Thermoelectric Properties of Single Crystal EuBiSe₃ Fiber

Xiuqi Wangᵃ, Shaoyi Shiᵃ, Xin Qiᵃ, Dong Wuᵇ, Weigang Maᵃ, and Xing Zhangᵃ

ᵃKey Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Engineering Mechanics, Tsinghua University, Beijing, China;ᵇSchool of Physics, International Center for Quantum Materials, Peking University, Beijing, China

ABSTRACT
EuBiSe₃, a narrow-band-gap semiconductor, is synthesized by introducing the rare earth element Eu into Bi₂Se₃. It can be a potential thermoelectric material due to the relatively complex crystal structure and large effective mass. In this study, the thermoelectric properties of a EuBiSe₃ fiber with a diameter of 167 μm have been characterized systematically for the first time from 80 to 290 K by applying our developed T-type method, including thermal conductivity, electrical conductivity and Seebeck coefficient. The thermal conductivity decreases from 1.08 to 0.88 W m⁻¹K⁻¹ dominated by three-phonon Umklapp scattering and then increases to 1.20 W m⁻¹K⁻¹ as the temperature increases to 290 K. The electrical conductivity varies from 4209 to 5240 S m⁻¹ in the studied temperature range. The absolute Seebeck coefficient increases slightly to 204 μVK⁻¹ with the increase of temperature. The highest value of the determined dimensionless figure of merit ZT is 0.05, obtained at 290 K.

ARTICLE HISTORY
Received 9 July 2018
Accepted 6 January 2019

KEYWORDS
EuBiSe₃; thermoelectric properties; thermal conductivity; electrical conductivity; Seebeck coefficient

Introduction
Thermoelectric material is a kind of functional material which can convert heat energy to electric energy through charge carriers without any moving parts or harmful gases [1–3]. It has been extensively used in aerospace, microelectronic devices, and energy conservation devices due to its high reliability and long service life [4, 5]. The thermoelectric performance of a material is characterized by the dimensionless figure of merit $ZT$, where $T$ is the absolute temperature and $Z = S^2σ/λ$, $S$ is the Seebeck coefficient, $λ$ is the thermal conductivity and $σ$ is the electrical conductivity, respectively. The larger the $ZT$ value, the better the thermoelectric properties of the material and the higher the thermoelectric conversion efficiency of the corresponding device. According to the theoretical analysis, there is no upper limit of $ZT$ value [6]. Thermoelectric materials with excellent performance must have high Seebeck coefficient, high electrical conductivity, and low thermal conductivity.

Bi₂Se₃ is a promising thermoelectric material near room temperature with 0.3 eV band gap since the narrow-band-gap semiconductor is very suitable for thermoelectric material [7–9]. The development and application of Bi₂Se₃ compound in the thermoelectric field have attracted much attention in recent years. Kadel et al. studied the thermoelectric properties of Bi₂Se₃ nanoparticles from 300 to 523 K and obtained a maximum $ZT$ of 0.096 at 523 K [10]. Min et al. synthesized Bi₂Se₃ nanosheets and achieved a maximum $ZT$ of 0.2 at 480 K [11]. Soni et al. studied the thermoelectric properties of Bi₂Te₃₋ₓSeₓ nanoplatelet composites from 5 to 300 K, in which Bi₂Se₃ obtained the best thermoelectric performance at 300 K with $ZT = 0.1$ [12]. Sun et al. found that the Bi₂Se₃ compound could achieve the $ZT$ value of 0.35 at 480 K, which is a breakthrough in the $ZT$ value of Bi₂Se₃.
material [13]. However, the thermoelectric device can be competitive with other energy conversion technologies only if the ZT value achieves to 4 [14]. Thence, it is of great importance to optimize the thermoelectric properties of Bi₂Se₃.

The introduction of rare-earth metal element Eu in Bi₂Se₃ may improve its thermoelectric properties. The special f electron shell of rare-earth element can produce hybrid effect with d electron shell of other elements, forming a complex energy band structure, the effective mass of rare-earth alloy material can be larger than that of ordinary semiconductors due to the strong interaction between the electrons, which is significant to improve the thermoelectric performance of rare-earth alloy material [15–17].

