Homo-composition and hetero-structure nanocomposite $Pnma\ Bi_2SeS_2 - Pnnm\ Bi_2SeS_2$ with high thermoelectric performance

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Nanocomposite engineering decouples the transport of phonons and electrons. This usually involves the in-situ formation or ex-situ addition of nanoparticles to a material matrix with hetero-composition and hetero-structure (heC-heS) interfaces or hetero-composition and homo-structure (heC-hoS) interfaces. Herein, a quasi homo-composition and hetero-structure (hoC-heS) nanocomposite consisting of $Pnma\ Bi_2SeS_2 - Pnnm\ Bi_2SeS_2$ is obtained through a Br dopant-induced phase transition, providing a coherent interface between the $Pnma$ matrix and $Pnnm$ second phase due to the slight structural difference between the two phases. This hoC-heS nanocomposite demonstrates a significant reduction in lattice thermal conductivity ($\sim 0.40\ W\ m^{-1}\ K^{-1}$) and an enhanced power factor (7.39 $\mu Wcm^{-1}K^{-2}$). Consequently, a record high figure-of-merit $ZT_{\text{max}} = 1.12$ (at 773 K) and a high average figure-of-merit $ZT_{\text{ave}} = 0.72$ (in the range of 323–773 K) are achieved. This work provides a general strategy for synergistically tuning electrical and thermal transport properties by designing hoC-heS nanocomposites through a dopant-induced phase transition.
hermoelectric (TE) technology, which directly converts heat into electricity, is a potential solution for securing an affordable green energy source by harvesting large-scale mid-grade waste heat (at/near mid-range temperatures)\(^1\)\(^2\). The dimensionless figure-of-merit (\(ZT = \sigma S^2 T/\kappa\)) and power factor (\(PF = \sigma S^2\)) are the material-level performance scales for energy conversion efficiency and output power factor, where \(S, \sigma, \kappa,\) and \(T\) are the Seebeck coefficient, electrical conductivity, thermal conductivity, and temperature, respectively\(^3\)\(^4\). Generally, \(ZT\) can be improved by lowering \(\kappa\) or enhancing \(PF\). However, simultaneously improving \(PF\) while reducing the value of \(\kappa\) is a significant challenge. Nanocomposite engineering, a vital strategy for decoupling the transport of phonons and electrons, involves the in-situ formation and ex-situ addition of nanoparticles to a material\(^5\)\(^6\). The composition difference between the matrix and second phases can induce mass fluctuation, strains\(^1\)\(^2\)\(^3\)\(^4\) or dislocation\(^1\)\(^5\)\(^6\)\(^7\) at their interfaces, which can dramatically scatter phonons and reduce lattice thermal conductivity. A nanocomposite with coherent nano-inclusions (e.g., hetero-composition and homo-structure)\(^8\)\(^9\) can cause the phase transition from one with incoherent nano-inclusions (e.g., hetero-composition and hetero-structure)\(^1\)\(^0\)\(^2\)\(^3\)\(^4\)\(^5\), PbTe-Ag\(_2\)Te\(^2\)\(^4\)\(^5\). Zhao et al. suggested that the band alignment between the matrix and second phases could play a critical role in minimizing electron scattering\(^2\)\(^5\).

Furthermore, extremely low thermal conductivities have been observed in various materials near their phase transition, caused by both pressure-induced and temperature-induced transitions. Near the phase transition point, a material can be considered as a metastable nanocomposite with a homo-composition and a hetero-structure. So far, some research has been carried out to investigate the structural changes with the symmetry reduction of specific phase change materials and their effect on TE properties under the influence of pressure or temperature\(^2\)\(^6\)\(^-\)\(^3\)\(^1\)\(^3\)\(^4\). However, the structural phase transitions and underlying driving force (temperature or pressure) of such materials have not yet been systematically investigated due to their undefined intermediate structures and internal atomic distortions. It is also very difficult to obtain precise regulation in pressure-induced transition, while temperature-induced transition may only be effective for the structural transition of specific materials in a narrow temperature range\(^2\)\(^6\)\(^3\)\(^1\)\(^3\)\(^4\).

