

Transport Properties of Bi_2S_3 and the Ternary Bismuth Sulfides $\text{KBi}_{6.33}\text{S}_{10}$ and $\text{K}_2\text{Bi}_8\text{S}_{13}$

Baoxing Chen and Ctirad Uher

Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

Lykourgos Iordanidis and Mercouri G. Kanatzidis*

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824

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We have studied transport properties (resistivity, Hall effect, thermopower, and thermal conductivity) of Bi_2S_3 and two new ternary bismuth sulfides, $\text{KBi}_{6.33}\text{S}_{10}$ and $\text{K}_2\text{Bi}_8\text{S}_{13}$, to explore their potential for thermoelectric applications. While both Bi_2S_3 and $\text{K}_2\text{Bi}_8\text{S}_{13}$ display an essentially metallic conduction, $\text{KBi}_{6.33}\text{S}_{10}$ has a distinctly semiconducting character. From the Hall measurements it follows that the dominant carriers in all three compounds are electrons and that the carrier density in $\text{K}_2\text{Bi}_8\text{S}_{13}$ is almost 2 orders of magnitude larger than in Bi_2S_3 and $\text{KBi}_{6.33}\text{S}_{10}$ over the whole temperature range from 4 to 300 K. While the room temperature thermopowers of $\text{KBi}_{6.33}\text{S}_{10}$ and $\text{K}_2\text{Bi}_8\text{S}_{13}$ are comparable ($\sim -100 \mu\text{V/K}$), the thermopower of Bi_2S_3 is a factor of 3 larger. All three compounds are poor conductors of heat, in particular the thermal conductivity of $\text{KBi}_{6.33}\text{S}_{10}$ is some 25% lower than the thermal conductivity of Bi_2Te_3 , the benchmark thermoelectric material. To make these materials useful thermoelectrics, ways must be found how to significantly increase their electrical conduction while preserving the reasonably large thermopower and low thermal conductivity.

Introduction

Semiconducting chalcogenide compounds have been receiving much attention because of their wide range of applications in various fields of science and technology. One of the most promising areas is their use in thermoelectric refrigeration. While the physical properties of Bi_2Te_3 and its isostructural alloys have been studied most intensely^{1–3} and this family of materials has been the backbone of the thermoelectric industry over the past 30 years, little effort has been extended to study new ternary bismuth chalcogenide compounds. We have recently synthesized two new ternary bismuth sulfides, $\text{KBi}_{6.33}\text{S}_{10}$ and $\text{K}_2\text{Bi}_8\text{S}_{13}$, and in this paper we provide a detailed assessment of their thermoelectric properties.

Experimental Section

Both compounds have a similar three-dimensional structure made up of Bi_2Te_3 -type blocks and CdI_2 -like fragments that connect to form K^+ ions-filled channels. $\text{KBi}_{6.33}\text{S}_{10}$ crystallizes with the orthorhombic structure, while $\text{K}_2\text{Bi}_8\text{S}_{13}$ has a monoclinic structure with two potassium atoms and one bismuth atom disordered over three sites. The structural and compositional difference and perhaps differences in doping give rise to a dramatically different transport behavior. The parent compound, Bi_2S_3 , was obtained by reaction of mixture of Bi and S at 500 °C in a vacuum-sealed Pyrex tube. The

compounds were prepared by a direct synthesis of K_2S with Bi_2S_3 at high temperatures ($>700 \text{ }^\circ\text{C}$) as described previously.⁴

Electrical resistivity and the Hall effect were measured under isothermal conditions in a cryostat equipped with a magnet capable of fields up to 5.5 T. Thermal conductivity and thermopower were determined using a longitudinal steady-state method over the temperature range 4–300 K. In this case samples were attached (using either a low melting point solder or silver-loaded epoxy) to the cold tip of the cryostat, while the other end of the sample is provided with a small strain gauge resistor (thin film) which serves as a heater. Temperature difference across the sample is measured using a differential chromel–constantan thermocouple.

