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**Entropy as a gene-like performance indicator promoting thermoelectric materials**

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#### Abstract text

High-throughput explorations of novel thermoelectric materials based on the Materials Genome Initiative paradigm only focus on digging into the structure-property space using non-global indicators to design materials with tunable electrical and thermal transport properties. As the genomic units, following the bio-gene tradition, such indicators include localized crystal structural blocks in real space or band degeneracy at certain points in the reciprocal space. However, this non-global approach does not consider how real materials differentiate from others. Here, we have successfully developed a strategy of using entropy as the global gene-like performance indicator that shows how multi-component thermoelectric materials with high entropy can be designed *via* a high-throughput screening method. Optimizing entropy works as an effective guide to greatly improve the thermoelectric performance through either a significantly depressed lattice thermal conductivity down to its theoretical minimum value and/or *via* enhancing the crystal structure symmetry to yield large Seebeck coefficients. The entropy engineering using multi-component crystal structures or other possible techniques provides a new avenue for an improvement of the thermoelectric performance beyond the current methods and approaches.

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**Main Text**

In response to the global energy crisis and the debilitating impact of fossil fuels on the environment, thermoelectric (TE) materials have attracted worldwide attention for their ability to collect and convert industrial waste heat into useful electricity. A criterion for what constitutes a high performing TE material is the dimensionless thermoelectric figure of merit  $zT$ , defined as  $zT = \alpha^2 \sigma T / \kappa$ , where  $\alpha$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity, and  $T$  is the absolute temperature. Strong correlations among the above transport parameters limit the materials base of thermoelectricity to a few classic TE materials, and the  $zT$  values have remained limited to a range of 1-2 in the past decades<sup>[1-3]</sup>. To meet the endlessly growing demands, the Materials Genome Initiative has been used for the fast design and screening of new thermoelectric materials by tailoring the real-space (R-space) structural building blocks or band degeneracy at certain reciprocal-space (K-space) points as a genome-like performance indicator based on first principles calculations<sup>[4,5]</sup>.

In thermodynamics, entropy ( $S$ ) measures the large number of microscopic configurations of a given material's macrostate from a global point of view. The entropy in a material can be enhanced through introducing element doping and alloying<sup>[2]</sup> various atomic vibration states<sup>[3,6]</sup>, liquid-like ionic migrations<sup>[7]</sup> or hierarchical structures<sup>[8]</sup>. Maximizing the entropy in a material makes a significant impact on the material's microstructure and macroscopic properties clearly beyond doping or band engineering within limited R- or K-space, which is especially useful for thermoelectrics requiring the optimization of multiple inter-related physical quantities at one given material state. Entropy indeed acts as an overall performance indicator to evaluate TE properties, just like a virtual but unique "gene" beyond

localized crystal structural blocks in R-space or band degeneracy at certain K-space points. A particular example is using multi-component alloying that specially alters configurational entropy, as shown in Figure 1A and Figure 1B. Compared with simple compounds characterized by single-component atoms located at respective atomic positions, multi-component materials have several structural components located at the same atomic sites and thus have highly tunable entropy capable of strongly scattering lattice phonons and potentially enhancing the crystal structure symmetry to yield good electronic properties. However, there is currently no effective criterion to predict and screen high performance multi-component TE materials due to the complexity of the crystal structure and chemical bonds in such materials. Since the solvent atoms are usually homogeneously distributed in materials, attempts to form a multi-component structure, i.e., a solid solution with multiple components, result in a material that has similar chemical bonds as the matrix material. This fact prompted us to develop an elastic model to study the stability of multi-component TE materials. We found that the maximum entropy for given multi-component materials depends on the overall material's solubility parameter  $\delta$  that is associated with the material's shear modulus, lattice constants and mismatch in the atomic radius (see below). For a multi-component material with given  $\delta$  value, it is very easy to find the maximum entropy based on Figure 1C. Then the high-throughput calculation for multi-component TE materials with the desired entropy is performed, and several candidate materials with the  $zT$  values significantly higher than in the matrix are identified (see Figure 1D). As an example, the maximum  $zT$  is up to 1.6 and 2.23 in (Cu/Ag)(In/Ga)Te<sub>2</sub>- and Cu<sub>2</sub>(S/Se/Te)-based multi-component TE materials, respectively (see in Supporting Information).

In multi-component materials (see Figure 1A), the substituted atoms ( $A'$ ,  $A''$ ...) in equivalent lattice sites definitely change the material's total free energy although they have similar chemical bonds and atomic coordination as the framework atom  $A$ . Because the substituted atoms ( $A'$ ,  $A''$ ...) have different atomic size and electronegativity compared to the matrix element ( $A$ ), the enthalpy change ( $\Delta H_{\text{total}}$ ) is simply considered as a combination of the internal strain energy ( $\Delta H_S$ ) due to atomic size mismatch and fluctuations of the internal ionic field energy ( $\Delta H_C$ ) arising from the electron cloud redistribution according to the Hume-Rothery rules<sup>[17]</sup>. In addition, the total energy is lowered by the entropy caused by multiple components located at the same atomic sites. Formally, the total free energy change ( $\Delta E$ ) is given by  $\Delta E = \Delta H_S + \Delta H_C - \Delta S \times T$ . Following Boltzmann's hypothesis, the configurational entropy ( $\Delta S$ ) is given by<sup>[18]</sup>

$$\Delta S = k_B \ln \Omega = -N_A k_B \sum_{i=1}^n x_i \ln x_i, \quad \sum_{i=1}^n x_i = 1, \quad (1)$$

where  $k_B$  is the Boltzmann constant,  $\Omega$  is the number of atomic occupation probability,  $n$  is the number of the substituted components,  $x_i$  is the mole content of the  $i$ -th component, and  $N_A$  is Avogadro's number. In semiconductors, the magnitude of  $\Delta H_C$  is very small (at the level of 0.01~0.1  $k_B T$ /f.u. at 300 K, see Table S1 in Supporting information) and thus can be ignored. Therefore, the change in enthalpy is dominated by the internal strain energy ( $\Delta H_S$ ) that is determined by the average shear modulus and the mismatch in the unit cell (see Equation S7 in Supporting information).

For a two-component TE semiconducting solid solution  $(1-x)AB + xA'B \rightarrow A_{1-x}A'_x B$ , the calculated change in enthalpy and atomic solubility reasonably agree with the

*ab initio* calculations and experimental observations (see in Supporting Figure S1 and Figure 2A). We then define a parameter  $\delta = \bar{G}\bar{R}^*(\Delta R^*)^2/Z$  with units of  $\text{GPa}\cdot\text{\AA}^3$  as a criterion for judging the atomic solubility. Here  $\bar{G}$  is the average shear modulus,  $R^*$  is the effective lattice constant (defined by  $R^* = \sqrt{\frac{a^2+b^2+c^2}{3}}$  for an orthorhombic structure and  $\sqrt{\frac{(2a)^2+c^2}{3}}$  for a hexagonal structure, where  $a$ ,  $b$  and  $c$  are the parameters of a unit cell, or the parameters of a supercell that is built close to a sphere),  $\bar{R}^*$  is the average effective lattice constant and  $\Delta R^*$  is the difference in the effective lattice constant between  $AB$  and  $A'B$  ( $\Delta R^* = |R^*_{AB} - R^*_{A'B}|$ ), and  $Z$  is the number of formula units in one unit cell or the corresponding supercell. For example, a supercell with lattice parameters of  $(4a^* \times 4b^* \times c^*)$  is required to run such calculations for hexagonal  $\text{Bi}_2\text{Te}_3$ -based materials, where  $a^*$ ,  $b^*$ , and  $c^*$  are the lattice parameters of a conventional unit cell. With the above definitions, a low  $\delta$  value means a low internal strain energy and high atomic solubility, and *vice versa*. As shown in Figure 2A, two-component solutions with  $\delta$  below  $2.08 \text{ GPa}\cdot\text{\AA}^3$  can form complete solid solutions, such as  $(\text{Cd}/\text{Hg})\text{Te}$ ,  $\text{Pb}(\text{S}/\text{Se})$ ,  $(\text{Rh}/\text{Ir})\text{Sb}_3$ ,  $\text{Cu}_2(\text{S}/\text{Se})$ ,  $\text{Cu}_2(\text{Se}/\text{Te})$ ,  $(\text{Bi}/\text{Sb})_2\text{Te}_3$ ,  $(\text{Cu}/\text{Ag})\text{InTe}_2$  and  $(\text{Cu}/\text{Ag})\text{GaTe}_2$ , while systems with  $\delta$  larger than  $2.08 \text{ GPa}\cdot\text{\AA}^3$  can only result in partial solid solutions, such as  $(\text{Co}/\text{Ir})\text{Sb}_3$ ,  $(\text{Co}/\text{Rh})\text{Sb}_3$ ,  $\text{Bi}_2(\text{Se}/\text{Te})_3$  and  $\text{Pb}(\text{Se}/\text{Te})$ . The systems with very large  $\delta$  values, such as  $\text{Pb}(\text{S}/\text{Te})$ , have very low atomic solubility.

