Enhanced thermoelectric performance in Sb–Br codoped Bi$_2$Se$_3$ with complex electronic structure and chemical bond softening†

Ju Zhang, Shiqi Zhong and San-Huang Ke*

Prior experimental work showed that Bi$_2$Se$_3$, as a sister compound of the best room-temperature thermoelectric material Bi$_2$Te$_3$, has remarkably improved thermoelectric performance by Sb–Br codoping. But the relationship between its crystalline structure and thermoelectric properties is still unclear to date. Here, we use first-principles calculations to explore the possible reasons for such improvement. The electronic structures of Bi$_{1-x}$Sb$_x$(Se$_{1-y}$Br$_y$)$_3$ (x = 0, 1, 2; y = 0, 0.08) are systematically investigated. Significant effects of 8% Br codoping in BiSbSe$_3$ are found. First, the Br atom acts as an electron donor, thus greatly increasing the carrier concentration. Second, similar to the effect of Sb doping, Br codoping further improves greatly the degeneracy of the conduction band edge, which leads to a remarkably increased density-of-states effective mass without deterioration of the carrier mobility, and simultaneously preserves a large Seebeck coefficient of ~254 μV K$^{-1}$ at 800 K. In addition, the Br codoping softens the chemical bonds, which enhances anharmonic scattering and further reduces the lattice thermal conductivity. We predict that the maximum $zT$ of BiSbS$_2$Te$_2$Br$_{10}$ at 800 K can reach 0.96 with the carrier concentration of 9.22 × 10$^{19}$ cm$^{-3}$. This study rationalizes a potential strategy to improve the thermoelectric performance of Bi$_2$Se$_3$-based thermoelectric materials.

Introduction

With about two-thirds of the world’s produced energy being lost as waste heat,† thermoelectric (TE) materials which can directly convert exhaust heat into usable electricity have been investigated widely as clean and sustainable energy materials.‡ The TE performance depends on the dimensionless figure of merit $zT = S^2σT/k$, where $S$, $σ$, $k$, and $T$ are the Seebeck coefficient, electrical conductivity, total thermal conductivity (including the lattice contribution $k_L$ and carrier contribution $k_e$), and absolute temperature, respectively.‡—‡ An excellent TE material requires a high value of $zT$ simultaneously with a high power factor (PF = $S^2σ$) and a low $k$.‡—‡ Because of the strong coupling between $S$, $σ$, and $k$, it is very difficult to enhance $zT$ by optimizing only one of these parameters.§ To date, decoupling of these electronic parameters by band engineering approaches through increasing the number of effective energy valley and minimizing $k_L$ (the only independent parameter) have proved to be effective strategies for enhancing $zT$.§ It is well known that the electrical transport properties of a material are dominated by the details of its band structure and scattering mechanism. The optimized electrical transport properties of a thermoelectric material depend on the weighted mobility, $μ(m_{DOS}^*/m_e)^{3/2}$, here $μ$, $m_{DOS}$ and $m_e$ are the mobility of carriers, density-of-states (DOS) effective mass and electron mass, respectively. The DOS effective mass is given as $m_{DOS}^*$ = $N^*/m_b^*$, where $N_b$ is the band degeneracy and $m_b^*$ is the band effective mass. Actually, for the charge carriers predominately scattered by acoustic phonons, the mobility is expected that $μ\propto 1/m_b^{5/2}$.‡ Consequently, increasing the $m_b^*$ should be detrimental to the thermoelectric performance. In contrast, the convergence of many charge carrying valleys has virtually no detrimental effects. Therefore, multiple degenerate valleys are generally desired, thanks to the separate pockets of Fermi surface with the same energy, which have the effect of producing large $m_{DOS}^*$ without explicitly increasing $m_b^*$. Besides, materials with soft chemical bonds and anharmonic lattice dynamics would suppress the lattice thermal conductivity.‡,†,‡,† However, the combination of all these features has been identified with a large challenge in achieving high-performance thermoelectrics through an avenue simultaneously possessing large band degeneracy and strong anharmonic lattice dynamics, which are highly inter-dependent. As the best commercialized thermoelectric material found so far, Bi$_2$Te$_3$ has excellent $σ$, $S$, and large $zT$ (for both n-type and p-type), and therefore have been widely applied for TE power generation and electronic cooling around room temperature.‡ However, Te is a scarce element in the crust of the earth and its cost would rise
Bi2Se3 in recent years. Liu et al. demonstrated that the key limitations for the zT of Bi2Se3 are its poor electrical transport properties and high κ. With the intrinsically small band gap (Eg) ~ 0.3 eV and low carrier concentration (n), Bi2Se3 displays bipolar effect. The excitation of minor carriers attenuates the S, while the κ is enhanced at the same time, suggesting a small PF and a high κeff. \(^{23}\) Shakouri et al. proposed that enlarging the band gap would be an effective method to avoid bipolar conduction. \(^{37}\) Increasing n directly is another adequate means to minify the effects of minority carriers. In addition, the single valley of conduction band minimum (CBM) (Nv = 1) will lead to a low DOS and also a small power factor for n-type Bi2Se3. \(^{22}\) In the meantime, suppression of phonon transport is also critical to largely enhance the zT of Bi2Se3. Recently, Zhao et al. successfully introduced Sb–Br into the intrinsic semiconductor Bi2Se3 and obtained a maximum zT of 1.4 for n-type BiSb(Se0.94Br0.06)\(_3\) at 800 K. That is analogous to the most n-type Te-free TE materials, indicating that Sb–Br codoping is an effective approach in improving TE properties of Bi2Se3 alloy compounds. They found that Sb doping reduced \(\mu\) on account of strong anharmonicity and soft bonds. \(^{23}\) But the electrical transport properties of BiSbSe3 is still poor because of the extremely low n and the imbalance between the effective mass and n. Then, via heavy Br-doping in BiSbSe3, Liu et al. acquired a high n and further optimized TE properties. Although there is a computational work about the electronic structure of BiSbSe3 alloy \(^{18}\) and a parameterized model theoretical analysis about the effects of Br doping, \(^{27}\) the detailed physical reasons in atomic level for Br codoping to further significantly improve TE properties have not been investigated yet. Particularly, the relationship between the crystalline atomic structure and the TE performance for Bi\(_{2-x}\)Sb\(_x\)(Se\(_1-y\)Br\(_y\))\(_3\) (\(x = 0, 1, 2; y = 0, 0.08\)) is still unclear so far.