Forbes et al. and Bang Jin et al. have introduced the rare-earth metal element Eu into the Bi₂Se₃ compound, synthesizing the EuBiSe₃ phase [18–20]. However, the thermoelectric properties of the EuBiSe₃ phase have not been characterized. In this study, we synthesized EuBiSe₃ single crystal fiber by the reported method and characterized the thermoelectric properties of EuBiSe₃ fiber with a diameter of 167 μm for the first time by applying our developed T-type method, including thermal conductivity, electrical conductivity and Seebeck coefficient. Moreover, we compared the thermoelectric properties of EuBiSe₃ fiber and Bi₂Se₃ phase reported in previous literatures.

**Experiment and results**

**Sample preparation and characterization**

The single-crystal EuBiSe₃ fiber was grown by the method reported by Bang Jin et al. [19, 20]. First, the starting material Bi₂Se₃ was synthesized by a direct reaction of Bi shots (99.999%) and Se powders (99.999%) in the stoichiometric ratio of 2:3. Second, EuBiSe₃ fiber was prepared by melting Eu, Bi₂Se₃ and Se in an optimized molar ratio of 2:1:3. All the raw materials were enclosed in a fused silica tube, which was evacuated to a pressure of 10⁻⁴ torr. The silica tube was carbon-coated to prevent the unexpected reactions of Eu and silica when the temperature was high. The following heating trend was used to synthesize the EuBiSe₃ fiber: heated the tube from room temperature to 873 K at a rate of 2 K min⁻¹, kept at this temperature for 1 h, then heated to 1173 K at a rate of 0.5 K min⁻¹, dwelt at this temperature for 4 days, after that, cooled down at a rate of 0.03 K min⁻¹, the reactions were kept for 1 day once at 773 K, finally cooled to 297 K at a rate of 0.5 K min⁻¹.

The phase composition of the sample was determined using a Rigaku D/max-2500/PC X-ray diffractometer with Cu Kα radiation (k = 1.5406 Å). The collected 2θ for the diffraction data was in the range of 3° to 60°. The microstructure of the sample was observed by Quanta FEG 450 scanning electron microscopy (SEM). The high-resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) pattern were obtained using a JEOL JEM-2010 microscope. The TEM sample was prepared as follows: the fiber was crushed and dispersed in ethanol completely under the effect of supersonic wave, then a drop of this suspension was placed on the holey carbon grid.

**Figure 1** shows the XRD pattern of the sample. The detailed comparison of the present measured XRD pattern and the simulated value according to the reported single crystal structure of EuBiSe₃ [18] are listed in the supplementary materials. It can be found that the XRD pattern of the present sample is in good agreement with the calculated result without other phase, i.e., Bi₂Se₃, indicating that the present sample is single crystal EuBiSe₃. **Figure 2a** shows the SEM photograph of the fractured surface for a representative sample, which reveals that the sample is fairly compact without any visible holes. The TEM image is presented in **Figure 2b**. According to the observation for the HRTEM image (**Figure 2c**), the sample is layered structure and the distance between adjacent layers is 0.33 nm. The SAED pattern (**Figure 2d**) reveals that the sample is a single crystal, which is consistent with the XRD pattern.

EuBiSe₃, belonging to P2₁2₁2₁ space group, is a member of the structure of compounds MPnSe₃ (M = Sr, Ba, and Pn = Sb, Bi). The crystal structure of EuBiSe₃ viewed along the c direction is illustrated in **Figure 3**. The light green, light gray, and pink balls represent selenium, bismuth, and europium atoms,
respectively. The Bi-Se slabs are regarded as the main part in the structure, which contains two net-shaped Bi\(_5\)Se\(_5\) units connected by the pyramid Bi\(_6\)Se\(_6\) units. The gap of the slabs is occupied by the nine-coordinate Eu\(^{2+}\) cations and V-shaped Se\(^{2-}\) anions. For a crystallographically center, EuBiSe\(_3\) can be described as four Eu\(^{2+}\) cations, four Bi\(^{3+}\) cations, four Se atoms, and a Se\(_3^{2-}\) anion [18–20].

The thermoelectric properties of the EuBiSe\(_3\) fiber with a diameter of 167 \(\mu\)m have been measured by applying our T-type method, including thermal conductivity, electrical conductivity and Seebeck coefficient. The method is widely used in the measurement of various conductive or non-conductive...
micro/nanoscale fibers [21–26]. The two ends of the Pt hot wire are suspended on the heat sinks which can be maintained at the set temperature $T_{\text{set}}$ because the specific heat capacity of the heat sinks is much larger than that of the hot wire. One end of the tested fiber is lapped in the middle of the hot wire, and the other end is overlapped on another heat sink.