Herein, we propose a quasi homo-composition and hetero-structure (hoC-heS) nanocomposite composed of \(Pnma\) Bi\(_2\)Se\(_3\) - \(Pnma\) Bi\(_2\)Se\(_2\), which provides a coherent interface between the matrix and second phase due to the slight structural difference between the two phases. Br element is familiarly donor in the Bi\(_2\)S\(_2\), Bi\(_2\)Se\(_3\), and Bi\(_2\)Se\(_2\)\(^1\)\(^1\)\(^2\)\(^3\)\(^4\). However, it was found that the Br dopant caused the phase transition from \(Pnma\) Bi\(_2\)Se\(_2\) to \(Pnma\) Bi\(_2\)Se\(_2\) in our work. And the initial orthorhombic \(Pnma\) phase also exhibits structural distortion. Due to the significant reduction in lattice thermal conductivity (\(\kappa_L\)) and low impact to carrier mobility (\(\mu\)) caused by the Br dopant, a record high figure-of-merit \(ZT_{\text{max}} = 1.12\) (at 773 K) and a record average \(ZT_{\text{ave}} = 0.72\) (in the range of 323–773 K) were achieved in the Bi\(_2\)Se\(_3\) family. It should be noted that the ZT value of most reported sulfide compounds is lower than 1.0 due to the low carrier mobility and high lattice thermal conductivity so far, although sulfide compounds with cheaper, low-toxicity, and high earth abundance elements have been extensively studied in recent years. This work provides a general strategy for designing hoC-heS nanocomposites through a dopant-induced phase transition to enhance TE properties.

**Results**

Figure 1 shows the structure of the as-fabricated \(Pnma\) Bi\(_2\)Se\(_3\) - \(Pnma\) Bi\(_2\)Se\(_2\) quasi hoC-heS nanocomposite induced by the Br dopant. This structure is very different from those of previously

![Fig. 1 Schematic representation of the nanocomposition and crystal structure of Bi\(_2\)Se\(_2\). a Summary of previously reported nanocomposites classified by the composition and crystal structure of their nanoinclusion and matrix. Most reported nanocomposites are hetero-composition and homo-structure (heC-heS) or hetero-composition and hetero-structure (heC-heS). b Structure and schematic illustration of transport mechanism inside \(Pnma\) Bi\(_2\)Se\(_3\) - \(Pnma\) Bi\(_2\)Se\(_2\) hoC-heS nanocomposite. c–d Crystal structure of Bi\(_2\)Se\(_2\) Pnma phase in the ac plane. e–f Crystal structure of Bi\(_2\)Se\(_2\) Pnma phase in the ab plane.](https://example.com/figure1.png)
reported nanocomposites with a hetero-composition and homo-structure (heC-hoS) or hetero-composition and hetero-structure (heC-heS) (Fig. 1(a, b)). The matrix phase \(\text{Pnma} \ Bi_2SeS_2\) demonstrates an orthorhombic layered structure with each quintuple layer assembled by weak Van der Waals interactions, a widely observed characteristic of polycrystalline \(\text{Bi}_2\text{SeS}_2\). Five distinct atomic sites (Bi1, Bi2, S1, S2, and Se) are presented in the unit cell due to lattice symmetry operation (S-Bi-S(Se)-Bi-S), in which all the Bi and S (or Se) atoms occupy the 4c Wyckoff positions in the \(\text{Pnma}\) space group (Fig. 1(c))\(^{9,35–37}\). This layered assembly possesses a highly confined S-coordination environment around both the Bi1 and Bi2 cations with three short and four long bonds (Fig. 1(d)). However, a new \(\text{Bi}_2\text{SeS}_2\) phase crystallized in a \(\text{Pnnm}\) orthorhombic structure can be found (Fig. 1(e, f)).

