Roles of Anion Sites in High-Performance GeTe Thermoelectrics

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Cationic doping is mainly used to improve the performance of rocksalt-structured GeTe thermoelectric materials. However, its counterpart anionic doping is scarcely facilitated. Here, a comprehensive discussion is provided on doping at the anion site of rocksalt-structured thermoelectric materials, surrounding its influence on bonding mechanisms, carrier and phonon transport characteristics, and thermoelectric figure-of-merit. To verify the viewpoint, a modified flux-assist method is adopted to synthesize anionic Iodine (I) doped GeTe samples, which show comparably optimized electrical and thermal properties with that of cationic Antimony (Sb) or Bismuth (Bi) doped GeTe samples. Further combining cationic Bi and anionic I co-doping, an enhanced figure-of-merit from 0.8 in pristine GeTe to 2.5 at 675 K can be realized in 8% (Bi and I) co-doped GeTe, which corresponds to a maximum heat-to-electricity conversion efficiency of 14.6% under a temperature difference of 430 K. This study rationalizes the influence of anionic doping on the electrical and thermal properties of the rocksalt-structured materials, which serves as an effective yet previously neglected strategy toward high-performance GeTe thermoelectrics.

1. Introduction

Thermoelectrics have attracted increasing interests from both academia and industries to alleviate the ever-growing energy crisis and climate-related concerns. A typical thermoelectric generator can convert waste heat to electricity, with its efficiency determined respective to the heat dissipation from an irreversible system. According to the Onsager’s reciprocal relations, a high efficiency requires a combination of large electrical potential difference, low Joule heat, and maintained temperature gradient.[1] These requirements are corresponding to the Seebeck coefficient (S), the electrical conductivity (σ), and the thermal conductivity (κ) of thermoelectric materials, then the figure-of-merit,

\[ zT = S^2 \sigma T / \kappa \] (1)

is defined to evaluate thermoelectric goodness. In most cases, \( \kappa \) refers to the sum of electronic (\( \kappa_e \)) and lattice (\( \kappa_l \)) tensor components; as \( \kappa_l \) is competing with power factor (\( S^2 \sigma \)) on carrier concentration (n, holes for p– and electrons for n–type conductance), a compromise is required for enhancing \( zT \).[2] In contrast, \( \kappa_l \) is mainly determined by lattice vibration that is quantified by phonons, and therefore can be independently minimized through intrinsic (e.g., tuning phonon modes) and/or extrinsic (e.g., inducing scattering centers) processes.[3]

In addition to \( zT \), an appropriate working temperature is also important for the application of thermoelectric materials. For example, Bi₂Te₃ and Mg₂Bi₃ mainly work near room temperatures, while half-Heusler alloys are suitable for higher temperatures.[4] For the mid-temperature range from 500 to 800 K, MTe (M = Ge, Sn, and Pb) are competitive thermoelectric materials thanks to their high intrinsic \( zT \).[5] Other considerations are that PbTe is highly toxic, and SnTe suffers from perversely low S, making GeTe the most prevalent.[6] Figure 1a summarizes...
the state-of-art MTe thermoelectric materials, indicating that optimizing \( n \), i.e., by manipulating the reduced chemical potential \( (\mu_r) \), is beneficial for enhancing \( zT \). Once an optimal \( n \) is attained, the highest achievable \( zT \) is proportional to quality factor \( (B) \), which is an autonomous physical parameter determined by the microscopic transport characteristics of electrons and phonons, and is mainly governed by weighed mobility \( (\mu_w) \).[7] Due to the semiconductor nature of MTe, doping should be a facile yet effective strategy to modify both \( \mu_r \) and \( \mu_w \), as has been extensively reported in cationic doped GeTe, SnTe, and PbTe thermoelectric materials. In comparison, unlike SnTe and PbTe, anionic doping has been scarcely facilitated for GeTe thermoelectric materials.