The whole test process was carried out in high vacuum that is pumped to $10^{-4}$ Pa by a mechanical pump (R5614Y-Z) and a molecular pump (Leybold, TW70H), which can avoid the effect of natural convection between sample and environment. The measurement cell was placed in a cryogenic thermostat (Oxford Instruments, Optistat DN-V). Through theoretical analysis, it can be found that the influence of thermal radiation can also be neglected. The temperature of the thermostat can be controlled by the temperature controller (Oxford Instruments, ITC601) with the accuracy of 0.1 K. The high precision dc power supply (Advantest R6243) provides the current for the thermal conductivity and electrical conductivity measurements. The dc voltage data are collected by two high precision digital multimeters (Keithley 2002, 8.5 digital). The signal generator (Aglient 3320A) is used to export ac current in the Seebeck coefficient measurement.

**Thermal conductivity**

The thermal conductivity of the EuBiSe$_3$ fiber is determined by the dc heating-dc detecting T-type method. The Pt hot wire is served as a Joule self-heating source and a resistance thermometer with calibrated resistance characteristics. First, the dc current is applied on the suspended hot wire before the tested fiber attached, the parabolic temperature distribution along the length direction of the hot wire is established. Then, one end of the sample is fixed to the center of hot wire and another end is attached to the heat sink. When the system is in steady state again, the temperature distribution on the hot wire will turn into double arched due to partial heat conduction along the measured sample. Comparing the change of the hot wire resistance before and after the attachment of the sample, the variation of average temperature of hot wire is calculated according to the calibrated temperature coefficient of resistance. Therefore, the thermal conductivity of sample can be obtained [21, 23],

![Figure 3. The crystal structure of EuBiSe$_3$ viewed along the c direction.](image-url)
\[
\lambda_s = \frac{\lambda_{Pt}A_{Pt}l_{Pt}q_v(I_{Pt}^2 - 12\lambda_{Pt}l_{Pt}\Delta T_v)}{A_sI_{Pt,1}I_{Pt,2}(12\lambda_{Pt}l_{Pt}\Delta T_v - q_v(l_{Pt,1} + l_{Pt,2}^2))}
\]  

(1)

where \(\lambda_s\) and \(\lambda_{Pt}\) are the thermal conductivity of the tested fiber and Pt hot wire. \(A_s\) and \(A_{Pt}\) are the cross section of the fiber and Pt hot wire. \(l_s\) is the length of the fiber, \(l_{Pt}\) is the whole length of the Pt hot wire while \(l_{Pt,1}\) and \(l_{Pt,2}\) are the length of the two sides of the Pt hot wire. \(\Delta T_v\) is the average temperature rise of the Pt hot wire. \(q_v = IV/(A_{Pt}l_{Pt})\) is the current heating power, \(I\) and \(V\) are current and voltage applied on the Pt hot wire [26].

The temperature-dependent thermal conductivity of the sample is plotted in Figure 4. The thermal conductivity decreases from 1.07 to 0.88 W m\(^{-1}\) K\(^{-1}\) as the temperature increases from 80 to 140 K and then increases to 1.20 W m\(^{-1}\) K\(^{-1}\) as the temperature increases to 290 K. Actually, we performed the same experiment on two sets of samples at different times, the temperature-dependent experimental data of two samples is plotted in supplementary materials (Figures S2–S5). The experimental data showed the same trend, with only minor fluctuations in the values. Since the section of the sample 2 is not uniform, we studied sample 1 in this paper. For most crystal materials, the thermal conductivity decreases with the increase of temperature in high temperature range. The thermal conductivity for the present EuBiSe\(_3\) fiber decreases first and then increases with the increase of temperature, which is repeatable and abnormal. We try to explain the mechanism as follows:

The electronic thermal conductivity \(\lambda_e\) can be calculated from the Wiedemann-Franz law, \(\lambda_e = L\sigma T\), where \(L\) is the Lorentz number of free electrons and \(\sigma\) is the electrical conductivity. For the Lorentz number, \(L = 2.45 \times 10^{-8} \text{V}^2\text{K}^{-2}\) is suitable for the degenerate electron gas while \(L = 2.0 \times 10^{-8} \text{V}^2\text{K}^{-2}\) is more proper for the present sample (a heavily doped semiconductor) so as not to overvalue the electronic thermal conductivity [27]. The value of the electronic thermal conductivity \(\lambda_e\) is nearly zero which is shown in Figure 4, indicating that the heat conduction is dominated by phonons in the EuBiSe\(_3\) fiber.