Figure 2 shows the XRD patterns of the \(\text{hoC-heS}\) nanocomposite with different \(\text{Bi}_2\text{Se}_{1-x}\text{Br}_x\text{S}_2\) compositions \((x = 0, 0.03, 0.06, 0.09, 0.12, \text{and } 0.15)\). The two phases (\(\text{Pnma}\) and \(\text{Pnnm}\)) appear when the Br content is higher than \(x = 0.01\) (Fig. 2(a), Figs. S1 and S2: \(\text{Bi}_2\text{Se}_{1-x}\text{Br}_x\text{S}_2, x = 0–0.21\)). Based on the Rietveld refinement (Figs. 2(b) and S3), the XRD peaks match well with those of orthorhombic \(\text{Pnma}\) (space group: 62) and \(\text{Pnnm}\) (space group: 58). It should be noted that the \(\text{Pnma}\) phase is widely reported for polycrystalline \(\text{Bi}_2\text{SeS}_2\) and \(\text{Bi}_2\text{S}_2\) compounds, while the \(\text{Pnnm}\) phase is still a theoretically predicted structure\(^{38,39}\). A noticeable and continuous variation in the \(\text{Pnma}\) crystal structure can be observed with increasing Br content in the normal \(\text{Bi}_2\text{Se}_{1-x}\text{Br}_x\text{S}_2\) composition. Figure 2(c) shows the molar fraction evaluation of \(\text{Pnma}\) \(\text{Bi}_2\text{SeS}_2\) and \(\text{Pnnm}\) \(\text{Bi}_2\text{SeS}_2\). The fraction of \(\text{Pnnm}\) \(\text{Bi}_2\text{SeS}_2\) increases with increasing Br content while \(\text{Pnma}\) \(\text{Bi}_2\text{SeS}_2\) shows the opposite trend. For instance, \(\text{Bi}_2\text{Se}_{1-x}\text{Br}_x\text{S}_2, x = 0.12\) consists of 71.3% \(\text{Pnma}\) phase and 28.7% \(\text{Pnnm}\) phase, while \(\text{Bi}_2\text{Se}_{1-x}\text{Br}_x\text{S}_2, x = 0.21\) consists of 44.4% \(\text{Pnma}\) phase and 55.6% \(\text{Pnnm}\) phase.

In addition to the Br dopant-derived phase change, the relative intensity of the (301), (011), (202), (402), (314), and (015) peaks of the \(\text{Pnma}\) phase significantly change with increasing Br content, indicating continuous lattice distortion before the transition into the \(\text{Pnnm}\) phase. In addition, it is reported that their surface energies can quantitatively describe the stability of various surfaces\(^{40}\). The calculated formation energy along the plane (011) and (301) indicates that the formation energy along the plane (011) has reduced, while it has increased along the plane (301) after Br doping. This means the plane (011) might be easy to form during the preparation due to the low energy after Br doping. Therefore, it is clear that the \(\text{Bi}_2\text{SeS}_2\) system experiences a two-fold structural evolution with increasing Br content. First, the initial orthorhombic \(\text{Pnma}\) phase exhibits some structural distortion, revealing planar transitions that preserve the unit cell and achieve complete orientation along the (011) plane when \(0.09 \leq x \leq 0.12\). Second, doping-induced structural variations simultaneously promote inter-orthorhombic phase transformation from \(\text{Pnma}\) to \(\text{Pnnm}\). Figure 2(d) shows the Br dopant-induced lattice parameter evolution. In the current \(\text{Pnma}\) phase, the \(b\)-axis does not show significant change. However, the \(a\)- and
c- axes approach each other and overlap without a significant expansion in the unit cell volume (Fig. S4 and Table S1) with increasing Br content from x = 0 to x = 0.015–0.03, indicating the absence of prominent structural disorder in the Pnma phase. When x is further increased from 0.03 to 0.105, the unit cell parameters show similar constant behavior while the unit cell volume significantly expands (Fig. S4). As the Br content increases from x = 0.12 to x = 0.18, the a- and c- axes move away from each other with a continuous expansion in the unit cell volume (Fig. S4). These discontinuities or deviations in the lattice parameters of the Br-doped Pnma phase Bi2Se2S2 indicate the existence of lattice distortion. For the Pnnm phase, the lattice parameters of b and c gradually reduce when the Br content x is higher than 0.105 (Fig. S5). However, the decrease is not significant for the samples with low Br content x (x < 0.105), mainly due to the lower dopant content and the slight difference in the ionic radius between Br (1.96 Å) and Se (1.98 Å).

