Intrinsically Low Thermal Conductivity in BiSbSe₃: A Promising Thermoelectric Material with Multiple Conduction Bands

Xiaoying Liu, Dongyang Wang, Haijun Wu,* Jinfeng Wang, Yang Zhang, Guangtao Wang, Stephen J. Pennycook, and Li-Dong Zhao*

Bi₂Se₃, as a Te-free alternative of room-temperature state-of-the-art thermoelectric (TE) Bi₂Te₃, has attracted little attention due to its poor electrical transport properties and high thermal conductivity. Interestingly, BiSbSe₃, a product of alloying 50% Sb on Bi sites, shows outstanding electron and phonon transports. BiSbSe₃ possesses orthorhombic structure and exhibits multiple conduction bands, which can be activated when the carrier density is increased as high as \(3.7 \times 10^{20} \text{ cm}^{-3}\) through heavily Br doping, resulting in simultaneously enhancing the electrical conductivities and Seebeck coefficients. Meanwhile, an extremely low thermal conductivity \((=0.6–0.4 \text{ W m}^{-1} \text{ K}^{-1}\) at \(300–800 \text{ K}\) is found in BiSbSe₃. Both first-principles calculations and elastic properties measurements show the strong anharmonicity and support the ultra-low thermal conductivity of BiSbSe₃. Finally, a maximum dimensionless figure of merit \(ZT \sim 1.4\) at \(800 \text{ K}\) is achieved in BiSb(Se₀.₉₄Br₀.₀₆)₃, which is comparable to the most \(n\)-type Te-free TE materials. The present results indicate that BiSbSe₃ is a new and a robust candidate for TE power generation in medium-temperature range.

1. Introduction

Thermoelectric (TE) technology that can directly and reversibly convert heat to electrical energy has received wide attention due to global energy and environmental demands.\(^{[1–7]}\) But the application of TE technology is limited by the low power generation conversion efficiency which is determined by the dimensionless figure of merit \(ZT\) defined as \(ZT = (S^2\sigma)/k T\), where \(S\), \(\sigma\), \(k\), and \(T\) denote the Seebeck coefficient, electrical conductivity, thermal conductivity, and working temperature in Kelvin, respectively. An efficient TE material needs high power factor \((PF = S^2\sigma)\) and low thermal conductivity \((k)\). However, the complex interrelation among these parameters makes it difficult to improve the overall efficiency. To date, many emerging methods have been effectively employed to optimize final \(ZTs\), including enhancing power factor through modifying electronic band structures,\(^{[8–11]}\) reducing lattice thermal conductivity through designing nanostructures,\(^{[12–14]}\) or all-length-scale hierarchical architectures.\(^{[15]}\) Alternatively, one can seek promising candidates, which intrinsically possess more than one of the main ingredients of good TE materials,\(^{[16–19]}\) such as a large Seebeck coefficient, high electrical conductivity, or low thermal conductivity.

As one narrow bandgap semiconductor, Bi₂Te₃ possesses excellent electrical conductivity and Seebeck coefficient, and thus it is one of classic room-temperature TE materials. \(ZTs\) for both \(n\)-type and \(p\)-type Bi₂Te₃-based systems are larger than unity, which have been widely applied for TE power generation and electronic cooling around room temperature for several decades.\(^{[20,21]}\) It is well known that Te is a scarce element in the crust of the earth, additionally, the cost of Te would rise sharply along with the Te-containing TE materials reach mass markets. A broad search for inexpensive alternatives is therefore warranted. In this case, the Te-free TE materials have attracted huge interest. As a sister compound of Bi₂Te₃, Bi₂Se₃ has drawn little attention due to its inferior TE performance \((ZT \sim 0.4)\).\(^{[21,22]}\) The key factors that limit the \(ZTs\) of Bi₂Se₃ are its poor electrical transport properties and high thermal conductivity.\(^{[21,23]}\)

In this work, to improve the TE performance of Bi₂Se₃, we introduced Sb substitutions on Bi sites. Interestingly, BiSbSe₃ has extremely low thermal conductivity \(=0.40–0.60 \text{ W m}^{-1} \text{ K}^{-1}\) at \(300–800 \text{ K}\), which is related to the phase transition from the rhombohedral structure of Bi₁Sb₁Se₃ to the orthorhombic structure of Sb₂Se₃. Therefore, it is expected that BiSbSe₃ could display a promising TE performance after optimizing carrier density via

