Manipulating Band Structure through Reconstruction of Binary Metal Sulfide for High-Performance Thermoelectrics in Solution-Synthesized Nanostructured Bi$_{13}$S$_{18}$I$_2$

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**Abstract:** Reconstructing canonical binary compounds by inserting a third agent can significantly modify their electronic and phonon structures. Therefore, it has inspired the semiconductor communities in various fields. Introducing this paradigm will potentially revolutionize thermoelectrics as well. Using a solution synthesis, Bi$_2$S$_3$ was rebuilt by adding disordered Bi and weakly bonded I. These new structural motifs and the altered crystal symmetry induce prominent changes in electrical and thermal transport, resulting in a great enhancement of the figure of merit. The as-obtained nanostructured Bi$_2$S$_3$I$_2$ is the first non-toxic, cost-efficient, and solution-processable n-type material with $zT = 1.0$.

Thermoelectrics, in which the waste heat can be converted into electricity in a silent and reliable way, have gained renewed interests. The semiconductor industry, of which thermoelectrics is a subset, has been primarily relying on binary compounds. Specifically, the state-of-the-art thermoelectric compounds are Bi$_2$Te$_3$ operating at low-temperature (300–500 K) and PbTe, SnS$_2$, and CoSb$_3$ at medium temperature (500–900 K). The conversion efficiency of thermoelectrics is evaluated by the figure of merit, $zT = S^2σT/d$. Typical ways to enhance the $zT$ of these binary compounds include increasing the power factor, $S^2σ$, through band engineering, such as energy filtering, resonant level, and/or diminishing $σ$ via structural engineering, as exemplified by the atomic-level defect nanoscale grain boundary.

Aside from performance, cost and toxicity also raise critical concerns. Since Co and Pb are toxic and Te is also scarce (0.001 ppm in earth crust), the earth-abundant (500 ppm) and eco-friendly sulfur-based counterparts have attracted attentions as potential alternatives. However, their performance is impaired by lower carrier mobility ($μ$) owing to the more ionic bonding and higher $σ$ ascribed to the lower atomic weight. The commonly used strategies to improve $zT$ have encountered a bottleneck to achieve $zT = 1.0$ in binary metal sulfides, especially for the n-type leg.

Recently, dismantling and reconstructing the canonical binary compound by inserting a third agent has inspired material explorations in various fields, such as electronic devices (SnS$_2$–(Ni,H)$_3$SnS$_3$) and radio detectors (Hg$_2$Cu$_2$Cd$_2$Sn$_4$). This strategy may also reconstruct the crystal structure of binary thermoelectric compounds, resulting in possible modifications of electronic and phonon structures. However, it has seldom been attempted, which is probably due to the synthetic complexity and the sophisticated interplay between the transport properties ($S$, $σ$, and $k$). Herein, we chose the n-type binary metal sulfide, Bi$_2$S$_3$, and inserted a third environmentally compatible and earth-abundant element, iodine. The resultant Bi$_2$S$_3$I$_2$ has the crystal symmetry changed and several novel structural motifs introduced, leading to substantially modified electronic and phonon structures. Consequently, it significantly outperformed the parent compound (Bi$_2$S$_3$). The high $zT$ (1.0 at 788 K), as well as eco-friendly and cost-efficient constituent elements qualify this material as a competitive alternative to conventional Te-based thermoelectrics.

Bi$_2$S$_3$I$_2$ has a complex crystal structure that belongs to a trigonal lattice with the space group $P3$–$2$–$c$. There are four sites for disordered Bi(X), each with a $1/4$ occupancy. These disordered Bi(X) atoms at the (1/3, 2/3, z) sites coordinate with six S atoms to form a wheel-like cluster (Figure 1a). The Bi(X) atom disorder and Bi–Bi bonding had been validated through both single-crystal and powder X-ray diffraction in previous studies. This unusual Bi–Bi bond had also been witnessed in CsBi$_2$Te$_3$ and BiTe. Between the disordered Bi(X) atoms, the Bi$_6$S$_8$ clusters serve as the connecting arms...
The Bi—I coordination styles in these clusters (Figure 1a) are almost the same with those in Bi$_2$I$_3$ (Figure 1b, circled region). These Bi and I atoms construct a 3D framework and create two one-dimensional tunnels propagating along the [001] axis in each unit cell, inside which the I atoms reside. It is noteworthy that the distance between iodine and the nearest atom (Bi) is around 3.57 Å, which is much longer than the sum (2.79 Å) of the covalent radii of Bi (1.46 Å) and I (1.33 Å). This is reminiscent of open framework compounds as exemplified by clathrate (Ba$_6$Ga$_8$Ge$_{30}$)\textsuperscript{[7]} or CoSb$_3$-based skutterudite\textsuperscript{[8]}. The addition of disordered Bi sites, Bi—Bi bonds, and the iodine sublattice going from Bi$_2$I$_6$ to Bi$_3$I$_6$I$_2$ are likely to alter its electronic and thermal properties.