Such a mismatch is intriguing, when on the one side considering the great success of anionic doping in analogous SnTe and PbTe thermoelectric materials, and on the other side envisaging that the cation and anion sites of GeTe can play an equivalent role in terms of crystal structure, bonding mechanism, transport properties, and thermoelectric performance.[8] In order to clarify our viewpoint, we used a modified flux-assist method to synthesize GeTe samples doped with cationic Bi or Sb, and/or anionic Br or I, which show that I-doped GeTe can have comparably optimized electrical and thermal properties to that of Sb/Bi doped GeTe, yet due to a different doping effect. Combining cationic Bi and anionic I co-doping can enhance \( zT \) from 0.8 in pure GeTe to 2.5 in 8% (Bi and I) co-doped GeTe at 675 K, which is equivalent to a maximum heat-to-electricity conversion efficiency \( (\phi) \) of 14.6% under a temperature difference of 430 K. The concurrently improved \( zT \) and \( \phi \) reported by this work should justify the great potential of anionic doping toward high-performance GeTe thermoelectrics.

2. Results and Discussion
2.1. Crystal Structure and Bonding Mechanism

Pure GeTe undergoes a ferroelectric phase transition from high-temperature cubic \((\beta, Fm\bar{3}m)\) to low-temperature rhombohedral \((\alpha, R3m)\) phase at \( 670 \) K, via a Peierls distortion in an arbitrary
diagonal direction.[9] As displayed in Figure 1b, β-GeTe shares the similar rocksalt structure with SnTe and PbTe, formed by cation and anion sub-lattices slipping along their [111] axes. Therefore, the cation and anion sites are spatially equivalent: in real space, they can interchange through the phase shift of a “periodic function”; whereas in reciprocal space, they can be folded into an identical k-point via the point group operations (Note S1, Supporting Information). This results in additional high-symmetry points in the first Brillouin zone of rocksalt structured β-GeTe, which forms exceptional vellaytronics to optimize n, meanwhile restricts intervalley scattering to retain B, being beneficial for a high intrinsic κT.[10]

In fact, from a chemical bonding perspective, β-GeTe is different from traditional ionic rocksalt compounds, e.g., NaCl or ZnTe considering its much lower ionicity. Moreover, β-GeTe has 10 valence electrons more than allowed by the 8-N rule, hypothetically due to bonding resonance or hyperbonding formed by s² lone pairs (compared to s⁰ states in NaCl and ZnTe. Note S2, Supporting Information),[11] which indicates that the anion and cation sites are equivalent in terms of bonding mechanism (Figure S1, Supporting Information), despite the density-based properties of Ge-Te bond in β-GeTe have not been fully revealed. Electrically, the stronger covalent nature of Ge-Te bond is responsible for the weakened orbital hybridization that strengthens band anisotropy and usually increases S²[12] while thermally, the long-range [001] polarity of Ge-Te bond can intensify the anharmonic phonon scattering and provide large phase space for three- and four-phonon scattering processes, which decreases κ and consequently enhance κT.[13]

However, a rocksalt coordinate can also be detrimental for the thermoelectric performance of β-GeTe. For instance, it is found that ~3.5% intrinsic Ge vacancies can be intrinsically formed during the melting synthesis of GeTe due to low formation energy (E_form), which is referred to the β-GeTe phase.[14] This exceeds n beyond its optimal value and deteriorates zT from 1.7 in stoichiometric GeTe to ~1.0 in Ge-deficient GeTe.[15] Figure 1c calculates the E_form of Ge vacancies in GeTe, which is elevated with respect to the chemical potential of anionic Te (μTe), therefore is more sensitive to anionic doping. Specifically, doping ~1.5% I in GeTe (Ge₆₄Te₆₃I₁) elevates the E_form from 0.49 eV in Ge₆₄Te₆₄ to 0.59 eV, which is a complementary factor in conjunction with the donor effect induced by I doping to decrease n from ~1 x 10²¹ to 8.3 x 10¹⁹ cm⁻³, toward the optimal value of ~1 x 10²⁰ cm⁻³ (Note S3, Supporting Information). To clarify this point, we synthesized cationic Sb or Bi, and/or anionic Br or I doped GeTe samples through a modified flux-assist method (Note S4, Supporting Information). The Rietveld refinement of X-ray diffraction (XRD, Figure S2, Supporting Information) indicates that the weight percentage of Ge impurities (due to Ge vacancies) is reduced from 2.7% in pure GeTe to 1.4% in 8% (Bi and I) co-doped GeTe. Besides, the lattice constant (a), interaxial angle (α, on the basis of the primitive rhombohedral cell), and central site displacement (disp., along diagonal axis) of synthesized samples are varying with increase of (Bi and I) co-doping concentration, as plotted in Figure 1d.