Ternary or multi-component solid solution systems can be regarded as being derived from a quasi-binary reaction of the type  $(1-x)A_{1-y}A''_yB + xA'_{1-y}A''_yB \rightarrow (A_{1-x}A'_x)_{1-y}A''_yB$ , where  $A_{1-y}A'_yB$ ,  $A'_{1-y}A''_yB$  are the quasi-matrices dissolving a third component  $A''B$  with an initial content  $y$ . Our

calculations show that the component  $A''B$  actually relaxes the crystal lattice by reducing the internal strain energy by the magnitude of the suppressed strain energy determined mainly by  $y$  under a relation  $(1-y)^{3.5}$  (see Equation S11 in Supporting information). By accumulating all the reactions of binary solid solutions and sub-reactions of quasi-binary solutions, the total free energy change in an equimolar multi-component solution is

$$\Delta E = MN_A \cdot \bar{\delta} \cdot \left[ \sum_{i=2}^n \left(1 - \frac{1}{i}\right) \frac{1}{i} \cdot \left(\frac{i}{n}\right)^{3.5} \right] - N_A k_B T \ln(n), \quad (2)$$

where  $\bar{\delta}$  is the average  $\delta$  value of all separate binary solutions and  $M$  is a dimensionless constant with an approximate value of 7.34 in semiconductors. The first term in Equation 2 represents the change in enthalpy, referred to the internal strain energy, and the second term represents the energy from the configurational entropy. Figure 2B shows the energy variation when increasing the number of substituted components. Due to the rapidly increasing configurational entropy, a complete solid solution is obtained when the number of substituted components is large enough, regardless of the intrinsic nature of the components. This is similar to cases of high entropy-stabilized alloys and oxides in which five or more substituted components with far different atomic sizes and electronegativities leads to a single *bcc* or *fcc* phase<sup>[19,20]</sup>. However, the number of substituted components in TE semiconductors usually does not exceed 4 or 5. Therefore, in order to form a complete solid solution, the parameter  $\bar{\delta}$  should be less than 2.92, 3.58, and 4.12 GPa·Å<sup>3</sup> for the multi-component materials with 3, 4, and 5 components, respectively.

Our model shown above provides a direct criterion by which to screen and identify candidate multi-component TE materials with high configurational entropy. The current elastic model works well for materials with identical crystal structures; thus, high-throughput selection can be performed based on the experimental lattice parameters or atomic sizes, and the materials' shear moduli. We looked at various typical TE materials with cubic or cubic-like structures, the physical properties of which are listed in Supporting Table S2 and Table S4. Our calculations show that (Ti/Zr/Hf)NiSn and (Ti/Zr/Hf)CoSb can form equimolar ternary solid solutions, which is reasonably consistent with the experiments<sup>[21]</sup>. Furthermore, our model shows that  $\text{Cu}_2(\text{S}/\text{Se}/\text{Te})$  can form equimolar ternary solid solutions, while (Cu/Ag)(In/Ga)Te<sub>2</sub> and (Mn/Ge/Sn/Pb)Te can be realized as equimolar quaternary solutions. In contrast, Pb(S/Se/Te) has a too large value of  $\bar{\delta}$  to form equimolar ternary solid solutions.

Aiming to form solid solutions and test our predictions experimentally, we selected and synthesized several candidate multi-component TE materials, e.g., (Cu/Ag)(In/Ga)Te<sub>2</sub>-,  $\text{Cu}_2(\text{S}/\text{Se}/\text{Te})$ -, and (Mn/Ge/Sn/Pb)Te-based materials. X-ray diffraction analysis (XRD) shows all these materials to be phase pure without any obvious impurity phases (see Figures S3-S5). Electron Probe Microanalysis (EPMA) reveals that all elements are homogeneously distributed throughout the entire sample without any obvious agglomeration of elements (see in Supporting information). Furthermore, we have performed a 3D-atom probe tomography (APT) analysis to check the distribution of elements on the atomic-scale. Taking  $\text{Cu}_2(\text{S}/\text{Se}/\text{Te})$ -based multi-component materials as an example, the ionic mass spectrum of  $\text{Cu}_2\text{S}_{1/3}\text{Se}_{1/3}\text{Te}_{1/3}$  is shown in Figure 3A. The reconstructed 3D atomic maps based on the ionic mass spectrum are shown in Figure 3B. No aggregation of chalcogen atoms is observed.



This is further confirmed by the analysis of the nearest-neighbor (NN) atomic distributions, as shown in Figure 3C. The measured NN atomic distance histograms of each element are completely overlapped with the calculated curves (black curve in Figure 3C) based on the assumption that all elements are randomly distributed in the sample. All these results unequivocally demonstrate that all components are extremely homogeneous on the macro-scale, the nano-scale, and even on the atomic-scale. This is consistent with our calculations because these multi-component TE materials are phase-pure and thermodynamically stable.

Beyond the high-throughput screening and identification of candidate multi-component TE materials, TE properties are also significantly optimized and improved by increasing the material's entropy because it is a gene-like performance indicator. Increasing entropy in a TE material definitely leads to a greater number of microscopic configurations that may significantly introduce extra phonon disorder and open a new window to tune electrons, and thus affect both electrical and thermal transports. First is a significantly decreased lattice thermal conductivity. Such a large number of microscopic configurations in the materials with high entropy implies the existence of numerous lattice defects that provide extra phonon point defect scattering to suppress heat conduction. Especially for the multi-component materials shown above, there exist strong mass and strain fluctuations among the various components that significantly depress the material's lattice thermal conductivity<sup>22</sup>. With the continuous enhancement of entropy by increasing the solute components, the phonon disorder is incessantly increased and finally may reach a critical state like a glass. Correspondingly, the lattice thermal conductivity is depressed down to the glass limit in a solid, i.e., the

minimum lattice thermal conductivity. This is illustrated in Figure 4A. When the number of solid solution components increases, a huge suppression in the lattice thermal conductivity is observed, with the value approaching the minimum thermal conductivity<sup>[6]</sup> ( $\kappa_{min}$ ) in solids. The required number of components to reach  $\kappa_{min}$  varies for different materials. For the systems with high initial thermal conductivity, such as half-Heusler alloys<sup>[22]</sup>, skutterudites<sup>[23]</sup> and chalcopyrites<sup>[24]</sup>, the required number of substituted components to reach  $\kappa_{min}$  at 300 K is at least 5 or 6. For example, the room temperature  $\kappa_L$  of around 6-9  $\text{Wm}^{-1}\text{K}^{-1}$  in the matrix of  $\text{CuInTe}_2$  or  $\text{CuGaTe}_2$  is reduced to 2-4  $\text{Wm}^{-1}\text{K}^{-1}$  for the two-component materials with an entropy of 0.69  $k_B/\text{f.u.}$ , and down to 1.4  $\text{Wm}^{-1}\text{K}^{-1}$  for the four-component materials with an entropy of 1.38  $k_B/\text{f.u.}$  in this study. For matrix compounds with a moderate initial  $\kappa_L$ , such as  $(\text{Ca/Yb})\text{Zn}_2\text{Sb}_2$ <sup>[25]</sup>,  $\text{Mg}_2(\text{Si/Ge/Sn})$ <sup>[26-28]</sup>,  $\text{Bi}_2(\text{S/Se/Te})_3$ <sup>[29]</sup> and  $\text{Pb}(\text{S/Se/Te})$ <sup>[9-11]</sup>, 3 or 4 different kinds of substituted components are required to reach  $\kappa_{min}$ . For example, the room temperature  $\kappa_L$  of around 2.5  $\text{Wm}^{-1}\text{K}^{-1}$  in the  $\text{PbTe}$  matrix<sup>[9]</sup> is reduced to 1.0  $\text{Wm}^{-1}\text{K}^{-1}$  (just a little higher than the  $\kappa_{min}$  in  $\text{PbTe}$ ) for three-component materials with an entropy of 0.7  $k_B/\text{f.u.}$ <sup>[11]</sup>. For matrix materials having an extremely low  $\kappa_L$ , such as liquid-like materials  $\text{Cu}_2(\text{S/Se/Te})$  and  $(\text{Cu/Ag})_8\text{Ge}(\text{Se/Te})_6$ , the  $\kappa_L$  values are already nearly equal to the  $\kappa_{min}$ , and these values are maintained in essentially all multi-component materials.