In this work, we report a systematic first-principles study on the TE properties of the Bi\(_{2-x}\)Sb\(_x\)(Se\(_1-y\)Br\(_y\))\(_3\) (\(x = 0, 1, 2; y = 0, 0.08\)) alloy. The calculations are based on the density functional theory (DFT) for the atomic and electronic structures and based on the Boltzmann transport theory for the electron and phonon transport processes. It has been shown in literature that DFT is one of the most common and successful theoretical tools for probing TE materials, such as Cu\(_{12}\)Sb\(_2\)S\(_{13}\). \(^{26}\) x = 0, 1 in the Bi\(_{2-x}\)Sb\(_x\)Se\(_3\) system is identified to be the transition boundary of the rhombohedral structure and orthorhombic structure. The strong hybridization between Sb and Se atoms in the complex crystal structure of orthorhombic BiSbSe\(_3\) with alloying 50% Sb on Bi sites makes it have a lower κ\(_L\). In addition, the increase of structural symmetry is helpful to obtain a large energy valley degeneracy (N\(_v\)), and a large σ can be achieved by increasing conductive channels. The N\(_v\) and chemical bond softening can be further improved significantly by codoping 8% Br at Se sites. The improved N\(_v\) will enhance the \(m_{BS}\) without reducing the \(\mu\). The further softened phonons are beneficial to enhancing anharmonic scattering and further decrease the κ\(_L\). The Br codoping also moves the Fermi level (E\(_F\)) into the conduction band (CB), resulting in a significant increase of n and σ. Interestingly, the increase of n does not reduce largely S because of the increased \(m_{BS}\). Eventually, a peak zT value of ~0.96 at 800 K can be realized in n-type alloy compounds BiSb(Se\(_{0.96}\)Br\(_{0.08}\))\(_3\) with the carrier concentration of 9.22 \(\times\) 10\(^{19}\) cm\(^{-3}\).