We then used electron microscopes to characterize microstructures and crystallography. The fracture cross sections observed by scanning electron microscopy (SEM, Figures S3–S5, Supporting Information) indicates an apparent evolution of the grain morphology, from nanometric flake grains in pure GeTe to micrometric polyhedron grains in 8% (Bi and I) co-doped GeTe. This should be consistent with the observed polished surface, consisted of nearly single crystal grains, in which a high density of twin structures with alternative contrast can be found. The twin structures are anisotropic along a set of orthogonal-based zone axes, as known from electron backscattered diffraction (EBSD, Figure S6, Supporting Information), with the misorientation angle between the twinned domains being either 88° or 92°. Transmission electron microscopy (TEM) images further observe fractally secondary-ordered twin structures in a single twin domain (Figure S7, Supporting Information), elsewhere known as herringbone structure,[16] which leads to numerous twin boundaries and Ge plane vacancies along with ubiquitous lattice strain, mainly devoting to extrinsic process to decrease κ.[17]

2.2. Carrier and Phonon Transport

The Ge–Te bond in β-GeTe can be represented by a generalized energy level diagram formed due to the interaction between cationic M and anionic X orbitals (Figure S8, Supporting Information). Specifically, E_M and E_X are on-site energies, which split into a bonding (E_MM) and an antibonding (E_M*X*) state. The energetic difference from E_M to E_M*X* to the average of E_M+E_X corresponds to the hypotenuse of a right-angled triangle with its legs equal to energy gap (A, governed by energy alignment) and overlap parameter (V, governed by momentum alignment), which can be expressed as:[18]

\[ E_{MM/MM*} = 1/2(E_M + E_X) \pm 1/2\sqrt{(E_M - E_X)^2 - 4V} \]  

(2)

Based on tight binding approach, Figure 1e sketches the energy level diagram of the conceived bonding in β-GeTe, as a linear combination of molecular orbitals,[19] where the p–p interaction in higher energy than s–s interaction dominates the thermoelectric transport. To simplify the analysis, the energy level is converted to the dispersion of a 1D diatomic chain from Γ (0) to L (π/a) point, e.g., along a [111] axis of β-GeTe, as shown in Figure 2a. Notably, the π-type p–p (ππ) bonding is symmetric along bonding axis, thus has the lowest energy at Γ (0) point, and an upward dispersion from Γ to L (π/a) point, in comparison to the σ-type σσ bonding that is antisymmetric along bonding axis thus has a downward dispersion.