The second effect concerns the increasing configurational entropy that may enhance the crystal structure symmetry and thus improve electronic transport properties, especially for matrix materials having low symmetry structures. When the configurational entropy increases, environmental heat activations and fluctuations lead to more disordered and homogenous atomic distributions throughout the crystal lattice in materials possessing multi-component-

occupied identical atomic sites. This may increase the material's crystal symmetry. When the entropy is high enough, all multi-component materials tend to possess a high symmetry cubic structure. When the entropy is not so high, the symmetry of the structure may still be improved or any structural transition temperature may be reduced. This has been shown in many experiments<sup>[30,31]</sup>, and is confirmed here by our studies. For example, single  $\text{Cu}_2\text{X}$  ( $\text{X} = \text{Te, Se or S}$ ) compounds generally crystallize with the monoclinic structure at room temperature ( $P2_1/c$  for  $\text{Cu}_2\text{S}$ <sup>[32]</sup> and  $C2/c$  for  $\text{Cu}_2\text{Se}$ <sup>[33]</sup>), but the symmetry is increased to hexagonal in  $\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}$ ,  $\text{Cu}_2\text{S}_{0.5}\text{Se}_{0.5}$ , and  $\text{Cu}_2\text{S}_{1/3}\text{Se}_{1/3}\text{Te}_{1/3}$  when the configuration entropy is above  $0.6 k_B/\text{f.u.}$  (see in Supporting Figure S3). This promotion of the crystal symmetry in multi-component TE materials definitely changes their electronic band structure. High symmetry crystal structures tend to form multiband electronic bands or overlapped bands near the Fermi level due to the high symmetry inducing more equivalent positions in both real and reciprocal space. This can significantly increase the electronic density-of-states and effective mass, and thus enhance the Seebeck coefficient. For the systems with initially high crystal symmetry, such as  $(\text{Cu}/\text{Ag})(\text{In}/\text{Ga})\text{Te}_2$ , there is no obvious trend in the variation of the Seebeck coefficient because there is either no structural variation or the structural variation is very weak (see Figure 4B). However, for the systems with initially low crystal symmetry, the Seebeck coefficient of multi-component TE materials is obviously superior to the matrix compounds. Taking  $\text{Cu}_2(\text{S}/\text{Se}/\text{Te})$  as an example, when the carrier concentration is in the range from  $1.0 \times 10^{21}$  to  $3.0 \times 10^{21} \text{ cm}^{-3}$ , the Seebeck coefficient at 300 K is merely  $20\text{-}40 \mu\text{VK}^{-1}$  in the monoclinic structure, but it significantly improves to  $70\text{-}130 \mu\text{VK}^{-1}$  in the hexagonal structure having large entropy (see Figure 4B). Specifically, the carrier concentrations of the

matrix compound  $\text{Cu}_{2-x}\text{Se}$  ( $1.51 \times 10^{21} \text{ cm}^{-3}$ ) and the multi-component solid solution compound  $\text{Cu}_2\text{S}_{1/3}\text{Se}_{1/3}\text{Te}_{1/3}$  ( $1.50 \times 10^{21} \text{ cm}^{-3}$ ) are almost the same, but the room temperature Seebeck coefficient of  $\text{Cu}_2\text{S}_{1/3}\text{Se}_{1/3}\text{Te}_{1/3}$  ( $130 \mu\text{V/K}$ ) is obviously larger than that in  $\text{Cu}_{2-x}\text{Se}$  ( $40 \mu\text{V/K}$ ). According to the single parabolic band model (see Supporting Figure S9), the effective mass of monoclinic  $\text{Cu}_2(\text{X} = \text{Te}, \text{Se} \text{ or } \text{S})$  compounds is mostly below  $2.0 m_e$ , but it is greatly enhanced to above  $4.5 m_e$  in the hexagonal structure. Such an enhancement means an increase in the electronic density of states, which is completely consistent with the upgrading of the material's crystal structure symmetry. Although there are other factors that affect the electronic properties of a material, it is very clear that the Seebeck coefficient is improved in multi-component TE materials with increased entropy based on our data.

According to our elastic model, high-throughput predictions have been made regarding the discovery of multi-component thermoelectric material systems, including  $(\text{Cu/Ag})(\text{In/Ga})\text{Te}_2$ ,  $\text{Cu}_2(\text{S/Se/Te})$  and  $(\text{Mn/Ge/Sn/Pb})\text{Te}$ . Good consistency between calculations and experiment reveals that the model presented here is reliable and effective for the screening, design, and realization of new multi-component materials. We also expect this model to work for other materials, beyond thermoelectrics. The enhanced  $zT$  values up to 1.6 and 2.23 in respective  $(\text{Cu/Ag})(\text{In/Ga})\text{Te}_2$ - and  $\text{Cu}_2(\text{S/Se/Te})$ -based multi-component TE materials demonstrate that the entropy is a gene-like performance indicator that has two significant effects on tuning and optimizing electronic and thermal transport properties, i.e., to lower  $\kappa_L$  by the presence of local mass and strain fluctuations and to improve the Seebeck coefficient by enhancing the crystal symmetry. While the magnitude of the two effects

depends on the initial state of the matrix compounds, entropy engineering emerges as a very effective approach to design and realize high performance TE materials.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