**Results and discussion**

**Crystal structure and electronic structure**

Bi\(_2\)Se\(_3\) compound has a rhombohedral crystal structure with space group D\(_{3d}\)(R\(_{3m}\)) no. 166 (Fig. 1(a)). In order to generate a reliable atomic structure for this compound, we first optimized its crystal structure with PBE functional as implemented in VASP in the total energy method. Its lattice constants \(a, b\) and \(c\) are found to be 4.19, 4.19 and 30.8 Å, respectively, which are in good agreement with the experimental values 4.14, 4.14 and 28.63 Å, \(^{27}\) proving the reliability of our theoretical modeling. The distinct layered structure consists of a regular octahedron structure with Bi atom as the center and Se atom as the vertex. On the other hand, Sb\(_2\)Se\(_3\) exhibits an orthorhombic structure composed of a tetragonal conical pentahedron with Sb as the bottom center and Se as the vertex, as shown in Fig. 1(b). According to the previous results of Zhao et al., \(^{23}\) the substitution of Sb for 50% Bi atoms in Bi\(_2\)Se\(_3\) will induce a phase transition from the rhombohedral structure to the orthorhombic structure. Therefore, we utilize Bi atoms to replace the two nonequivalent sites of Sb\(_1\) atom in Sb\(_2\)Se\(_3\), and adopt a structure with the lower energy to simulate the BiSbSe\(_3\). It displays a significant chain-like structure of orthorhombic phase by forming an octahedral structure with Bi atom as the center and Se atom as the vertex, and a triangular pyramidal tetrahedron with Sb and three Se atoms as the vertex is also formed (Fig. 1(c)).

This complex crystal structure of BiSbSe\(_3\) is favorable to reducing the \(\kappa\) because of the structural phase transition and the formation of the chain-like structure. Since the structural rhombohedral–orthorhombic phase transition is related to the breakage of part of the cation–anion bonds, half of the octahedral coordination cations are converted to five coordination, as reported previously by Yang et al. \(^{23}\) Finally, we consider the possible substitution of single Br atom for Se. There are three nonequivalent sites of Se atom in BiSbSe\(_3\), therefore, three possible structures can be formed. It is found by calculation that the total energies per cell of the three structures are \(-78.373, -78.285\) and \(-78.308\) eV, respectively. Furthermore, we calculate the energy band structures and thermoelectric transport properties for the three structures, respectively. The results are compared in Fig. S1 and S2, which show that the
results are qualitatively similar. Herein, we take the lowest energy structure with Se3 replaced by Br atom to model the BiSb(Se0.92Br0.08)3.

As shown in Fig. 1(d), this structure also possesses a stable orthorhombic structure (space group Pnma) but is more complex: not only an octahedral structure with Bi atom as the center and Se atom as the apex, and a triangular pyramidal tetrahedron with one Sb and three Se atoms as the apex are formed, but also formed is an octahedral structure with Bi as the center and both Se and Br atoms as the vertices. This more complex structure may be helpful to further suppressing the lattice thermal conductivity.

The conduction band and valence band model can be used to analyze how the carrier concentration and the band gap affect the TE properties. The calculated electronic band structures of Bi2Se3 (a), Sb2Se3 (b), BiSbSe3 (c), and BiSb(Se0.92Br0.08)3 (d), with Bi, Sb, Se, and Br atoms shown as red, brown, green, and blue spheres, respectively.

One can see in Table 1 that the previous PBE-GGA result of the $E_g$ of Sb2Se3 (~0.7 eV) is largely underestimated with respect to the experimental value (~1.17 eV), while our TB-mBJ result (~1.11 eV) is in good agreement. In order to ensure the accuracy of the calculated results, we use TB-mBJ to calculate the band structures of Bi2-xSb2x(Se1-yBry)3 (x = 1, 2; y = 0, 0.08). The SOC are considered in our calculations due to the heavy element. As can be seen in Table 1 and Fig. 2, the Bi2-xSb2x(Se1-yBry)3 (x = 1, 2; y = 0, 0.08) have much larger band gaps than Bi2Se3, which can largely suppress the intrinsic excitation and the bipolar effect to prevent them from reaching a higher $zT$ value. In addition, the 8% Br codoping further makes the Fermi level ($E_F$) shifted to deeper conduction states, indicating that the Br codoping increases significantly the majority carrier concentration.