Bulk polycrystalline samples of Bi$_3$I$_6$I$_2$ (6.70 g cm$^{-3}$, relative density: 96.4%) could be prepared from spark plasma sintering (SPS) commercial Bi$_2$I$_6$ and BiI$_3$ (the molar ratio is 5.60:1) at 600°C. We have conducted an analysis of the powder X-ray diffraction (PXRD) profile of the bulk Bi$_3$I$_6$I$_2$ and confirmed this single-phase product (Figure 1c). The Rietveld refinement was also carried out (Supporting Information, Table S1 and Figure S2). Energy dispersive spectrum (EDS) detected the chemical compositions (measured at. %: Bi 40.1, S 53.6, I 6.3, theoretical at. % of Bi$_3$I$_6$I$_2$: Bi 39.3, S 54.5, I 6.1).

Along with the bulk Bi$_3$I$_6$I$_2$ prepared, we have also adopted a solution-phase method to synthesize the nanocrystalline counterpart, which was then unequivocally characterized by various techniques. First, the PXRD pattern agreed well with the simulated one (Supporting Information, Figure S6). Furthermore, EDS confirmed the chemical composition (at. %: Bi 39.0, S 55.0, I 6.0, theoretical at. %: Bi 39.3, S 54.5, I 6.1). Finally, transmission electron microscopy (TEM) depicted the microstructure of the product. As expected from the trigonal crystal structure of Bi$_3$I$_6$I$_2$, an anisotropic rod-like shape could be found (Figure 2a). The axial direction of the nanorod was indexed as [001] by high-resolution transmission electron microscopy (HRTEM, Figure 2b,c).

The scalable (9.0 g per batch) synthesis of Bi$_3$I$_6$I$_2$ nanopowder enabled us to consolidate it into a macroscopic cylinder (diameter 10 mm × height 12 mm, 6.33 g cm$^{-3}$ relative density = 91.1%). After SPS, the crystal phase was preserved according to PXRD (Figure 2e). From the TEM (Figure 2f) of the focused-ion-beam (FIB)-cut nanosample, the grain size was estimated to be 800 ± 300 nm. EDS corroborated the nearly identical atomic percentages of Bi, S, and I (at. %: Bi 39.4, S 54.3, I 6.3) to nominal values (at. %: Bi 39.3, S 54.5, I 6.1). HRTEM clearly revealed the lattice fringe of (100), (001) plane and honeycomb-like pattern along [001] axis (Supporting Information, Figure S7). The atomically resolved high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image taken along [001] zone axis was in good accordance with the atomic model (Figure 2g). BiCl$_3$ was mixed with the Bi$_3$I$_6$I$_2$ nanopowder (Supporting Information, Figure S8c–f) and then SPSed to study the dopant effect.

Interestingly, the as-compressed nanostructured material manifested a strong crystallographic anisotropy (Figure 2e). In the cross-plane (\(\perp\) pressing) XRD, (hk0) reflection peaks, such as (310), (410) and (520), were notably enhanced. In stark contrast, in the in-plane (|| pressing) XRD, (002) peak was relatively much stronger. This anisotropy might stem from the anisotropic grain structure of the starting crystalline...
of nanorods as the long axis ([001] direction) of the nanorod tended to lie perpendicular to the pressing direction (Figure 2d). Contrarily, for the bulk polycrystalline sample of Bi$_2$S$_3$I$_2$ that was synthesized via sintering randomly oriented Bi$_2$S$_3$ and BiI powder, almost no anisotropy was observed (Supporting Information, Figure S2).