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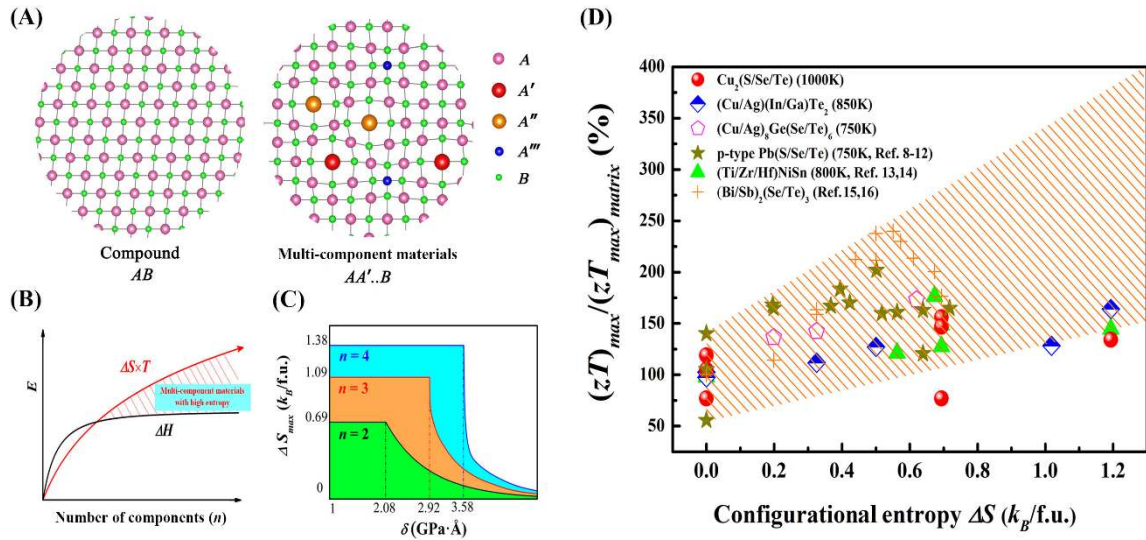
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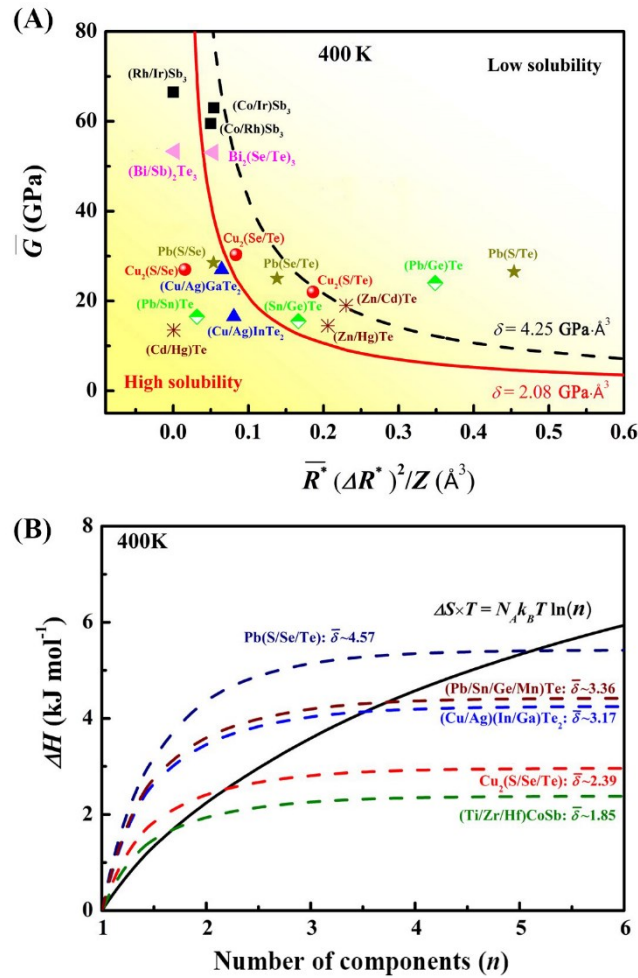
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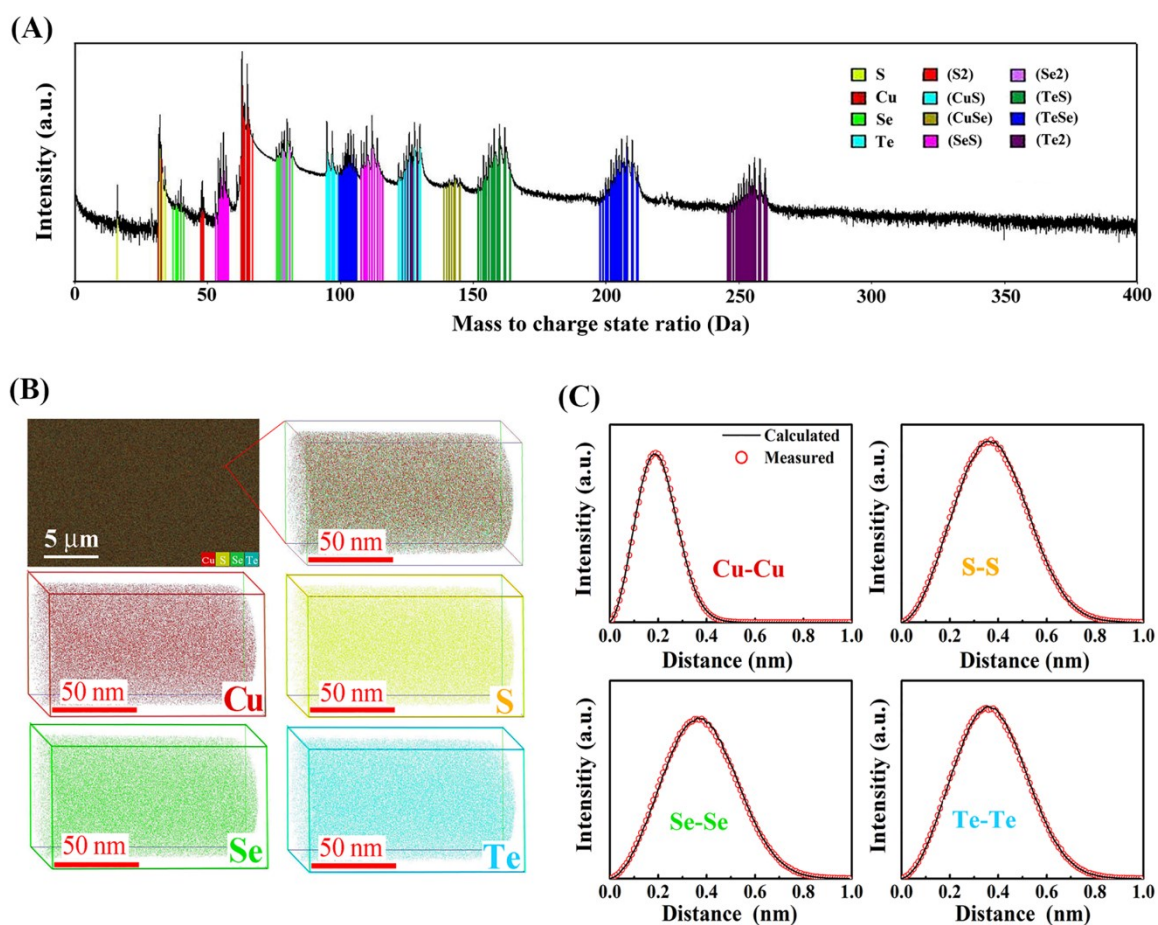




**Figure 1.** Enhanced TE properties through entropy engineering. (A) Schematic diagram of the lattice framework in multi-component materials compared to an ordinary binary compound. (B) Schematic diagram of the entropy engineering with multi-component TE materials. The red line and black line represent energies contributed by the configurational entropy ( $\Delta S$ ) and by the formation enthalpy ( $\Delta H$ ), respectively. (C) The maximum configurational entropy (in units of  $k_B$  per formula unit) as a function of a material's solubility parameter  $\delta$  for given multi-component TE materials, where  $n$  is the number of components. (D) Maximum TE Figure of merit ( $zT$ ) as a function of the configurational entropy in  $Cu_2(S/Se/Te)$ -,  $(Cu/Ag)(In/Ga)Te_2$ -, and  $Cu_8Ge(Se/Te)_6$ -based multi-component TE materials. The  $zT$ s of  $Pb(S/Se/Te)$ - and  $(Ti/Zr/Hf)NiSn$ -based materials are taken from Ref. 8-16.

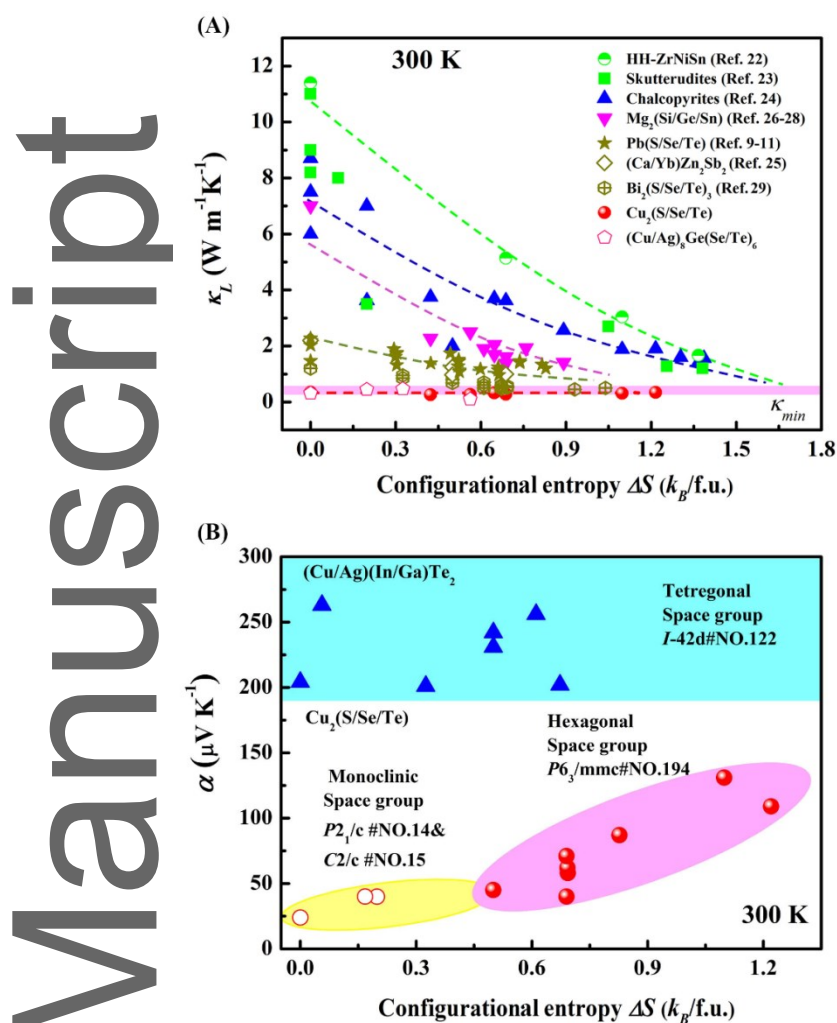


**Figure 2.** Energies in multi-component TE materials. (A) Average shear modulus ( $\bar{G}$ ) as a function of  $\bar{R}^2 (\Delta R^*)^2 / Z$  in two-component solutions. The red and black lines represent the curves with the solubility of 0.5 and 0.01, respectively. (B) Internal strain energy as a function of the number of components ( $n$ ). The black solid line represents the energy contributed by configurational entropy. The dashed lines illustrate the relation in particularly useful TE materials.



**Figure 3.** 3D-Atomic Probe Tomography detection for  $\text{Cu}_2\text{S}_{1/3}\text{Se}_{1/3}\text{Te}_{1/3}$ . (A) Ionic mass spectrum, (B) 3D-atomic maps, and (C) nearest-neighbor atomic distribution histograms of the four elements. The black lines represent the calculated curves assuming all elements are homogeneously and randomly distributed in the material.