As is well known, a large $N_v$ is beneficial to a large DOS effective mass ($m^*_\text{DOS}$) without deterioration of the carrier mobility. $N_v$ is the effective total number of independent carrier pockets or valleys in the Brillouin zone, including both symmetry and orbital degeneracies. For Bi2Se3, it can be seen that alloying 50% Sb on Bi sites increases the valley number of effective energy from the degeneracy 2 to 10. As one can see in

![Fig. 1 Crystal structure of Bi2Se3 (a), Sb2Se3 (b), BiSbSe3 (c), and BiSb(Se0.92Br0.08)3 (d), with Bi, Sb, Se, and Br atoms shown as red, brown, green, and blue spheres, respectively.](image)

![Fig. 2 Calculated electronic band structures of Bi2Se3 (a), Sb2Se3 (b), BiSbSe3 (c), and BiSb(Se0.92Br0.08)3 (d).](image)
Sb2Se3 11.77
BiSb(Se0.92Br0.08)3 respectively, as shown in Fig. 4(a). It should traversed by Fermi level from bottom to top, respectively.

Fig. 2(c), the energy difference between the CBM and the fourth valence valley is less than ~0.14 eV, which is smaller than the 0.15 eV between the first and the second valence bands of PbTe.48 Such small energy difference can be easily crossed at elevated temperatures, making it possible to improve the electrical transport properties. Furthermore, 8% Br subsequent codoping at Se12 position exhibits remarkably distinct electronic structures, which further significantly increases the effective Nv, accompanied by pushing the Ef deep into the band structure, which significantly enlarges the n. A high Nv number generally results in a larger mcσσ for the conduction band and eventually maintains a high S for n-type samples in spite of the increased n. Interestingly, the conduction bands of BiSb(Se0.92Br0.08)3 are much more complex than those of BiSbSe3: the activated multiple conduction-band minima lie close together in energy, forming complex multiband valence states. Another illustration of the complex band structure is shown in the Fermi surface, which has multiple types of valleys coming from the four conduction bands of Ef crossing, all within a small energy window (see Fig. 3(a)–(d)). Such a good band feature may be associated with excellent thermoelectric properties, as found in other thermoelectric materials.39,41

To clearly understand the states near the Ef, we calculate the total density of states (TDOS) for Bi2Se3, BiSbSe3, and BiSb(Se0.92Br0.08)3, respectively, as shown in Fig. 4(a). It should be noted that TDOS near the Fermi level of doped Bi2Se3 is larger than that of pristine Bi2Se3, 50% Sb doping on Bi sites of Bi2Se3 slightly increased the TDOS near the Ef. This is mainly originated from the substitution of Sb for Bi, which increases Nv. Furthermore, 8% Br codoping at Se12 site in BiSbSe3 tremendously increases the TDOS in the vicinity of the Ef, which will enhance σ significantly. These results manifest that Sb and Br dual doped Bi2Se3 can be expected to have enhanced electrical transport and thermoelectric properties. To analyze the reasons for the enhanced TDOS by Br substitution, we calculate the partial density of states (PDOS) of BiSb(Se0.92Br0.08), As can be seen in Fig. 4(b), the bottom of CB edge is mainly contributed by the hybridized p orbitals from Bi, Se, Br, and Sb atoms (see the next section for more details). Thus, the Br atom replacement on the Se12 site can effectively adjust the band structure near the CB edge, and strongly enhances the thermoelectric performance.

Table 1   Lattice parameters and band gaps of Bi2–xSbx(Se1−yBry)3 (x = 0, 1; y = 0, 0.08)

| Compounds            | Experimental value | Previously calculated value | Our calculated value |
|----------------------|--------------------|-----------------------------|---------------------|
|                      | a      | b      | c      | E_f   | a      | b      | c      | E_f   | a      | b      | c      | E_f   |
| Bi2Se3              | 4.14a  | 4.14a  | 28.63a | 0.25a | 4.17a  | 4.17a  | 30.29a | 0.16a | 4.19   | 4.19   | 30.80  | 0.17  |
| Sb2Se3              | 11.77b | 3.96b  | 11.62b | 1.17b | 11.53b | 3.96b  | 11.22b | 0.75b | 12.82  | 4.03   | 11.53  | 1.11  |
| BiSbSe3             | 11.70c | 3.91c  | 11.62c | 0.88c | 12.59c | 4.10c  | 11.65c | 0.63c | 12.63  | 4.10   | 11.62  | 1.05  |
| BiSb(Se0.92Br0.08)3 | 10.52d | 5.26d  | 10.17d | —     | 11.84d | 4.07d  | 11.67d | —     | 12.36  | 4.16   | 11.65  | 1.02  |

* Result from ref. 27.  
* Result from ref. 28.  
* Result from ref. 29.  
* Result from ref. 23.