Results and Discussion

Figure 1 shows the temperature dependence of resistivity for the three compounds. $\text{K}_2\text{Bi}_8\text{S}_{13}$ displays a positive slope of the resistivity over most of the temperature range with a shallow minimum around 30 K. The minimum arises from freezing of the carriers at low temperatures, and the material is thus a very narrow gap semiconductor. $\text{KBi}_{6.33}\text{S}_{10}$ indicates a robust activated behavior at temperatures above 80 K with the activation energy of 5.8 meV. Most surprisingly, Bi_2S_3 shows a positive slope of the resistivity even though it nominally has a large bandgap^{5,6} of 1.3 eV. The origin of such metallic conduction stems from a substoichiometry of sulfur whereby the sulfur vacancies serve as the source of electrons. As pointed out recently by Mizogu-

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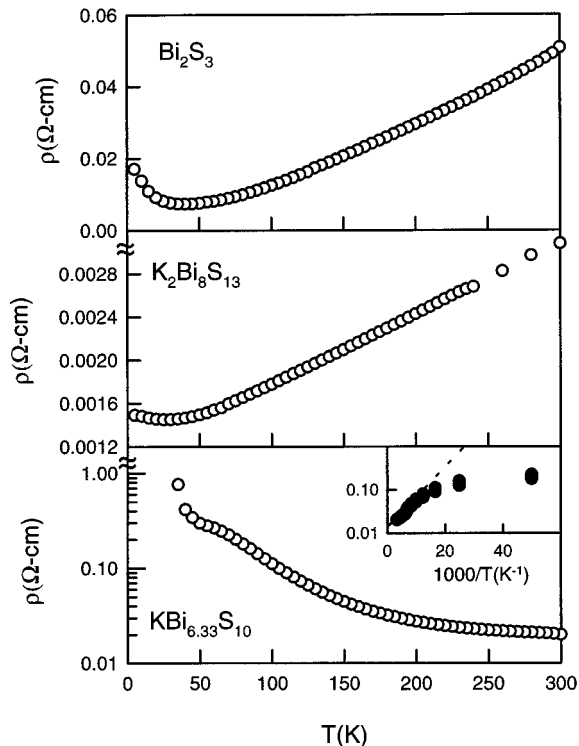


Figure 1. Temperature dependence of the resistivity of Bi_2S_3 (top panel), $\text{K}_2\text{Bi}_8\text{S}_{13}$ (middle panel), and $\text{KBi}_{6.33}\text{S}_{10}$ (bottom panel). The inset in the bottom panel shows the logarithmic plot of the resistivity vs $1000/T$. The dashed line is a guide for eyes.

chi et al.,⁷ annealing of Bi_2S_3 in a sulfur-rich atmosphere leads to a drastic decrease in the electrical conduction as the sulfur vacancies are being filled.

In Figure 2 we show the temperature dependence of the Hall coefficient, R_H , for the three samples. The Hall voltages through the temperature range investigated are linear with field up to the highest field of 5 T, which indicates that the Hall coefficients are all field independent. The Hall coefficients are negative, which suggests that the majority carriers are electrons. The magnitude of the Hall coefficient for $\text{KBi}_{6.33}\text{S}_{10}$ is almost 2 orders of magnitude larger than that for $\text{K}_2\text{Bi}_8\text{S}_{13}$. The Hall coefficient of Bi_2S_3 implies a carrier density on the order of 10^{20} cm^{-3} . The peak in R_H near 25 K observed in $\text{K}_2\text{Bi}_8\text{S}_{13}$ coincides with the minimum in the resistivity. Making use of the data for the electrical resistivity and the Hall coefficient, the Hall mobility $\mu_H = R_H/\rho$ is plotted as a function of temperature in Figure 3. In Bi_2S_3 , the Hall mobility at $T > 70 \text{ K}$ has a power law scaling $\mu_H \propto T^n$, with $n = -1.4$, while for $\text{K}_2\text{Bi}_8\text{S}_{13}$, the Hall mobility at comparable temperatures has an exponent $n = -0.9$. These exponents suggest a combination of phonon-limited mobility ($n = -1.5$) and impurity-limited conduction. The mobility of $\text{KBi}_{6.33}\text{S}_{10}$ has a very different exponent, $n = -2.5$. This value suggests the carriers interact dominantly with the acoustic phonon modes ($\lambda = 0.5$) via two-phonon processes⁸ ($\mu_H \propto T^{\lambda-2}$). Similar functional forms have been reported for Bi_2Te_3 and related compounds.²

Thermal conductivity of the compounds is displayed in Figure 4. We note a pronounced peak observed on

