High thermoelectric performance enabled by convergence of nested conduction bands in Pb$_7$Bi$_4$Se$_{13}$ with low thermal conductivity

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Thermoelectrics enable waste heat recovery, holding promises in relieving energy and environmental crisis. Lillianite materials have been long-term ignored due to low thermoelectric efficiency. Herein we report the discovery of superior thermoelectric performance in Pb$_7$Bi$_4$Se$_{13}$ based lillianites, with a peak figure of merit, $zT$ of 1.35 at 800 K and a high average $zT$ of 0.92 (450–800 K). A unique quality factor is established to predict and evaluate thermoelectric performances. It considers both band nonparabolicity and band gaps, commonly negligible in conventional quality factors. Such appealing performance is attributed to the convergence of effectively nested conduction bands, providing a high number of valley degeneracy, and a low thermal conductivity, stemming from large lattice anharmonicity, low-frequency localized Einstein modes and the coexistence of high-density moiré fringes and nanoscale defects. This work rekindles the vision that Pb$_7$Bi$_4$Se$_{13}$ based lillianites are promising candidates for highly efficient thermoelectric energy conversion.
Worldwide energy and environmental crisis have an urgent requirement on clean and sustainable energy sources due to the combustion of fossil fuels. Thermoelectric (TE) semiconductors provide promising opportunities in enabling the conversion of waste heat into electrical energy, especially favorable for relieving the current dilemma. The crucial issue is the relatively limited energy conversion efficiency, related to the TE figure of merit, $zT = S^2TD/(\kappa_e + \kappa_l)$. Here, $S$ and $\kappa$ are the Seebeck coefficient and electrical conductivity; $T$ is absolute temperature; $\kappa_e$ and $\kappa_l$ are electronic and lattice thermal conductivities, respectively. Electronically, the intertwining of $S$, $\kappa_e$, and $\kappa_l$ complicates efforts to optimize TE performance. With the single parabolic band assumption, the $zT$ can be described as $zT = zT(\eta, B)$ by the conventional quality factor analysis. This description correlates $zT$ solely with two independent physical parameters, i.e., tunable reduced Fermi level, $\eta$ and quality factor, $B$. This $B$ value is an effective descriptor with considering band degeneracy ($N_d$), ineffective mass ($m^*$), deformational potential ($\varepsilon$), and lattice thermal conductivity, according to the relationship of $B = N_d/(m^*\varepsilon)^{3/2}$.

The optimization of electrical properties and simultaneous suppression of heat transport are essential and critical for advanced TE materials. To achieve the optimal electrical properties, effective strategies on electronic band engineering are indispensable, such as electronic band convergence, resonant level introduction, band inversion and flattening. Meanwhile, low lattice thermal conductivity is equivalently favorable. Intrinsically, the reduced heat transport requires large lattice anharmonicity, complex crystal structure, and suppressed transverse acoustic phonon branches. Extrinsically, lattice imperfection engineering, including point defect, dislocation, grain boundary and interface, coherent nanostructure, etc., is equally prevalent to scatter all-length scale phonons and thus impede heat propagation.

The alignment of multiple electronic bands and intrinsically low lattice thermal conductivity are highly beneficial for promising TE materials. Ternary heavy metal chalcogenides have transport requires large lattice anharmonicity, complex crystal structures, and localized Einstein modes, and suppressed transverse acoustic phonon branches. Externally, lattice imperfections, such as point defect, dislocation, grain boundary and interface, coherent nanostructure, etc., are also accessible with enhanced quality factors. Equally significantly, the lattice thermal conductivity is exceptionally low of 0.17 W m⁻¹ K⁻¹ at 800 K, which originates from large lattice anharmonicity, low-frequency localized Einstein modes, and the coexistence of high-density moiré fringes and nanoscale defects, especially periodic defective stripes with high-density stacking faults and intense lattice strains. Our work demonstrates that PbₓBi₂Se₃ based lillianites hold a great potential to be efficient TEs. Importantly, this work also develops an unconventional approach to calculate quality factors, highly favorable for accelerating the screen and evaluation of advanced TE systems.