For a more complicated 3D lattice, its electron band structures should be rationalized based on density-functional-theory (DFT, Figures S9–S11) calculations. Figure 2b projects the constituent orbitals of Ge, Te, and I along the calculated band structures for Ge₁₇Te₂₇, Ge₁₇Te₂₀I₁, and Ge₁₆Bi₁Te₁₉I₁, with the fatness being proportional to orbital weight. In pure GeTe, a direct bandgap (E_g) opens at L (π/a, π/a, π/a) point between the fully occupied valence band maximum (VBM) and the vacant conduction band minimum (CBM), which are dominated by Te_5p⁰ and Ge_4p⁰ orbitals, respectively. The n of GeTe is dependent on the position of Fermi potential (E_F) relative to VBM, and can be suppressed if doping Te with elements that has more p valence electrons or higher p orbital on-site energy, which explains the elevated E_F from 5.517 eV in Ge₁₇Te₂₇ to 5.594 eV in Ge₁₆Te₁₉I₁.
and from 5.067 eV in Ge\textsubscript{26}Te\textsubscript{27} to 5.110 eV in Ge\textsubscript{26}Te\textsubscript{26}I\textsubscript{1}. Valleytronics is another character influencing electronic transport, e.g., the convergence of $V_B^L$ and $V_B^\Sigma$ ($\approx \pi/a$, $\approx \pi/a$, 0) by suppressing their energy offset ($\Delta E$) can increase band degeneracy ($N_v = 4 + 12 = 16$), which can be fulfilled through doping Te by elements with weaker s–p splitting, given that Te$_5p$ orbitals are more hybridized with s$_2$ lone pairs at $V_B^L$ than $V_B^\Sigma$.[20] This is consistent with the reduced $\Delta E$ from 0.217 eV in Ge\textsubscript{27}Te\textsubscript{27} to 0.181 eV in Ge\textsubscript{27}Te\textsubscript{26}I\textsubscript{1} and 0.193 eV in Ge\textsubscript{26}Bi\textsubscript{1}Te\textsubscript{26}I\textsubscript{1}.

Figure 2c plots phonon wavefunction in the first Brillouin of a simplified 1D diatomic chain, where the mass of two adjacent atoms is closed with each other to account for a small optical-acoustic gap. Under the harmonic presumption, phonon frequency ($\omega$) from L to $\Gamma$ point can be expressed as:

$$\omega = \sqrt{2F/M} \cdot \sin \left( \frac{\pi}{2} \cdot \frac{k}{k_c} \right)$$

where $F$ and $M$ are force constant and average atomic mass, respectively, and $k_c$ is cut-off wave vector. In overall, the $\kappa_\ell$ of an isotropic semiconductor, i.e., polycrystalline GeTe, is determined by phonon velocity ($v$, proportional to the slope of $\omega$ versus $k$) and mean-free-path ($l$, inversely proportional to optical and acoustic phonon scattering). Therefore, a low $\kappa_\ell$ is rooted in either a large $M$ and low $v$, which can be realized by doping Te with heavier elements; or a small $F$ and short $l$, which is relating to doping induced lattice defects and strain, being sensitive to doping concentration. Moreover, the discordant doping in generally symmetric $\beta$-GeTe can greatly strengthen the local anharmonicity,[22] which on the one hand has an equivalent influence of flattening the dispersion to lower $v$,[23] on the other hand can reduce the optical-acoustic bandgap to shorten $l$,[24] usually resulting in ultralow $\kappa_\ell$.

We also calculated phonon band structures based on a $2 \times 2 \times 2$ parent supercell substituted by cationic and/or anionic doping atoms, as displayed in Figure S12 (Supporting Information). Figure 2d projects the atomic displacement of Ge, Te, and I to the band structures of Ge\textsubscript{8}Te\textsubscript{8}, Ge\textsubscript{8}Te\textsubscript{7}I\textsubscript{1}, and Ge\textsubscript{7}Bi\textsubscript{1}Te\textsubscript{7}I\textsubscript{1}, with the fatness being proportional to displacement amplitude. In pure GeTe, anionic Te mainly contributes to acoustic
phonons because of its heavier atomic mass than Ge, which determines $\chi_I$ in a wide temperature range. At $\Gamma$ point, one longitudinal (LA) and two transverse (TA) acoustic branches are triply degenerated, with an overall $\omega$ reduced from 5.9 THz in Ge$_8$Te$_8$ to 5.1 THz in Ge$_7$Bi$_1$Te$_7$I$_1$, then to 4.9 THz in Ge$_7$Bi$_1$Te$_7$I$_1$, meaning the decreased $\nu$ thus $\chi_I$ is mainly due to doping of I. Meanwhile, a slight imaginary $\omega$ is observed in Ge$_7$Bi$_1$Te$_7$I$_1$, which increases to $\approx 0.5i$ THz in Ge$_7$Bi$_1$Te$_7$I$_1$, indicating that anionic I (compared to the real $\omega$ in Ge$_7$Bi$_1$Te$_8$) might intensify the anharmonicity by fluctuating local dipole, and in turn give rise to phonon scattering rates to shorten $l$ and further decrease $\chi_I$.