Fig. 3   The energy isosurfaces at 0.37 eV of BiSb(Se0.92Br0.08)3 (space group: Pnma, no. 62). (a), (b), (c) and (d) are the four conduction bands traversed by Fermi level from bottom to top, respectively.
Bi, Sb, Se and Br are 2.02, 2.05, 2.55, and 2.96, respectively. The electropositive elements Bi and Sb dedicate all of their valence electrons to the more electronegative elements Se and Br, ultimately, BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ can be described as (BiSb)$_3^+$(Se$_{0.92}$Br$_{0.08}$)$_3^{2-}$. It coincides with the above analysis that, in BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$, Bi and Sb atoms tend to lose electrons, while Se and Br atoms tend to gain electrons owing to their larger electronegativity. These also manifest that Br–Bi has a stronger interaction than Se–Bi. In fact, the stronger hybridization between Br and Bi atoms would lead to increasing the DOS near the CB edge, as indicated in Fig. 4(d). The electrons between the Bi and Br atoms mainly localize around Br, while a certain number of electrons appear near the center position between Bi and Se, and Sb and Se atoms, indicating Bi and Br atoms incline to form an ionic bond, while there is a distinct covalent bond characteristics between Bi and Se, and Sb and Se atoms. The ionicity of the bonding in a material usually is characterized by the electronegativity difference ($\Delta\chi$). The larger $\Delta\chi$ ($\approx$ 0.9 between Br and Bi atoms), the more likely there will be interaction between carriers and the optical vibrations of the lattice atom, thus suppressing the $\kappa_L$. For instance, observations by Ioffe et al. showed a decrease of $\kappa$ with an increase of the ionicity of the bonds between atoms.\(^\text{44}\) Spitzer reported a correlation between increasing coordination number (CN) in a crystal structure and decreasing $\kappa_L$ (by relating the $\kappa_L$ to the strength of the chemical bonds in a material).\(^\text{42}\) In our case, the bond lengths between atoms after Br doping become longer, namely, Se$_{12}$–Bi bond lengths (2.81, 3.12 Å) in the BiSbSe$_3$ are shorter than the corresponding Br–Bi bond lengths (3.05, 3.23 Å) in BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$. This implies that the Br–Bi bond could be relatively weaker according to the bonding descriptor contact developed by Deringer et al.\(^\text{28}\) The weaker chemical bond among Br and Bi atoms will be also a factor leading to the low $\kappa_L$ (see the next section), as also recognized recently in x-MgAgSb.\(^\text{43}\) In addition, the big “mushroom” CDD shape around Bi/Sb is a clear indicator of the existence of lone-pair electrons, which is alike to the case of CuSbS$_2$.\(^\text{44}\) According to the valence shell electron pair repulsion (VSEPR) theory, the lone-pair electrons almost occupy one bonding site. Hence, the unsymmetrical and disorderly coordinated environment of bonds in BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ indicates the possibility of strong interactions.
anharmonicity by significantly enhancing heat carrying phonon scatterings. This will also result in ultralow $\kappa_L$.

**Low lattice thermal conductivities**

To achieve a high thermoelectric figure of merit, a low lattice thermal conductivity is essential. Therefore, insights into the origin of the extremely low thermal conductivity is meaningful for exploiting high performance thermoelectric materials. Previous work predicted that BiSbSe$_3$ could possess a low $\kappa_L$. Nevertheless, the prediction was based on a strong dependence of the elastic properties on volume, and the resulting large Grüneisen parameter ($\gamma$, an indicator of anharmonicity) suggests a strong anharmonicity. In this work, we precisely calculate the $\kappa_L$ as a function of temperature for BiSbSe$_3$ and BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ using the full linearized ShengBTE code combined with DFT, which is well known for quantitative predictive power. The results are presented in Fig. 5.