Having successfully synthesized and characterized both bulk and nano Bi$_2$S$_3$I$_2$ samples on a large scale, we studied their thermoelectric properties (Figure 3). First, the electrical conductivities (σ) of the so-called bulk Bi$_2$S$_3$I$_2$, nano Bi$_2$S$_3$I$_2$, and nano Bi$_2$S$_3$I$_2$ + 2% BiCl$_3$ samples all increased with ascending temperature, 313–788 K (Figure 3a). This was indicative of a semiconductor-like transport behavior. Nearly no anisotropy was found in σ of the bulk Bi$_2$S$_3$I$_2$ sample due to the random grain orientation (Supporting Information, Figure S5c–h). Contrarily, σ showed pronounced differences in two directions of the nanosamples (Figure 3a). σ of the undoped nanosample was similar with that of the bulk sample, while doping had induced a significant enhancement of σ in the nano Bi$_2$S$_3$I$_2$ + 2% BiCl$_3$ sample (Figure 3a). The carrier concentration (n$_{\text{H}}$) of undoped nanosample showed a steady increase as temperature rose (Figure 3b). This again corroborated the semiconductor-like characteristics. Upon doping of BiCl$_3$, n$_{\text{H}}$ was higher than that of the undoped nanosample over the whole temperature range (Figure 3b; Supporting Information, Table S2).

The Seebeck coefficients (S, Figure 3c) of all the samples had negative signs throughout the temperatures of interest, indicating that electron was the majority carrier. The nano and bulk undoped samples exhibited quite similar Seebeck coefficients (Figure 3c), implying their nearly identical carrier concentration. On the other hand, the lower magnitude of Seebeck coefficient of the BiCl$_3$-doped nanosample (Figure 3c; Supporting Information, Figure S10) compared to the undoped nanosample might be attributed to its higher carrier concentration (Figure 3b). The power factor was then calculated as $S^2\sigma$ (Figure 3d). The BiCl$_3$-doped sample exhibited a much larger (ca. 2 times) power factor compared with the undoped sample. The highest power factor attained in the nano Bi$_2$S$_3$I$_2$ + 2% BiCl$_3$ sample was 0.59 mW m$^{-1}$ K$^{-2}$ at 788 K.

The total thermal conductivity (Figure 3e), $\kappa_{\text{total}}$, was calculated from $D_T C_p \rho$, in which $D_T$ (thermal diffusivity; Supporting Information, Figure S9d) was measured using a laser flash method, $C_p$ (specific heat; Supporting Information, Figure S9c) was assessed by differential scanning calorimetry (DSC) and $\rho$ (mass density) was determined geometrically. For the bulk-grain sample, $\kappa_{\text{total}}$ was 0.55 W m$^{-1}$ K$^{-1}$ at 363 K, and then decreased to 0.43 W m$^{-1}$ K$^{-1}$ at 763 K. For the nano Bi$_2$S$_3$I$_2$ + 2% BiCl$_3$ sample, the in-plane $\kappa_{\text{total}}$ was 0.53 W m$^{-1}$ K$^{-1}$ at 313 K, and then decreased to 0.48 W m$^{-1}$ K$^{-1}$ at 788 K. The cross-plane $\kappa_{\text{total}}$ of the nano Bi$_2$S$_3$I$_2$ + 2% BiCl$_3$ sample was even lower.

Combining all the transport properties, the maximum figure of merit, $z\tau (S^2\sigma T)^{-1}$ of 1.0 was achieved at 788 K along the in-plane direction of nano Bi$_2$S$_3$I$_2$ + 2% BiCl$_3$ sample (Figure 3f). Along the cross-plane direction of this sample, $z\tau$ was 0.8 at 738 K. The nano-undoped sample showed lower $z\tau$ as compared to the doped sample in two directions. For the bulk undoped Bi$_2$S$_3$I$_2$, the highest $z\tau$ attained was 0.7 at 763 K.