Results

**TE performance.** PbₓBi₂Se₃ crystallizes in a monoclinic structure with the space group (No. 12) of C2/m. This monoclinic structure consists of diverse polyhedra, including PbSe₆, PbSe₅, and BiSe₆ (Fig. S1a). The synthesis of PbₓBi₂Se₃ includes ball-milling and long-term annealing with details presented in the experimental section. A series of heterogeneous elemental doping has been carried out by introducing Ga, In, Ag, and I, according to the nominal compositions (Pbₓ-xGaₓ)ₓBi₂Se₃ (x = 0.02, 0.05, and 0.1), (Pbₓ-xAgₓ)ₓBi₂Se₃ (x = 0.05 and 0.1), (Pbₓ-xIₓ)ₓBi₂Se₃ (x = 0.4 and 0.8). The XRD patterns of pristine and doped PbₓBi₂Se₃ are presented in Fig. S1b. This distinct doping achieves varied electron concentrations at 300 K, ranging from 1.0 × 10²⁰ to 1.2 × 10²¹ cm⁻³. For the convenience of comparison and discussion, PbₓBi₂Se₃ with different element doping are denoted as the corresponding electron concentration (n_H) measured at 300 K, as shown in the inset of Fig. 1. The composition, carrier concentration, Hall mobility, and geometry density are tabulated in Table S1. It should be noted that there exists a certain degree of anisotropy of TE properties, due to the monoclinic structure of PbₓBi₂Se₃. The measurement geometry and TE properties parallel and perpendicular to the spark plasma sintering (SPS) directions of two different samples are presented in Fig. S3. In this work, only the TE properties parallel to the SPS direction is presented and discussed for convenience. It should be noted that $zT$ value calculations are consistent from the direction of electrical conductivity, Seebeck coefficient, and thermal conductivity. For instance, (Pb₀.95Ga₀.05)ₓBi₂Se₃ corresponds to the sample with $n_H$ of 1.2 × 10²⁰ cm⁻³ (also denoted as Ga2). As shown in Fig. 1a, the electrical conductivities, $\sigma$ of PbₓBi₂Se₃ alloys with $n_H$ larger than 1.6 × 10²⁰ cm⁻³, show a decreasing tendency with increasing temperature, which is a characteristic of degenerated semiconductors. The $\sigma$ of PbₓBi₂Se₃ decreases firstly and then increases slightly with rising temperature. Specifically, $\sigma$ of PbₓBi₂Se₃ with $n_H$ of 1.2 × 10²⁰ cm⁻³ decreases from 250 Scm⁻¹ at 300 K to 104 Scm⁻¹ at 723 K, followed by a slight increase to 119 Scm⁻¹ at 800 K. The magnitude of Seebeck coefficient, $S$, of PbₓBi₂Se₃ with $n_H$ higher than 2.8 × 10²⁰ cm⁻³ increases monotonously with increasing temperature. And the $|S|$ of samples with lower $n_H$ demonstrates broad extrema at high temperatures, attributed to the contribution from the minority carrier. Taking the sample with $n_H$ of 1.2 × 10²⁰ cm⁻³ as an example, the $S$ at 300 K is ~89 μV K⁻¹ and decreases to ~217 μV K⁻¹ at 723 K and then increase to ~213 μV K⁻¹ at 800 K. According to Goldsmidt–Sharp bandgap, $E_g = 2[|S|/m_{max}]^{1/2}$, the $|S|_{max}$ and $m_{max}$ are the maximum of the magnitude of Seebeck coefficient, and its corresponding temperature, respectively. The bandgap is estimated to be about 0.33 eV, close to the reported value of 0.29 eV. The total thermal conductivities of PbₓBi₂Se₃ demonstrate low values at 300 K, e.g., 0.48 Wm⁻¹ K⁻¹ in PbₓBi₂Se₃ with $n_H$ of 1.2 × 10²⁰ cm⁻³, which further decreases to 0.32 W m⁻¹ K⁻¹ at 800 K. By systematic doping, a series of $zT$ is achieved. And the peak $zT$ of 1.35 is obtained at 800 K for the composition of (Pb₀.95Ga₀.05)ₓBi₂Se₃ with $n_H$ of 1.2 × 10²⁰ cm⁻³.
(Fig. 1d). It is worth noting that this is the highest \( zT \) achieved to date not only in illianitene homologous series, but also in a series of compounds with similar structures, such as Tetradyomite, Pavo-nite, Cannizzarite, Galenobismuthite, complex rare-earth sulfides, and other structure-similar compounds. The total number of 37 different compounds was enumerated and compared in Fig. S2. Compared to the state-of-the-art TE materials, like PbTe\(_7\), SnSe\(_3\), GeTe\(_3\), and Mg\(_3\)Sb\(_2\), etc., this result demonstrates a great potential for realizing high TE performance in illianitene-type or similar structures. These promising high peak and average \( zT \) values enable Pb\(_7\)Bi\(_4\)Se\(_{13}\) to be applicable for middle-temperature power generation, such as waste heat recovery, remote sensor power, and emergency power sources. Besides, it also could be employed in the marine engines of ships by utilizing waste heat from exhaust pipes.