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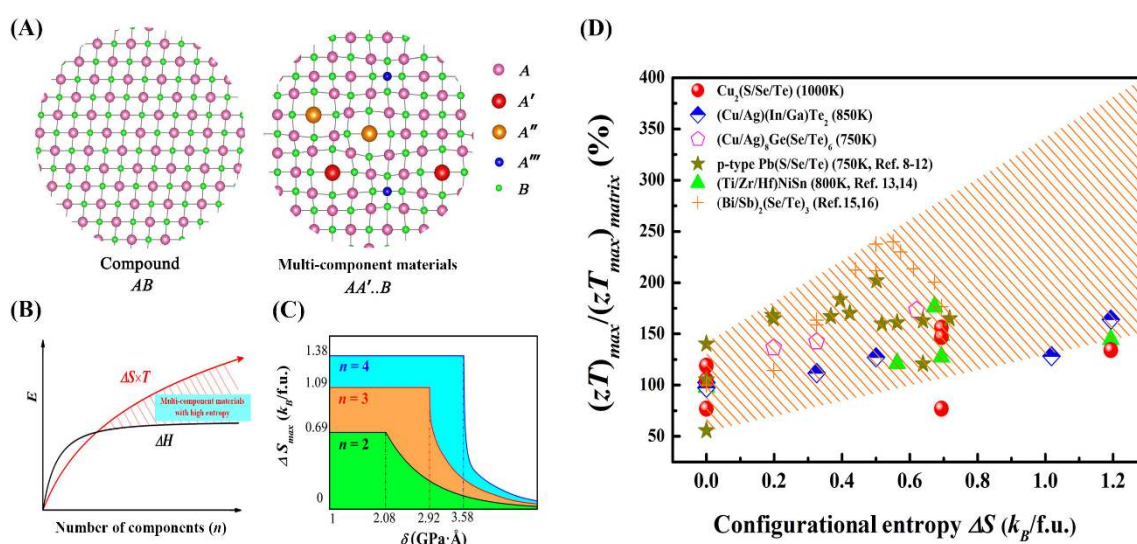


**Figure 4.** Lowered lattice thermal conductivity ( $\kappa_L$ ) and improved Seebeck coefficient ( $\alpha$ ) in multi-component TE materials. (A)  $\kappa_L$  as a function of the configurational entropy. The red zone presents the  $\kappa_{min}$ , and the dashed lines are guides to the eyes. (B) Room temperature  $\alpha$  as a function of the configurational entropy in (Cu/Ag)(In/Ga)Te<sub>2</sub>- and Cu<sub>2</sub>(S/Se/Te)-based multi-component materials with respective carrier concentrations in the range of  $(1.0 - 2.0) \times 10^{19}$  and  $(1.0 - 3.0) \times 10^{21}$  cm<sup>-3</sup>. The data for (Cu/Ag)(In/Ga)Te<sub>2</sub>- and Cu<sub>2</sub>(S/Se/Te)-based materials are listed in Supporting Table S3.

thermoelectric, entropy, high-throughput

Ruiheng Liu<sup>†</sup>, Hongyi Chen<sup>†</sup>, Kunpeng Zhao, Yuting Qin, Binbin Jiang, Tiansong Zhang, Gang Sha, Xun Shi<sup>\*</sup>, Ctirad Uher, Wenqing Zhang<sup>\*</sup>, Lidong Chen<sup>\*</sup>

### Entropy as a gene-like performance indicator promoting thermoelectric materials



A strategy of using entropy as the global gene-like performance indicator is developed to show how multi-component thermoelectric materials with high entropy can be designed *via* a high-throughput screening method. Optimizing entropy works as an effective guide to greatly improve the thermoelectric performance through either a significantly depressed lattice thermal conductivity down to its theoretical minimum value and/or *via* enhancing the crystal structure symmetry to yield large Seebeck coefficients.

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## Supporting Information

### Entropy as a gene-like performance indicator promoting thermoelectric materials

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#### Experimental Section.

Cu shot (99.999%, Alfa Aesar), Ag shot (99.999%, Alfa Aesar), S pieces (99.9999%, Alfa Aesar), Se shot (99.999%, Alfa Aesar), Ge pieces (99.999%, Alfa Aesar), Ga shot (99.9999%, Alfa Aesar), Mn, Sn, and Pb shots (99.999%, Alfa Aesar), Te shot (99.999%, Alfa Aesar). For  $\text{Cu}_{2-z}\text{Ag}_z\text{S}_{1-x-y}\text{Se}_x\text{Te}_y$ , the sealed tubes were slowly cooled to 650 °C from 1100 °C at a rate of 10 °C/h and then kept at 650 °C for 8 days. The obtained ingots were crushed into fine powders and followed by Spark Plasma Sintering (Sumitomo SPS 2040) under a pressure of 60 MPa at 600 °C for 20 min. For  $\text{Cu}_{1-y}\text{Ag}_y\text{In}_{1-x}\text{Ga}_x\text{Te}_2$ , the silica tubes were quenched into ice cold water from 1100 °C and then annealed at 650 °C for 5 days. The obtained ingots were crushed into fine powders followed by hot press sintering (MRF Inc., USA) under a pressure of 65 MPa at 650 °C for 30 min. For  $\text{Mn}_x\text{Ge}_y\text{Sn}_z\text{Pb}_{1-x-y-z}\text{Te}$ , the silica tubes were slowly cooled to 550 °C at a rate of 10 °C/h from 1000 °C and kept at 550 °C for 3 days. The obtained ingots were crushed into fine powders and followed by hot press sintering (MRF Inc., USA) under a pressure of 65 MPa at 550 °C for 30 min. For  $(\text{Cu}_{1-y}\text{Ag}_y)_8\text{Ge}(\text{Se}_{1-x}\text{Te}_x)_6$ , the silica tubes were quenched into ice cold water from 1100 °C and then annealed at 600 °C for 5 days. The obtained ingots were

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crushed into fine powders and followed by Spark Plasma Sintering (Sumitomo SPS 2040) under a pressure of 60 MPa at 550 °C for 20 min.

X-ray diffraction (XRD) analysis (Cu  $K\alpha$ , D8 ADVANCE, Bruker Co.Ltd) was employed to examine phase purity and crystal structures. Phase composition analysis at the micrometer scale was carried out by Electron Probe Microanalysis (EPMA, ZEISS Supra 55). APT was performed at 20 K in a CAMECA instrument (LEAP 4000X Si) by applying ultraviolet laser pulsing with a wavelength of 355 nm, an energy of 10 pJ, a pulse repetition rate of 200 kHz, and a target ion collection rate of 5%. We used CAMECA IVAS 3.6.8 software to analyze the data. Samples in the form of sharp needles for APT analysis were prepared by a focused ion beam lift-off methodology (Zeiss Augraga FIB/SEM) by using Ga ion beam milling. High-temperature Seebeck coefficient ( $\alpha$ ) and electrical conductivity ( $\sigma$ ) were measured using a ZEM-3 instrument (ULVAC Co. Ltd.) under a sealed chamber with a small amount of helium gas. The thermal diffusivity ( $\lambda$ ) and heat capacity ( $C_p$ ) from 300 K to 1000 K were measured using the laser flash method (Netzsch, LFA427) and differential scanning calorimetry (Netzsch DSC 404F3), respectively. The density ( $d$ ) was measured using the Archimedes method. The thermal conductivity was calculated from  $\kappa = \lambda \times C_p \times d$ . Room temperature Hall coefficient ( $R_H$ ) measurements were performed using Quantum Design PPMS by sweeping the magnetic field up to 3 T in both positive and negative directions. The hole concentration ( $p$ ) is calculated from  $p = 1/qR_H$ , where  $q$  is the elementary charge.

For a binary solution reaction



the change in enthalpy  $\Delta H_{A_{1-x}A'_xB}$  is

$$\Delta H_{A_{1-x}A'_xB} = H_{A_{1-x}A'_xB} - (1-x)H_{AB} - xH_{A'B} = x \int_1^x \Delta H_{cell} \cdot \frac{N_A}{Z} dt + (1-x) \int_0^x \Delta H_{cell} \cdot \frac{N_A}{Z} dt, \quad S2$$

where  $N_A$  is the Avogadro's number, and  $\Delta H_{cell}(t)$  is the enthalpy change due to one  $A'B$  unit cell replacing one  $AB$  unit cell in  $A_{1-t}A'_tB$ .  $\Delta H_{cell}(t)$  has two components, the internal strain energy  $\Delta H_{cell}^S(t)$  caused by the atomic size mismatch and the internal ionic field energy  $\Delta H_{cell}^C(t)$  caused by electron cloud redistribution.