To elucidate the origin of the excellent figure of merit, we have conducted a series of theoretical studies. First, the electronic band structure (Figure 4a) is computed by density
functional theory (DFT; see the Supporting Information, Figure S1 for details). As seen from the total density of states (DOS, Figure 4b), the band gap ($E_g$) of Bi$_3$S$_5$I$_3$ is found to be around 0.70 eV, which is in good agreement with previous optical measurement (0.82 eV).\cite{14} Intuitively, the alloying of Bi$_2$S$_3$ ($E_g = 1.3$ eV) and BiI$_3$ ($E_g = 1.67$ eV) would yield a compound with $E_g = 1.5$ eV. However, based on the analysis of orbital characters, the Bi(X) atoms with Bi–Bi bond contributed an in-gap state that is located at 0.70 eV below the conduction band minimum (CBM, Figure 4b), resulting in the anomalous shrinkage of the band gap. This $E_g$ (0.70 eV) is within the proper range (6–10 $k_B T$, 0.41–0.69 eV at 800 K) of those of typical mid-temperature thermoelectric materials, such as 0.31 eV of PbTe, 0.41 eV of PbS, and 0.86 eV of SnSe. The narrower band gap (0.70 eV) of Bi$_3$S$_5$I$_3$ as compared to that of Bi$_2$S$_3$ (1.3 eV) leads to the more favored activation of charge carrier and concomitant larger electrical conductivity (Supporting Information, Figure S5).

Deeper investigation unveils the double band extrema at the CBM (Figure 4a) that are located between the high symmetry points, Γ–M, and Γ–K, in the Brillouin zone (Supporting Information, Figure S1). They result in a very high valley degeneracy ($N_v$) of 12 in total (PbS, $N_v = 4$),\cite{18} Bi$_3$S$_5$, $N_v = 2$\cite{19} and a moderate effective mass of electron, $m^* = 0.30 m_e$ (PbS 0.39 $m_e$,\cite{18} Bi$_3$S$_5$, 0.40 $m_e$). This is attributable to the increased symmetry in Bi$_3$S$_5$I$_3$ (trigonal) as compared to Bi$_2$S$_3$ (orthorhombic). This high $N_v$ can also be hinted from the extremely high Seebeck coefficient ($S = -400 \mu V K^{-1}$ at 313 K (Figure 3c) with $n_{el} = 4.0 \times 10^{20}$ cm$^{-3}$ (Figure 3b)) of our nano Bi$_3$S$_5$I$_3$ + 2 % BiCl$_3$ sample as compared to those of other metal sulfide compounds ($-330 \mu V K^{-1}$ of Bi$_3$S$_5$\cite{20} and $-206 \mu V K^{-1}$ of PbS\cite{21}) with the same carrier concentration and similar effective mass. This is because $S$ at a certain $n_{el}$ increases with respect to $N_v$\cite{19} and $m^*$\cite{21}. These features would also favor a high power factor, as $S^2$ is proportional to $N_v$ and inversely proportional to $m^*$ at a certain carrier concentration.\cite{21} Although our nano Bi$_3$S$_5$I$_3$ + 2 % BiCl$_3$ sample had not been optimized in terms of carrier concentration, its peak power factor (0.59 mW m$^{-1}$ K$^{-2}$ at 778 K) is comparable to those of the reported metal sulfide thermoelectric compounds (0.70 mW m$^{-1}$ K$^{-2}$ for AgBiS$_2$\cite{22}) and exceeds that of the optimized Bi$_3$S$_5$ materials (0.47 mW m$^{-1}$ K$^{-2}$).\cite{23} We expect that through appropriate doping to tune the carrier concentration, an even higher power factor in Bi$_3$S$_5$I$_3$ may be achieved.

Besides the electrical transport, we have also studied the atomic vibrational properties that may lead to the low thermal conductivity. First, we obtain the potential wells using DFT (Figure 4c). The disordered Bi(X) and I atoms have the flattest potential wells as compared to S and other Bi atoms, especially along the $c$ direction. This indicates that the Bi(X) and I atoms have much weaker bonding with their neighboring atoms than the other atoms have. Additionally, we have calculated the electron localization function (ELF) as displayed in Figure 4d. It is clearly seen that only the ELFs of the Bi(X) and I atoms are spherical, indicating their off-centering instability.\cite{24} To directly observe their vibrations, we have conducted ab initio molecular dynamics (AIMD) simulations, and found that the amplitudes of vibration of Bi(X) and I atoms are much larger than other atoms. These data indicate that the Bi(X) and I atoms with relatively weak bonds may lead to low-energy optical modes. These flat optical modes have low group velocities and scatter other phonons much like so-called rattler modes.\cite{24,25} As a result, the complex-structured bulk and nano Bi$_3$S$_5$I$_3$ have exceedingly low $\kappa_T$ and $\kappa_{total}$ as compared to state-of-the-art n-type