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electrons doping. Meanwhile, we aimed at investigating the origins of the low thermal conductivity of BiSbSe₃, and found that BiSbSe₃ possesses very low elastic properties (phonon velocity $v_a$, Young's modulus $E$) and large Grüneisen parameter $\gamma$, which are related to its strong anharmonicity caused by lone-pair electrons come from Sb/Bi in BiSbSe₃. These experimental results are well supported by theoretical calculations on phonon dispersions. Additionally, the multiple conduction bands of BiSbSe₃ imply a possibility to improve the electrical transport properties (power factor) by manipulating these bands through introducing a higher density of electron carriers. Our results show that the carrier density can be increased to as high as $\approx 3.7 \times 10^{20} \text{ cm}^{-3}$ through Br doping, which could activate Fermi electron pockets and enhance Seebeck coefficients. Finally, we obtained a $ZT \sim 1.4$ at 800 K due to enhanced power factor ($\approx 7.4 \text{ µW cm}^{-1} \text{ K}^{-2}$) and favorable thermal conductivity ($\approx 0.43 \text{ W m}^{-1} \text{ K}^{-1}$), the superior performance of BiSbSe₃ is competing with most of the state-of-the-art medium-temperature n-type TE materials, such as Bi₂Se₃ ($ZT \sim 0.4$ at 600 K), Bi₂(Te,Se)₃ ($ZT \sim 1.0$ at 400 K),[24] SnSe polycrystalline ($ZT \sim 1.2$ at 800 K),[25] PbS ($ZT \sim 0.9$ at 800 K),[26] Bi₂S₃ ($ZT \sim 0.6$ at 760 K),[27] etc.

2. Results and Discussions

In this work, we first optimized the Bi substitution by Sb which can induce the phase transition and selected the best Sb substitution fractions based on TE transport properties, and then optimized its electrical transport properties through Br doping. The X-ray diffraction patterns of Bi₂₋ₓSbxSe₃ show a rhombohedral structure for Bi₂Se₃ and Bi₁.₅Sb₀.₅Se₃ samples, while the samples of BiSbSe₃, Bi₀.₅Sb₁.₅Se₃, and Sb₂Se₃ show an orthorhombic structure, as shown in Figure S1a in the Supporting Information. For $x = 0.02$–0.08, all samples display a single phase without noticeable impurities, as shown in Figure S1b in the Supporting Information. There is a clear evidence of an additional phase for $x = 0.10$ (Bi₁.₅Sb₀.₅Br), revealing the solubility limit of Br in BiSbSe₃. To clearly confirm the structure of (Br-doped) BiSbSe₃, compared with the two end terminal members of Bi₂Se₃ and Sb₂Se₃, we employed electron diffraction and scanning transmission electron microscopy (STEM) imaging techniques.[28] The Bi₂Se₃ exhibits five-layer structure (−Se⁴(1)−Bi−Se⁴(2)−Bi−Se⁴(1)−) as Bi₂Te₃,[29] as shown in Figure 1a,b. Through 50% alloying with Sb on Bi site, the BiSbSe₃ totally changes to the structure of Sb₂Se₃ without any precipitates.

Figure 1. Structural characterizations of BiSbSe₃, and comparisons with two terminal compounds of Bi₂Se₃ and Sb₂Se₃. a1,a2) Experimental and simulated electron diffraction patterns of Bi₂Se₃ along [210] zone axis. b) Atomically resolved STEM HAADF image of Bi₂Se₃ along [210] zone axis, with enlarged image inset. c1,c2,e1,e2,g1,g2) Experimental and simulated electron diffraction patterns along [100], [010], and [011] zone axes. d,f,h) Atomically resolved STEM HAADF images of BiSbSe₃ or Sb₂Se₃ along [100], [010], and [011] zone axes, with enlarged images insets.
To further investigate the characteristics of BiSbSe₃, we measured the bandgap of Bi₂₋ₓSbₓSe₃ as shown in Figure S2 in the Supporting Information. Compared with the narrow bandgap of Bi₂Se₃ (~0.25 eV), BiSbSe₃ shows a larger bandgap of ~0.88 eV, comparable to that of Sb₂Se₃ (~1.17 eV). The first-principles density of functional theory (DFT) calculations were also performed and results are shown in Figure 2 and Figure S3 in the Supporting Information. Considering the two nonequivalent sites of Sb atom in Sb₂Se₃ (Figure S4a, Supporting Information), two possible structures can be formed and the lower energy structure with Sb1 substituted by Bi atom was adopted to modeling the BiSbSe₃ (Figure S4b, Supporting Information). The calculated bandgaps are ~0.16, 0.75, and 0.63 eV for Bi₂Se₃, Sb₂Se₃, and BiSbSe₃, respectively, as shown in Figure 2 and Figure S3 in the Supporting Information. Although the DFT calculations cannot give quantitatively accurate predictions of the bandgap, the trends are more reliable. For Bi₂Se₃, both the valence band maximum (VBM) and conduction band minimum (CBM) are located along Γ–Z direction, identifying them as direct bandgap semiconductors. The energy difference between CBM and the fourth valence valley is less than