As mentioned previously, the substitution of Sb for 50% Bi in Bi$_2$Se$_3$ decreases the $\kappa_L$ partly due to the structural phase transition from rhombohedral to orthorhombic, and partly due to the formation of the more complex chain-like structure with respect to the layered structure, which induces enhanced intrinsic phonon scatterings. In Fig. 5 our ab initio results are compared with the experimental $\kappa_L$ values of polycrystalline samples cited from ref. 23. It is worth mentioning that the calculated values are averaged over the three principal axes for the purpose of better vision and comparison with the experimental measurements on polycrystalline samples. It can be seen that the predicted values of BiSbSe$_3$ are below 1.2 W m$^{-1}$ K$^{-1}$ at 300 K, which is pretty low in thermoelectric materials. However, the experimental values are even much lower at low temperatures though the agreement between theory and experiment is improved at high temperatures. The large discrepancy in $\kappa_L$ at low temperatures may not be entirely attributed to grain boundary scattering, since this effect is usually small in materials with intrinsically low $\kappa_L$, where heat carrying phonons have smaller mean free paths than the size of the grains. It has to be noted that the theoretical calculation does not take into account the phonon scattering due to dynamic disorder, an omission that may be responsible for the overestimation of $\kappa_L$.

Here a possible mechanism is that the underlying atomic disorder plays an appreciable role in reducing $\kappa_L$ at relatively low temperatures. While at high temperatures atoms occupy higher-symmetry positions, and intrinsic phonon–phonon scattering then dominates, as described by Eivari et al. For example, the previously mentioned lone-pair electrons may provide an origination of this disorder which can act as a phonon-blocking mechanism that may help facilitate an ultralow $\kappa_L$. Moreover, we find that 8% Br codoping is also effective to further reduce $\kappa_L$ as shown in Fig. 5. BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ shows a lower $\kappa_L$ than that of BiSbSe$_3$ at the entire temperature. For instance, their $\kappa_L$ are 0.29 and 0.44 W m$^{-1}$ K$^{-1}$ at 800 K, respectively. Clearly, the chemical bond softening between Br and Bi atoms is considerably higher than that between Se12 and Bi. As we know, the strong anharmonicity usually not only relies directly on the unsymmetrical and chemical bonds between the atoms in the crystal but also is often associated with atoms and their near neighbors (large coordination numbers). The calculated $\kappa_L$ of BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ is found to be in good agreement with an available experimental value 0.22 W m$^{-1}$ K$^{-1}$ at 800 K.

**Promising electrical transport properties**

To shed light on the influences of Sb–Br codoping, herein the electrical transport properties of BiSbSe$_3$ and BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ are calculated as functions of carrier concentration ($n$) at 300 K, 600 K, and 800 K within the framework of the semiclassical Boltzmann transport theory. While it is possible to calculate $\sigma/T$ as a function of $n$ and $T$, but it is not possible to calculate $\sigma$ itself without the scattering rate $\tau^{-1}$. Here, the strategy previously used by Ong et al. is adopted with available experimental data to estimate the relaxation time $\tau = \frac{3n}{C_0 T^{3/2}}$ with $T$ in K, $\tau$ in s, $n$ in cm$^{-3}$. The specific details are that we used 800 °C data from Liu and coworkers, who measured transport properties on the material. They report a thermopower $S = 202.462$ μV K$^{-1}$ at this temperature. By comparing with the calculated $S(T,n)$, we obtain a value $n = 1.77 \times 10^{20}$ cm$^{-3}$ for this sample. The reported experimental $S$ is 172.899 S cm$^{-1}$, which combined with the calculated $\sigma/T$ yields $\tau = 2.345 \times 10^{-15}$ s for this particular sample at 800 °C. As mentioned, we then calculate $\sigma$ as $\sigma = \frac{n}{\tau}$ of $T$. Ultimately, the results for BiSbSe$_3$ and BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ are plotted in Fig. 6.

