**Rational Design from Material to Device Enables Efficiency of 10.5% Based on Thermoelectric (Bi, Sb)$_2$Te$_3$ and Mg$_3$(Bi, Sb)$_2$ for Power Generation**

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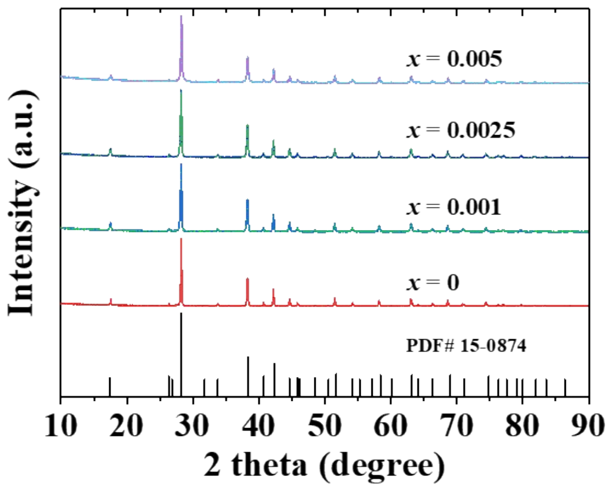


Figure S1. The XRD pattern of Li$_x$(Bi$_{0.4}$Sb$_{1.6}$)$_{1-x}$Te$_3$ samples.

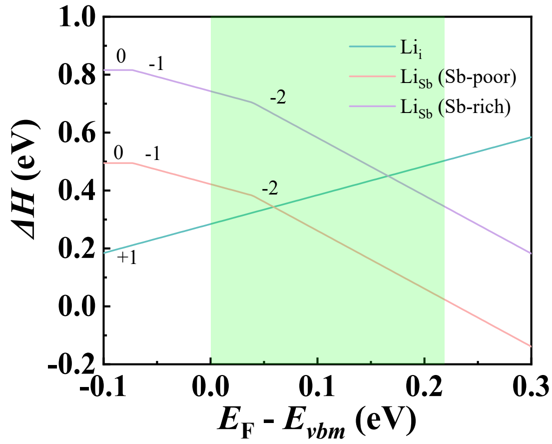


Figure S2. Formation enthalpy ($\Delta H$) of $Li_i$, $Li_{Sb}$(Sb-poor), and $Li_{Sb}$(Sb-rich) in $Sb_2Te_3$ as a function of $E_F$-$E_{vbm}$ value.

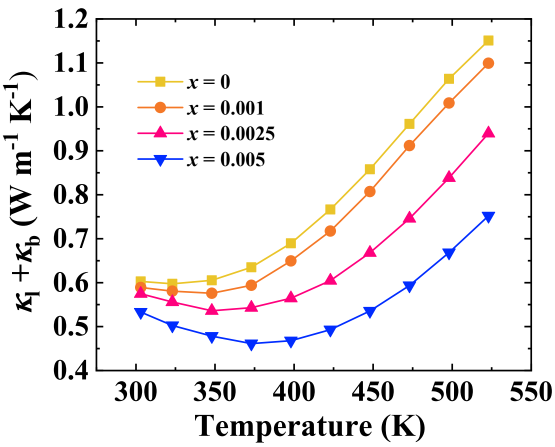


Figure S3. The sum of lattice thermal conductivity and bipolar thermal conductivity of $Li_x(Bi_{0.4}Sb_{1.6})_{1-x}Te_3$ samples.

