Supplementary information

Realizing high thermoelectric performance in GeTe by defect engineering on cation sites

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1. First-principles calculation methods

The path to calculate band structure for rhombohedral and cubic GeTe is P–Γ–L–B–F–B₁–Z–Γ–X and K–Γ–L–U–W–X–W–U–L–Γ–K, respectively. The coordinates of high-symmetry points in the Brillouin zone are derived from the developed framework,¹ as shown in Table.S1. The maximum and secondary valance bands of GeTe-based materials, as well as the minimum conduction band, are important factors for thermoelectric properties. Therefore, parts of the band structures on the path of P–Γ–L–B (rhombohedral GeTe) and K–Γ–L–U–X (cubic GeTe)² containing these features are shown in Fig.1.

<table>
<thead>
<tr>
<th>Table.S1 Coordinates of high-symmetry points in Brillouin zone of rhombohedral and cubic GeTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>rhombohedral GeTe</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>P  (0.756, 0.372, 0.372)</td>
</tr>
<tr>
<td>Γ  (0, 0, 0)</td>
</tr>
<tr>
<td>L  (0.5, 0, 0)</td>
</tr>
<tr>
<td>B  (0.756, 0.5, 0.244)</td>
</tr>
<tr>
<td>F  (0.5, 0.5, 0)</td>
</tr>
<tr>
<td>B₁ (0.5, 0.244, -0.244)</td>
</tr>
<tr>
<td>Z  (0.5, 0.5, 0.5)</td>
</tr>
<tr>
<td>X  (0.372, 0, -0.372)</td>
</tr>
</tbody>
</table>

2. Phase structures

2.1 XRD patterns
Fig. S1 The XRD patterns of (a) Ge$_{1-x}$Ti$_x$Te ($x = 0, 0.005, 0.01, 0.015, 0.02$) series and (c) Ge$_{0.925+y}$Ti$_{0.015}$Bi$_{0.06}$Te ($y = -0.02, -0.01, 0, 0.02, 0.04$) series at RT. Composition dependent lattice parameters and volume for (b) Ge$_{1-x}$Ti$_x$Te and (d) Ge$_{0.925+y}$Ti$_{0.015}$Bi$_{0.06}$Te series based on the hexagonal unit cell at RT.

2.2 Lattice parameters for hexagonal, trigonal, and pseudo cubic GeTe unit cells

When describing the crystal structures of the rhombohedral GeTe, all three different lattice parameters / interaxial angles based on hexagonal, trigonal, and pseudo cubic GeTe unit cells are often used. As shown in Fig. S2(a), the hexagonal GeTe unit cell has lattice parameters $a$ and $c$, the trigonal GeTe unit cell has lattice parameter $a_2$ and interaxial angle $\alpha_2$, and the pseudo cubic GeTe unit cell has lattice parameter $a_1$ and interaxial angle $\alpha_1$. The coordinate of one kind of atom in a hexagonal unit cell is (0, 0, 0), (2/3, 1/3, 1/3), and (1/3, 2/3, 2/3). According to the coordinate
transformation from hexagonal coordinate to rectangular coordinate (Fig.S2(b)), the lattice parameters and interaxial angles based on the other two unit cells can be calculated according to the following formulas: 

\[ a_2 = \left| \overrightarrow{OA} \right|, \quad a_1 = \left| \overrightarrow{OE} \right|, \quad \cos \alpha_2 = \frac{\overrightarrow{OA} \cdot \overrightarrow{OB}}{|\overrightarrow{OA}| |\overrightarrow{OB}|}, \quad \cos \alpha_1 = \frac{\overrightarrow{OE} \cdot \overrightarrow{OF}}{|\overrightarrow{OE}| |\overrightarrow{OF}|}, \]

see **Table.S2**.