Figure 3 (a–d) shows high-resolution TEM images of the as-fabricated hoC-heS nanocomposite Bi$_{2}$Se$_{1-x}$Br$_{x}$S$_{2}$ (x = 0.12). The existence of the Pnma and Pnnm phases can clearly be seen. The Pnnm phase has a typical irregular oval-like morphology and is coherently embedded within the Pnma phase films. The inverse fast Fourier transform (IFFT) image shown in Fig. 3 (b) displays a defect-free phase boundary between these two phases. In addition, energy dispersive X-ray spectroscopy (EDS) shows that the elements, including Br, are homogeneously distributed in the Pnma and Pnnm phases, with the exception of excess Bi observed in the Pnnm phase (Fig. S6). Figure 3 (e, f) shows high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of Bi$_{2}$Se$_{1-x}$Br$_{x}$S$_{2}$ (x = 0, 0.12) along the c-axis. Bi-centric atomic distributions are prominent, well-arranged atoms along the c-axis of the undoped Bi$_{2}$Se$_{2}$S$_{2}$ (Fig. 3(e)). However, the Br dopant clearly induces atomic disarrangement and lattice distortion with uniform and distinctive elongation or contraction (Fig. 3(f)), with the doped materials displaying local phase structural variations without disturbing the symmetry. By comparing the peak intensity profiles of line 1 (or line 2) to line 3 (or line 4), it can be predicted that the significant contrast in strain causes atomic disarrangement within the frame structure of the orthohombic Pnma phase due to Br doping. The lattice variations along the c-axis are related to modifications of the bond distances. The calculated bond lengths indicate that the short Bi1-S1(S) and Bi2-S2(S) bonds and the long Bi1-S1(L) and Bi2-S2(L) bonds do not significantly change after doping (Fig. S7). However, the increased Bi-Se bond length and decreased Bi2-Se bond length (Fig. S7) suggest that Br elongates the orthohombic layered structure (Fig. 3). This lattice evolution with disordered bond length can lead to lattice anharmonicity, which is an important phonon scattering mechanism in TE materials. Figure 4 (a–d) shows that the Pnnm phase particles are tensile strained, with the maximum tensile strain reaching 3%. The strains in the $\varepsilon_{xx}$ and $\varepsilon_{yy}$ directions show continuous contrast across the grain boundary (Fig. 4(a–d)). The rotational strain profile ($\varepsilon_{rot}$) also shows continuous contrast across the phase boundaries (Fig. S8). This means that the strain at the interface is insignificant, suggesting that the corresponding phase boundary between the Pnma and Pnnm phases is defect-free.

Figure 5 shows the electrical transport properties of as-fabricated hoC-heS nanocomposite Bi$_{2}$Se$_{1-x}$Br$_{x}$S$_{2}$ (x = 0, 0.015, 0.03, 0.06, 0.09, 0.105, 0.12, 0.15, 0.18, and 0.21). The transport properties change with increasing doping content x, and this change can be roughly divided into three parts. The undoped Bi$_{2}$Se$_{2}$S$_{2}$ exhibits poor electrical conductivity (σ) at room temperature due to its low carrier concentration (n) (Fig. 5(a)). However, the room temperature σ value significantly increases from 0.25 × 10$^{4}$ Sm$^{-1}$ to 6.26 × 10$^{4}$ Sm$^{-1}$ with a low amount of Br (x = 0.015), corresponding to an enhanced n value from 1.28 × 10$^{19}$ to 46.6 × 10$^{19}$ cm$^{-3}$ (Fig. 5(b)). Thus, Br is a very effective dopant. However, the room temperature σ decreases from 5.62 × 10$^{4}$ Sm$^{-1}$ to 2.42 × 10$^{4}$, 1.49 × 10$^{4}$, and then 0.59 × 10$^{4}$ Sm$^{-1}$ as the Br content further increases from x = 0.03 to x = 0.06, 0.09, and 0.105 (Fig. 5(c)). For these doped nanocomposite samples, the Pnnm phase appears and increases with increasing Br content but remains lower than 40%. A further increase in Br content (from x = 0.105 to 0.12 and 0.15) results in a slight increase in σ (with slightly enhanced n and moderate μ), but σ declines again when x ≥ 0.18 (Fig. 5(h)). It means that when the Pnnm phase fraction is higher than 40% and x ≥ 0.18, the value of σ deteriorates due to the decrease of μ (Fig. 5(a)). The nano Pnnm phase would be a new electron scattering center. The temperature-dependent σ exhibits two trends. When 0.015 ≤ x ≤ 0.03, the value of σ decreases monotonically with increasing temperature, acting as a degenerate semiconductor. In contrast, when 0.06 ≤ x ≤ 0.21, the value of σ first decreases and increases with increasing temperature, acting as a thermally activated semiconductor.