Based on the estimated $\tau$, we can calculate the $\kappa_L$ using the BoltzTraP2 code. Unfortunately, with the significant increase of $n$, the $\kappa_L$ augments from ~0.05 W m$^{-1}$ K$^{-1}$ of BiSbSe$_3$ at 300 K, to ~0.34 W m$^{-1}$ K$^{-1}$ of BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ at 800 K. However, as discussed previously, Br codoping notably reduces the $\kappa_L$ from ~1.11 W m$^{-1}$ K$^{-1}$ at 300 K to ~0.29 W m$^{-1}$ K$^{-1}$ at 800 K. Therefore, a favorable $\kappa$ (~0.63 W m$^{-1}$ K$^{-1}$) could still be obtained for BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ at 800 K. Then, by combining the calculated $\kappa_L$, $\kappa_e$, $S$, and $\sigma$ of BiSbSe$_3$ and BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$, we determine their $zT$s at different temperatures and carrier concentrations. Fascinatingly, compared with 50% Sb doped...
BiSbSe$_3$ (maximum $zT \sim 0.23$ with the optimal $n$ of $1.163 \times 10^{19}$ cm$^{-3}$ at 800 K, see Fig. 6(a)), further 8% Br codoping enhances $\sigma$, hence strikingly improves the $zT$ (maximum $\sim 0.96$ with the optimal $n$ of $9.224 \times 10^{19}$ cm$^{-3}$ at 800 K, see Fig. 6(b)). BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ exhibits a still high $S$ that may originate from the increase of $m^*_\text{DOS}$ owing to the increase of $N_v$ through Br codoping. On the other hand, the remarkably enhanced $\sigma$ shown in Fig. 6(b) may originate from the increases of $n$ and/or $\mu$.

To show this more clearly, we calculate $n$ and $\mu$ as functions of temperature for BiSbSe$_3$ and BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$, as depicted in Fig. 7. $\mu$ is obtained from the calculated $\sigma$ and $n$ by using the expression $\mu = \sigma n/\tau e$. One can see that, 8% Br codoping dramatically enlarges $n$, and in the meantime, $\mu$ is still promoted at medium high temperatures. The significant increase of $n$ in BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ is essentially due to the one more electron of Br atom with respect to Se. Thus, Br atom acts as an electron donor though it has a large electronegativity. Consequently, the $E_F$ shifts deeper in the CB and the differential conductivity turns into more symmetric regarding the Fermi level. Our Bader charge analyses show consistently that each nearest neighbor Bi atom of Br averagely obtains more 0.44 electrons from the Br atom than that from Se. In addition, the hybridization of the electronic states then provides a large DOS around the Fermi level, as already shown in Fig. 4(d). A direct result is the remarkably enhanced $\sigma$. However, the dramatically increased $n$ in the Sb–Br codoping system does not significantly reduce the $S$: it is $-261.93$ $\mu$V K$^{-1}$ for BiSbSe$_3$ at 300 K and $-254.12$ $\mu$V K$^{-1}$ for BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ at 800 K. Based on the aforementioned data and analyses, this explicit increase is most likely due to the $N_v$ augment, which is the key parameter for making a compromise between $n$ and $S$. Normally, the optimum $n$ for most good TE materials is in the range of $10^{19}$ to $10^{21}$ cm$^{-3}$. Optimization of the carrier concentration is still one of the most effective approaches for improving TE performance. Especially, in the case of some TE materials with intrinsically low thermal conductivity, a high $zT$ can be obtained solely through doping.

**Methods**

**First-principles calculations**

The atomic structures of Bi$_{2-x}$Sb$_x$(Se$_{1-y}$Br$_y$)$_3$ ($x = 0, 1, 2; y = 0, 0.08$) are optimized utilizing the plane-wave projector augmented wave (PAW) method$^{24}$ as implemented in the Vienna *ab initio* simulation package (VASP)$^{25}$ based on DFT. The
Perdew–Burke–Ernzerhof parametrization of the generalized gradient approximation (PBE-GGA) is used for the exchange–correlation potential. The wave function is expanded using plane waves with a kinetic energy cutoff of 400 eV. A $(5 \times 15 \times 5)$ Monkhorst–Pack\textsuperscript{26} $k$-point mesh is used for the Brillouin zone (BZ) sampling. The spin–orbit coupling (SOC) is considered in all the calculations due to the heavy element. The geometry optimization is performed for every Br doping configuration by relaxing both atomic positions and lattice constants. The energy convergence criterion is chosen to be $10^{-7}$ eV. The Hellmann–Feynman forces on each ion are less than 0.001 eV Å$^{-1}$. The residual stress is set to be less than 0.1 GPa. Here, we discuss only the configuration with the lowest total energy. The calculated lattice constants are listed in Table 1. These values agree well with previous results reported in literature.\textsuperscript{21,27–29}