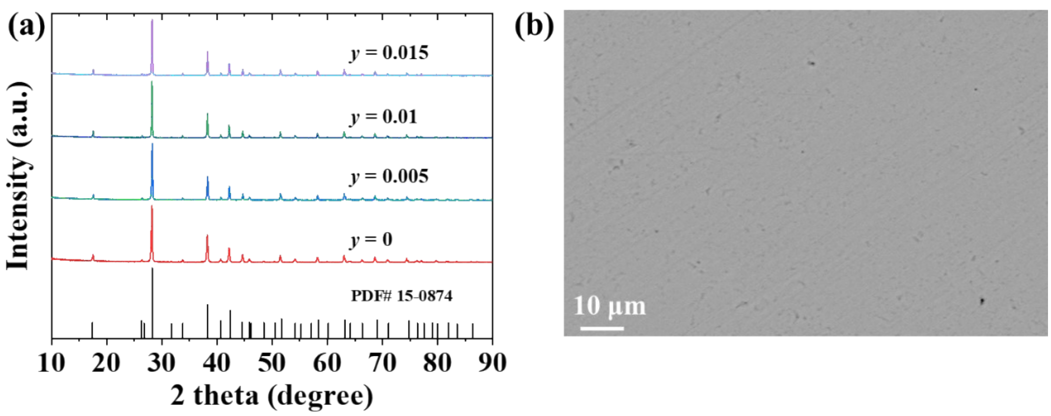

Figure S4. (a) The XRD pattern of $Li_{0.0025}(Bi_{0.4}Sb_{1.6})_{0.9975}Te_{3+y}$ samples ($y = 0.005$, 0.01, 0.015). (b) Backscattered electron (BSE) image of $Li_{0.0025}(Bi_{0.4}Sb_{1.6})_{0.9975}Te_{3.01}$ sample.

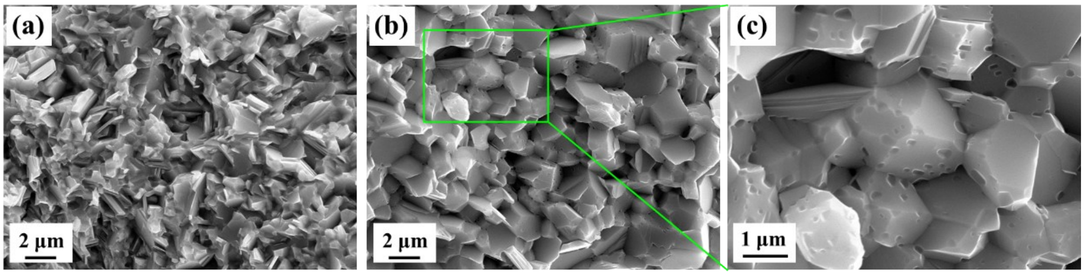


Figure S5. Fractured secondary electron (SE) images of (a) $Li_{0.0025}(Bi_{0.4}Sb_{1.6})_{0.9975}Te_3$, (b) $Li_{0.0025}(Bi_{0.4}Sb_{1.6})_{0.9975}Te_{3.01}$. (c) The enlarged view of the selected interface area in (b).

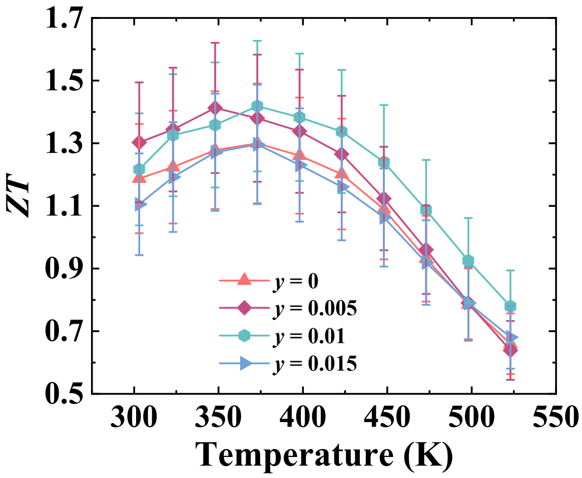


Figure S6. The *ZT* value of $Li_{0.0025}(Bi_{0.4}Sb_{1.6})_{0.9975}Te_{3+y}$ samples with uncertainty.