### 2.3. Electrical and Thermal Properties

Figure 3a,b and Figures S13–S17 (Supporting Information) show measured temperature-dependent $\sigma$ and $S$ of pure, cationic Sb/Bi and anionic Br/I doped, and (Bi and I) co-doped GeTe, with the uncertainties estimated using propagation law (Note S5, Figure S18, and Table S2, Supporting Information). All above aliovalent dopants serve a donor effect to reduce $n$ (Figure S19, Supporting Information), making $\sigma$ decreases with increasing the doping concentration, down to 100 S cm$^{-1}$ in 8% (Bi and I) co-doped GeTe at 300 K. By increasing the temperature, $\sigma$ behaves a metallic downward tendency, in contrast to the upward tendency of $S$, leading to an improved electronic quality factor as revealed by the plot of $S$ versus logarithmic $\sigma$ with a slope approximating to $k_B/e$ (Figure S20, Supporting Information). A desirable $S$ of over 220 µV K$^{-1}$ is attained in both cationic Sb/Bi and anionic I doped GeTe; however, when coming to room temperature, Sb/Bi doped GeTe maintains an $S$ as large as 150 µV K$^{-1}$, which is merely $\approx 70$ µV K$^{-1}$ for Br/I doped GeTe, because cationic doping is more efficient for modifying $n$ in $\alpha$-GeTe. By combining the cationic Bi and anionic I doping with equivalent ratio of doping concentration, a high $S^2\sigma$ of over 40 µW cm$^{-1}$ K$^{-1}$ at 700 K is achieved in 8% (Bi and I) co-doped GeTe, which is comparable to that of pure GeTe.

The optimized electrical properties can be rationalized through numerical modeling based on Boltzmann equation. For instance, in pure GeTe, $S$ is primarily determined by $VB_L$...
because of large $\Delta E$ and $E_g$, whereas in Bi or I doped, and (Bi and I) co-doped GeTe, both $\Delta E$ and $E_g$ are decreased with the increase of (co-) doping concentration, making $\text{VB}_L$ and $\text{CB}_L$ gradually contribute to $S$ by:

$$
S = \frac{S_{\text{VB}_L}\sigma_{\text{VB}_L} + S_{\text{VB}_L}\sigma_{\text{VB}_L} - S_{\text{CB}_L}\sigma_{\text{CB}_L}}{\sigma_{\text{VB}_L} + \sigma_{\text{VB}_L} + \sigma_{\text{CB}_L}}
$$  \hspace{1cm} (4)

As $\text{VB}_L$ is beneath $\text{VB}_L$, it can be regarded as degenerated band edge with a parabolic dispersion. In contrast, $\text{VB}_L$ and $\text{CB}_L$ are adjacent to $E_g$ with a nonparabolic Kane dispersion: \cite{28}

$$
E(1 + E/E_g) = \frac{\hbar^2 k^2}{2m^*}
$$  \hspace{1cm} (5)