Figure 2. TE transport properties as a function of temperature for BiSb(Se₁₋ₓBrₓ)₃ with different Br doping fractions x (x = 0–0.08) and calculated band structures: a) electrical conductivity; b) and c) Seebeck coefficient; d) power factor; and e) calculated Pisarenko line of BiSbSe₃ (m⁎ = 2.0 mₑ) by using the single parabolic model at 300 K. The experimental Seebeck coefficients (black spots) deviate to the theoretical line with increasing carrier density, suggesting the contribution of the multiple conduction bands of BiSbSe₃. The experimental Seebeck coefficients from the BiSbSe₃[31] fall in the Pisarenko line. Calculated band structures f) BiSbSe₃ in which the Fermi levels were set to zero. The horizontal lines in f) refer to the carrier densities (in cm⁻³) and the corresponding chemical potentials at room temperature.
Table 1. Room-temperature carrier density and mobility for BiSb(Se_{1-x}Br_x)₃ (x = 0–0.08), indicating Br is an effective dopant that could dramatically enhance carrier density.

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<th>Samples</th>
<th>n_H</th>
<th>μ_H</th>
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<tr>
<td>BiSbSe₃</td>
<td>0.0014</td>
<td>23.1</td>
</tr>
<tr>
<td>BiSb(Se₀.₉₈Br₀.₀₂)₃</td>
<td>21.59</td>
<td>6.33</td>
</tr>
<tr>
<td>BiSb(Se₀.₉₂Br₀.₀₈)₃</td>
<td>32.89</td>
<td>3.96</td>
</tr>
<tr>
<td>BiSb(Se₀.₉₂Br₀.₀₈)₃</td>
<td>35.98</td>
<td>4.40</td>
</tr>
<tr>
<td>BiSb(Se₀.₉₂Br₀.₀₈)₃</td>
<td>36.89</td>
<td>4.57</td>
</tr>
</tbody>
</table>

≈0.10 eV, which is smaller than that of ≈0.13 eV between the first and third valence bands in SnSe.[30] Such small energy difference can be easily crossed at elevated temperature, leading to enhancements in electrical transport properties.

After optimizing Sb substitutions by Bi, Figure S5 in the Supporting Information, we found that BiSbSe₃ could exhibit the lowest thermal conductivity as that of Sb₂Se₃, but the low bandgap (Figure S2, Supporting Information) suggests us to optimize its carrier density to enhance the TE performance of BiSbSe₃ via Br doping. Figure 2 shows the temperature dependent electrical transport properties of BiSb(Se₁₋ₓBrₓ)₃ (x = 0–0.08). The undoped BiSbSe₃ has a poor electrical conductivity at room temperature, due to its extremely low carrier density (Table 1). With the increase of temperature, the electrical conductivity (σ) increases for BiSbSe₃ (Figure 2a), while decreases for Br contained samples, which is consistent with heavily doped semiconductor behavior. As the content of Br rises, the room-temperature electrical conductivity significantly increases from undoped BiSbSe₃ to ≈219 S cm⁻¹ for BiSb(Se₀.₉₂Br₀.₀₈)₃, and further to ≈278 S cm⁻¹ for BiSb(Se₀.₉₂Br₀.₀₈)₃, which results from the increase of carrier density (Table 1). The carrier density increases from ≈1.4 × 10¹⁶ to ≈2.2 × 10²⁰ cm⁻³ with only 2% Br doping, indicating Br is an effective dopant to increase the carrier density and the electrical conductivity. Absolute Seebeck coefficients (S) undergoes a significantly decrease from ≈756 µV K⁻¹ for undoped BiSbSe₃ to ≈110 µV K⁻¹ for Br contained samples at room temperature (Figure 2b,c). It is noted that S increases with temperature due to Br doping, which is different from BiSbSe₃. The strengthened electrical conductivities and carrier density with increasing Br doping fractions indicate that electron doping has been successful achieved in BiSbSe₃.