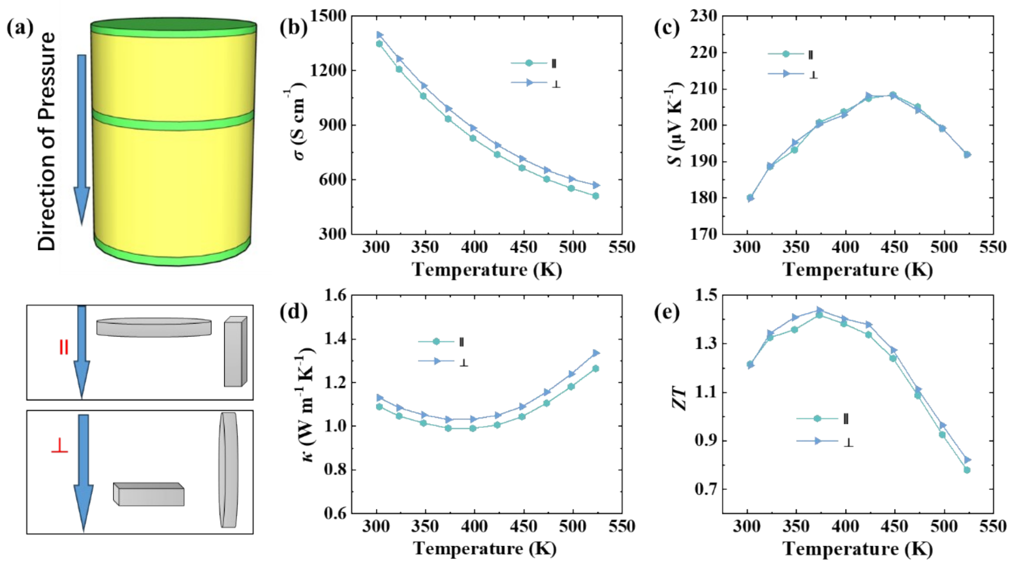


Figure S7. (a) Schematic diagram of sampling positions in two different directions. (b-e) The TE properties along two directions (perpendicular and parallel).

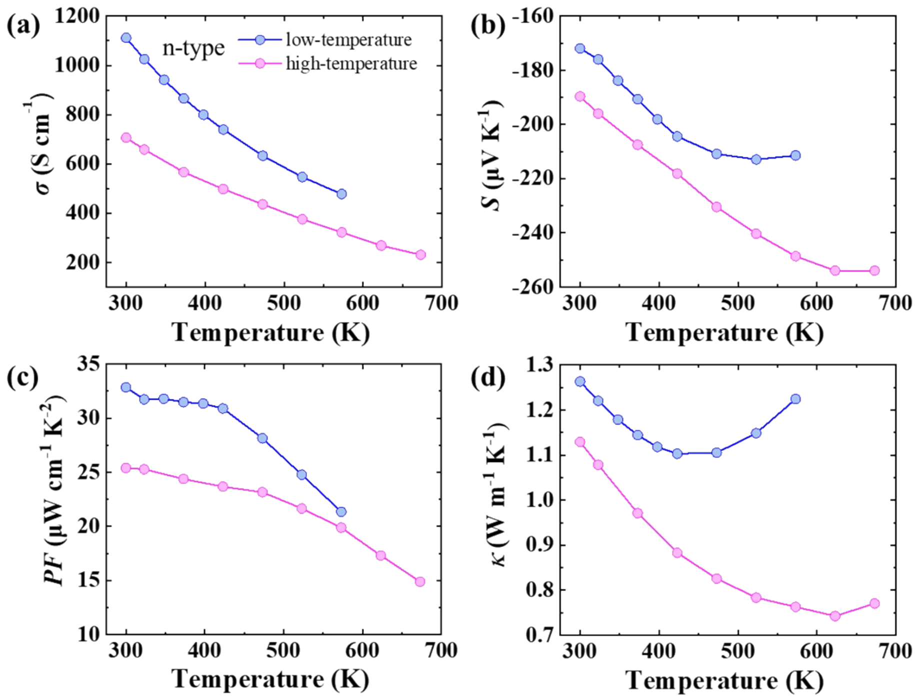


Figure S8. The thermoelectric properties for $Mg_{3.2}Sb_{0.5}Bi_{1.495}Mn_{0.02}Te_{0.005}$ and $Mg_{3.2}Sb_{1}Bi_{0.995}Mn_{0.02}Te_{0.005}$: (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, and (d) thermal conductivity.

**Note S1:**

**3D finite element model:**

According to the energy conservation equation and charge continuity equation under steady-state conditions:

$$\nabla\vec{q} = \dot{q}$$

$$\nabla\vec{j} = 0$$

and the thermoelectric coupling constitutive equation

$$\vec{q} = [\alpha]T\vec{j} - [\kappa]\nabla T$$

$$\vec{j} = -[\sigma]\nabla\varphi - [\sigma][\alpha]\nabla T$$

The governing equations describing the temperature and potential distribution and the thermoelectric coupling effect can be obtained:

$$\nabla([\kappa]\nabla T) + \frac{\vec{j}}{\sigma} - T\vec{j}\left(\frac{\partial\alpha}{\partial T}\right)\nabla T - T\vec{j}(\nabla\alpha)_T = 0$$

$$\nabla([\sigma]\nabla\varphi + [\sigma][\alpha]\nabla T) = 0$$

where $\vec{q}$ is the heat flux vector, $\dot{q}$ is the rate of heat production per unit volume, $\vec{j}$ is the current density vector, $[\alpha]$ is the Seebeck coefficient matrix, $[\kappa]$ is the thermal conductivity coefficient matrix, $[\sigma]$ is the electrical conductivity coefficient matrix.