The lattice thermal conductivity is described as \(\lambda_L = C_v l v/3\), where \(C_v\) is heat capacity, \(l\) is phonon mean free path and \(v\) is velocity of the phonons, respectively. Below 140 K, the effect of the phonon mean free path is dominant in this temperature range. Under the action of three-phonon Umklapp
scatter mechanism, the mean free path greatly reduces, and the thermal conductivity decreases. According to the Umklapp-limited intrinsic thermal conductivity described by Klemens [28, 29], the thermal conductivity should follow the relationship $\lambda \propto 1/T$. Fitting the determined data $\lambda$ versus $1/T$ in Figure 4, $\lambda$ has a good linear relationship with $1/T$, which is agreeable with above formula, confirming that the thermal conductivity decrease is due to the three-phonon Umklapp scattering. As the temperature rises further, the thermal conductivity goes up. This trend has also been found in the EuSbSe$_3$ at 300–600 K, which has the same crystal structure [18]. It is concluded that the bipolar diffusion mechanism cannot be applied to the present sample due to the inconsistent temperature dependence of the electrical conductivity and Seebeck coefficient. According to the measured electrical conductivity data, we hypothesize that the insulator-metal second order phase transition occurs at about 140 K. The increasing thermal conductivity with temperature may be related to the transition, and the specific underlying mechanism need to be explored further.

It can be found that although the addition of the rare-earth metal Eu increases the point defects in the structure, strengthening the scattering of the short-wave phonon, the thermal conductivity of the EuBiSe$_3$ is still larger than that of most Bi$_2$Se$_3$ [7–13, 30, 31]. This could be due to the fact that Bi atom is heavier than Eu atom in the relative atomic mass, which can decrease the frequency of phonon. The thermal conductivity could be cut down by reducing the grain size to nanoscale and increasing grain boundaries, which will also decrease the electrical conductivity. It is expected to improve the thermoelectric performance by decreasing the thermal conductivity more than the electrical conductivity in the present EuBiSe$_3$ sample. However, it should be noted that this outcome is possible only when the phonon mean free path in the bulk material is larger than that of electron and it is not a universal trend.

**Electrical conductivity**

The standard four probe T-type method is applied to measure the electrical conductivity of the sample. The direct current $I_\sigma$ is provided to the sample, the voltage $V_\sigma$ at two ends of the sample can be measured, then the resistance and the corresponding electrical conductivity of the sample can be calculated based on Ohm’s Law,

$$\sigma = \frac{I_\sigma l_\sigma}{V_\sigma A_S}$$  \hspace{1cm} (2)

Figure 5 shows the electrical conductivity as a function of temperature. It can be seen that with the temperature increases from 80 to 170 K, the electrical conductivity increases from 4209 to 5240 S m$^{-1}$, exhibiting typical semiconductor characteristics. Then the electrical conductivity decreases slightly to 4599 S m$^{-1}$ as the temperature rises to 290 K, which is described as metallic or degenerate semiconductor behavior. For a typical semiconductor, its electrical conductivity should satisfy the Arrhenius equation, expressed as follows:

$$\sigma = \sigma_0 \exp\left(-\frac{E_0}{k_B T}\right)$$  \hspace{1cm} (3)

where $\sigma_0$ is the pre-exponential factor, $k_B$ is the Boltzmann constant ($8.62 \times 10^{-5}$ eV K$^{-1}$) and $E_0$ is the activation energy, respectively. As shown in Figure 5, $\ln(\sigma)$ and $1000/T$ are linear in the temperature range from 80 to 140 K. It can be inferred that the sample is a typical semiconductor within this temperature range. According to the fitting slope and intercept, the activation energy ($E_0$) and pre-exponential factor of the sample ($\sigma_0$) can be obtained as 3.5 meV and 7104 S m$^{-1}$, respectively.