Furthermore, thermomechanical properties are also investigated in Pb\(_7\)Bi\(_4\)Se\(_{13}\). The compression test shows an ultimate compressive strength of 85 MPa and the strain can reach 1.2% (Fig. S6). Nanoindentation investigation indicates the hardness of 2.88 ± 0.04 GPa (Fig. S7). And the microstructural investigation shows no obvious precipitates and micropores in the sample after annealing under vacuum conditions for 2 weeks (Fig. S8), which shows its reasonably robust thermal stability. The heating and cooling measurements is also presented in Fig. S9.

**Convergence of nested conduction bands.** To understand the origin of such high TE performance, we performed DFT calculations to study the electronic structure of Pb\(_7\)Bi\(_4\)Se\(_{13}\). Figure 2a shows the band structure along with the high symmetry \( \Gamma \)-\( M \)-\( M' \)-\( Y' \)-\( Y'' \)-\( M'' \)-\( Y''' \)-\( M''' \) path. The conduction bands at \( M_2 \) and \( Y_2 \) points demonstrate large \( E - k \) dispersion, implying the light band characteristic. The feature is the band nesting especially occurred at \( M_2 \) and \( Y_2 \). These bands have nearly the same energies, i.e., the difference in the conduction band minimum (CBM) at \( M_2 \) point is around 100 meV, which can synergistically participate in the electrical transport. More significantly, the effectively nested conduction bands at \( M_2 \) and \( Y_2 \) also demonstrate nearly indiscernible energy separations. In details, the energy difference of CBMs of \( M_2 \) and \( Y_2 \) is as small as 8 meV. In this way, the nested conduction bands at \( M_2 \) and \( Y_2 \) reveal a high number of valley degeneracy, comparable to many decent TE materials, such as \( n \)-type Si\(_3\), Bi\(_3\)Se\(_3\), and PbTe\(_7\), as well as \( p \)-type elemental Te\(_3\). The convergence of nested bands enables multiple conducting channels without the deterioration on the Seebeck coefficient, highly favorable for superior electrical performances. A recent study suggests the convergence of electronic bands at distant \( k \) points is superior. However, for semiconductors with lower symmetries, this favorable band configuration is a grand challenge. Alternatively, the convergence of nested bands could be significant to advance electrical properties for lower-symmetry TE materials. The convergence of nested bands plays an important role in charge transport properties than the situation with only heavy bands, even though it introduces a certain degree of intervalley scattering. This situation is confirmed by the theoretical calculation in the recent work, in which the power factors in band configuration of nested bands are still higher than that in band configuration of the heavy band only. Experimentally, the band nesting is proven to be an advanced method in the Tellurium TE compound with space for improvement. Furthermore, the convergence of nested bands holds great potential for TE materials, if nested bands could be removed away from the same \( k \) point by chemical modifications.

In regard to valence band structure, the valence band maximum (VBM) exhibits flatten dispersion along \( \Gamma - Y_2 \) and \( \Gamma - M_2 \) lines, which is a characteristic of high valence valleys. The VBM lies in the middle of \( Y_2 \) and \( M_2 \) paths, implying high valley degeneracy. Therefore, the multiband feature in both conduction and valence valleys enables Pb\(_7\)Bi\(_4\)Se\(_{13}\) alloys to be promising for high TE efficiency. The spin–orbit coupling (SOC) effect on the band structure is also considered. The introduction of SOC has an indiscernible effect on the band dispersions of CBM and VBM, as shown in Fig. S9. The calculated \( E_0 \) is suppressed from 0.67 eV (without SOC) to 0.22 eV (with SOC). Figure 2b exhibits the orbital projected density of states.
(DOS). In the region from the CBM to 1 eV above the Fermi level ($E_F$), the states are dominated by $p$ orbitals of Pb, Bi, and Se, with minor components from $s$ orbitals of Se. The valence bands ranging from 1 eV below the $E_F$ to the VBM is dominated by Se-4$p$ and Pb-6$s$ states with minor mixed contributions of Bi-6$s$, Bi-6$p$, and Pb-6$p$ states. The 6$s^2$ electrons of Pb and Bi are deeply located below Se 4$p$, forming lone-pair electrons. In the band structure shown in Fig. 2a, the orange and red dashed lines represent the $E_F$ calculated from DFT for the 0.05 electron-doped and 0.05 hole-doped Pb$_7$Bi$_4$Se$_{13}$, respectively. In the electron-doped Pb$_7$Bi$_4$Se$_{13}$, the $E_F$ goes across two bands at both $Y_2$ and $M_2$, which forms a nested Fermi surface consisting of two cylindrical-like electron sheets, visible in Fig. 2c. On the other hand, Fig. 2a shows that the Fermi level only lies in one band at both $Y_2$ and $M_2$, in the case of hole-doped Pb$_7$Bi$_4$Se$_{13}$, and the hole pocket at $M_2$ is obviously larger than $Y_2$, confirmed by the Fermi surface in Fig. 2d. It should be noted that nested bands could trigger strong electron–phonon scattering by the center valley phonons, which is a detrimental effect on charge transport. It is meaningful to calculate the scattering rates for each band and valley by using the electron–phonon coupling calculations based on density-functional perturbation theory, which will be the subject of our future work separately.