The significantly increased electrical conductivities and slightly declined Seebeck coefficients result in remarkable enhancements in power factors in the whole temperature range, as shown in Figure 2d. The power factor significantly increases from ≈0.03 to ≈2.6 µW cm⁻¹ K⁻² at room temperature due to Br doping. Compared to the experimental carrier densities at room temperature (Table 1), it is clearly shown that BiSbSe₃ exhibits a characteristic of multiple bands transport as discussed before. This result is also validated by the Pisarenko plot, the relationship between carrier concentration and Seebeck coefficient, which shows the enhanced Seebeck coefficients due to activating conduction bands through Br doping, as shown in Figure 2e. The solubility limit of Br in BiSbSe₃ (≤8%) is higher than that of I in BiSbSe₃ (≤3%) since the carrier concentration of Br-doped BiSbSe₃ samples is more than three times higher than those of I-doped BiSbSe₃,[31] which confirms the multiple band conduction in BiSbSe₃. Considering that the energy difference (≈0.10 eV) is smaller between CBM and the fourth band valley, the multiple band characteristic (Figure 2f) can be easily achieved through tuning the carrier density (Table 1).

As shown in Figure 3a, the total thermal conductivity Ktot of all samples decreases with increasing temperature. All Br-doped samples display higher Krot than that of undoped BiSbSe₃, which is the result of higher electronic thermal conductivity Kele (Figure S5d, Supporting Information), according to Wiedemann–Franz law, Kele = LσT. L is the Lorenz number and can be extracted based on fitting of the respective Seebeck coefficient values to the reduced chemical potential (η).[32,33] The heat capacity (Cp), thermal diffusivity (D), Lorenz number (L), and electrical thermal conductivity (κele) were presented in Figure S6 in the Supporting Information. The lattice thermal conductivity K_L can be calculated by subtracting the electronic thermal conductivity from the total thermal conductivity and the results are shown in Figure 3a. The room-temperature K_L decreases from ≈0.60 W m⁻¹ K⁻¹ for undoped BiSbSe₃ to ≈0.47 W m⁻¹ K⁻¹ for BiSb(Se₀.₉₂Br₀.₀₈)₃ as shown in Figure 3a. The reduction of K_L is ascribed to the enhanced phonon scattering by point defects due to the solid solution of Br atom in the Se sublattice. It is worth mentioning that K_L of undoped BiSbSe₃ already shows a very low value of ≈0.6 W m⁻¹ K⁻¹ at room temperature, which is comparable to those well-known TE materials with intrinsically low lattice thermal conductivities, e.g., BiCuSeO (≈0.88 W m⁻¹ K⁻¹),[34] SnSe (≈0.62 W m⁻¹ K⁻¹),[35] AgSbTe₂ (≈0.40 W m⁻¹ K⁻¹),[36] K₆Bi₄Se₁₁ (≈0.43 W m⁻¹ K⁻¹) as displayed in Figure 3b.

Different from the well-known layered TE material SnSe,[36] Sb₂Se₃ exhibits a chain-like structure along b axis (Figure S4, Supporting Information), although both of them possess the same space group Pnma (#62). There are five nonequivalent atoms in the Sb₂Se₃ unit cell, including two Sb and three Se atoms. These interchain bonding couplings are weaker than that in intrachain, therefore Bi–Se (Sb–Se) bonds could be relatively weaker. To understand the bonding characteristic of BiSbSe₃, the electron localization function (ELF) was calculated.[37] Figure 4 shows the calculated 3D and projected 2D ELF (isosurface level of 0.93) of Sb₂Se₃ and BiSbSe₃, respectively. The “mushroom” ELF shape around Sb atoms is a clear indicator of the existence of lone-pair electrons. The lone-pair electrons are mainly located along the a and c axes. The electronic repulsion between the lone-pair electrons and Sb–Se/Sb–Se bonding electrons could lead to strong anharmonicity along the two axes of Sb₂Se₃ and BiSbSe₃, which is similar to those in CuBiS₂[38] and SnSe.[39] These structural and electronic features suggest that ionic bond of Bi–Se and covalent bond in Sb–Se.