Based on the measured experimental data, the sample has not entered the intrinsic excitation region in the test temperature range, so the carrier is mainly ionized by impurity, and the scattering mechanism is dominated by the scattering between carriers. The expression of electrical conductivity
is \( \sigma = n q \mu \), where \( n \) is carrier concentration, \( q \) is quantity of electric charge and \( \mu \) is carrier mobility \((\mu = e \tau / m^*\)) \( \tau \) is the relaxation time of carrier, \( m^* \) is the effective mass of the carrier, respectively. With the increase of temperature, the inter carrier scattering is enhanced and the relaxation time is shortened, so the carrier mobility decreases. The carrier concentration of impurity ionization increases with increasing temperature. Before 170 K, the increase in carrier concentration has a greater effect on electrical conductivity than the decrease in carrier mobility, which is reversed after 170 K. So the electrical conductivity increases with the increase of temperature before 170 K, and shows a slight downward trend after 170 K. Furthermore, in order to verify the above conjecture, the temperature dependences of the carrier concentration and mobility have been calculated based on the measured electrical conductivity and Seebeck coefficient [32]. The calculated results (Figure S6) are consistent with the theoretical analysis.

Comparing the electrical conductivity of sample with that of Bi\(_2\)Se\(_3\) shown in previous literatures [7–13, 30, 31], the present EuBiSe\(_3\) sample exhibits a better electrical transport characteristic. The phenomenon can be explained as follows: The hybrid effect induced by the \( f \) electron shell of rare-earth element and the \( d \) electron shell of other elements makes complex band structure in the rare-earth alloy. Then the rare-earth element presents the intermediate valence electron state in the rare-earth alloy, which increases the band gap and the density of state near Fermi level [15–17].

**Seebeck coefficient**

The Seebeck coefficient is detected by ac heating-dc detecting T-type mode. Supplying the ac current in the form of \( I = I_0 \sin(\omega t) \) to the hot wire, the temperature of the hot wire will be risen up, which includes static and harmonic components,

\[
T_{Pt}(x_{Pt}, t) = T_{Pt, static}(x_{Pt}) + T_{Pt, harmonic}(x_{Pt}, t)
\]

The temperature of the heat sink will be kept at the ambient temperature because of the larger specific heat capacity. Hence, the temperature difference along the tested fiber between the junction

![Figure 5. Temperature dependence of electrical conductivity of EuBiSe\(_3\) fiber.](image-url)
point, hot end, and the heat sink, cold end, can also be the superposition of the static and the harmonic component,

\[ \Delta T_s(t) = \Delta T_{s,\text{static}} + \Delta T_{s,\text{harmonic}}(t) \]  

(5)

Solving one-dimensional heat conduction differential equation, the static component of temperature difference at junction point \( \Delta T_{s,\text{static}} \) can be calculated,

\[ \Delta T_{s,\text{static}} = \frac{I_0^2 R_{Pt} l_{Pt,1} l_{Pt,2} l_s}{4(A_1 \lambda_{Pt} l_{Pt,1} l_{Pt,2} + l_s A_{Pt} \lambda_{Pt} l_{Pt})} \]  

(6)

The dc thermoelectric voltage \( V_s \) on the sample will be established due to the static component \( \Delta T_{s,\text{static}} \). Measuring the dc voltage \( V_s \) between the two ends of sample, the Seebeck coefficient can be obtained under the definition of Seebeck coefficient,

\[ S = -\frac{V_s}{\Delta T_{s,\text{static}}} \]  

(7)

It should be noted that the Seebeck coefficient calculated with this method is the Seebeck coefficient difference between sample and hot wire \([33]\), and the Seebeck coefficient of the tested sample can be obtained by subtracting that of the Pt hot wire.

The temperature dependence of the Seebeck coefficient from 80 to 290 K for the sample is illustrated in Figure 6. With the increasing temperature, the value of the Seebeck coefficient decreases slightly from \(-178 \) to \(-204 \) µV K\(^{-1}\), which shows that the intrinsic excitation has not taken place in the studied temperature range. The mobility of electrons and holes determines whether the sign of Seebeck coefficient is “+” or “-” \([24]\). The negative Seebeck coefficient over the measured temperature range of the sample indicates that the present fiber is a kind of n-type material, the mobility of electrons is much higher than that of holes, and electrons are the main carriers in the fiber. The Seebeck coefficient can be expressed as \([32]\),

\[ S = \frac{k_B}{q} \left[ \frac{5}{2} + \gamma \right] + \ln \left( \frac{2 \pi m^* k_B T^3}{\hbar^3} \right) \]  