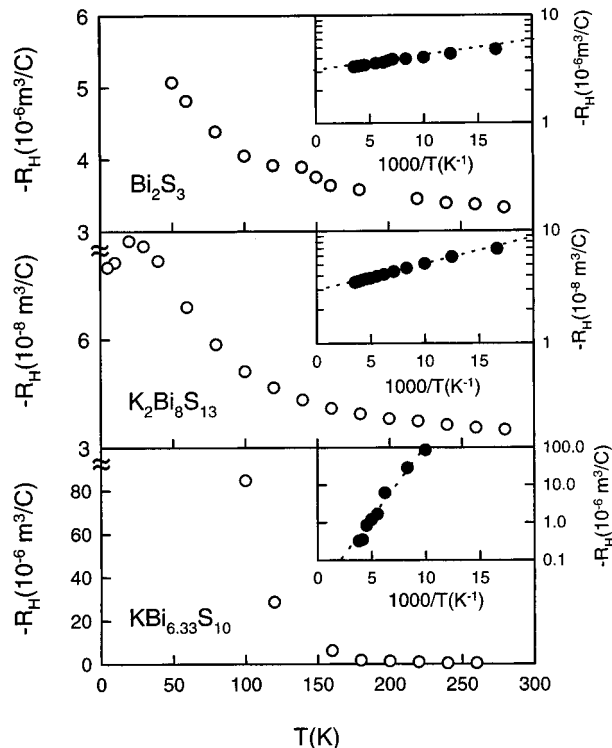


Figure 2. Temperature dependence of the Hall coefficient in Bi_2S_3 (top panel), $\text{K}_2\text{Bi}_8\text{S}_{13}$ (middle panel), and $\text{KBi}_{6.33}\text{S}_{10}$ (bottom panel). The dashed line in the insets represents $\log R_H$ vs $1/T$ dependence.

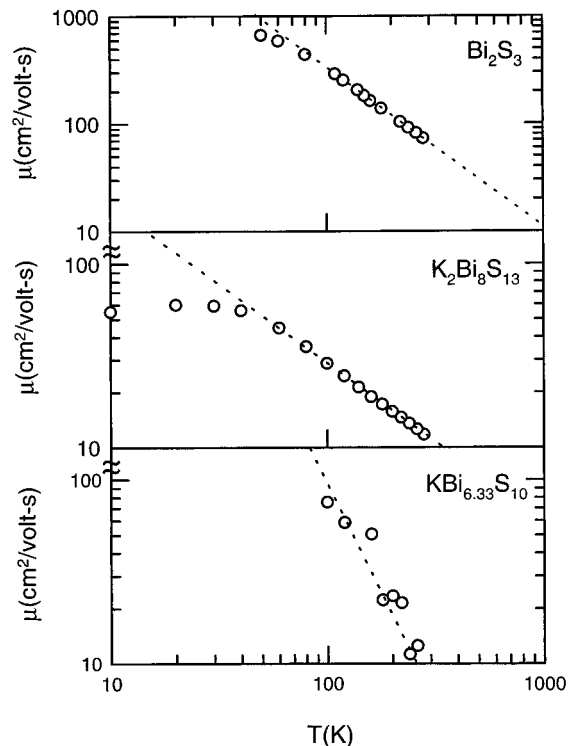


Figure 3. log-log plots of the temperature dependence of the Hall mobility in Bi_2S_3 (top panel), $\text{K}_2\text{Bi}_8\text{S}_{13}$ (middle panel), and $\text{KBi}_{6.33}\text{S}_{10}$ (bottom panel).

both Bi_2S_3 and $\text{K}_2\text{Bi}_8\text{S}_{13}$ at 15 K, which reflects a competition between phonon-boundary scattering and umklapp phonon-phonon interactions. Bi_2S_3 has a more pronounced peak on account of its simple and less defective structure. Invoking the Wiedemann-Franz law and the measured electrical resistivity, we estimate

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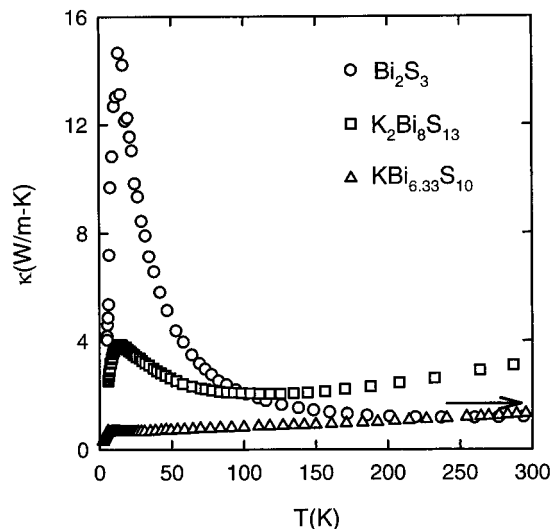