**Fig.S2** (a) The crystal structures of GeTe in hexagonal coordinate system O-abc (black axes) and rectangular coordinate system O-xyz (red axes), and the hexagonal, trigonal, and pseudo cubic GeTe unit cells. (b) Projection of the lattice on the ab/xy plane and the corresponding coordinates in two coordinate systems. OA, OB, and OC are the projection of trigonal GeTe’s edges and OD, OE, and OF are the projection of pseudo cubic GeTe’s edges.
Fig. S3 Composition-dependent (a) lattice parameters ratio ($c/a$) based on hexagonal unit cell, and (b) lattice parameter $a_2$ and interaxial angle $\alpha_2$ based on trigonal unit cell.
The lattice parameters of samples in this work based on hexagonal, trigonal, and pseudo cubic unit cells at room temperature

<table>
<thead>
<tr>
<th>Samples</th>
<th>Hexagonal unit cell</th>
<th>Trigonal unit cell</th>
<th>Pseudo cubic unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a (\text{Å}))</td>
<td>(c (\text{Å}))</td>
<td>(c/a)</td>
</tr>
<tr>
<td>Ge(_{1-x})Ti(_x)Te</td>
<td>(x = 0)</td>
<td>A0</td>
<td>4.1622</td>
</tr>
<tr>
<td></td>
<td>(x = 0.005)</td>
<td></td>
<td>4.1637</td>
</tr>
<tr>
<td></td>
<td>(x = 0.01)</td>
<td></td>
<td>4.1641</td>
</tr>
<tr>
<td></td>
<td>(x = 0.015)</td>
<td>A1</td>
<td>4.1669</td>
</tr>
<tr>
<td></td>
<td>(x = 0.02)</td>
<td></td>
<td>4.1661</td>
</tr>
<tr>
<td>Ge(<em>{0.94})Bi(</em>{0.06})Te</td>
<td>(x = -0.02)</td>
<td>A2</td>
<td>4.1947</td>
</tr>
<tr>
<td>Ge(<em>{0.925+y})Ti(</em>{0.015})Bi(_{0.06})Te</td>
<td>(y = -0.02)</td>
<td></td>
<td>4.1863</td>
</tr>
<tr>
<td></td>
<td>(y = -0.01)</td>
<td></td>
<td>4.1886</td>
</tr>
<tr>
<td></td>
<td>(y = 0)</td>
<td>A3</td>
<td>4.1933</td>
</tr>
<tr>
<td></td>
<td>(y = 0.02)</td>
<td>A4</td>
<td>4.1958</td>
</tr>
<tr>
<td></td>
<td>(y = 0.04)</td>
<td></td>
<td>4.1953</td>
</tr>
</tbody>
</table>

Trigonal unit cell

\[
\begin{align*}
\alpha_2 &= \sqrt{\frac{3a^2 + c^2}{3}} \\
\cos \alpha_2 &= \frac{\left| \frac{c^2}{9} - \frac{a^2}{6} \right|}{a_2^2} \\
\text{or} \\
\sin \frac{\alpha_2}{2} &= \frac{3}{2} \sqrt{\frac{1}{\sqrt{3} + \left( \frac{c}{a} \right)^2}} \\
\end{align*}
\]

Pseudo cubic unit cell

\[
\begin{align*}
\alpha_1 &= \sqrt{\frac{12a^2 + c^2}{3}} \\
\cos \alpha_1 &= \frac{\left| \frac{c^2}{9} - \frac{2a^2}{3} \right|}{a_1^2} \\
\text{or} \\
\sin \frac{\alpha_1}{2} &= \frac{3}{2} \sqrt{\frac{1}{\sqrt{3} + \left( \frac{c}{2a} \right)^2}} \\
\end{align*}
\]
3. Microstructure

Fig. S4 SEM images of the fractured surfaces of Ge$_{1-x}$Ti$_x$Te ($x = 0, 0.015, 0.02$) series.

Fig. S5 SE, BSE and Ge-mapping images of the polished surfaces for Ge$_{1-x}$Ti$_x$Te ($x = 0, 0.015, 0.02$).
Fig.S6  SE, BSE and Ge-mapping images of the polished surfaces for Ge$_{0.925+y}$Ti$_{0.015}$Bi$_{0.06}$Te ($y = -0.01, 0, 0.02$).
4. Thermoelectric properties

4.1 Electronic transport properties

Fig.S7 The temperature-dependent (a, d) conductivity $\sigma$, (b, e) Seebeck coefficient $S$, and (c, f) power factor $PF$ of $\text{Ge}_{1-x}\text{Ti}_x\text{Te}$ series and $\text{Ge}_{0.925+y}\text{Ti}_{0.015}\text{Bi}_{0.06}\text{Te}$ series, respectively.