To further investigate the origin of the low thermal conductivity, we carried out the evaluations on elastic properties through ultrasonic pulse echo measurements for BiSbSe₃ and Sb₂Se₃. It is worth mentioning that it is impossible to extract the directional dependence of the different moduli from measurement of polycrystalline samples, especially for an orthorhombic system. Therefore, the values presented in this work are considered to be directionally averaged estimated.[40] Then we
obtained the longitudinal (LA) ($\nu_l$) and shear ($\nu_s$) phonon velocities, Young's modulus ($E$), Grüneisen parameter ($\gamma$), and Debye temperature ($\theta_D$). As we known, elastic properties are widely used to evaluate the interatomic bonding strength and lattice vibration anharmonicity in a crystal lattice. Usually, a large Grüneisen parameter ($\gamma$), a small Debye temperature ($\theta_D$) and Young's modulus ($E$) result in a low lattice thermal conductivity via the formula as follows:[34,41,42]

$$\kappa_L = \frac{3.0 \times 10^{-5} M \rho a_0^3}{T \gamma' \nu_0^{1/3}}$$  \hspace{1cm} (1)

$$\kappa_L \propto \rho^{1/5} E^{1/2} \left( \frac{M}{m} \right)^{1/5}$$  \hspace{1cm} (2)

where $\rho$ is the sample density, $M$ is the mean atomic weight of all the constituent atoms, $a_0$ is the average volume occupied by one atom, $\gamma'$ is the number of atoms in the unit primitive cell, $M$ is the atomic weight of the molecule of the compound, and $m$ is the number of atoms in the molecule. As shown above, Equations (1) and (2) summarize the key-variable interconnections quite nicely.

In this work, average sound velocity ($v_s$), Young's modulus ($E$), shear modulus ($G$), Poisson ratio $\nu_p$, and Grüneisen parameter ($\gamma$) can be calculated from the sound velocity through following relationships:[34,41,42]

$$v_s = \left[ \frac{1}{3} \left( \frac{1}{\nu_l} + \frac{2}{\nu_s} \right) \right]^{-1/3}$$  \hspace{1cm} (3)
where \( \rho \) is the sample density, \( \nu_p \) is the Poisson ratio, \( \nu_l \) is the longitudinal phonon velocity and \( \nu_s \) is the shear phonon velocity which can be acquired directly by the ultrasonic pulse echo measurements, as listed in Table 2.

The low lattice thermal conductivity values in BiSbSe\(_3\) system can be partly explained in terms of vibrations of phonon modes. The calculated phonon dispersion is shown in Figure 3c.d. There is no imaginary frequency, indicating the thermodynamic stability of the two structures. It can be seen that Bi doping leads to a soften in the acoustic mode, due to the weak bonding interaction along \( a \) and \( c \) directions as analyzed above. Bi substitution also leads to a clear mode soften and significant decrease in group velocities, i.e., longitudinal (LA) 2478 m s\(^{-1}\) and transverse (TA) 1008 m s\(^{-1}\) and 1014 m s\(^{-1}\) velocities for BiSbSe\(_3\) along \( a \) axis. The mode Grüneisen parameters, an indicator of anharmonicity, are shown in Figure 3e.f. It can be seen that soft acoustic modes also give rise to larger mode Grüneisen parameters. Near the zone center, Grüneisen parameter is close to 10, larger than that of SnSe.\(^{[16]}\) The physical origin of the large anharmonicity in BiSbSe\(_3\) may be ascribed to the repulsion between the 5s\(^2\) lone-pair electrons of Sb and 3p orbital of Se, similar to other reported strong anharmonicity and low lattice thermal conductivity in SnSe,\(^{[16]}\) AgSbSe\(_2\),\(^{[43]}\) NaSbSe\(_2\),\(^{[43]}\) and Tl\(_3\)VSe\(_4\).\(^{[44]}\) Therefore, the combination of very low group velocities and strong anharmonicity governs the low lattice thermal conductivity of BiSbSe\(_3\).