where $\hbar$ is reduced Planck constant, $m^*$ is dependent on $E_g$ (and temperature). Figure S21 (Supporting Information) shows the plot of $S$ versus $n$ at 700 K, considering the addition of $\text{VB}_L$ and $\text{CB}_L$ (Note S6, Supporting Information). It indicates that the $S$ of pure and lightly doped GeTe are mainly determined by $\text{VB}_L$. By increasing the doping concentration, the plot behaves an upward tendency approximating $\text{VB}_L + \text{VB}_L$, because of the increased $N_s$ by band convergence. Noteworthy, as illustrated in Figure 3c, the measured $S$ of 8% (Bi and I) co-doped GeTe are approximating to the plot of $\text{VB}_L + \text{VB}_L + \text{CB}_L$ in the $\beta$-GeTe temperature range. This is mainly because that the smaller ground-state $E_g$ of $\beta$-GeTe than that of $\alpha$-GeTe is suppressed with increase of temperature, in the accordingly enlarged value of $k_BT$, making the energy gap from $E_g$ to $\text{CB}_L$ being less than several $k_BT$, and therefore the $\text{CB}_L$ can partially contribute to electronic transport.

Likewise, the measured temperature-dependent $\kappa$ is presented in Figure 3d, which behave a similar tendency with $\sigma$, indicating the nonnegligible contribution of $\kappa_L$ to $\kappa$. In addition, $\kappa$ is decreased with increasing doping concentration, down to 0.94 W m$^{-1}$ K$^{-1}$ in 8% (Bi and I) co-doped GeTe, which is attributed to both decreased $\kappa_S$ and $\kappa_L$. We further calculated the $\kappa_S$ quantitatively by subtracting $\kappa_L$ from $\kappa$, which is estimated based on the Wiedemann–Franz law, and the results are shown in Figure 3e. As can be seen, Sb/Bi doped GeTe has apparently lower $\kappa_S$ than that of Br/I doped GeTe near room temperature, mainly due to Sb and Bi can enlarge the $\alpha$ of $\alpha$-GeTe to strengthen the long-range phonon scattering, \cite{29} whereas in $\beta$-GeTe temperature, all $\kappa_L$ tends to merge. With co-doping Bi and I, the $\kappa_L$ is further decreased down to 0.39 W m$^{-1}$ K$^{-1}$ at 675 K, in accordance with the reduced $\alpha$ in Ge$_7$Bi$_1$Te$_7$I$_1$, which is lower than that of the state-of-art GeTe thermoelectric materials, and is even lower than the conceptional inferior limits of lattice thermal conductance.\cite{30}

In addition to the intrinsically lowered $\omega$, $\kappa_L$ can also be decreased due to extrinsic lattice defects as phonon scattering centers based on the phenomenological Debye–Callaway model: \cite{31}

$$
\kappa = \frac{k_B \left( \frac{k_BT}{B} \right) \int \tau_p(z) \frac{z^2 e^z}{(e^z - 1)^2} dz}{2\pi^2v\hbar^2}
$$  \hspace{1cm} (6)

where $\tau_p$, $z$, and $\theta_0$ are phonon relaxation time, reduced frequency, and the Debye temperature, respectively. Known from Matthiessen’s rule, $\tau_p$ is the addition of participant phonon scattering processes, \cite{32} including intrinsic Umklapp (U) and normal (N) processes that can be extracted from phonon dispersion, and extrinsic scattering processes due to various types of lattice defects. Here, we take grain boundaries (B), nanoprecipitates (NP), and point defects (PD) into account for phonon scattering (Note S7 and Table S3, Supporting Information). The integral spectral lattice thermal conductivity ($\kappa_L$) of each process is calculated via fitting the $\kappa_L$ of 8% (Bi and I) co-doped GeTe at 300 K, as shown in Figure 3f. The area between two adjacent curves represents the decreased magnitude $\kappa_L$ due to additional phonon scattering. As can be seen, $\kappa_L$ is reduced throughout a full range of phonon spectrum, where B, NP, and PD take over low-, medium-, and high-frequency phonon scattering, respectively.