4.1.1 Single parabolic band model

Based on the single parabolic band (SPB) approximation, the effective mass $m^*$ can be derived by:15, 16

$$F_j(\eta) = \int_{0}^{\infty} \frac{e^j}{1+\exp(\varepsilon-\eta)} d\varepsilon$$  \hspace{1cm} (S1)

$$S = \pm \frac{k_B}{e} \left[ \frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \eta \right]$$  \hspace{1cm} (S2)

$$m^* = \frac{\hbar^2}{2k_B T} \left[ \frac{n}{4\pi F_{1/2}(\eta)} \right]^{2/3}$$  \hspace{1cm} (S3)

$F_j(\eta)$ is the Fermi integral function and $\eta = E_F/k_B T$, which is related to the carrier concentration $n$. As it is considered that the GeTe-based materials basically obey phonon-dominated scattering, the scattering factor $r = -1/2$ is always taken.5, 16
Table S3: The electronic transport parameters of samples in this work at room temperature.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( n_H (10^{20} \text{ cm}^{-3}) )</th>
<th>( \mu_H (\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}) )</th>
<th>( \sigma (\text{S} \cdot \text{cm}^{-1}) )</th>
<th>( S (\mu\text{V} \cdot \text{K}^{-1}) )</th>
<th>( m^*/m_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge( _{1-x} )Ti( _x )Te</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( x = 0 )</td>
<td>A0</td>
<td>8.21</td>
<td>52.59</td>
<td>7032.02</td>
<td>26.12</td>
</tr>
<tr>
<td>( x = 0.005 )</td>
<td></td>
<td>8.01</td>
<td>46.09</td>
<td>6461.60</td>
<td>33.36</td>
</tr>
<tr>
<td>( x = 0.01 )</td>
<td></td>
<td>7.80</td>
<td>43.27</td>
<td>6077.52</td>
<td>35.15</td>
</tr>
<tr>
<td>( x = 0.015 )</td>
<td>A1</td>
<td>7.08</td>
<td>39.42</td>
<td>4745.08</td>
<td>43.87</td>
</tr>
<tr>
<td>( x = 0.02 )</td>
<td></td>
<td>8.08</td>
<td>42.11</td>
<td>5926.92</td>
<td>33.61</td>
</tr>
<tr>
<td>Ge( _{0.94} )Bi( _{0.06} )Te</td>
<td></td>
<td>3.85</td>
<td>40.86</td>
<td>2218.57</td>
<td>71.28</td>
</tr>
<tr>
<td>Ge( _{0.925+y} )Ti( _{0.015} )Bi( _{0.06} )Te</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( y = -0.02 )</td>
<td></td>
<td>5.75</td>
<td>20.08</td>
<td>1964.32</td>
<td>77.58</td>
</tr>
<tr>
<td>( y = -0.01 )</td>
<td></td>
<td>5.32</td>
<td>25.67</td>
<td>2177.20</td>
<td>72.44</td>
</tr>
<tr>
<td>( y = 0 )</td>
<td>A3</td>
<td>3.25</td>
<td>49.72</td>
<td>2415.30</td>
<td>70.18</td>
</tr>
<tr>
<td>( y = 0.02 )</td>
<td>A4</td>
<td>3.00</td>
<td>52.64</td>
<td>2410.81</td>
<td>75.03</td>
</tr>
<tr>
<td>( y = 0.04 )</td>
<td></td>
<td>2.81</td>
<td>45.37</td>
<td>2024.90</td>
<td>78.04</td>
</tr>
</tbody>
</table>

Since both \( S \) and \( \sigma \) are the function of carrier concentration and are related to each other, the transport coefficients \( \sigma_{E0} \) and the weighted mobility \( \mu_W \) are introduced to describe the intrinsic transport properties of materials.\(^5\), \(^17\) And they can be expressed as:

\[
\sigma = \sigma_{E0} \ln(1 + e^{\eta}) \tag{S4}
\]

\[
\sigma_{E0} = \frac{2^{3/2} e \pi (m_e k_B T)^{3/2}}{3h^3} \mu_W \tag{S5}
\]

\[
\mu_W = \mu_0 \left(\frac{m^*}{m_e}\right)^{3/2} \tag{S6}
\]

And \( k_B \), \( h \), and \( \eta \) are the Boltzmann constant, Planck constant, and the reduced Fermi level. It can be seen from the above formulas that the parameter \( \sigma_{E0} \) is a conductivity expression independent of the carrier concentration, which excludes the error of the carrier concentration in the Hall measurement. The \( \sigma_{E0} \) characterizes how well a
material conducts electricity for a given \( \eta \) (i.e., at a given \( n \)). The larger \( \sigma_{E0} \) generally reflects the good crystallinity of the material. The parameter \( \sigma_{E0} \) can be expressed by the weighted mobility \( \mu_{W} \), which is closely related to the effective mass. Therefore, the change in \( \mu_{W} \) can also explain the relationship between \( S \) and \( \sigma \), and the \( \mu_{W} \) can initially reflect the scale of \( PF \).