Figure 4. Temperature dependence of the thermal conductivity of Bi_2S_3 (open circles), $\text{K}_2\text{Bi}_8\text{S}_{13}$ (open squares), and $\text{KBi}_{6.33}\text{S}_{10}$ (open triangles) from 2 to 300 K. The arrow indicates the room-temperature value of the lattice thermal conductivity of Bi_2Te_3 .

the electronic contribution to the thermal conductivity in the vicinity of the peak to be no more than 1% of the total heat conduction. The electronic contribution increases with increasing temperature, and near the room temperature amounts to about 10% of the total heat conduction. A part of the upturn observed above 150 K is associated with this increasing contribution of carriers to the heat transport. In contrast, the thermal conductivity of $\text{KBi}_{6.33}\text{S}_{10}$ is much depressed at all temperatures; the low-temperature peak is barely resolved and is shifted down to near 8 K. Furthermore, the thermal conductivity is essentially a linear function of temperature right up to room temperatures. The value of the thermal conductivity at 300 K is some 25% below the value for Bi_2Te_3 . Thus, from the point of view of phonon transport, $\text{KBi}_{6.33}\text{S}_{10}$ looks far more disordered than $\text{K}_2\text{Bi}_8\text{S}_{13}$.

One thing we would like to point out is that there is inevitable radiation loss for the thermal conductivity measurements at high temperatures. However, we estimate that the radiation loss in our measurements at room temperatures is no more than 8%. For example, our Bi_2S_3 sample is a cylinder with a length $l = 3$ mm and a diameter $D = 2$ mm. At room temperatures, with a heat power of 0.3 mW, the temperature difference ΔT across the sample is roughly 0.3 K; thus the heat lost by radiation E_l from the sample and the thin-film heater attached at the hot end is given approximately by

$$E_l = \int_0^l \sigma \left[\left(T_c + \frac{x}{l} \Delta T \right)^4 - T_c^4 \right] 2\pi \frac{D}{2} dx + \sigma \pi \left(\frac{D}{2} \right)^2 \left[(T_c + \Delta T)^4 - T_c^4 \right] \quad (1)$$

Here σ is the Stefan-Boltzmann constant, T_c is the temperature of the cold end of the sample as well as that of the radiation shield, and we have considered the worst-case scenario by assuming that the sample is an ideal radiator. Using the values given above, we found that $E_l \approx 0.0231$ mW at 300 K, which is less than 8% of the total heat power, 0.3 mW, applied to the heater. This radiation loss will tend to overestimate the thermal conductivity.

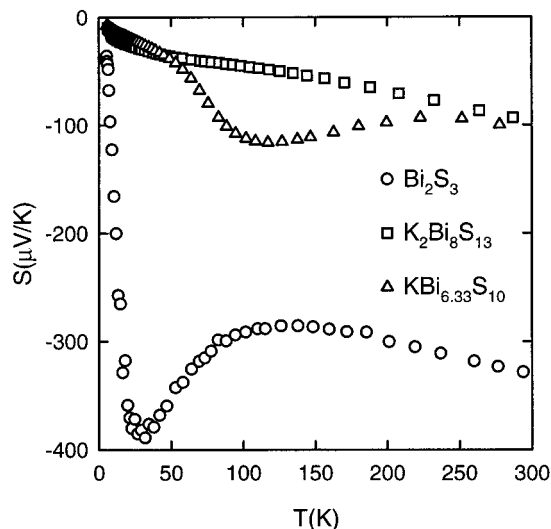


Figure 5. Temperature dependence of the thermopower of Bi_2S_3 (open circles), $\text{K}_2\text{Bi}_8\text{S}_{13}$ (open squares), and $\text{KBi}_{6.33}\text{S}_{10}$ (open triangles).

Thermopower data are shown in Figure 5. In accord with the Hall measurements, the thermopower of all three samples is negative. In particular, Bi_2S_3 has a very large thermopower of about $-325 \mu\text{V/K}$ at room temperature. In addition, a pronounced dip, believed to be associated with a phonon drag contribution, is observed near 25 K. While the two ternary compounds have quite similar room-temperature values on the order of negative $100 \mu\text{V/K}$, they have very different temperature dependences. $\text{K}_2\text{Bi}_8\text{S}_{13}$ shows a weak dependence on temperature consistent with its degenerate semiconductor character. In contrast, $\text{KBi}_{6.33}\text{S}_{10}$ has a deep minimum near 115 K where the absolute value of the thermopower is actually larger than at 300 K. With further decrease in temperature the thermopower rapidly diminishes, and below about 50 K the two compounds have again comparable thermopowers.