(8)

where \( h \) is the Planck constant \((6.626 \times 10^{-34} \text{ J/s})\), \( \gamma \) is the scattering factor, respectively. The Seebeck coefficient of tested n-type EuBiSe\(_3\) single crystal fiber is much larger than those reported for Bi\(_2\)Se\(_3\), which is generally in the range of \(-50 \) to \(-100 \) µV K\(^{-1}\) \([7–13, 30, 31]\). This can be attributed to the addition of rare-earth element Eu. The density of states near the Fermi level is enhanced. According to Mahan Sofo theory, large density of states near the Fermi level corresponds to a large carrier effective mass \([34]\). Introducing Eu into the Bi\(_2\)Se\(_3\) material, leads to a shift in scattering mechanism from acoustic dominance to ionizing impurity dominance, the scattering factor \( \gamma \) increases from \(-1/2 \) to 3/2 correspondingly. The carrier concentration increases after doping based on the increasing electrical conductivity while the mobility of carriers decreases. The calculated carrier concentration and effective mass in the supplementary materials (Figures S6, S7) support the above deductions. According to the Eq. (8), large carrier effective mass, scattering factor and low carrier concentration lead to a higher Seebeck coefficient of materials. The enhancement of the Seebeck coefficient in the present experiment can mainly attribute to the improvement of carrier effective mass and scattering factor, although the increase of carrier concentration causes a slight decrease.
Figure of merit

The temperature-dependent $ZT$ for the present EuBiSe$_3$ fiber is shown in Figure 7. It increases obviously as the temperature increases from 80 to 260 K, then the increase becomes slow in the temperature range of 260–290 K. The maximum value of $ZT$ is 0.05 at 290 K, in the same order of magnitude for the reported $ZT$ value of Bi$_2$Se$_3$ [7–13, 30, 31]. The thermoelectric properties have not
been improved significantly with the addition of rare-earth metal element Eu. According to the comparative analysis of thermoelectric properties between the EuBiSe$_3$ and Bi$_3$Se$_3$, this is primarily due to the enhancement in the thermal conductivity, although the electrical conductivity and Seebeck coefficient have been raised at the same time.

**Conclusions**

In this study, the thermoelectric properties of a EuBiSe$_3$ single crystal fiber have been studied for the first time by applying the developed T-type method, including thermal conductivity, electrical conductivity and Seebeck coefficient. The thermal conductivity increases from 0.88 to 1.20 W m$^{-1}$ K$^{-1}$ in the temperature range of 80–290 K. The electrical conductivity increases from 4209 S m$^{-1}$ to 5240 S m$^{-1}$ as the temperature is in the range of 80–170 K, then it decreases slightly to 4599 S m$^{-1}$ at 290 K. The value of Seebeck coefficient decreases with the increasing temperature, reaches to $-204$ $\mu$V K$^{-1}$ at 290 K. The $ZT$ value increases obviously as the temperature increases from 80 K to 260 K and then the increase becomes slow at higher temperature. The maximum value of $ZT$ is 0.05 at 290 K, although it is not a remarkable enhancement compared with that of Bi$_3$Se$_3$. Since the thermoelectric properties of EuBiSe$_3$ compound have not been studied before, it is expected to provide reference value for further development of new thermoelectric Eu-Bi-Se compounds.

**Funding**

This work was supported by the National Natural Science Foundation of China Grant Nos. [51576105,51636002].