As shown in Table 2, the average sound velocity (\( \nu_v \)) of BiSbSe\(_3\) (\( \approx \) 1629 m s\(^{-1}\)) is much lower than that of Bi\(_2\)Se\(_3\) (\( \approx \) 2104 m s\(^{-1}\)) and BiCuSeO (\( \approx \) 2107 m s\(^{-1}\)). What is more, a small average sound velocity (\( \nu_v \)) leads to a small Young’s modulus (\( E \)) (\( \approx \) 34.9 GPa) of BiSbSe\(_3\), which is not only much smaller than that of Bi\(_2\)Se\(_3\) (\( \approx \) 70.3 GPa) and BiCuSeO (\( \approx \) 76.5 GPa) but also comparable to those of ultra-low thermal conductivity materials AgSbTe\(_2\) (\( \approx \) 39.2 GPa) and K\(_2\)Bi\(_6\)Se\(_{13}\) (\( \approx \) 37.1 GPa). The Grüneisen parameter (\( \gamma \)) of BiSbSe\(_3\) is (\( \approx \) 1.89), which is linked to strong anharmonicity of the crystal structure. As we known, the origin of the low thermal conductivity of SnSe, with a large average Grüneisen parameter (\( \gamma \)) (\( \approx \) 3.13), can be attributed to the high degree of lattice anharmonicity partially due to lone-pair electrons of Sn.\(^{[16,43,45–47]}\) Here, BiSbSe\(_3\)
shows a large Grüneisen parameter ($\gamma$) of ($\approx$1.89), which is comparable to AgSbTe$_2$ ($\approx$2.05) and K$_2$Bi$_8$Se$_{13}$ ($\approx$1.77),\cite{36,45} because of the lone-pair electrons of Sb.

Apart from these elastic parameters (sound velocity, Young’s modulus, shear modulus, and Grüneisen parameters), the value of Debye temperature could also reflect the thermal conductivity to some extent. Debye temperature $\theta_D$ can be estimated as follows:\cite{41}

$$\theta_D = \frac{h}{k_b} \left( \frac{3N}{4\pi V} \right)^{1/3} v_a,$$

where $h$ is Planck’s constant, $k_B$ is the Boltzmann constant, $N$ is the number of atoms in a unit cell, $V$ is the unit-cell volume, and $v_a$ is the average phonon velocity, respectively. As listed in Table 2, the Debye temperature ($\theta_D$) of BiSbSe$_3$ is $\approx$165 K, which is much smaller than that of Bi$_2$Se$_3$ ($\approx$205 K). It is consistent with the lower lattice thermal conductivity at room temperature ($\approx$0.6 W m$^{-1}$ K$^{-1}$) of BiSbSe$_3$ compared to that of Bi$_2$Se$_3$ ($\approx$1.3 W m$^{-1}$ K$^{-1}$), as displayed in Figure 3b.

Because of the intrinsically low thermal conductivity and the effectively optimized power factor, we finally obtain the maximum $ZT \sim 1.4$ at 800 K for the sample BiSb(Se$_{0.94}$Br$_{0.06}$)$_3$ (Figure 5a). Compared to Bi$_2$Te$_3$ and Bi$_2$Se$_3$, Sb/Se substitutions successfully push the peak of $ZT$ to high temperature. Moreover, $ZT$ of optimized BiSbSe$_3$ is more competitive than most of the state-of-the-art medium-temperature $n$-type TE materials, as shown in Figure 5b. In addition, the Figure S7 in the Supporting Information shows that the sample displays an anisotropic behavior since the electrical conductivity and thermal conductivity measured perpendicular to spark plasma sintering (SPS) pressure direction are higher than those parallel to SPS direction. As a result, a higher $ZT$ $\sim$ 1.4 is obtained for the sample perpendicular to SPS direction than $ZT$ $\sim$ 0.8 for the sample parallel to SPS direction.