The \( \kappa_{e} \) is calculated according to the Wiedemann–Franz law \( \kappa_{e} = L\sigma T \), where \( L \) is the Lorenz number based on the SPB approximation:\textsuperscript{15, 18}

\[
L \equiv \left( \frac{k_B}{e} \right)^2 \left\{ \frac{(r+7/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} \right\}^2 \tag{S7}
\]

**Fig.S8** The temperature-dependent (a, d) transport coefficients \( \sigma_{E0} \), (b, e) weighted mobility \( \mu_{W} \), and (c, f) Lorenz number \( L \) of Ge\(_{1-x}\)Ti\(_{x}\)Te series and Ge\(_{0.925+y}\)Ti\(_{0.015}\)Bi\(_{0.06}\)Te series, respectively. The \( \mu_{W} \) is compared with the doped-GeTe\textsuperscript{17, 19} and other works\textsuperscript{10, 20} in (b) and (e).
4.2 Thermal transport properties

Table S4 The heat capacity $C_p$ and density $\rho$ used for each sample in this work

<table>
<thead>
<tr>
<th>$x$</th>
<th>Ge$_{1-x}$Ti$_x$Te</th>
<th>$C_p$ (J·g$^{-1}$·K$^{-1}$)</th>
<th>$\rho$ (g·cm$^{-3}$)</th>
<th>$y$</th>
<th>Ge$<em>{0.925+y}$Ti$</em>{0.015}$Bi$_{0.06}$Te</th>
<th>$C_p$ (J·g$^{-1}$·K$^{-1}$)</th>
<th>$\rho$ (g·cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>A0</td>
<td>0.2491</td>
<td>6.11</td>
<td>-0.02</td>
<td>0.2391</td>
<td>6.16</td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td></td>
<td>0.2493</td>
<td>6.02</td>
<td>-0.01</td>
<td>0.2394</td>
<td>6.21</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td></td>
<td>0.2494</td>
<td>6.02</td>
<td>0</td>
<td>A3</td>
<td>0.2398</td>
<td>6.15</td>
</tr>
<tr>
<td>0.015</td>
<td>A1</td>
<td>0.2496</td>
<td>5.93</td>
<td>0.02</td>
<td>A4</td>
<td>0.2405</td>
<td>6.12</td>
</tr>
<tr>
<td>0.02</td>
<td></td>
<td>0.2498</td>
<td>5.97</td>
<td>0.04</td>
<td></td>
<td>0.2412</td>
<td>6.13</td>
</tr>
<tr>
<td>Ge$<em>{0.94}$Bi$</em>{0.06}$Te</td>
<td>A2</td>
<td>0.2394</td>
<td>6.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.2.1 Debye–Callaway model for calculating the lattice thermal conductivity

According to the Debye–Callaway model,$^{21-24}$ $\kappa_L$ can be defined as a sum of the spectral lattice thermal conductivity $\kappa_S(f)$ from different frequencies ($f$):

$$\kappa_L = \int \kappa_S(f) \, df = \frac{1}{3} \int_0^{f_D} C_S(f)v_g(f)^2\tau_{\text{tot}}(f) \, df \quad (S8)$$

The $\kappa_S(f)$ is determined by the spectral heat capacity $C_S(f)$, the phonon group velocity $v_g(f)$, and the total relaxation time $\tau_{\text{tot}}(f)$. For simple approximation, $v_g(f)$ is assumed as a constant value $v_s$ (sound velocity). The Debye frequency $f_D$ can be expressed as:

$$f_D = \frac{k_B\theta_D}{\hbar} = \left(\frac{6\pi^2N}{V}\right)^{1/3} v_s \quad (S9)$$

where $\theta_D$ is Debye temperature, $N$ is the number of atoms in a unit cell volume, $V$ is the unit-cell volume, $k_B$ is the Boltzmann constant and $\hbar$ is the reduced Plank constant. The $C_S(f)$ can be expressed as:

$$C_S(f) = \frac{3k_Bf^2}{2\pi^2v_s^3} \quad (S10)$$

Thus, $\kappa_L$ and $\kappa_S$ are calculated by

$$\kappa_L = \frac{k_B}{2\pi^2v_s}\left(\frac{k_BT}{\hbar}\right)^2 \int_0^{\theta_D/T} \tau_{\text{tot}}(x) \frac{x^4\exp(x)}{[\exp(x)-1]^2} dx \quad (S11)$$
\[
\kappa_S = \left(\frac{k_B^2}{2\pi^2 v_s}\right)^3 \tau_{\text{tot}}(x) \left(\frac{x \exp(x)}{[\exp(x)-1]^2}\right)
\]  
(S12)

where \(x = hf/k_B T\) is the reduced phonon frequency. According to Matthiessen’s rule,\textsuperscript{25} \(\tau_{\text{tot}}(x)\) is the reciprocal sum of the relaxation times from different phonon scattering mechanisms including the Umklapp phonon-phonon scatterings (U), normal phonon-phonon scatterings (N), grain boundaries scatterings (B), point defects scatterings (PD), nano-precipitates phonon scatterings (NP) and stacking fault phonon scatterings (SF).

So, \(\tau_{\text{tot}}\) is calculated by

\[
\tau_{\text{tot}}^{-1} = \tau^{-1}_U + \tau^{-1}_N + \tau^{-1}_B + \tau^{-1}_{\text{PD}} + \tau^{-1}_{\text{NP}} + \tau^{-1}_{\text{SF}} + \cdots
\]  
(S13)

The \(\tau_U^{-1}\) is calculated by

\[
\tau_U^{-1} = \frac{\hbar y^2 f^2 T}{M_{\text{av}} v_s^2 \theta_D} \exp\left(-\frac{\theta_D}{3T}\right)
\]  
(S14)

where \(M_{\text{av}}\) and \(\gamma\) are the average atomic mass and Grüneisen parameter respectively.

The \(\tau_N^{-1}\) can be simply expressed as \(\tau_U^{-1}\) with an additional factor \(\beta\), as

\[
\tau_N^{-1} = \beta \tau_U^{-1}
\]  
(S15)

The \(\tau_B^{-1}\) is calculated by

\[
\tau_B^{-1} = \frac{v_s}{D}
\]  
(S16)

where \(D\) is the average grain size of polycrystalline materials.

The \(\tau_{\text{PD}}^{-1}\) is calculated by

\[
\tau_{\text{PD}}^{-1} = \frac{V_{\text{av}} f^4}{4\pi v_s^3} \Gamma
\]  
(S17)

where \(V_{\text{av}}\) is the average atomic volume. The disorder scattering parameter \(\Gamma = \Gamma_M + \Gamma_S\) describes the mass and atomic size contrast with the lattice, which are calculated by\textsuperscript{26, 27}
\[ \Gamma_M = \frac{\sum_{i=1}^{n} c_i \left( \frac{M^i_{\text{av}}}{M_{\text{av}}^i} \right)^2 f^i_1 f^i_2 \left( \frac{M^i_{\text{av}}}{M^i} \right)^2}{\sum_{i=1}^{n} c_i} \] (S18)

\[ \Gamma_S = \frac{\sum_{i=1}^{n} c_i \left( \frac{M^i_{\text{av}}}{M_{\text{av}}^i} \right)^2 f^i_1 f^i_2 \left( \frac{r^i_{\text{av}}}{r^i} \right)^2}{\sum_{i=1}^{n} c_i} \] (S19)

where \( n \) is the number of sublattices, \( c_i, M_{\text{av}}^i \) and \( r_{\text{av}}^i \) are the relative fraction, average mass, and atomic radius for the \( i \)th sublattice respectively. For GeTe, there are two different sublattices (the Ge site and the Te site); thus, \( n = 2 \) and \( c_1 = c_2 = 1 \). The \( M_{\text{av}}^i, r_{\text{av}}^i \), and \( f^i \) represent the \( j \)th atomic mass, atomic radius, and atomic fraction on the \( i \)th sublattice, respectively.