From experimental values of the thermopower and the carrier concentration we can estimate the carrier effective masses in the three materials. For a single-band semiconductor, the thermopower and the carrier density can be written as³

$$S = \pm \frac{k_B}{e} \left[\frac{2F_1(\eta)}{F_0(\eta)} - \eta \right] \quad (2)$$

$$n = \frac{4}{\sqrt{\pi}} \left[\frac{2\pi m^* k_B T}{h^2} \right]^{3/2} F_{1/2}(\eta) \quad (3)$$

where $\eta = E_F/k_B T$ is the reduced Fermi energy and F_n are Fermi integrals. Using eqs 2 and 3, we found that the carrier effective masses in Bi_2S_3 , $\text{K}_2\text{Bi}_8\text{S}_{13}$, and $\text{KBi}_{6.33}\text{S}_{10}$ are $0.587m_e$, $1.635m_e$, and $0.372m_e$, respectively, with m_e being the mass of the electron.

To be a useful thermoelectric, a material must have large thermoelectric figure of merit defined as $Z = S^2/\kappa\rho$, or its dimensionless equivalent ZT . Experimental values of the transport coefficients of the compounds studied yield the dimensionless figure of merit shown in Figure 6. Using as a benchmark the value of $ZT = 1$ which is approached in optimized Bi_2Te_3 -based alloys, substantial improvement in electrical conductivity and thermopower needs to be achieved for the materials

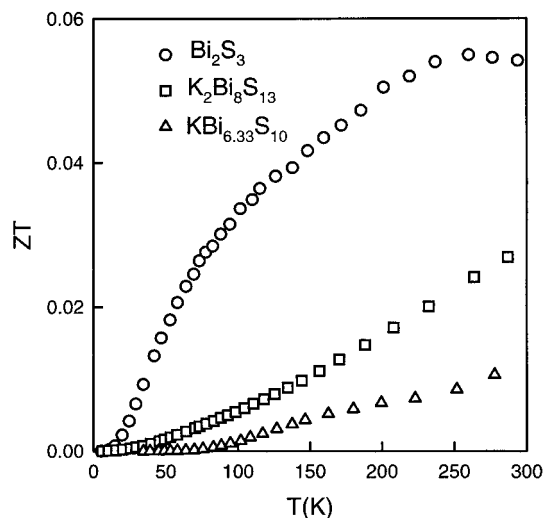


Figure 6. Dimensionless figure of merit as a function of temperature for the three samples.

reported here to be competitive. While the values of the thermopower and thermal conductivity are encouraging, particularly for Bi_2S_3 and $\text{KBi}_{6.33}\text{S}_{10}$, the electrical resistivity is simply too high. Resistivity improvements may come through better sample morphologies and larger crystallite sizes and via judicious doping processes.

The most significant findings of this study are (a) we have demonstrated that bismuth sulfide compounds can have thermal conductivities comparable to or even lower

than that of Bi_2Te_3 . Given that in the field of thermoelectrics there is the tendency to employ compounds with heavy elements to keep the thermal conductivity low, this work carries important implications on the entire class of metal sulfides as candidate materials for thermoelectric applications. This is important from the point of view of environmental compatibility and materials costs. (b) The thermoelectric data reported for sulfur-deficient Bi_2S_3 are quite encouraging given that the intrinsic material is a wide-gap semiconductor (1.3 eV) with room-temperature conductivity of $10^{-4} \Omega^{-1} \text{cm}^{-1}$. That the conductivity can be increased by 5–6 orders of magnitude by introducing sulfur vacancies in the lattice and at the same time maintain a very large thermopower ($>300 \mu\text{V}/\text{K}$) suggests that introducing vacancies may be profitable in these kinds of materials. The surprisingly low thermal conductivity of the sulfur deficient Bi_2S_3 could be due to enhanced phonon scattering on the sulfur vacancies. In future work we will investigate quantitatively the effect of sulfur vacancies on ZT , and we shall attempt to raise their density to even higher levels. It is possible that the vacancy route may also lead to an improvement in the figure of merit of the ternary compounds such as $\text{K}_2\text{Bi}_8\text{S}_{13}$ and $\text{KBi}_{6.33}\text{S}_{10}$.

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