**References**

[1] M. S. Dresselhaus, et al., “New directions for low-dimensional thermoelectric materials,” Adv. Mater., vol. 19, pp. 1043–1053, 2007. DOI: 10.1002/adma.200600527.
[2] T. C. Harman, P. J. Taylor, M. P. Walsh, and B. E. Laforge, “Quantum dot superlattice thermoelectric materials and devices,” Science, vol. 297, pp. 2229–2232, 2002. DOI: 10.1126/science.1072886.
[3] M. He, F. Qiu, and Z. Lin, “Towards high-performance polymer-based thermoelectric materials,” Energy Environ. Sci., vol. 6, pp. 1352–1361, 2013. DOI: 10.1039/c3ee24193a.
[4] T. Pan, T. R. Gong, W. Yang, and Y. J. Wu, “Numerical study on the thermal stress and its formation mechanism of a thermoelectric device,” J. Therm. Sci., vol. 27, pp. 249–258, 2018. DOI: 10.1007/s11630-018-1006-3.
[5] H. W. Ma, L. Shi, and Y. T. Tian, “Role of a single shield in thermocouple measurements in hot air flow,” J. Therm. Sci., vol. 26, pp. 523–532, 2017. DOI: 10.1007/s11630-017-0969-9.
[6] T. M. Tritt, “Thermoelectric materials, phenomena, and applications: a bird’s eye view,” MRS Bull., vol. 31, pp. 188–198, 2006. DOI: 10.1557/mrs2006.44.
[7] S. K. Mishra, S. Satpathy, and O. Jepsen, “Electronic structure and thermoelectric properties of bismuth telluride and bismuth selenide,” J. Phys.: Condens Matter., vol. 9, pp. 461–470, 1997.
[8] A. A. Bayaz, A. Giani, A. Foucaran, F. Pascal-Delannoy, and A. Boyer, “Electrical and thermoelectrical properties of Bi$_3$Se$_3$ grown by metal organic chemical vapour deposition technique,” Thin Solid Films, vol. 441, pp. 1–5, 2003. DOI: 10.1016/S0040-6090(03)00675-8.
[9] B. J. Stanbery, “Copper indium selenides and related materials for photovoltaic devices,” Crit. Rev. Solid State, vol. 27, pp. 73–117, 2002. DOI: 10.1080/20014091104215.
[10] K. Kadel, L. Kumari, W. Z. Li, J. Y. Huang, and P. P. Provencio, “Synthesis and thermoelectric properties of Bi$_2$ Se$_3$ nanostructures,” Nanoscale Res. Lett., vol. 6, pp. 57–63, 2011. DOI: 10.1007/s11671-010-9795-7.
[11] Y. Min, et al., “Surfactant-free scalable synthesis of Bi$_2$Te$_3$ and Bi$_2$Se$_3$ nanoflakes and enhanced thermoelectric properties of their nanocomposites,” Adv. Mater., vol. 25, pp. 1425–1429, 2013. DOI: 10.1002/adma.201203764.
[12] A. Soni, et al., “Enhanced thermoelectric properties of solution grown Bi$_2$Te$_3$–Se$_x$ nanoplatelet composites,” Nano Lett., vol. 12, pp. 1203–1209, 2012. DOI: 10.1021/nl2034859.
[13] Y. F. Sun, et al., “Atomically thick bismuth selenide freestanding single layers achieving enhanced thermoelectric energy harvesting,” J. Am. Chem. Soc., vol. 134, pp. 20294–20297, 2012. DOI: 10.1021/ja3102049.
[14] F. J. Disalvo, “Thermoelectric cooling and power generation,” Science, vol. 285, pp. 703–706, 1999.
[15] P. S. Riseborough, “Theory of the dynamic magnetic response of Ce$_6$Bi$_3$Pt$_3$: a heavy-fermion semiconductor,” Phys. Rev. B, vol. 45, pp. 13984–13995, 1992. DOI: 10.1103/PhysRevB.45.13984.
[16] Y. H. Zhang, T. J. Zhu, J. P. Tu, and X. B. Zhao, “Flower-like nanostructure and thermoelectric properties of hydrothermally synthesized La-containing Bi$_2$Te$_3$ based alloys,” Mater. Chem. Phys., vol. 103, pp. 484–488, 2007. DOI: 10.1016/j.matchemphys.2007.02.059.

[17] D. M. Rowe, G. Min, and L. Kuznestov, “Electrical resistivity and Seebeck coefficient of hot-pressed YbAl$_3$ over the temperature range 150–700 K,” Phil. Mag. Lett., vol. 77, pp. 105–108, 1998. DOI: 10.1080/095008398178679.

[18] S. Forbes, Y. C. Tseng, and Y. Mozharivskyi, “Crystal cluster growth and physical properties of the EuSbSe$_3$ and EuBiSe$_3$ phases,” Inorg. Chem., vol. 54, pp. 815–820, 2015. DOI: 10.1021/ic501808y.