The \( \tau_{\text{NP}}^{-1} \) is calculated by\(^{28,29}\)

\[ \tau_{\text{NP}}^{-1} = v_3 \left[ (2\pi R_{\text{NP}}^2)^{-1} + \left( \pi R_{\text{NP}}^2 \frac{4}{9} \left( \frac{\Delta \rho}{\rho} \right)^2 \left( \frac{f R_{\text{NP}}}{v_3} \right)^4 \right)^{-1} \right] N_{\text{NP}} \] (S20)

where \( R_{\text{NP}} \) and \( N_{\text{NP}} \) are the radius and number density for the nano-precipitates, \( \rho \) and \( \Delta \rho \) are the matrix density and density difference between the precipitate and matrix.

The \( \tau_{\text{SF}}^{-1} \) is calculated by\(^{30}\)

\[ \tau_{\text{SF}}^{-1} = 0.7 \frac{a^2}{v_3} \gamma^2 f^2 N_{\text{SF}} \] (S21)

where \( a \) is the lattice parameter based on c-GeTe and \( N_{\text{SF}} \) is the number of stacking faults induced by herringbones domain boundaries\(^{23}\) or planar vacancies\(^{28}\) crossing a line of unit length. The parameters for modelling \( \kappa_L \) in this work are shown in Table.S5 and Table.S6.
Table S5 Parameters for modelling the lattice thermal conductivity

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grüneisen parameter $\gamma$</td>
<td>1.56$^{31}$</td>
</tr>
<tr>
<td>Sound velocity $v_s$ (m·s$^{-1}$)</td>
<td>1967$^{31}$</td>
</tr>
<tr>
<td>Debye temperature $\theta_D$ (K)</td>
<td>194.88</td>
</tr>
<tr>
<td>Lattice parameter $a$ (Å)</td>
<td>5.986</td>
</tr>
<tr>
<td>Average atomic mass $M_{av}$ (kg)</td>
<td>$1.6625 \times 10^{-25}$</td>
</tr>
<tr>
<td>Grain size $D$ (µm)</td>
<td>50</td>
</tr>
<tr>
<td>Matrix density $\rho$ (g·cm$^{-3}$)</td>
<td>6.0$^28$</td>
</tr>
<tr>
<td>Density difference between matrix and precipitates $\Delta \rho$ (g·cm$^{-3}$)</td>
<td>0.7$^28$</td>
</tr>
<tr>
<td>Radius for the nano-precipitates Ge $R_{NP}$ (nm)</td>
<td>55$^{6}$</td>
</tr>
<tr>
<td>Number density of nano-precipitates $N_{NP}$ (m$^{-3}$)</td>
<td>$3 \times 10^{18}$ ref$^{28}$</td>
</tr>
<tr>
<td>Number of stacking faults crossing a line of unit length $N_{SF}$ (m$^{-1}$)</td>
<td>$1 \times 10^6$ (fitted)</td>
</tr>
</tbody>
</table>

Table S6 Parameters for modelling point defect scattering. Based on the elasticity theory,$^{32, 33}$ the longitudinal/transverse sound velocity $v_i = a(\delta/M_{av})^{1/2}$, where $\delta$ is the force constant in the lattice. The $a$ and $\delta$ are assumed to be constant because of the same structure. The average sound velocity $v_s = [(2v_t^{-3} + v_l^{-3})/3]^{-1/3}$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$M_{av}$ (10$^{-25}$ kg)</th>
<th>$v_t$ (m·s$^{-1}$)</th>
<th>$v_l$ (m·s$^{-1}$)</th>
<th>$v_s$ (m·s$^{-1}$)</th>
<th>$\theta_D$ (K)</th>
<th>$\Gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeTe</td>
<td>1.6625</td>
<td>1780$^{31}$</td>
<td>2930$^{31}$</td>
<td>1967$^{31}$</td>
<td>194.88</td>
<td>0</td>
</tr>
<tr>
<td>Ge$<em>{0.995}$Ti$</em>{0.005}$Te</td>
<td>1.6614</td>
<td>1780.55</td>
<td>2930.90</td>
<td>1967.29</td>
<td>194.91</td>
<td>0.00964</td>
</tr>
<tr>
<td>Ge$<em>{0.99}$Ti$</em>{0.01}$Te</td>
<td>1.6604</td>
<td>1781.10</td>
<td>2931.81</td>
<td>1967.90</td>
<td>194.97</td>
<td>0.01912</td>
</tr>
<tr>
<td>Ge$<em>{0.985}$Ti$</em>{0.015}$Te</td>
<td>1.6594</td>
<td>1781.65</td>
<td>2932.72</td>
<td>1968.51</td>
<td>195.03</td>
<td>0.02844</td>
</tr>
<tr>
<td>Ge$<em>{0.98}$Ti$</em>{0.02}$Te</td>
<td>1.6583</td>
<td>1782.21</td>
<td>2933.63</td>
<td>1969.12</td>
<td>195.09</td>
<td>0.03761</td>
</tr>
<tr>
<td>Ge$<em>{0.94}$Bi$</em>{0.06}$Te</td>
<td>1.7304</td>
<td>1744.71</td>
<td>2871.92</td>
<td>1927.70</td>
<td>190.99</td>
<td>0.085 (fitted)</td>
</tr>
<tr>
<td>Ge$<em>{0.925}$Ti$</em>{0.015}$Bi$_{0.06}$Te</td>
<td>1.7273</td>
<td>1746.27</td>
<td>2874.48</td>
<td>1929.42</td>
<td>191.16</td>
<td>0.15 (fitted)</td>
</tr>
<tr>
<td>Ge$<em>{0.945}$Ti$</em>{0.015}$Bi$_{0.06}$Te</td>
<td>1.7394</td>
<td>1740.21</td>
<td>2864.50</td>
<td>1922.72</td>
<td>190.49</td>
<td>0.17 (fitted)</td>
</tr>
</tbody>
</table>