Assuming  $A_{1-t}A'_tB$  is an elastic continuous sphere with a vacancy of one unit cell, the internal strain energies by inserting  $A'B$  ( $\Delta H_{A'B}^S(t)$ ) or  $AB$  ( $\Delta H_{AB}^S(t)$ ) unit cells into the vacancy are calculated by using the elastic deformation equation<sup>[1,2]</sup>

$$\Delta H_{A'B}^S(t) = \int_0^\infty \frac{1}{2} \bar{\epsilon} \bar{\sigma} 4\pi r^2 dr = 8\pi G_{AA'} R_{AA'}^3 \chi_{A'}^2 c_{A'}, \quad S3$$

where  $\chi_{A'} = \frac{R_{A'} - R_{AA'}}{R_{AA'}}$ ,  $c_{A'} = \frac{3K_{A'}}{4G_{AA'} + 3K_{A'}}$ ,  $K_{A'}$  is the bulk modulus of  $A'B$ ,  $R_{AA'}(t)$  and  $G_{AA'}(t)$  are the circumradius and shear modulus of the matrix  $A_{1-t}A'_tB$ , respectively, which can be regarded as the linear combination of  $AB$  and  $A'B$ . Assuming there are  $tN$   $A'B$  unit cells dispersed in a spherical matrix with a cut-off radius  $\hat{R}$ , by adding the extra increased internal energy by the first-order effect of surface tension,  $\Delta H_{A'B}^S(t)$  becomes<sup>[3,4]</sup>

$$\Delta H_{A'B}^S(t) = 8\pi G_{AA'} R_{AA'}^3 \chi_{A'}^2 c_{A'} (1 - 2t). \quad S4$$

$\Delta H_{AB}^S(t)$  is obtained by the same approach. Then,

$$\Delta H_{cell}^S(t) = \Delta H_{A'B}^S(t) - \Delta H_{AB}^S(t) = 8\pi G_{AA'} R_{AA'}^3 \chi_{A'}^2 c_{A'} (1 - 2t) - 8\pi G_{AA'} R_{AA'}^3 \chi_A^2 c_A (2t - 1), \quad S5$$

The total increased internal strain energy ( $\Delta H_S(x)$ ) is

$$\begin{aligned} \Delta H_S(x) &= x \int_1^x \frac{\Delta H_{cell}^S(t)}{Z} \cdot N_A dt + (1-x) \int_0^x \frac{\Delta H_{cell}^S(t)}{Z} \cdot N_A dt \\ &\approx 8\pi \frac{N_A}{Z} G_{AA'} R_{AA'}^3 (R_A - R_{A'})^2 \frac{3K_{A'}}{4G_{AA'} + 3K_{A'}} f_0 - 8\pi \frac{N_A}{Z} G_{AA'} R_{AA'}^3 (R_A - R_{A'})^2 \frac{3K_A}{4G_{AA'} + 3K_A} f_1, \quad S6 \end{aligned}$$

where  $f_0 = x \int_1^x (1-t)^2 (2t-1) dt + (1-x) \int_0^x (1-t)^2 (2t-1) dt$ , and  $f_1 = x \int_1^x t^2 (1-2t) dt + (1-x) \int_0^x t^2 (1-2t) dt$ .



When  $x = 0.5$ ,  $\Delta H_S$  achieves its maximum value, and then  $f_0 = -f_1 \approx 0.09375$ . Furthermore, in semiconductors,  $G/K$  is about  $0.5^{[5]}$ , and  $\Delta H_S(x)$  is then well-fitted by the 2nd-degree Taylor polynomial at  $x = 0.5$ ,

$$\Delta H_S(x) \approx MN_A \cdot [\bar{G} \bar{R}^* (\Delta R^*)^2 / Z] \cdot (1-x)x = MN_A \cdot \delta \cdot (1-x)x, \quad S7$$

where  $\delta$  is the solubility parameter (defined by  $\delta = \bar{G} \bar{R}^* (\Delta R^*)^2 / Z$ ),  $R^*$  is the effective lattice constant (defined by  $R^* = \sqrt{\frac{a^2+b^2+c^2}{3}}$  for an orthorhombic structure and  $\sqrt{\frac{(2a)^2+c^2}{3}}$  for a hexagonal structure, where  $a$ ,  $b$  and  $c$  are the parameters of a unit cell, or the parameters of a supercell that is built close to a sphere),  $\bar{G}$  and  $\bar{R}^*$  are the average shear modulus and the effective lattice constant of  $AB$  and  $A'B'$ ,  $\Delta R^*$  is the difference in effective lattice constants between  $AB$  and  $A'B'$  ( $\Delta R^* = |R_{AB}^* - R_{A'B'}^*|$ ),  $M = \frac{72\sqrt{3}\pi \times 0.09375}{4G/K+3} \approx 7.34$ .

A ternary solution  $(A_{1-x}A'_x)_{1-y}A''_yB$  can be divided into three binary solutions

$$(1-y)AB + (1-y)A''B \rightarrow A_{1-y}A''_yB, \quad S8-1$$

$$(1-y)A'B' + (1-y)A''B \rightarrow A'_{1-y}A''_yB, \quad S8-2$$

$$(1-x)A_{1-y}A''_yB + xA'_{1-y}A''_yB \rightarrow (A_{1-x}A'_x)_{1-y}A''_yB, \quad S8-3$$

The change in the internal strain energy of the first two binary solutions  $\Delta H_1(y)$ ,  $\Delta H_2(y)$  can be calculated according to Equation S7. For the third quasi-binary solution,  $\Delta H_3(x, y)$  is

$$\Delta H_3(x, y) \approx 8\pi \frac{N_A}{Z} G'_A R'_A (R'_A - R'_{A'})^2 \frac{3K'_A}{4G'_A + 3K'_A} f_0 - 8\pi \frac{N_A}{Z} G'_{A'} R'_{A'} (R'_A - R'_{A'})^2 \frac{3K'_A}{4G'_{A'} + 3K'_A} f_1, \quad S9$$

where  $R'_A, R'_{A'}, R'_{AA'}, K'_A, K'_{A'}, G'_A, G'_{A'}$ , have the same definitions as those in binary systems. However, Equation S9 neglects the internal stress and strain caused by the first-order effect of surface tension of the  $A''B$  unit cell, which has to be considered and added. Then,  $f_0$  and  $f_1$  in Equation S9 are modified as

$$\begin{aligned} \hat{f}_0 &= x \int_1^x (1-t)^2 \left( 2t - 1 - 2 \frac{R_{A''} - R'_{AA'}}{R'_A - R'_{AA'}} y \right) dt + (1-x) \int_0^x (1-t)^2 \left( 2t - 1 - 2 \frac{R_{A''} - R'_{AA'}}{R'_A - R'_{AA'}} y \right) dt \quad \text{and} \\ \hat{f}_1 &= x \int_1^x t^2 \left( 1 - 2t - 2 \frac{R_{A''} - R'_{AA'}}{R'_{A'} - R'_{AA'}} y \right) dt + (1-x) \int_0^x t^2 \left( 1 - 2t - 2 \frac{R_{A''} - R'_{AA'}}{R'_{A'} - R'_{AA'}} y \right) dt. \end{aligned}$$

To simplify  $\Delta H_3(x, y)$ , it can be written as a product of two terms

$$\Delta H_3(x, y) \approx \Delta H_3(x, 0) \cdot f\left(y, \frac{R_{A''}}{R_{AA'}}\right). \quad \text{S10}$$

where  $\Delta H_3(x, 0)$  is the internal strain energy for a binary solution  $A_{1-x}A'_xB$ , and  $f\left(y, \frac{R_{A''}}{R_{AA'}}\right)$  is a function representing the effect of an extra component  $A''B$ . As shown in Figure S2, the  $f\left(y, \frac{R_{A''}}{R_{AA'}}\right)$  can be well fit by  $(1-y)^{3.5}$  when  $\frac{R_{A''}}{R_{AA'}}$  varies from 80% ~ 120%. Thus,

$$\Delta H_3(x, y) \approx MN_A \cdot \delta_{AA'} \cdot (1-x)x \cdot (1-y)^{3.5}, \quad \text{S11}$$

where  $\delta_{AA'}$  is the solubility parameter of a binary solution  $A_{1-x}A'_xB$ .

Consequently, the calculated total internal strain energy of the ternary solution in Equation S8 is

$$\Delta H_{\text{total}} = x\Delta H_1(y) + (1-x)\Delta H_2(y) + \Delta H_3(x, y), \quad \text{S12}$$

Considering all the different solution routes, the average  $\Delta H_{\text{total}}$  for achieving an equimolar ternary solution is

$$\Delta \bar{H}_{\text{total}} = MN_A \cdot \bar{\delta} \cdot \left[ \sum_{i=2}^3 \left(1 - \frac{1}{i}\right) \frac{1}{i} \cdot \left(\frac{i}{3}\right)^{3.5} \right], \quad \text{S13}$$

where  $\bar{\delta}$  is the average  $\delta$  value of all separate binary solutions.