**Non-parabolic charge transport.** Parabolic band assumption is dominant for TE materials with wide bandgaps. For semiconductors with narrow band gaps, like PbTe$^8$ and CoSb$_3^8$, the non-parabolicity of electronic bands occurs, which stems from interactions between conduction and valence bands$^8,39$. As shown in Fig. 3a, three-dimensional (3D) plots of parabolic and Kane bands are presented. The color bar is indicative of the relative energy levels. Clearly, the parabolic band reveals an ellipsoid-shaped energy surface. By contrast, the Kane band demonstrates a non-parabolic energy surface deviating from band edges. The conduction band nesterification in parabolic and Kane bands are also considered. Two conduction bands are located at the same $k$ point and flat valence bands are shown in the Brillouin zone. Figure 3b presents the two-dimensional (2D) dispersion relations, $E(\mathbf{k})$ ($E$ energy, $\mathbf{k}$ wave vector). With respect to the parabolic band, $E$ is proportional to $k^2$, complying with the relationship, $E = \frac{\hbar^2 k^2}{2m^*}$. Here its effective mass, $m^*$ keeps as constant ($m^* = m^*_0$ effective mass at band edge). For the Kane band, it remains parabolicity at the energy extrema of electronic bands but deviates from parabolicity in a linear $k$ tendency with departing from band edges. And the $E(\mathbf{k})$ dispersion could be well described by $E(1 + \frac{E}{E_F}) = \frac{\hbar^2 k^2}{2m^*}$. Its effective mass, $m^*$ varies with Fermi level, following this relationship, $m^* = m^*_0(1 + \frac{E}{E_F})^8$.

To capture the effective mass of Pb$_7$Bi$_4$Se$_{13}$ at room temperature, the pisarenko plot based on single Kane band (SKB) and single parabolic band (SPB) assumptions could be well-simulated by the effective mass, $m^*_H$ of 1.1 $m^*_0$, as suggested in Fig. 3c. The temperature dependence of effective mass verifies its band nonparabolicity, as shown in Fig. S10b. It should be noted that the Seebeck effective mass, $m^*_S$ is defined as the density of state effective mass in TE community, which predicts the Seebeck coefficient with Hall carrier concentration, $n_H$ in both the SPB and SKB models. However, it should be also realized that the qualitative difference between $m^*_H$ (Seebeck effective mass) and $m^*_S$ (effective mass from the $E \sim k$ dispersion). The Seebeck effective mass is defined by Eqs. (1) and (2), which remain unchanged with increasing $n_H$. Differentially, the effective mass, $m^*_S$ defined by $m^*_S = h(dE/dk^2)^{-1}$, increases with increasing $E$. The temperature-dependent $n_H$ of two compositions of (Pb$_{0.98}$Ga$_{0.02}$)$_7$Bi$_4$Se$_{13}$ (Ga$_1$, $n_H = 2.0 \times 10^{20}$ cm$^{-3}$) and (Pb$_{0.95}$Ga$_{0.05}$)$_7$Bi$_4$Se$_{13}$ (Ga$_2$, $n_H = 1.2 \times 10^{20}$ cm$^{-3}$) is presented in the inset of Fig. 3c. The $n_H$ of the two compositions remains unchanged up to 600 K. Meanwhile, the Hall mobility, $\mu_H$ of all compositions as a function of $n_H$ follows the Kane-type charge transport characteristic, demonstrated by the red solid line.

This $n_H$ dependent $\mu_H$ considering SKB model is calculated based on the non-degenerate mobility, $\mu_0$ at 300 K. This relationship is presented as below$^{40}$

\[
\mu_H = \frac{e}{\sqrt{2m^*_1}} \cdot \frac{\pi \hbar^4 v^2 d}{(m^*_1 k_B T)^{3/2}} \cdot \frac{3(K + 1) \cdot 3F_{1/4}^{3/2}}{(2K + 1)^2 \cdot 0F_{1/4}^{3/2}},
\]

where $k_B$ is the Boltzmann constant, $h$ is the reduced Planck constant, $K$ is the anisotropy of Fermi surface, defined by $K = \frac{m^*_1}{m^*_1 + m^*_1} \cdot \frac{m^*_1 + m^*_1}{m^*_1 + m^*_1}$ exhibit the longitudinal and transverse effective mass. $K$ is assumed to be 1 here. $nF_{m_1}$ is the generalized Fermi integral. $v_l$ is the speed of sound, $d$ is the sample density, $m^*_1$ and $m^*_0$ are inert and single-valley effective mass.