[19] F. M. Schappacher, R. Pottgen, G. Bang Jin, and T. E. Albrecht-Schmitt, “$^{151}$Eu and $^{125}$Sb Moessbauer spectroscopy of EuSbSe$_3$ and EuBiSe$_3$,” J. Solid State Chem., vol. 180, pp. 3035–3038, 2007. DOI: 10.1016/j.jssc.2007.08.014.

[20] G. Bang Jin, S. J. Crerar, A. Mar, and T. E. Albrecht-Schmitt, “Syntheses, structures, and magnetic properties of the europium(II) selenido pnictogenates(III), EuPnSe$_3$ (Pn=Sb, Bi),” J. Solid State Chem., vol. 179, pp. 1596–1601, 2006. DOI: 10.1016/j.jssc.2006.02.017.

[21] W. G. Ma, et al. “A T-type method for characterization of the thermoelectric performance of an individual free-standing single crystal Bi$_2$S$_3$ nanowire,” Nanoscale, vol. 8, pp. 2704–2710, 2016. DOI: 10.1039/c5nr05946a.

[22] X. Zhang, X. G. Shi, and W. G. Ma, “Development of multi-physical properties comprehensive measurement system for micro/nanoscale filamentary materials,” Sci. Sin. Technol., vol. 48, pp. 403–414, 2018.

[23] T. T. Miao, W. G. Ma, X. Zhang, J. Q. Wei, and J. L. Sun, “Significantly enhanced thermoelectric properties of ultralong double-walled carbon nanotube bundle,” Appl. Phys. Lett., vol. 102, pp. 053105, 2013. DOI: 10.1063/1.4790190.

[24] W. G. Ma, et al. “Systematic characterization of transport and thermoelectric properties of a macroscopic graphene fiber,” Nano Res., vol. 9, pp. 3536–3546, 2016. DOI: 10.1007/s12274-016-1231-6.

[25] W. G. Ma, et al. “Chemically doped macroscopic graphene fibers with significantly enhanced thermoelectric properties,” Nano Res., vol. 11, pp. 741–750, 2016. DOI: 10.1007/s12274-017-1683-3.

[26] T. T. Miao, et al. “Integrative characterization of the thermoelectric performance of an individual multiwalled carbon nanotube,” J. Appl. Phys., vol. 120, pp. 124302, 2016. DOI: 10.1063/1.4962942.

[27] B. C. Sales, D. Mandrus, B. C. Chakoumakos, V. Keppens, and J. R. Thompson, “Filled skutterudite antimonides: electron crystals and phonon glasses,” Phys. Rev. B, vol. 56, pp. 15081–15089, 1997. DOI: 10.1103/PhysRevB.56.15081.

[28] P. G. Klemens, “Theory of the a-plane thermal conductivity of graphite,” Wide Bandgap Mater., vol. 7, pp. 332–339, 2000. DOI: 10.1106/7FP2-QBNL-TIPA-NC66.

[29] P. G. Klemens, “Theory of thermal conduction in thin ceramic films,” Int. J. Thermophys., vol. 22, pp. 265–275, 2001. DOI: 10.1023/A:1006776107140.

[30] X. F. Qiu, L. N. Austin, P. A. Muscarella, J. S. Dyck, and C. B. Prof, “Nanostructured Bi$_2$Se$_3$ films and their thermoelectric transport properties,” Angew. Chem., vol. 45, pp. 5656–5659, 2006. DOI: 10.1002/anie.200600848.

[31] J. Navrátil, et al. “Conduction band splitting and transport properties of Bi$_2$Se$_3$,” J. Solid State Chem., vol. 177, pp. 1704–1712, 2004. DOI: 10.1016/j.jssc.2003.12.031.

[32] S. Johnsen, et al. “Nanostructures boost the thermoelectric performance of PbS,” J. Am. Chem. Soc., vol. 133, pp. 3460–3470, 2011. DOI: 10.1021/ja109138p.

[33] Y. X. Wang, et al. “Terahertz photodetector based on double-walled carbon nanotube macrobundle-metal contacts,” Opt. Express, vol. 23, pp. 13348–13357, 2015. DOI: 10.1364/OE.23.013348.

[34] J. P. Heremans, et al. “Enhancement of thermoelectric efficiency in PbTe by distortion of the electronic density of states,” Science, vol. 321, pp. 554–557, 2008. DOI: 10.1126/science.1159725.