The electronic structures of Bi$_2$$_x$Sb$_3$(Se$_{1-y}$Br$_y$)$_3$ ($x = 0, 1, 2; y = 0, 0.08$) are then calculated using the linearized augmented plane wave (LAPW) method,\textsuperscript{30} as implemented in the WIEN2k code.\textsuperscript{31} The muffin-tin radii (RMT) are set to 2.5, 2.46, 2.46, and 2.5 a.u. for Bi, Sb, Se, and Br, respectively. The cutoff parameter RMT $\times K_{\text{max}}$ $= 9$ ($K_{\text{max}}$ is the magnitude of the largest $k$ vector) is used. The self-consistent DFT calculations are performed with a $(5 \times 15 \times 5)$ $k$-point mesh in the irreducible BZ, and the total energy is converged to within 0.0001 Ry. Since the local or semilocal exchange–correlation approximation underestimates band gaps as the presence of artificial self-interaction and the absence of the derivative discontinuity in the exchange–correlation functional,\textsuperscript{32} band gaps with better accuracy are calculated using the Tran–Blaha modified Becke–Johnson (TB-mBJ) functional.\textsuperscript{33} The calculated electronic structures with the TB-mBJ functional are further used to obtain electrical transport properties. The transport calculations are carried out using the semiclassical Boltzmann theory, as implemented in the BoltzTraP code\textsuperscript{34} within the constant scattering time approximation, by taking 20 000 $k$ points in the irreducible BZ.

The lattice thermal conductivity can be determined by using an iterative self-consistent method for solving the phonon Boltzmann transport equation as implemented in the ShengBTE code.\textsuperscript{35,36} The harmonic lattice dynamics and the second-order interatomic force constants (IFCs) are determined by the density functional perturbation theory (DFPT)\textsuperscript{37} implemented in VASP with a supercell of $1 \times 3 \times 1$ and the PHONOPY code\textsuperscript{38} interfaced to VASP. The third-order anharmonic IFCs are extracted from the DFT calculations by applying the finite displacement method with a supercell of $1 \times 3 \times 1$ and a truncation for next–nearest–neighbor interactions up to the tenth order. As for the $k$-point sampling of the BZ, our test calculations adopting a $1 \times 3 \times 1$ and a $3 \times 3 \times 3$ $k$-point mesh show that the thermal conductivities are converged very well. In this work, a $3 \times 3 \times 3$ mesh is used for all the supercell calculations.

**Summary and conclusion**

In this work, we performed comprehensive investigations of both the thermal and electrical transport properties of BiSbSe$_3$ and BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ by using first-principles calculations combined with the Boltzmann transport theory. The results demonstrate that the dual doping of Sb–Br in Bi$_2$Se$_3$ leads to both low $\kappa$, and promising electrical transport properties. First, the chemical bond softening between Br and Bi atoms and lone-pair electrons act as a phonon-blocking mechanism which greatly suppresses $\kappa$ with strong anharmonicity. Second, the one more electron of Br atom with respect to Se makes the Br atom acts as an electron donor, which dramatically increases the carrier concentration $n$ in BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$. As a result, the DOS near the $E_F$ is significantly increased and more conduction bands participate in the electron transport, leading to a remarkably enhanced $\sigma$. Third, the 8% Br subsequent codoping exhibits remarkably distinct electronic structures and transport properties, which further significantly increases the effective $N_v$. This multiple degeneracy of conduction band edges is a distinctive feature of BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$, enabling an extraordinary high PF by giving rise to a large $m^*_{\text{DOS}}$ and thus preserving a large $S$ in spite of the dramatically increased $n$. Combined with the low $\kappa$ and excellent electrical transport properties, the n-type BiSb(Se$_{0.92}$Br$_{0.08}$)$_3$ presents an outstanding thermoelectric performance, especially around 800 K: the maximum $zT$ can reach 0.96 with the optimal $n$ of $9.224 \times 10^{19}$ cm$^{-3}$. This work shows theoretically the possibility for crystalline materials to achieve a high thermoelectric performance without introducing defects and/or nanostructures, and provides a possible guidance and inspiration for seeking new promising Te-free thermoelectric materials.

**Data availability**

The data that support the findings of this study are available from corresponding author upon reasonable request.

**Author contributions**

S.-H. Ke conceived the idea. J. Zhang conducted the simulation and analysis. S. Zhong provided advices on this work. All authors participated in the writing and correction of the manuscript.

**Conflicts of interest**

The authors declare no competing interests.

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