**Unique quality factor analysis.** Conventional quality factor ($B$) analysis provides an insight into TE physics. It decouples $zT$ into the tunable reduced Fermi level, $\eta$ and $B$, based on the SPB model.
Fig. 3 Electronic transport properties. a 3D illustration of Parabolic and Kane bands with asymmetric conduction and valence bands. The features of conduction band nesting and relative flat valence band are presented. b $E - \mathbf{k}$ dispersions of parabolic (solid blue line) and Kane bands with different band gaps, $E_g$, and Fermi level, $E_F$. c Hall electron concentration, $n_H$, dependence of the temperature. The inset shows the temperature dependence of $n_H$ of two compositions, Ga1 (red circle) and Ga2 (blue circle). d Hall mobility, $\mu_H$, as a function of $n_H$. The red solid line is calculated based on the single Kane band (SKB) model. The inset shows the temperature dependence of $\mu_H$ of Ga1 and Ga2.

(see Supplementary Note 2). However, this SPB model is limited to fully describe TE semiconductors with band nonparabolicity and bipolar effect. At first, the discernible difference between parabolic and Kane bands, shown in Fig. 3a, b, enables non-negligible deviations by using SPB to describe the electronic transport of non-parabolic bands. Secondly, the bipolar effect frequently emerges in semiconductors with small band gaps. This effect leads to a decrease in the carrier relaxation time, and degrades the Seebeck coefficient. Thirdly, this SPB model is limited to describe TE semiconductors with band nonparabolicity and bipolar effect. Herein, this unique quality factor, $B^Kane$, is developed by using two Kane band (TKB) models. Distinct from the traditional quality factor, the $zT$ here is closely correlated with the reduced Fermi level, $\eta (\eta = (E - E_F)/k_BT)$, and the reduced bandgap, $\xi (\xi = E_g/k_BT)$, which is summarized as follows

$$zT = \frac{S(y + S_h)^2}{(\gamma + 1) \left[ \frac{(k_y/\xi)^2}{3B^Kane^2\xi^2} + (L_y + L_h) \right] + \gamma(S_c - S_h)^2}.$$  

(3)

And this unique quality factor $B^Kane^*$ is generalized as below

$$B^Kane^* = \frac{k_B}{e} \frac{\sigma_{xx} E_g}{\kappa_L}$$  

(4)

in which the $S$ denotes the Seebeck coefficient, $L$ is the Lorenz number, $\sigma_{xx}$ is the transport coefficient, $\gamma$ is the electrical conductivity ratio. The subscripts, $c$ and $h$, denote conduction and holes. The derivation is presented in Supplementary Note 3.

With the determination of physical parameters of the conduction and valence bands, we could obtain a series of $zT$ values by changing $B^Kane$. This $B^Kane$ considers band nonparabolicity, band degeneracy $N_v$, inertial effective mass $m_I^*$, and deformation potential $\Xi$. An example is provided based on Pb$_7$Bi$_4$Se$_{13}$ with a specific $B^Kane = 6$. Figure 4a depicts the theoretical $zT$ as functions of $\eta$ and $\xi$. A maximum $zT$ could be achieved with simultaneously optimized $\xi$ and $\eta$. A contour plot is presented in Fig. 4b with the $B^Kane^*$ of 6. The progressive changes in the color bar from blue to red correspond to $zT$ from 0 to 1.48. Contour lines with representative $zT$ values, such as 0.4, 0.8, and 1.4, are marked by dash-dot lines in Fig. 4b. Taking Pb$_7$Bi$_4$Se$_{13}$ with $n_H$ of $1.2 \times 10^{20} \text{cm}^{-3}$ as an example, its $\eta$ and $\xi$ at 800 K could be estimated to be $-0.5$ and $4.6$, which is indicated by the yellow dot in Fig. 4b. The estimation of $\eta$, $\xi$, and $B^Kane^*$ is presented in Supplementary Note 4. It is worth noting that the difference in conduction and valence band is considered and included in this model by using the band anisotropy, $\Lambda$.

A maximum $zT$ of 1.48 is predicted as represented by the red point in Fig. 4b. It can be achieved by further optimizing $\eta$ and $\xi$, indicated by the yellow arrow. For the tuning of bandgap, the chemical substitution of selenium by sulfur or tellurium tends to enlarge and decrease band gaps, respectively. This quality factor could be further optimized via chemical modifications on electronic band structures. The introduction of coherent nanoscale defects is favorable for improving quality factors, which could guarantee unchanged carrier mobilities, concomitantly strengthen...
This elaborately developed plots of three different quality factors are presented in Fig. S12. It can in evaluating and predicting TE performance in Pb7Bi4Se13. It can as shown by the red point of Fig. 4c. Figure 4d shows that the maximum zT is predicted to be 1.76 as shown by the red point of Fig. 4c. Figure 4d shows that the maximum zT is proportional to the enhanced B*Kane which can be used as an insightful guide to exploiting high-performance TE materials.

It should be noted that the quality factor with SKB model has already been established, which could evaluate and predict the TE performance. However, its application is limited at low temperatures, due to thermally excited minority carriers with increasing temperatures. The contribution of minority carriers becomes inevitable and considerably deteriorates TE performances. A lack of effective quality factors brings a great challenge to evaluate and predict TE performances in semiconductors with narrow band gaps, especially at high temperatures. To resolve this issue, this unique quality factor is established with TKB model, which can provide an effective and time-saving method. The derivations on previously reported quality factors established on SPB and SKB models (B*Para and B*Kane for clarity) and developed B*Kane are presented in Supplementary Note 5. With regard to previously reported quality factors, zT values only correlate with the B*Para (or B*Kane) and reduced chemical potential, ƞ. By contrast, the zT in this unique quality factor depends on three independent variables, B*Kane ƞ and ξ. The 3D and contour plots of three different quality factors are presented in Fig. S12. This elaborately developed B*Kane not only plays a significant role in evaluating and predicting TE performance in Pb7Bi4Se13. It can also be extended to more TE materials with narrow bandgaps, such as prototypical (Bi,Sb)2Te3 and van der Waals crystal Ta4SiTe4. By adopting this B*Kane the highest zT of 1.54 and 0.27 are predicted in (Bi,Sb)2Te3 and Ta4SiTe4, which could be achieved by further optimizing the ƞ and ξ.

Understanding low lattice thermal conductivity. Lattice thermal conductivities, η of Pb7Bi4Se13 samples are presented in Fig. 5a. The η is estimated by subtracting electronic thermal conductivity, η from total thermal conductivity. The η is estimated by using the Wiedemann–Franz equation, κL = LσT. The η ranges from 0.44 to 0.29 Wm⁻¹K⁻¹ at 300 K, and decreases with rising temperature. This decline deviates from the T⁻¹ tendency dominated by Umklapp phonon-phonon scattering, which implies strong defect-phonon scattering. Specifically, the η for Pb7Bi4Se13 with nH of 1.2 × 10²⁰ cm⁻³ decreases from 0.33 Wm⁻¹K⁻¹ at 300 K to 0.17 Wm⁻¹K⁻¹ at 800 K. This low η is comparable to that of state-of-the-art TE materials, such as 0.18 Wm⁻¹K⁻¹ for CaAgTe, 0.13 Wm⁻¹K⁻¹ for both (Ge,Mn, Sb)Te and Bi₁₋ₓPbₓCuSeO₆. To further assess the intrinsic Umklapp phonon interaction, sound speeds were measured. The related physical parameters were calculated and tabulated in Table S6. The mean sound speed for Pb7Bi4Se13 is as low as 1553 ms⁻¹, and the Grüneisen parameter γ is 2.2. This large γ is indicative of soft chemical bonding and strong lattice vibration anharmonicity, which is comparable with γ of 2.6 for Ag₃GaSe₆, 2.1 for Ag₃SbTe₄, 1.7 for K₃Bi₆Se₁₃, 1.7 for BiSe₄, and 1.6 for Cu₁₋ₓFeₓ₄Se₂·. The calculated Debye temperature (ΘD) is as low as 148 K, comparable to 147 K in Ag₃GaSe₆ with liquid-like thermal conductivity. The large Grüneisen parameter and low Debye temperature lead to large lattice anharmonicity and strong Umklapp phonon–phonon scattering.

The low-temperature heat capacity in Fig. S13 shows the non-linear relationship of C_p/T vs. T². This inconsistency with the conventional Debye model implies the existence of localized...
characteristic temperatures are full description of the measured data. And the Einstein
Three low-frequency Einstein vibration modes are utilized for a
experimental data and the line is established by using a Debye and three
phonon modes, frequently found in TEs with low thermal
contribution to heat capacity is a signature of localized optical
Einstein oscillator modes. A broad maximum appears around
a Lattice thermal conductivity,
Fig. 5 Lattice thermal conductivity and phonon-related calculations.

Coexistence of diverse defects. Nanoscale defects also play a
significance role in the low thermal conductivity. To elucidate
defect-phonon scattering sources, a microstructural investigation by using a spherical aberration-corrected scanning transmission electron microscope (Cs-corrected STEM) was employed on Pb-Bi-5Se3 with \( n_{\perp} = 1.2 \times 10^{20} \text{cm}^{-3} \). High-angle annular dark-field (HAADF)-STEM images in Fig. 6a, b clearly show the periodic defective stripes, with a length beyond 30 nm and a width of ~3 nm, embedded in the host matrix of Pb-Bi-5Se3. The defective stripes include high-density of stacking faults, shown by the white arrows in Fig. 6b. The elemental mapping in Fig. S15 verifies the homogeneously distributed elements along with defective stripes. The strain map profiles (\( \epsilon_{x} \)) in Fig. 6a1, b1 are derived by geometric phase analysis (GPA), which semi-quantitatively evaluate spatially distributed strain fields. Intriguingly, the periodic strain lines are captured (labeled by black arrows) and demonstrate the intense strains along with these defective stripes in Fig. 6a, b. The strain analysis of \( \epsilon_{x} \) is presented in Fig. S15. In addition, dislocation cores are also observed, highlighted by white circles. Figure 6c presents the irregularly shaped nanoscale precipitates embedded in the host matrix, marked by the blue dotted circles. These high number density of nanoscale precipitates demonstrates the size of several nanometers. Diverse lattice imperfections have been evidently observed in Fig. 6d. The moiré fringes, marked by the yellow ellipses, distribute around the dark-contrast precipitates. These strong moiré fringes originate from the interference between different sets of lattice planes, indicating local mass and strain fluctuations. Figure 6e shows the enlarged region from the inverse fast Fourier transform of Fig. S16c. In sharp contrast to the slightly distorted lattice in Fig. 6e, another two regions in Fig. 6f, g
highlight the crystal imperfections. In Fig. 6f, moiré patterns are highlighted by the pleated structure, marked by the yellow lines. In Fig. 6g, the coexistence of dislocation arrays and nanoscale twined structures, demonstrated by green symbols and parallel brown lines, respectively. Numerous nano-precipitates and dislocations can also be observed in Fig. S16. The coexistence of periodic defective stripes, nanoprecipitates, dislocation, and Moiré fringes play a significant role in scattering phonon with different length scales, which strongly suppresses lattice thermal conductivity.

Discussion

In this work, we report the discovery of a unique TE material, Pb$_7$Bi$_4$Se$_{13}$ based lillianites. A high peak $zT$ of 1.35 at 800 K and a decent average $zT$ of 0.92 from 450 to 800 K are achieved for $n$-type (Pb$_{0.95}$Ga$_{0.05}$)Bi$_4$Se$_{13}$. This is the highest TE performance realized in lillianites. For Pb$_7$Bi$_4$Se$_{13}$, conduction bands are highly nested at Y$_2$ and M$_2$ points. Besides, these nested conduction bands at Y$_2$ and M$_2$ also share similar energies, demonstrating a strong signature of band convergence. The synergistic effect of band nesting and convergence leads to higher band degeneracy and superior electrical properties. It provides an alternative approach to improve valley degeneracy for low-symmetry TE systems. These electronic band features are rarely documented in compounds with lower crystal symmetries and are comparable to typical $n$-type TE materials, such as PbTe and CoSb$_3$, which both demonstrate multiple degenerated bands as well as narrow-band gaps ($E_g = -0.3$ eV for PbTe and $\sim 0.23$ eV for CoSb$_3$). For PbTe, conduction bands consist of one Kane band at the L point. The full valley degeneracy, $N_v$, for L are 4. For CoSb$_3$, conduction bands are composed of one Kane band at Γ point ($N_v = 3$) and one parabolic band along the Γ–N line ($N_v = 12$).

The conventional quality factor neglects the features of band nonparabolicity and bandgap, whose application is severely limited in narrow-gap TE materials. A unique quality factor, $B'_{\text{Kane}}$, is deliberately established here, which can break previous limitations and provide an effective method to predict and evaluate TE properties. Furthermore, a low lattice thermal conductivity, 0.17 Wm$^{-1}$K$^{-1}$ is achieved at 800 K. The intrinsic and extrinsic phonon scattering sources synergistically suppress phonon transport and achieve the ultralow lattice thermal conductivity. The intrinsic component stems from strong anharmonicity of an acoustic phonon with large Grüneisen parameter ($\gamma_G = 16$), localized low-frequency optical phonons (<0.6 THz), and low Debye temperature ($\Theta_D = 148$ K). Moreover, the extrinsic nanoscale lattice imperfections, including periodic defective stripes, nano-precipitates, dislocations, and Moiré fringes, facilitate to impede heat transport. This work could rekindle the hope and vision of lillianites as promising high-performance TE materials. Furthermore, the unique quality factor paves an attractive route to accelerate the exploration for TE compounds with resembling band characteristics.
Methods

Synthesis. Pb shots (99.999%), Ag shots (99.999%), Ga chunks (99.999%), In shots (99.999%), Se shots (99.999%), and I pieces (99.999%) were purchased from Sigma-Aldrich. Firstly, precursors of Pb$_{1-x}$M$_x$(Se$_x$I$_{1-x}$)$_3$ (M = Ga in Ag, Ag) were pressed into pellets in the glove box and then sealed. The pellets were then ball-milled in a glove box with the 3:5:2 mass ratio of the pellets, Ag chunks, and In shots. The powders were then heated to 450 °C for 4 h. The powders were then pressed into pellets in the glove box, which were then heated to 450 °C to form Pb$_{1-x}$M$_x$(Se$_x$I$_{1-x}$)$_3$ (M = Ga in Ag, Ag) for 10 h. The pellets were then cooled down to room temperature in the glove box. After the long-term ball-milling, the powders were pressed into pellets in the glove box. The pellets were subsequently characterized using X-ray diffraction, micro-X-ray fluorescence, and energy-dispersive spectrometry (EDS).

Characterization. The electronic and transport properties of Pb$_{1-x}$M$_x$(Se$_x$I$_{1-x}$)$_3$ (M = Ga in Ag, Ag) were determined using the Van der Pauw method (Bio-Rad Microscience, model MS-5000, USA). The Seebeck coefficient was measured using a three-point probe setup. The electrical conductivity was measured using a four-point probe setup. The thermal conductivity was determined using a laser flash method (DSC 1200, TA Instruments, USA). Room temperature carrier concentration was determined from the Hall coefficient measurement using the Van der Pauw method. The Seebeck coefficient and the thermal conductivity were determined using the van der Pauw method in Bio-Rad Microscience, model MS-5000, USA. High-temperature carrier concentration, Hall coefficient, and thermal conductivity were determined using the refined electronic band structure and the density of states.

Electronic structure and phonon calculations. First-principles density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package58. The generalized gradient approximation in the Perdew–Burke–Ernzerhof parameterization59 was used as the exchange-correlation functional. The cutoff energy was set to 400 eV which has been sufficient to guarantee accuracy. We used a primitive cell of Pb$_{1-x}$M$_x$(Se$_x$I$_{1-x}$)$_3$, including 24 atoms in modeling the electronic properties. The energy convergence threshold and force convergence threshold in the structural optimization were 10$^{-6}$ eV and 10$^{-4}$ eV Å$^{-1}$, respectively. A k-mesh of 5 × 5 × 5 was used to sample the Brillouin zone. The rigid band approximation was used to model the p-type and n-type Pb$_{1-x}$M$_x$(Se$_x$I$_{1-x}$)$_3$. Specifically, the electronic/hole doping in Pb$_{1-x}$M$_x$(Se$_x$I$_{1-x}$)$_3$ was achieved by adding extra electrons/holes to the system with the same amount of uniform positive/negative charge in the background. Within the framework of rigid band approximation, we find the overall shape of band structures are almost unchanged except for the Fermi level shift, hence we only show the calculated Fermi surface of the n-type and p-type Pb$_{1-x}$M$_x$(Se$_x$I$_{1-x}$)$_3$. In Fig. 2a of the main text. The resulting Fermi surfaces were calculated by using a very dense 45 × 45 × 15 k-mesh to ensure the accuracy of calculations for metallic states. To evaluate the lattice dynamic properties, we used the finite displacement supercell method to calculate the phonon spectrum and phonon density of states and used the quasi-harmonic method to calculate the Grünisen parameter. Both the finite displacement supercell method and quasi-harmonic method implemented in Phonopy were used. In addition, the finite displacement supercell method was used with the 3 × 3 × 1 supercell (216 atoms) of the primitive cell with a finite displacement of 0.1 Å. The crystal structures and displacement patterns were all visualized using VESTA software60. When computing the phonon density of states of mode-averaged Grünisen, we used a q-mesh of 20 × 20 × 20.

Data availability

The authors declare that all data supporting the findings of this work are available from the corresponding authors upon reasonable request.

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