Using the same approach, for a multi-component material  $(A_{1-x}A'_x)_{1-y_1-y_2\dots}A''_{y_1}A'''_{y_2} \dots B$ ,  $\Delta H_5(x, y_1, y_2 \dots)$  we write

$$\Delta H_5(x, y_1, y_2 \dots) \approx MN_A \cdot \delta_{AA'} \cdot (1-x)x \cdot (1-y_{\text{total}})^{3.5}, \quad \text{S14}$$

where  $y_{\text{total}} = y_1 + y_2 + \dots$ . For equimolar multi-component solutions,  $\Delta \bar{H}_{\text{total}}$  is given by

$$\Delta \bar{H}_{\text{total}} = MN_A \cdot \bar{\delta} \cdot \left[ \sum_{i=2}^n \left(1 - \frac{1}{i}\right) \frac{1}{i} \cdot \left(\frac{i}{n}\right)^{3.5} \right]. \quad \text{S15}$$

For the change in the internal ionic field energy  $\Delta H_{cell}^c(t)$ , the effective charge ( $Q$ ) of  $A$  (or  $A'$ ) in  $AB$  (or  $A'B$ ) is estimated and calculated based on the developed Pauling electronegativity<sup>[6]</sup>. For  $A_{1-t}A'_tB$ , the average effective charge of  $A$  ( $A'$ ) atomic positions can be assumed to be a linear combination of  $Q_A$  and  $Q_{A'}$ . Then, according to the Born–Landé equation<sup>[7]</sup>,  $\Delta H_{cell}^c(t)$  is

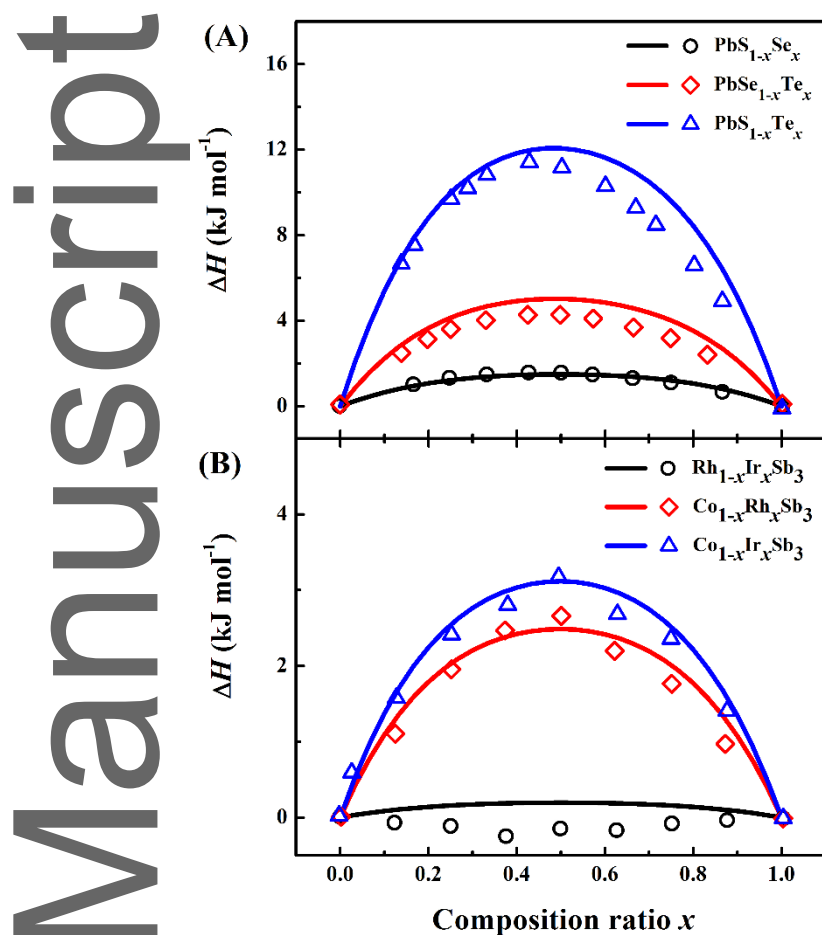
$$\Delta H_{cell}^c(t) = -\frac{M_A \cdot Q_{AA'}(Q_A - Q_{A'})}{4\pi\epsilon_0 R_{AA'}} - \frac{M_B \cdot Q_B \cdot (Q_A - Q_{A'})}{4\pi\epsilon_0 R_{AA'}}, \quad S16$$

where  $\epsilon_0$  is the vacuum permittivity, and  $M_A$  and  $M_D$  are the Madelung constants for atom  $A$  ( $A'$ ) and  $B$ .  $\Delta H_c(x)$  then becomes

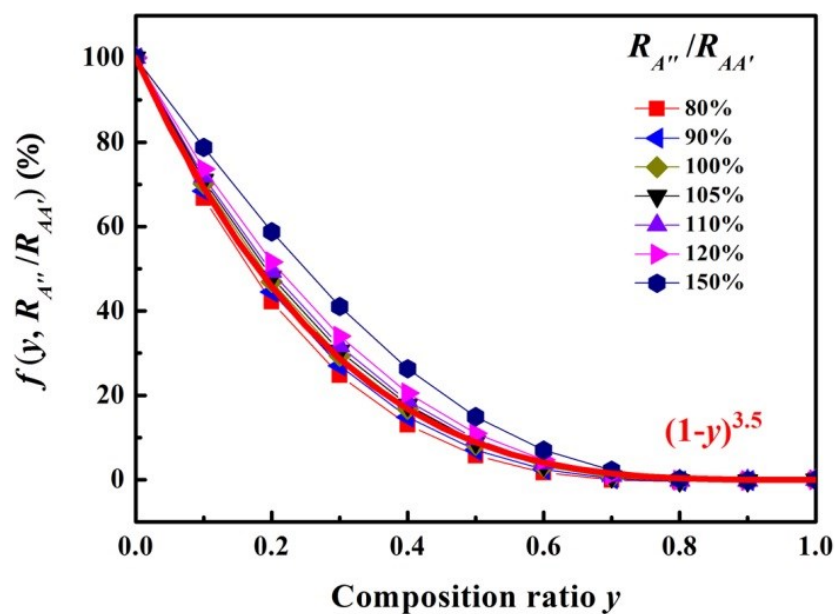
$$\Delta H_c(x) = x \int_1^x -\Delta H_{cell}^c(t) \cdot N_A dt + (1 - x) \int_0^x -\Delta H_{cell}^c(t) \cdot N_A dt. \quad S17$$

The calculated  $\Delta H_S$  and  $\Delta H_c$  for several TE materials are listed in Table S1.

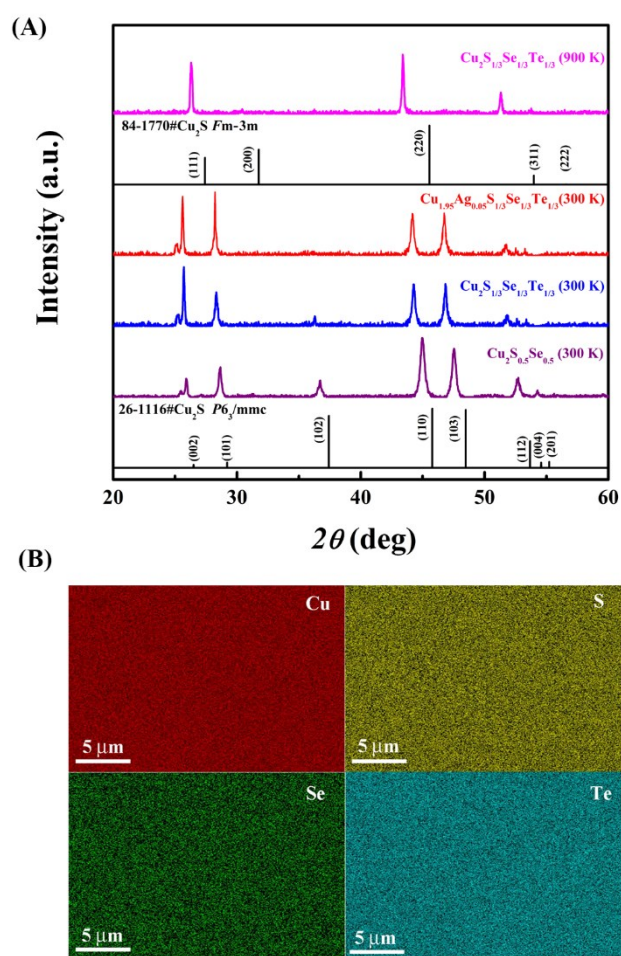
Figures S1 to S9.