### 2.4. Figure-of-Merit and Conversion Efficiency

Owing to high $S^2\sigma$ and low $\kappa$, (Bi and I) co-doped GeTe can have an evidently enhanced $zT$ in both $\alpha$- and $\beta$-GeTe temperature range. Specifically, the peak $zT$ is enhanced from 0.8 in pure GeTe to 2.5 in 8% (Bi and I) co-doped GeTe at 675 K (Figure 4a). The temperature-dependent average $zT$ ($zT_{\text{avg}}$) of 8% (Bi and I) co-doped GeTe approximates to the modeling of $\text{VB}_L + \text{VB}_L + \text{CB}_L$, as shown in Figure 4b, which confirms the

![Figure 4](https://www.afm-journal.de/)

**Figure 4.** Thermoelectric performance. a) Temperature-dependent figure-of-merit ($zT$) of GeTe thermoelectric materials. b) Comparison of measured and modeled $zT$ of 8% (Bi and I) co-doped GeTe. The modeling considers the additional contribution from the light valence band (VB), heavy valence band (VB), and conduction band (CB), while the lattice thermal conductivity ($\kappa_L$) is assumed constant, namely $\text{VB}_L$, $\text{VB}_L + \text{VB}_L$, and $\text{VB}_L + \text{VB}_L + \text{CB}_L$. c) Temperature difference-dependent conversion efficiency ($\phi$) of the module reported by this work with other GeTe thermoelectric modules.
contribution of CB$_2$. It is also noticed the ultrahigh $zT_{\text{avg}}$ of 8% (Bi and I) co-doped GeTe being over 1.5 from 625 to 800 K can refer to a promising engineering $zT$ ($zT_{\text{avg}}$) of $\approx 1.47$ given cold side ($T_c$) at 300 K and hot side ($T_h$) at 800 K, which implies the great potential of (Bi and I) co-doped GeTe materials for thermoelectric generation application.

To evaluate the application propose, we propose a single-leg model posed under a thermal boundary condition of $T_c$ at 300 K and $T_h$ at 800 K using finite-element analysis (FEA). The actual temperature difference ($\Delta T$) estimated based on the temperature-dependent profile of $S$, $\sigma$, and $\kappa$ of 8% (Bi and I) co-doped GeTe is $\approx 430$ K. [33] The maximum heat-to-electricity conversion efficiency ($\phi_{\text{max}}$) can be therefore calculated as 14.6% by neglecting Thomson heat, given:

$$\phi_{\text{max}} = \phi_C \cdot \frac{1 + zT_{\text{avg}}(a/\phi_C - 1/2) - 1}{1 + zT_{\text{avg}}(a/\phi_C - 1/2) - \phi_C}$$

where $\phi_C$ is Carnot efficiency and $a$ is dimensionless intensity factor of Thomson coefficient. [34] As shown in Figure 4c, due to highly favorable $zT$ and $zT_{\text{avg}}$, the estimated $\phi_{\text{max}}$ of single-leg thermoelectric module made of (Bi and I) co-doped GeTe is competitive with that of other state-of-art thermoelectric devices, including GeTe, PbTe, and skutterudites. [5, 9, 33–35]

3. Conclusion
To conclude, this work provides a comprehensive discussion on the anionic doping effect in high-performance GeTe thermoelectrics. Theoretically, we elucidate that anion and cation sites play an equivalent role in the crystal structure and bonding mechanisms of rocksalt $\beta$-GeTe, on the basis of point group operation, molecular orbital theories, tight binding approach, and DFT calculations. Experimentally, we adopt a modified flux-assist method to synthesize cationic Sb/Bi or anionic Br/I doped, and (Bi and I) co-doped GeTe samples. Subsequent measurements indicate that Sb/Bi and Br/I doped GeTe can comparably optimized electrical and thermal properties, however, due to different doping effects. Further (Bi and I) co-doped GeTe can obtain an enhanced $zT$ up to 2.5 at 675 K and average $zT$ over 1.5 from 625 to 800 K when the co-doping concentration reaching 8%, which corresponds to a max heat-to-electricity $\phi$ of 14.6% under a $\Delta T$ of 430 K. The ultrahigh material and device performance reported by this work can justify the significant potential of anionic doping for high-performance GeTe thermoelectrics.