Figure 5 (c), (f), and (i) shows the temperature-dependent Seebeck coefficient (S) of the as-fabricated hoC-heS nanocomposite Bi$_{2}$Se$_{1-x}$Br$_{x}$S$_{2}$ (x = 0, 0.015, 0.03, 0.06, 0.09, 0.105, 0.12, 0.15, 0.18, and 0.21), which presents good consistency with σ. The Br-free Bi$_{2}$Se$_{2}$S$_{2}$ nanocomposite shows a high room temperature S value of ~300 μV K$^{-1}$. The S values decrease at low Br doping concentrations (0.015 ≤ x ≤ 0.09) due to the higher n values of these nanocomposites compared with the undoped nanocomposite. At high Br doping concentrations (0.105 ≤ x ≤ 0.21), the magnitude of S increases to 200 μV K$^{-1}$, and the bipolar transport shifts to lower temperatures. By using the S and n data and assuming that acoustic phonon scattering is prominent in the Bi$_{2}$Se$_{2}$S$_{2}$ matrix, a Pisarenko relation (at 300 K) can be obtained for Bi$_{2}$Se$_{1-x}$Br$_{x}$S$_{2}$ (Fig. 5(c)). The S values of the Br-doped samples deviate from the Pisarenko relation when x > 0.06, suggesting that the electronic density of states N(E) changes due to activation of the conduction bands (CBs) via doping. In addition, the density of state (DOS) effective mass ($m^{*}$) was obtained using the equations (S2)–(S4) in the Supporting Information, assuming the as-fabricated nanocomposite as quasi-single uniform phase (Fig. S9). A increased $m^{*}$ values from 1.62m$_{e}$ (x = 0) to 6.90m$_{e}$ (x = 0.21) with Br content of Bi$_{2}$Se$_{1-x}$Br$_{x}$S$_{2}$ was observed. The variations in $m^{*}$ values with Br content results from the band structure change and the interface effect. The enhanced σ and moderate S exhibited by all the doped samples result in a remarkable enhancement in their power factors (PF) across the whole temperature range (Fig. 5(d), (g), and (j)). The largest PF of ~7.39 μW cm$^{-1}$ K$^{-2}$ at 773 K is achieved by Bi$_{2}$Se$_{1-x}$Br$_{x}$S$_{2}$ (x = 0.12). This value is seven times higher than that of pure Bi$_{2}$Se$_{2}$S$_{2}$ and is also the highest value reported thus far among Bi$_{2}$Se$_{2}$S$_{2}$ and Bi$_{2}$S$_{3}$-based materials reported in the literature$^{8-11}$.

Figure 6 illustrates the evolution of the Br-free and Br-doped Bi$_{2}$Se$_{1-x}$Br$_{x}$S$_{2}$ band structure in both the Pnma and Pnnm phases. First, Fig. 6 (a–d) shows the Br-free and Br-doped Bi$_{2}$Se$_{1-x}$Br$_{x}$S$_{2}$ Pnma phase band structures, both of which are direct bandgap semiconductors with conduction band minima (CBM) and valence band maxima (VBM) near the G point along the high symmetric line of the Brillouin zone. However, the CBM and VBM of the Br-doped Bi$_{2}$Se$_{2}$S$_{2}$ and Bi$_{2}$Se$_{2}$S$_{2}$-based materials reported in the literature$^{8-11}$.
Fig. 3 Structural characterization. **a** TEM micrograph of Bi$_2$Se$_{1-x}$Br$_x$S$_2$ ($x = 0.12$), where the yellow dotted regions show the Pnmm nanophase. **b** HRTEM micrograph of the red dotted square [1] in (a), where the inset is the HRTEM micrograph of region [3]. **d** HRTEM micrograph of the red dotted square [4] in (c). e-f STEM-HAADF images of undoped and Br-doped Bi$_2$SeS$_2$ samples showing the orthorhombic Pnma structure along the c-direction. (e1)-(e2) Intensity line profiles corresponding to line 1 and line 2 in (e). (f1)-(f2) Intensity line profiles corresponding to line 3 and line 4 in (f).
The calculated formation energy of Bi$_2$Se$_2$S$_2$. Besides, the calculated formation energy of this Br-doped system, due to defect states, indicates that modifications can be made in the structure to utilize the overcharge. In addition, the partial density of states (DOS) of Bi primarily contributes to the total DOS in the CBM for both the Pnma and Pnnm phases (Fig. 6(c) and (g)). The DOS in the CBM along the y-axis shows that the intensity of peaks in the Pnma phase of Bi$_2$Se$_2$S$_2$ is reduced, which can be mainly ascribed to lattice distortions (Fig. 6(f)). This results in a reduction in energy. Here, distortions yield an orthorhombic Pnma Bi$_2$Se$_2$S$_2$ structure with a slightly reduced symmetry. Overall, these results indicate that the Br dopant acts as a donor, causing significant structural distortion and the inter-orthorhombic transformation of Pnma to Pnnm. This phase transformation optimizes the electrical transport properties of Bi$_2$Se$_2$S$_2$. Besides, the calculated formation energy also shows that the formation energy value for Br doping at Se site is much lower than that at S site (Fig. S10(a)). This means Br should prefer to occupy the Se site in Bi$_2$Se$_2$S$_2$.

Figure 7 shows the thermal conductivity and $ZT$ values of as-fabricated hoC-heS nanocomposite of Pnma Bi$_2$Se$_2$S$_2$ - Pnnm Bi$_2$Se$_2$S$_2$ in a nominal composition of Bi$_2$Se$_{1-x}$Br$_x$S$_2$ ($x = 0, 0.09, 0.12, 0.15, 0.21$). Other Bi$_2$Se$_{1-x}$Br$_x$S$_2$ with $x = 0.015, 0.03, 0.06, 0.105,$ and $0.18$ are shown in the Fig. S11. The undoped Bi$_2$Se$_2$S$_2$ shows a lower $\kappa$ of 0.72 W m$^{-1}$ K$^{-1}$ (Fig. 7(a)). While the value of $\kappa$ increases with a very low amount of Br ($x = 0.015$) due to the contribution from carriers (Fig. S11(a)), it gradually decreases to 0.60 W m$^{-1}$ K$^{-1}$ with an increase in Br content to $x = 0.09$ and further reduces to $\sim 0.5$ W m$^{-1}$ K$^{-1}$ when $x \geq 0.12$. Furthermore, the value of $\kappa$ shows temperature-independent behavior for the heavily doped samples ($0.09 \leq x \leq 0.21$), maintaining a minimum at $\sim 725$ K and then slightly shifting to higher values with a further increase in temperature due to the bipolar effect. As shown in Fig. 7(b), the value of $\kappa_L$, which can be estimated by subtracting the electronic thermal conductivity $\kappa_e$ from $\kappa$ ($\kappa_L = \kappa - \kappa_e$, where $\kappa_L$ is the lattice thermal conductivity and $\kappa_e$ is the electronic thermal conductivity (Fig. S11(b))), is $\sim 0.72$ W m$^{-1}$ K$^{-1}$ at room temperature for pure Bi$_2$Se$_2$S$_2$. The value of $\kappa_L$ declines with increasing temperature until 550 K, then increases due to the bipolar effect. However, for a Br content of $x = 0.09$, the value of $\kappa_L$ at room temperature is only 0.52 W m$^{-1}$ K$^{-1}$. This further declines to $\sim 0.40$ W m$^{-1}$ K$^{-1}$ for $x = 0.12$. For the Br-doped sample where $x \geq 0.15$, the value of $\kappa_L$ slightly increases to $\sim 0.47$ W m$^{-1}$ K$^{-1}$. The contribution of the bipolar effect becomes negligible with increasing Br content (Fig. S11(d)). Because of this, the value of $\kappa_L$ of the highly doped samples is temperature-independent (Fig. 7(b)). The theoretical lattice thermal conductivity was calculated via the Debye-Callaway model by combining all the substantial factors (presented in the Supporting Information). In the Bi$_2$Se$_{1-x}$Br$_x$S$_2$ system, the dominant phonon-scattering mechanisms involve scattering processes from point defects/ alloy elements, nanophase, phonon-phonon Umklapp scattering, boundaries between the Pnma and Pnnm phases, and electron-phonon interactions. Figure 7(b) shows that the calculated value of $\kappa_L$ is in good agreement with the experimental results before the onset of the bipolar effect, which is the main reason for the deviation between the calculated $\kappa_L$ and the experimental data. Parameter A (Table S3), which is the preset parameter for point defects (including nanophase boundaries) in the expression of total phonon relaxation time, shows a reduction due to doping. However, parameter A increases from 3.48 to 10.4 as $x$ increases from 0.015 to 0.12, which indicates enhanced phonon blocking due to the presence of intensive nanophase boundaries or impurity centers. A further increase in $x$ from 0.15 to 0.21 causes a decrease in the value of $A$ (Table S3). This explains the increase in $\kappa_L$ when $x \geq 0.15$. At high values of $x$, the nanophase boundaries between the Pnma and Pnnm phases agglomerate due to the high density of Pnnm nanoinclusions, which causes a reduction in the number of effective phonon scattering centers and increases the value of $\kappa_L$. Therefore, $x = 0.12$ is the optimum Br dopant level with the appropriate Pnma phase fraction in this nanocomposite.