When a current value is given, the potential distribution and temperature distribution can be obtained by solving the above equation, and then the output voltage ($V$), output power ($P$) and heat absorption at the hot side ($Q_h$) can be obtained by mathematical operations. The thermoelectric conversion efficiency ($\eta$) is calculated by the following formula.

$$\eta = \frac{P}{Q_h} = \frac{IV}{Q_h} \times 100\%$$

The $I$-$P$ and $I$-$\eta$ curves can be obtained by changing the current value in the loop, and the $P_{max}$ and $\eta_{max}$ can be obtained by optimizing the current.

**Boundary conditions:**

Thermal boundary conditions:

$$-\vec{n}\cdot\vec{q} = 0$$

$$T = T_0$$

$$-\vec{n}\cdot\vec{q} = q_0$$

$$q_0 = h\cdot\Delta T$$

where $\vec{n}$ is normal vector, $\vec{q}$ is heat flux vector, T is temperature, $T_0$ is ambient temperature, h is coefficient of heat transfer, $\Delta T$ is temperature difference.

Electrical boundary conditions:

$$\int_{\partial\Omega} \vec{J}\,\vec{n}\,dS = I_0$$

$$V=0$$

$$\vec{n}\vec{J}_1 = h_c(V_1 - V_2)$$

$$\vec{n}\vec{J}_2 = h_c(V_2 - V_1)$$

where $\vec{J}$ is current density, V is voltage, and h is conductivity value per unit area. V=0 represents ground contact.

The meshing type is Hexa dominant as follows. The number of mesh is 42000 for the single pair.

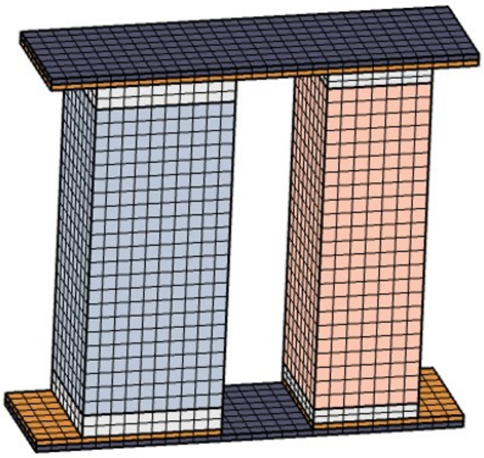

Figure S9. Thermoelectric module with grid division.

Table S1. Details regarding material parameters used in the simulation.

| Sample | Description | Thermal conductivity ($W\ m^{-1}\ K^{-1}$) | Electrical resistivity ($\Omega$ m) |
|---|---|---|---|
| Cu | electrode | 380 | $6\times10^{-7}$ |
| $Al_2O_3$ | Insulting ceramic plate | 33-14 (293 K-673 K) | --- |

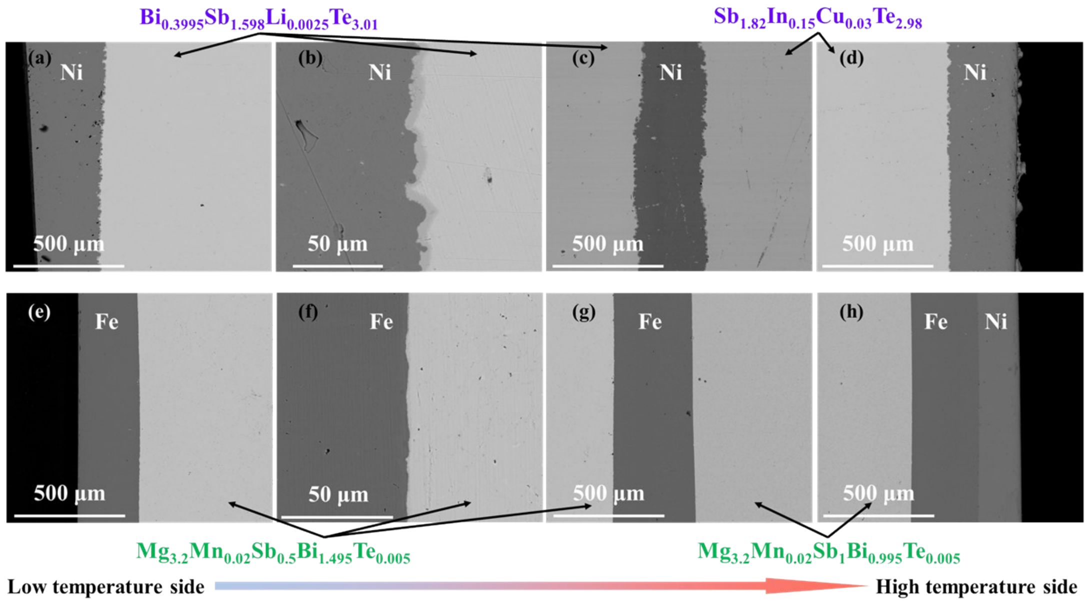


Figure S10. The BSE image of p-type junction (a-d) and n-type junction (e-h). (b) and (f) are enlarged images of (a) and (e).