### 3. Conclusions

In summary, BiSbSe$_3$ is a new promising material in the medium-temperature range. It shows extremely low thermal conductivity because of the low elastic properties (phonon velocity $v_l$ $\approx$ 1629 m s$^{-1}$ and Young’s modulus $E$ $\sim$ 34.9 GPa) and a big Grüneisen parameter $\gamma$ ($\approx$1.89), which are related to the lone-pair electrons of Sb. Additionally, the point defects attributed to solid solution of Br could further reduce the lattice thermal conductivity. Therefore, an ultra-low thermal conductivity ($\approx$0.43 W m$^{-1}$ K$^{-1}$) at 800 K could be obtained. The Br doping effectively increases the carrier density to a high level of ($\approx$3.7 $\times$ 10$^{20}$ cm$^{-3}$), which simultaneously improves the electrical conductivities and the Seebeck coefficients through activating the multiple band conduction. Therefore, the power factor is optimized to $\approx$7.4 $\mu$W cm$^{-1}$ K$^{-2}$ at 800 K. The combination of improved power factor and low thermal conductivity contributes to a high $ZT$ of $\approx$1.4 at 800 K.

### Table 2. Comparisons of room-temperature elastic properties of BiSbSe$_3$ and other thermoelectric materials with low thermal conductivity.

<table>
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<tr>
<th>Parameters</th>
<th>BiSbSe$_3$</th>
<th>Bi$_2$Se$_3$\cite{48}</th>
<th>Sb$_2$Se$_3$</th>
<th>BiCuSeO\cite{49}</th>
<th>SnSe\cite{46}</th>
<th>AgSbTe$_2$\cite{45}</th>
<th>K$_2$Bi$<em>8$Se$</em>{13}$\cite{36}</th>
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<td>1882</td>
<td>2107</td>
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<td>$E$ [GPa]</td>
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### Figure 5. Dimensionless figure of merit $ZT$ values and its comparisons: a) BiSb(Se$_{1-x}$Br$_x$)$_3$ ($x$ = 0–0.08), Bi$_2$Te$_2$Se$_{0.8}$,\cite{24} and Bi$_2$Se$_3$: b) $ZT$ comparisons for BiSb(Se$_{0.94}$Br$_{0.06}$)$_3$ and other typical medium-temperature $n$-type TE materials: Bi$_2$Se$_3$ ($ZT$ $\sim$ 0.4 at 600 K), Bi$_2$Te$_2$Se$_{0.8}$ ($ZT$ $\sim$ 1.0 at 400 K),\cite{24} BiSb(Se$_{0.7}$Te$_{0.3}$)$_3$ ($ZT$ $\approx$ 1.0 at 800 K),\cite{31} Sn$_{0.5}$Pb$_{0.5}$Se$_{0.95}$Br$_{0.05}$ polycrystalline ($ZT$ $\approx$ 1.2 at 800 K),\cite{25} (PbS)$_{0.53}$(PbSe)$_{0.25}$(PbTe)$_{0.22}$Bi$_2$Se$_3$ ($ZT$ $\approx$ 0.9 at 800 K),\cite{26} Bi$_2$S$_3$–0.5%BiCl$_3$ ($ZT$ $\approx$ 0.6 at 760 K).\cite{27}
4. Experimental Section

All samples were prepared by melting method followed a subsequent SPS technique. Starting materials were loaded into quartz tubes, which were sealed under a high vacuum (10⁻³ bar), slowly heated up to 1173 K and soaked at 1173 K for 5 h. The tubes were ice quenched to room temperature, and then annealed at 673 K for 48 h. The obtained ingots were ground into powders, and subsequently sintered using SPS. The phases were identified by XRD and the bandgaps were measured by a UV–vis–NIR Spectrophotometer (SHIMADZU UV-3600 Plus). The electrical resistivity and Seebeck coefficient were measured simultaneously in a helium atmosphere at 300–800 K using a Cryoall CTA measurement system. Hall coefficients were measured using a Hall measurement system (Lake Shore 8400 Series, Model 8404). The thermal conductivity was calculated from \( k = D \cdot C_p \cdot p \), where the thermal diffusivity coefficient (D) was measured using the laser flash diffusivity method in a Netzsch LFA457, the specific heat capacity (C_p) was calculated using Debye model in the range 300–800 K, and the sample density (p) was determined using the dimensions and mass of the sample, the sample density was also reconfirmed by gas pycnometer (Micromeritics AccucPyC1340) measurements. STEM and TEM were conducted with a JEOL ARM200F under 200 kV equipped with a cold field emission gun, and ASCOR probe corrector. The thin TEM specimens were prepared using a Cryoall CTA measurement system. Hall coefficients were measured using a Hall measurement system (Lake Shore 8400 Series, Model 8404).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

anharmonicity, BiSbSe₃, low thermal conductivity, multiple conduction bands, thermoelectric

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