Due to the combination of a significantly enhanced PF and reduced $\kappa$, a record high $ZT_{\text{max}}$ of 1.12 (at 773 K) and a record high average $ZT_{\text{ave}}$ of 0.72 (in 323–773 K) are achieved for the doped Bi$_2$Se$_{1-x}$Br$_x$S$_2$ system when $x = 0.12$ (Fig. 7(c)). The average $ZT_{\text{ave}}$ is calculated by integrating the area under the $ZT$ curves in
Fig. 7(c) according to the following formula,

$$ZT_{\text{ave}} = \frac{1}{T_\text{h} - T_\text{c}} \int_{T_\text{c}}^{T_\text{h}} ZT \, dT$$

where $T_\text{c} = 323 \text{ K}$ and $T_\text{h} = 773 \text{ K}$ are the hot-side and cold-side temperatures. These TE transport properties show good reproducibility and thermal stability (Fig. S12). The optimized nanocomposite of Bi$_2$Se$_{1-x}$Br$_x$S$_2$ is composed of 71.3% Pnma Bi$_2$SeS$_2$ and 28.7% Pnnm Bi$_2$Se$_2$. When the Pnnm phase fraction increases, the value of $ZT$ decreases (Fig. 7(d)) due to deterioration of electrical conductivity and a slight enhancement of thermal conductivity, demonstrating that a moderate amount of Pnnm phase in the nanocomposite is ideal for achieving good TE transport properties.

As a comparison, Table S4 and Fig. S13 present the TE properties, including $\sigma$, $S$, $\kappa$, and $ZT$ value, of some representative Bi$_2$S$_3$ related systems. Both the $ZT_{\text{max}}$ (1.12 at 773 K) and $ZT_{\text{ave}}$ (0.72 in 323–773 K) values of as-fabricated hoC-heS nanocomposite of Pnma Bi$_2$SeS$_2$ - Pnnm Bi$_2$Se$_2$ are much higher than previously reported Bi$_2$Se$_2$ and Bi$_2$S$_3$-based materials, and other reported sulphide
Fig. 6 Electronic band structure and density of state (DOS) calculations. a and c Electronic band structure and DOS of pure Bi$_2$SeS$_2$ with Pnma structure. b and d Electronic band structure and DOS of Br-doped Bi$_2$SeS$_2$ with Pnma structure. e and g Electronic band structure and DOS of pure Bi$_2$SeS$_2$ with Pnnm structure. f and h Electronic band structure and DOS of Br-doped Bi$_2$SeS$_2$ with Pnnm structure.
Our work shows that the hoC-heS nanocomposite of Pnma Bi$_2$Se$_2$ - Pnnm Bi$_2$Se$_2$ is a promising TE material. The hoC-heS nanocomposite through a dopant-induced phase transition is an effective strategy to decouple the transport of electrons and phonons and boost the TE figure-of-merit.