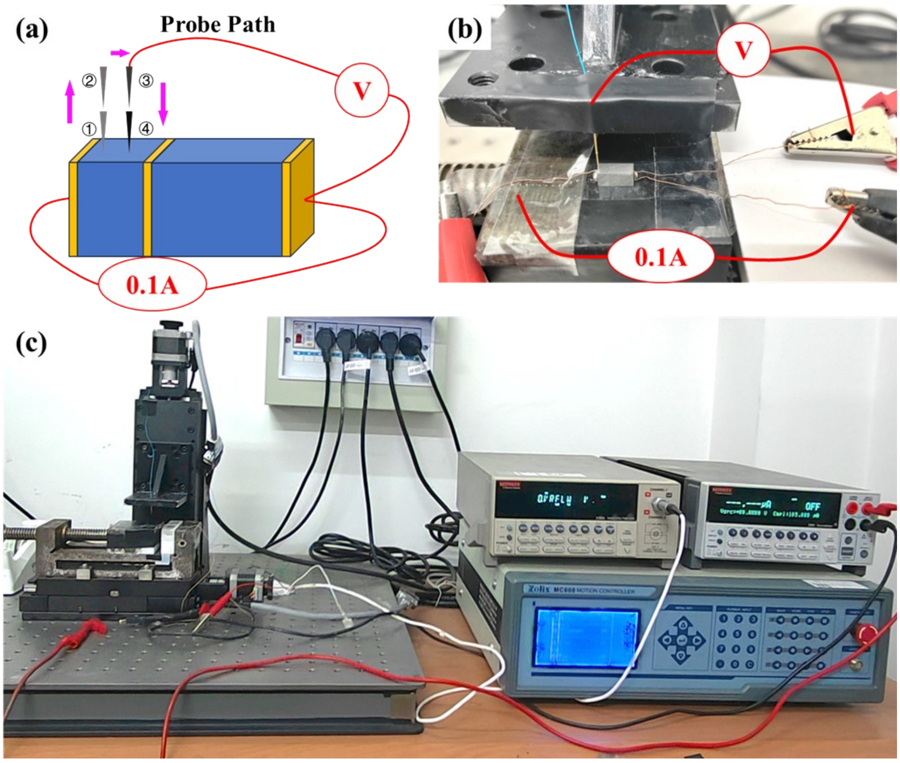


Figure S11. (a) The schematic diagram of the probe path. (b) The optical photo during testing (c) The optical photo of the overall device for testing contact resistivity.

**Note S2:**

Once a temperature difference (hot side temperature $T_h$, cold side temperature $T_c$) is established, the corresponding device output voltage $V_{out}$ and voltage drop $V_S$ on the standard resistor $R_S$ under different loads can be measured by changing the load resistance value under this temperature difference. The output current $I_{out}$ of the module can be obtained through the formula $I_{out} = V_S/R_S$. Heat output from the cold side $Q_{out}$ is obtained through the formula, $Q_{out} = \lambda\times(T_1\text{-}T_2)\times\mathrm{L}\times\mathrm{W}/\mathrm{H}$, where $\lambda$ is the thermal conductivity of the heat flux meter, L and W are the length and width of the cross-section of the heat flux meter, and H is the vertical distance between the two temperature measurement points $T_1$ and $T_2$. According to the formula $\eta = P_{out}/(P_{out} + Q_{out})\times100\%$, efficiency is calculated.

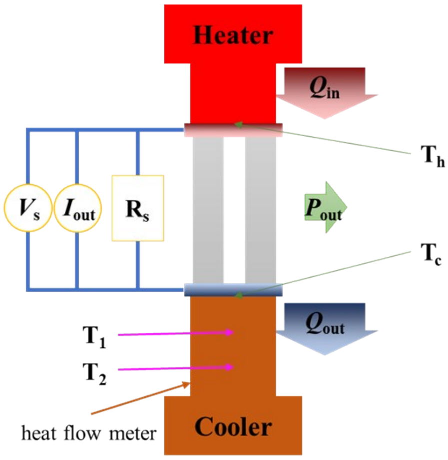

Figure S12. The schematic diagram of the conversion efficiency evaluation system for thermoelectric power generation modules.