4.2.2 Cahill–Watson–Pohl (CWP) model for calculating the minimum lattice thermal conductivity

The lower limit to the lattice thermal conductivity of this model $\kappa_{CWP}$ is derived from the Einstein’s random-walk model, but replacing Einstein temperature/frequency
with oscillators defined within the Debye model, which can be calculated as shown below:\textsuperscript{34}

\[
\kappa_{\text{Lmin}} = \kappa_{\text{CWP}} = \frac{k_B}{2\pi^2 v_s} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{\theta D/T} \frac{x^4 \exp(x)}{[\exp(x)-1]^2} \, dx
\] (S22)

**Fig.S9** The temperature-dependent (a, d) total thermal conductivity $\kappa_{\text{total}}$, (b, e) electronic thermal conductivity $\kappa_e$, and (c, f) lattice thermal conductivity $\kappa_{\text{L}}$ of Ge$_{1-x}$Ti$_x$Te series and Ge$_{0.925+y}$Ti$_{0.015}$Bi$_{0.06}$Te series, respectively.

**Fig.S10** The spectral lattice thermal conductivity ($\kappa_S$) as a function of phonon frequency ($f$) based on different scatterings of Ge$_{1-x}$Ti$_x$Te series.
4.3 Quality factor $B$ and $ZT$

The $ZT$ can be treated as a function of two independent variables: $\eta$ (reduced electron chemical potential) and the material quality factor $B$. The $\eta$ is related to doping and temperature, but $B$ just dependent on temperature and retains only the inherent material properties that determine $ZT$:35

\[
B = \left(\frac{k_B}{e}\right)^2 \frac{\sigma_{\eta_0}}{\kappa_L} T
\]  
(S23)

Above all, $ZT$ can be calculated by the $\eta$–dependent parameters:35

\[
ZT = \frac{S^2 \sigma T}{\kappa_L + \kappa_e} = \frac{S^2}{\kappa_L + L} = \frac{S^2(\eta)}{\sigma_{\eta_0} \ln(1 + e^{\eta/T}) + L(\eta)} = \frac{S^2(\eta)}{B \ln(1 + e^{\eta/T}) + L(\eta)} 
\]  
(S24)

Fig.S11 The temperature-dependent $ZT$ of (a) Ge$_{1-x}$Ti$_x$Te series compared with Ti-doping samples in references3, 36, 37 and (b) Ge$_{0.925+y}$Ti$_{0.015}$Bi$_{0.06}$Te series. (c) The $ZT_{\text{max}}$ vs. $\eta$ relation of Ge$_{1-x}$Ti$_x$Te at different $B$, compared with other works.3, 17, 19, 36, 37
4.4 Repeated thermoelectric properties measurement

Fig.S12 The temperature-dependent (a) $\sigma$, (b) $S$, (c) $\kappa_{\text{total}}$, and (d) ZT for the repeated thermoelectric properties measurement for the A4 sample.

References:


