)–Bi(1)–S(3)</td>
<td>88.0(4)</td>
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<td>S(2)–Bi(5)–S(10)</td>
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<td>S(7)–Bi(5)–S(7')</td>
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<td>S(1)–Bi(2)–S(1')</td>
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<td>S(1)–Bi(6)–S(1')</td>
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<td>S(5)–Bi(7)–S(10')</td>
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<td>S(3)–Bi(3)–S(8)</td>
<td>84.6(4)</td>
<td>S(5)–Bi(7)–S(10')</td>
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<td>S(4)–Bi(3)–S(4')</td>
<td>93.7(3)</td>
<td>S(10')–Bi(7)–S(10'')</td>
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<td>S(2'')–Bi(7)–S(5)</td>
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<td>S(1)–Bi(4)–S(6')</td>
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<td>S(4)–Bi(4)–S(6')</td>
<td>94.5(3)</td>
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<tr>
<td>S(4)–Bi(4)–S(9)</td>
<td>92.7(3)</td>
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</tr>
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the presence of small triangular-shaped empty channels
that are lined by Bi(7)–S(8)–Bi(4)–S(4)–Bi(3)–S(9).
The same type of channels has been observed in β-BaBi₂S₄.¹¹

The existence of Bi₂Te₃- and CdI₂-type fragments,
with Bi in an octahedral coordination site, is a common
structural motif that runs through much of the known
bismuth chalcogenide chemistry. The structure of
CsBi₃S₅ is comprised of Bi₂Te₃-type single chains that
extend along the b direction and share corners in the a–c
plane to form a three-dimensional tunnel structure filled
with Cs⁺ ions. In Cs₅Bi₉Se₁₃,¹² the [Bi₄Se₉]₃⁻ anions are slabs.
They contain CdI₂- and Bi₂Te₃-type fragments that connect in an edge-sharing manner to form
a lamellar structure. In Sr₂Bi₅Se₁₃,¹³ the highly charged
[ Bi₅Se₉ ]³⁻ anion has a very interesting structure. It
contains two-dimensional sheets made up of edge-sharing
CdI₂- and Bi₂Te₃-type fragments. One-dimen-
sional double chains, comprised of Bi₇Te₃-type blocks,
extend along the b direction and separate these layers.
In BaBiSe₃¹⁴ and in BaBiTe₃¹⁵ one-dimensional single
chains, comprised of Bi₂Te₃-type blocks, are linked by
unusual zig-zag (S₆)²⁻ and (Te₆)²⁻ chains respectively
to form a layered structure.

Atoms Bi(3,4) possess only slightly distorted octahe-
dral coordination with Bi–S bond distances ranging from 2.80(1) to 2.94(1) Å for Bi(3) and 2.812(9) to 2.86-
(1) Å for Bi(4). These distances are similar to those reported in CsBi₃S₅ (Bi₁,₂).³⁸ In contrast, the octahedral
coordination environments in Bi(1), Bi(2), Bi(5), and Bi-
(6) are highly distorted with a short bond that is trans
to a long bond (Figure 6). This type of coordination
environment is very prevalent in bismuth chalcogenide
chemistry and results from the influence of the non-
bonded, stereochemically active 6s² electron lone pair.
For example, the Bi(2)–S(9) bond distance of 2.572(7) Å
is trans to a long Bi(2)–S(1) distance of 3.282(2) Å. This
same type of distorted octahedral coordination, border-
ing on square-pyramidal coordination, is found in many
compounds including CsBi₃S₅ (Bi₁,₂),³⁸ Tl₄Bi₂S₅,¹⁰ and
α-(β'-)BaBi₄S₉.¹³ The sites of Bi(6) and Bi(7) are partially
occupied at 81% and 53%, respectively. Bi(7) possesses
a distorted seesaw structure or a trigonal-bipyramidal
coordination if one includes the lone pair, with four
normal Bi–S bonds ranging from 2.791(1) to 3.21(2) Å.
The lone pair is directed at four squarely arranged

sulfur atoms with long Bi–S distances of 3.47(1) and
3.48(1) Å. The axial S(2'')–Bi(7)–S(5) angle is much
less than 180° at 148.3(5)°, and the equatorial S(10')–
Bi(7)–S(10'') angle is 94.5(5)°. These angles are influ-
ced by the stereochemically active lone pair. If the four
sulfur atoms (i.e., S(9), S(9), S(8), and S(8)) are
included in the coordination sphere of Bi(7), then the
overall polyhedron becomes a bicapped trigonal prism
(see Figure 6).

Structure of K₂Bi₆S₁₀. This compound also posses-
ses a three-dimensional structure made up of NaCl
or Bi₂Te₃- and CdI₂-type rod-shaped fragments that
connect to form a structure with tunnels. Here too,
the highly coordinated Bi(8) atoms serve to stitch the rods
together. The K⁺ cations are disordered with one of the
Bi₃⁺ ions over three distinct crystallographic sites. This,
although not expected, can be rationalized by the similar
sizes of K⁺ and Bi₃⁺. This structure is quite different
from that of its selenium analogue K₂Bi₆Se₁₀.²¹ Selected
bond distances and angles for K₂Bi₆S₁₀ are given in Tables 7 and 8.

2.96(2) Å for Bi(4) and 2.80(2) to 2.86(1) Å for Bi(6). As to Bi of 1:4 (i.e., K₂S[Bi₂S₃]₄). The corresponding K₂S/K₂Bi₈S₁₃ can be viewed as a derivative of the well-known Bi(7) in a bicapped prismatic geometry. For Bi-S distances and S-Bi-S angles see Tables 3 and 6.

Figure 7 shows the extended [Bi₈S₁₃]₂⁻ framework down the b axis. As in K₂Bi₆.₃₃S₁₀, this framework is based on structural features from the Bi₂Te₃ and CdI₂ lattices and contains the small triangular-shaped empty channels. The tunnels of K₂Bi₆.₃₃S₁₀, which can be better viewed in Figure 8, are more open than those of K₂Bi₆.₃₃S₁₀ because more K⁺ is present per formula unit. K₂Bi₆.₃₃S₁₀ can be viewed as a derivative of the well-known Bi₆S₅ compound generated by breaking down the Bi₁₃S₅ framework by incorporation of K₂S in the molar ratio of 1:4 (i.e., [K₂S] [Bi₂S₃]₄). The corresponding [K₂S]/[Bi₂S₃] ratio in K₂Bi₆.₃₃S₁₀ is 1:6.33, so less K⁺ ions are present resulting in smaller channels.

Bi(4) and Bi(6) possess regular octahedral coordination with Bi-S bond distances ranging from 2.77(1) to 2.96(2) Å for Bi(4) and 2.80(2) to 2.86(1) Å for Bi(6). As in K₂Bi₆.₃₃S₁₀, the octahedral coordination environments of Bi(1), Bi(2), Bi(3), Bi(5), and Bi(7) are distorted with a short bond that is trans to a long bond but with normal octahedral angles, (Figure 9). For example, the Bi(2)-S(8) bond distance of 2.61(2) Å is trans to a long Bi(2)-S(3′) distance of 3.29(2) Å. Bi(8) is disordered over three sites with K(1,2). The Bi(8) site contains approximately 60% Bi and 40% K, while the other two sites contain mainly K (~80%). Bi(8) possesses the same type of distorted bicapped trigonal prismatic as found for Bi(7) (in K₂Bi₆.₃₃S₁₀), with four normal Bi-S bonds ranging from 2.75(1) to 3.06(2) Å and four longer distances from 3.43(1) to 3.50(1) Å. Bi(4) and Bi(6) possess regular octahedral coordination with Bi-S bond distances ranging from 2.77(1) to 2.96(2) Å for Bi(4) and 2.80(2) to 2.86(1) Å for Bi(6). As in K₂Bi₆.₃₃S₁₀, the octahedral coordination environments of Bi(1), Bi(2), Bi(3), Bi(5), and Bi(7) are distorted with a short bond that is trans to a long bond but with normal octahedral angles, (Figure 9). For example, the Bi(2)-S(8) bond distance of 2.61(2) Å is trans to a long Bi(2)-S(3′) distance of 3.29(2) Å. Bi(8) is disordered over three sites with K(1,2). The Bi(8) site contains approximately 60% Bi and 40% K, while the other two sites contain mainly K (~80%). Bi(8) possesses the same type of distorted bicapped trigonal prismatic as found for Bi(7) (in K₂Bi₆.₃₃S₁₀), with four normal Bi-S bonds ranging from 2.75(1) to 3.06(2) Å and four longer distances from 3.43(1) to 3.50(1) Å.
and 2.72(2) to 3.66(2) Å for K(2). These distances are similar to those found for the predominantly Bi(8) site. The K–S distances below 3.0 Å are unusual and presumably a result of averaging over the mixed K/Bi sites. Since the Bi(8) and the potassium sites have similar coordination characteristics and similar pocket sizes, it is not surprising, after all, that a site occupancy exchange exists between these ions. To the best of our knowledge, there are no known systems that have alkali metal/Bi disorder. The closest example is Cu$_{1+2x}$Bi$_{5}$S$_{8}$, where Cu$^{+}$ and Bi$^{3+}$ ions are disordered over one site.

Electrical Conductivity and Thermoelectric Power Measurements. Four-probe electrical conductivity measurements on polycrystalline chunks of KBi$_{6.33}$S$_{10}$ showed that the material is a semiconductor with room temperature conductivity $\sigma \sim 10^2$ S/cm which drops to $10^{-4}$ S/cm at 5 K. Figure 10a shows the log conductivity vs temperature plot for KBi$_{6.33}$S$_{10}$. The data can be fit to the equation shown below suggesting an activation energy of $E_a = 0.045$ eV:

$$\sigma = \sigma_0 e^{-E_a/k_B T}$$

Figure 10b shows the log conductivity as a function of temperature for K$_2$Bi$_8$S$_{13}$. The conductivity of $\sim 10^2$ S/cm (room temperature) and the weak temperature dependence between 5 and 300 K coupled with the IR optical data (vide supra) suggests that this compound is a semi-metal or a narrow-bandgap semiconductor. It is noteworthy that the conductivity of both these ternary compounds is significantly higher than that of the parent Bi$_2$S$_3$. The latter possesses a much higher bandgap of 1.1 eV. The conductivity of $\sim 10^2$ S/cm is compared to the values of other semi-metals such as Bi$_2$-Te$_3$ ($2.2 \times 10^3$ S/cm)$^{35}$ and Bi$_2$Se$_3$ (($1.6 \sim 2.0) \times 10^3$ S/cm, Bi$_2$Te$_3$-type)$^{36}$ obtained from single crystals of these materials.

The conductivity measurements alone cannot unequivocally characterize the electrical behavior of KBi$_{6.33}$S$_{10}$ and K$_2$Bi$_8$S$_{13}$. A complementary probe to address this issue is thermoelectric power (TP) mea-
measurements as a function of temperature. TP measurements are typically far less susceptible to artifacts arising from resistive domain boundaries in the material because they are essentially zero-current measurements. This is because temperature drops across such boundaries are much less significant than voltage drops. The TP of KBi$_6$S$_{10}$ is negative throughout the temperature range studied (80 < T < 300 K) with values of ∼−30 µV/K at room temperature. This indicates electron (as opposed to hole) charge transport. The TP becomes slightly more negative as the temperature is decreased from 300 to 80 K, (see Figure 11). This behavior in combination with the high electrical conductivity is characteristic of a degenerate semiconductor. The semiconducting character of this material is in accord the fact that an optical gap exists in this material in the infrared region (see Figure 1a). The TP of K$_2$Bi$_8$S$_{13}$ is also negative throughout the temperature range studied (80 < T < 300 K) with similar magnitudes of TP at room temperature suggestive of an n-doped material. The material displays weak temperature dependence of the TP is consistent with a degenerate semiconductor. The optical gap of K$_2$Bi$_8$S$_{13}$ (Figure 1b) is quite small (<0.25 eV) similar to that of Bi$_2$Te$_3$ ($E_g$ = 0.16 eV). Interestingly, the TP of this material varied greatly in samples of different preparations. Seebeck coefficients as small as −2 µV/K were observed in some samples indicative of a heavily doped material. This discrepancy could be a result of possible nonstoichiometry (K$_{2-3x}$Bi$_8$-$_x$S$_{13}$), caused by the site occupancy disorder between K and Bi found in the high coordinate Bi(8) site. The K/Bi distribution could vary from sample to sample slightly, thus affecting the electronic band structure of the Bi/S framework. Nonstoichiometry and the presence of impurities can have dramatic effects on the physical properties such as electrical conductivity and optical reflectance measurements.

**Thermal Conductivity.** For prospective materials to be competitive for thermoelectric applications, they must possess very low thermal conductivity at the temperature range of interest. Therefore, the thermal transport properties of these materials were measured over a wide temperature region. Thermal conductivity of the two compounds is shown in Figure 12. The data show a characteristic peak at low temperatures (near 7 K for KBi$_6$S$_{10}$ and at around 13 K for K$_2$Bi$_8$S$_{13}$) and


(38) For example, SnTe is p-type with an $E_g$ of 0.5 eV. The uncertainty as to whether SnTe is a semiconductor or a semimetal. The high carrier concentration favors the semimetallic character of the material; however, thermoelectric power measurements suggest a semiconductor.

![Figure 10. Variable-temperature electrical conductivity data for polycrystalline chunks of (a) KBi$_6$S$_{10}$ and (b) K$_2$Bi$_8$S$_{13}$.](image)

![Figure 11. Variable-temperature thermoelectric power data for polycrystalline rod of KBi$_6$S$_{10}$.](image)

![Figure 12. Temperature dependence of the thermal conductivity of polycrystalline cylindrical samples of KBi$_6$S$_{10}$ (open squares) and K$_2$Bi$_8$S$_{13}$ (open circles). The arrow indicates the room-temperature value of the lattice thermal conductivity of Bi$_2$Te$_3$.](image)
underscore an overall low value of thermal conductivity in these materials. K₂Bi₈S₁₃ shows a more pronounced peak than the one seen on the KBi₁₆.₃₃S₁₀ sample and, depending on the temperature, its thermal conductivity is a factor of 2–4 larger. Using the measured values of the electrical resistivity in conjunction with the Wiedemann–Franz law, we estimate the maximum possible value of the electronic thermal conductivity contribution to be below 1% of the total thermal conductivity for K₂Bi₈S₁₃ and not to exceed 1–2% in the case of KBi₁₆.₃₃S₁₀. Thus, essentially all heat in these compounds is carried by lattice phonons. Taking as a bench mark the room temperature value of the lattice thermal conductivity of Bi₂Te₃ (κ_L \sim 1.7 \text{ W/m K}), we note that the total thermal conductivity of KBi₁₆.₃₃S₁₀ is actually lower than this number. Hence, at least from the perspective of thermal transport, these compounds satisfy one of the key requirements for a useful thermoelectric material, they possess very low lattice thermal conductivity. This is an important finding because the KBi₁₆.₃₃S₁₀ is a sulfide and, compared to the heavier tellurides, is expected to possess higher thermal conductivity. This is because of the higher frequency lattice phonons present in the sulfide. The surprisingly low thermal conductivity of KBi₁₆.₃₃S₁₀ suggests other factors such as actual structure and lattice size and symmetry play an important role. If ways could be found to enhance the electrical conductivity and, at the same time, preserve or even increase the thermopower, at least in the case of KBi₁₆.₃₃S₁₀, one indeed might have a promising thermoelectric material. To achieve this we need additional information regarding the transport properties including carrier concentrations and mobilities. Then optimization of these properties could be accomplished by controlling accurately the stoichiometry of these materials. This work is currently underway.  

Concluding Remarks

In summary, our investigations of the K₂S/Bi₂S₃ system have revealed two new phases, KBi₁₆.₃₃S₁₀ and K₂Bi₈S₁₃ with new structure types. These compounds are n-type semiconductors with optical bandgaps < 0.25 eV and very good room-temperature conductivity. Although the thermoelectric power is too low for practical applications as thermoelectric materials, the product of electrical conductivity and thermopower are promising enough to warrant more systematic explorations in the A₂Q/Bi₂Q₃ (A = K, Rb, Cs; Q = S, Se, Te) and related systems.

It is noteworthy that both compounds possess rather low thermal conductivity with that of KBi₁₆.₃₃S₁₀ being extraordinarily low and much lower than that of Bi₂Te₃. This has the important implication that, as a class of materials, the sulfides are excellent candidates for exploration as potential thermoelectrics. The advantage of the sulfides relative to the tellurides, of course, lies in the significantly lower cost and weight savings that could be realized during manufacturing.

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Supporting Information Available: Tables of atomic coordinates of all atoms and anisotropic and isotropic thermal parameters of all non-hydrogen atoms, bond distances and angles (22 pages); a listing of calculated and observed (10F/10F) structure factors (21 pages). Ordering information is given on any current masthead page.

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