**Figure 4.** a) Electronic band structure, b) density of states, c) potential wells, and d) electron localization function. e),f) Comparison of $\kappa_{total}$ and $\kappa_T$ of our “nano Bi$_3$S$_5$I$_3$ + 2 % BiCl$_3$” with those of PbS,\cite{18} Bi$_3$S$_5$,\cite{18} Cu$_2$I$_3$Te$_2$,\cite{18} and AgBiS$_2$.\cite{22}
metal sulfide thermoelectric materials, such as Bi$_3$S$_2$$_{1.06}$, PbS$^{[18]}$, Ti$_5$S$_{1.04}$, and Ag$_2$Bi$_3$S$_6$$_{2.22}$ (Figure 4e).

According to the aforementioned theoretical analyses, Bi$_3$S$_2$$_{1.06}$ has featured distinct electronic and phonon structure motifs that may be responsible for its high power factor, low thermal conductivity, and excellent thermoelectric properties. Although the bulk Bi$_3$S$_2$$_{1.06}$ had not been optimized in terms of doping or nanostructuring, its peak $zT$ (0.69) is comparable to that of the optimized Bi$_3$S$_2$ materials (0.72).$^{[23]}$ For the nanostructured Bi$_3$S$_2$$_{1.06}$, doping, nano-grain boundary scattering (Supporting Information, Figure S12e) and texturization further improve its performance. The $zT$ of our n-type nano Bi$_3$S$_2$$_{1.06}$ + 2% BiCl$_3$ sample even outperformed that of n-type PbS$^{[18]}$ and was nearly identical with that of n-type Ag$_2$Bi$_3$S$_6$$_{2.22}$ at 500–800 K (Figure 4f), without the use of scarce or toxic element. This peak $zT$ of 1.0 is the highest up to date among n-type, environmentally friendly, and inexpensive thermoelectric metal sulfides.

Last but not least, as a strong candidate for mid temperature (500–800 K) thermoelectrics, our n-type Bi$_3$S$_2$$_{1.06}$ holds great advantages in terms of stability, cost, and processability, when compared with state-of-the-art n-type counterparts. PbQ$^{[3,18]}$ (Q = Te, Se, S) has used large amounts of toxic Pb. In half Heusler compound (HfZrNiSn)$_{2.22}$ MgSnGe$_{2.27}$ and In$_5$Se$_{12.28}$ the use of expensive Hf ($607$ kg$^{-1}$), Ge ($1250$ kg$^{-1}$), or In ($520$ kg$^{-1}$) impedes their widespread applications, whereas our Bi$_3$S$_2$$_{1.06}$ consists of very cheap elements (Bi $17$ kg$^{-1}$, S $0.09$ kg$^{-1}$, and I $27$ kg$^{-1}$). SnSe seems to have circumvented all the problems with a $zT = 2.2$ achieved in n-type single crystals$^{[4]}$ and $zT$ around 1.0 obtained in n-type polycrystalline samples.$^{[20]}$ However, the constituent elements (Sn (2.2 ppm), Se (0.05 ppm)) still have much lower abundance than those of Bi$_3$S$_2$$_{1.06}$ (S (500 ppm), I (0.49 ppm), Bi (0.05 ppm)) in the earth’s crust. MgSiSn meets the criteria of both low cost and non-toxicity, yet requires high-temperature solid-state processing,$^{[30]}$ whereas our low-temperature, solution-phase procedure is energy-saving and time-efficient (only 4 h).

We finally demonstrate the chemical tunability by synthesizing analogous Bi$_3$S$_2$$_{1.06}$Br$_{0.2}$ nanorods and its nanostructured material (Supporting Information, Figure S11). We foresee that based on proper solution-phase methods, other open-framework compounds derived from canonical binary metal sulfides (selenides), such as Sn$_2$Bi$_3$I$_{2.06}$ and Bi$_3$Se$_2$Cl$_{0.22}$ can be synthesized. This strategy can strongly modify the electronic band structure and the phonon transport, thus their thermoelectric properties can be improved. This will enrich the multinary metal sulfides (selenides) as a new family of eco-friendly, cost-efficient, and solution-processable thermoelectric materials.

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**Conflict of interest**

The authors declare no conflict of interest.

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