4. Experimental Section
Sample Preparation and Characterization: Polycrystalline samples were synthesized through a modified flux-assist process. Specifically, pristine Ge, Te, Bi, Sb, and chloride BiI$_3$, TeBr$_4$, and TeI$_4$ were chosen as reagent, and 50% NaCl + 50% KCl molten salt was chosen as flux medium. The acquired power samples were consolidated using spark plasma sintering (SPS-211X, Fuji Electronic) at 500 °C under Argon atmosphere, applied with a uniaxial pressure of 55 MPa. The phase purity of the synthesized samples was identified by X-ray diffraction (XRD, D8 Advance MKII, Bruker) equipped with monochromatized Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å).

XRD Rietveld refinement was conducted using GSAS-II software. [36] The microstructures were characterized by a field-emission scanning electron microscope (SEM, JSM-7001F, JEOL) using secondary electron (SE), backscattered electron (BSE), and energy-dispersive X-ray spectroscopy (EDS) techniques. The lattice structures were investigated using an aberration-corrected transmission electron microscope (TEM, HF-5000, Hitachi), assisted with Wiener filter, average background subtraction filter, and geometric phase analysis. [37] The lamella specimens were prepared using focus ion beam (FIB) lift out technique (FEI Scios Dualbeam system, Thermo Scientific). The overall grain morphology and twin structures were characterized by electron backscattered diffraction (EBSD) coupled in the FIB system.

Thermoelectric and Transport Measurement: Temperature-dependent Seebeck coefficient ($S$) and electrical conductivity ($\sigma$) were measured by four-probe method (ZEM-3, ULVAC-RIKO). The thermal conductivity ($\kappa$) is calculated by:

$$\kappa = D \times C_p \times \rho$$

where $D$ is thermal diffusivity measured by a laser flash method (LFA 467, NETZSCH), $\rho$ is density measured by Archimedes’ method. $C_p$ is specific heat capacity measured by the differential scanning calorimeter (DSC 404 F3, NETZSCH), which is overall higher than the Dulong–Petit’s value, therefore is taken as 0.28 J g$^{-1}$ K$^{-1}$, constantly throughout the measured temperature range.

Hall transport properties relative to increasing temperature were measured by Van der Pauw method (homemade instrument) with a sweeping magnetic field of up to $\pm 1.5$ T. Hall carrier concentration ($n_H$) and Hall mobility ($\mu_H$) are calculated based on:

$$n_H = \frac{1}{e \times R_H}$$

$$\mu_H = \frac{\sigma}{R_H}$$

where $R_H$ and $e$ are Hall coefficient and electron charge, respectively.

DFT Calculation: The DFT calculations were performed using a projector-augmented wave (PAW) method implemented in the Vienna Ab initio Simulation Package (VASP). [38] Fully relativistic Perdew–Burke–Ernzerh of generalized gradient approximation functional (GGA-PBE) was adopted to deal with exchange correlation interaction. [39] The 3 × 3 × 3 and 2 × 2 × 2 supercells were built for electron and force calculations, then sampled by a 9 × 9 × 9 and a 15 × 15 × 15 Monkhorst–Pack k-mesh, respectively. [40] All supercells were fully relaxed with plane wave cut-off energy of 500 eV, and convergence criterion of $1 \times 10^{-7}$ eV per electron and $1 \times 10^{-9}$ eV Å$^{-1}$ per atom. The dispersion relations were calculated along the line-mode k-path according to Brillouin path features of the AFLOW framework. [41] The electron band structures were calculated considering spin-orbital-coupling (SOC) effect. The phonon band structures were calculated without considering SOC effect, by solving the harmonic force constant near $\Gamma$ point using Phonopy package. [41]

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.

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

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