Discussion
This work experimentally showed that the quasi hoC-heS nanocomposite Pnma Bi$_2$Se$_{1-x}$Br$_x$S$_2$ - Pnnm Bi$_2$Se$_2$, whose phase composition was induced by a Br dopant, demonstrated excellent TE properties. The properties of this hoC-heS nanocomposite are very different from those of previously reported nanocomposites with heC-hoS or heC-heS interfaces. Br served as an effective carrier donor and also induced a partial Bi$_2$Se$_2$ phase transition from Pnma to Pnnm, forming the hoC-heS nanocomposite. The observed Bi–Se elongated bond length clearly predicted the doping-dependent local structural disorder in the doped orthorhombic Bi$_2$Se$_2$ system. The coherent interface between the Pnnm nanoprecipitates and Pnma matrix resulted in strongly enhanced phonon scattering and only slightly impacted the transport of electrons. As a result, a high PF of more than 7.30 μW cm$^{-1}$ K$^{-2}$ at 773 K was obtained, inducing a record high ZT$_\text{max}$ of 1.12 and a record high ZT$_\text{ave}$ of 0.72 (at 323–773 K) in the optimal Br-doped Pnma Bi$_2$Se$_{0.88}$Br$_{0.12}$S$_2$. This work provides a general strategy for enhancing TE properties by designing hoC-heS nanocomposites through a dopant-induced phase transition.

Methods
Polycrystalline Bi$_2$Se$_{1-x}$Br$_x$S$_2$ (where x = 0, 0.015, 0.03, 0.06, 0.09, 0.0105, 0.12, 0.15, or 0.21) powders were prepared by melting stoichiometric amounts of high-purity elements (>99.99%) packed under vacuum in glass ampoules at 1173 K for 10 h, followed by annealing at 773 K for 48 h. The obtained ingots were pulverized into fine micron-sized powders by hand grinding. The powders were then compacted at 773 K by spark plasma sintering for 10 min in vacuum under a pressure of 60 MPa.

X-ray diffractometry (XRD) (Rigaku, Japan) analysis was performed on all specimens with Cu Ka radiation, a wavelength of λ = 1.5406 Å, and a scanning speed of 4°/min. Rietveld refinement analyses were carried out by using the Generalized Structural Analysis System (GSAS-II) program. Field emission scanning electron microscopy (FE-SEM) (Ultra 55, Zeiss) was utilized to perform microstructure analysis of the freshly fractured surfaces of specimens.
resolution transmission electron microscopy (HRTEM) (JEOL-F2010, acceleration voltage of 200 kV) was employed to characterize the microstructures. A ZEM-3 apparatus (ULVAC-Riko) was employed to measure the Seebeck coefficient and electrical resistivity in a helium atmosphere from 300 to 550 K. A laser flash method with a commercial system (Netzsch, LFA-427) was employed to determine the thermal diffusivity (D) in the identical direction (in-plane) in electrical resistivity measurements to avoid overvaluing from the corresponding author (lifu@szu.edu.cn) upon reasonable request.

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Author contributions
The paper was prepared though the contribution of all authors. B.J., F.L. and W.L. designed the work. B.L., Z.Z., C.L. and D.A. prepared the nanocomposite and measured the thermoelectric transport properties. B.L. and Y.C. performed structural nanocomposite characterization. A.M. and Y.Z. performed simulation. Z.Z. and P.F. planed and supervised the work. F.L. and W.L. wrote the paper. B.L. and G.L. had major input in the writing of the paper. All the authors edited the paper.

Competing interests
The authors declare no competing interests.

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