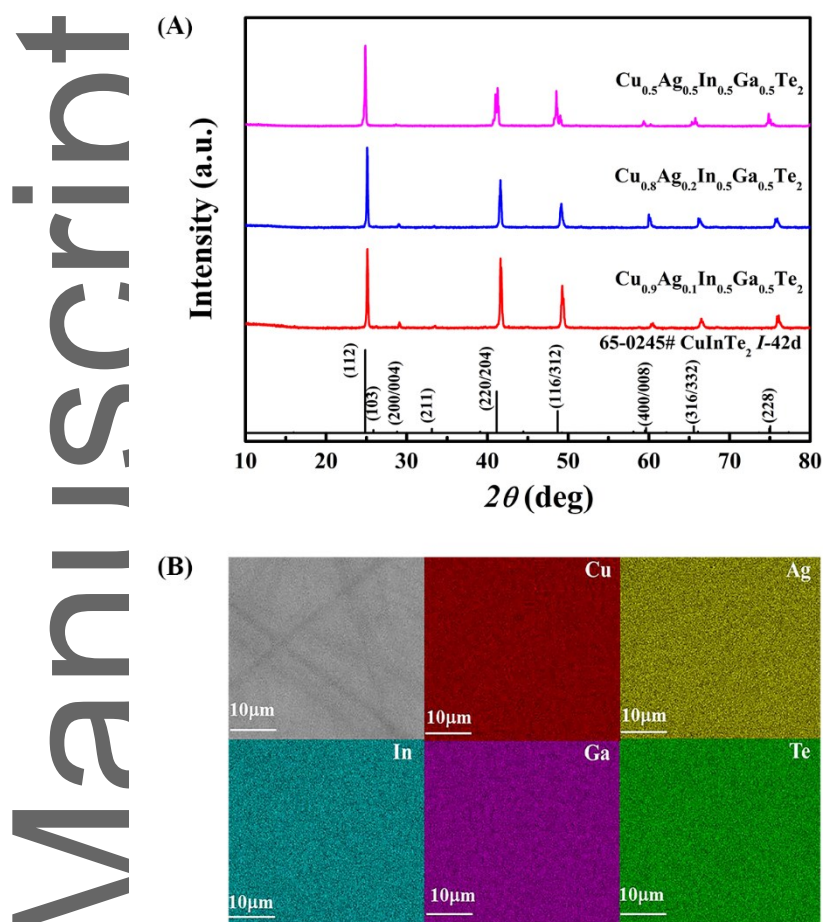
**Figure S1.** Calculated changes in enthalpy ( $\Delta H$ ) based on Equation S6 for several two-component TE materials. The lines are calculated according to our model. The dots are calculated by *ab initio* calculations taken from Supporting Ref. 8 and 9.



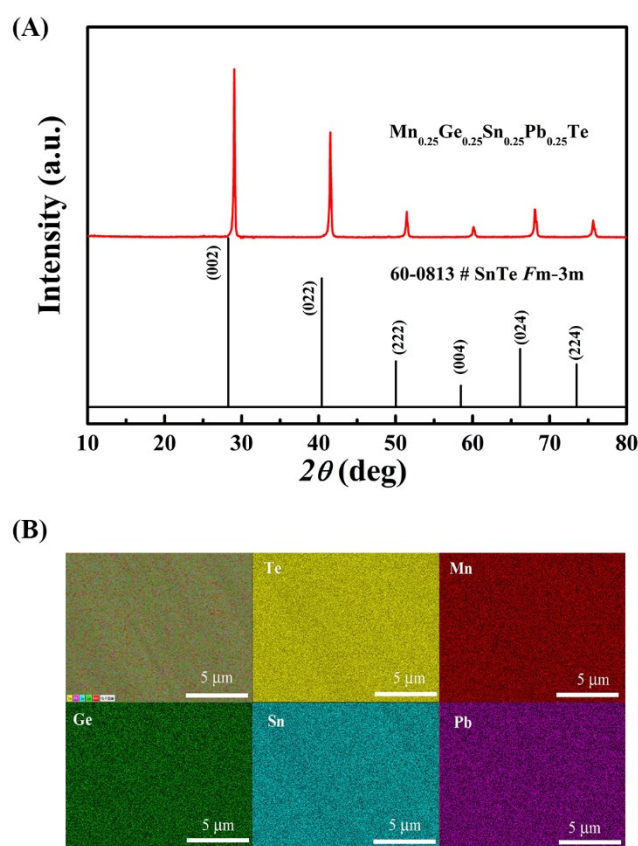
**Figure S2.** Function  $f(y, \frac{R_{A''}}{R_{AA'}})$  depending on  $y$  and  $\frac{R_{A''}}{R_{AA'}}$ . Curves marked with symbols are calculated according to Equation S9, and the red curve is the fitting result represented by  $(1-y)^{3.5}$ .



**Figure S3.** (A) Powder X-ray diffraction patterns of  $\text{Cu}_2\text{S}_{0.5}\text{Se}_{0.5}$ ,  $\text{Cu}_2\text{S}_{1/3}\text{Se}_{1/3}\text{Te}_{1/3}$ , and  $\text{Cu}_{1.95}\text{Ag}_{0.05}\text{S}_{1/3}\text{Se}_{1/3}\text{Te}_{1/3}$ . They exhibit a hexagonal structure with the space group of  $P6_3/mmc$  at 300 K. The uppermost trace shows a cubic structure of  $\text{Cu}_2\text{S}_{1/3}\text{Se}_{1/3}\text{Te}_{1/3}$  with the space group of  $Fm\bar{3}m$  at 900 K. (B) Elemental maps of  $\text{Cu}_2\text{S}_{1/3}\text{Se}_{1/3}\text{Te}_{1/3}$  obtained by Electron Probe Microanalysis (EPMA).

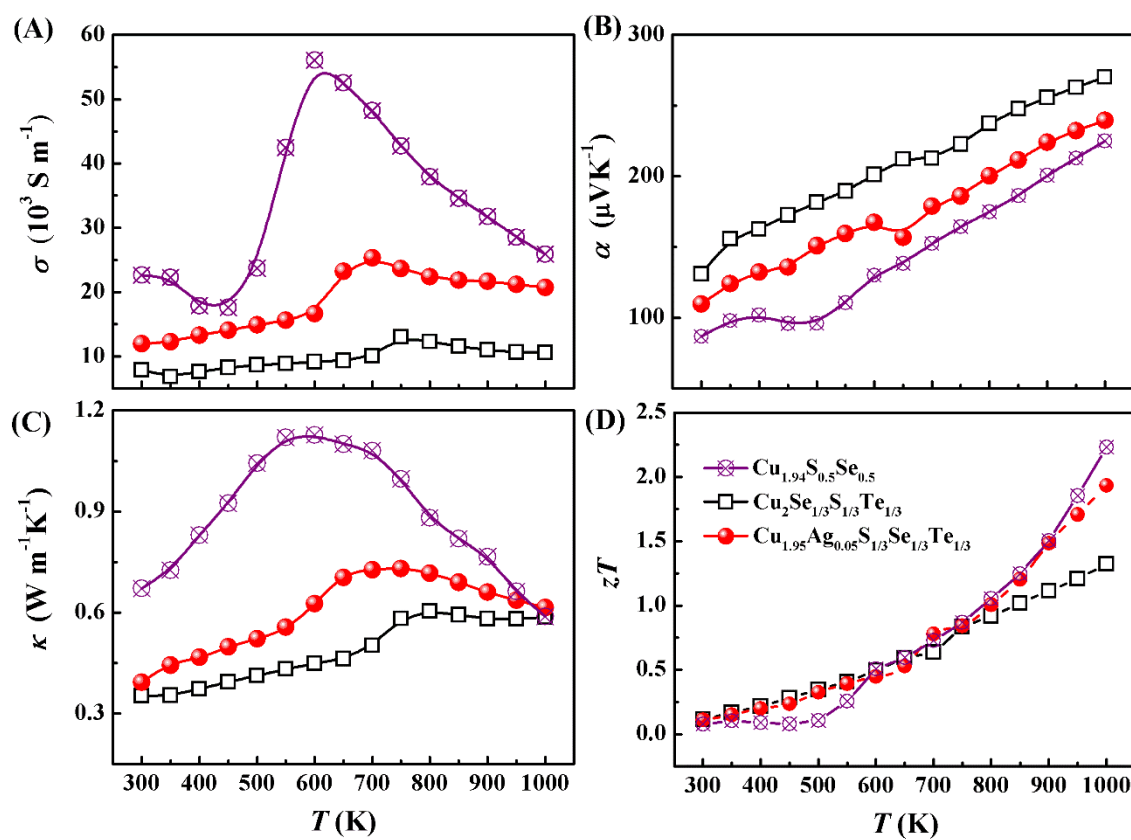


**Figure S4.** (A) Powder X-ray diffraction patterns of a series of (Cu/Ag)(In/Ga) $\text{Te}_2$ -based multi-component TE materials. (B) Elemental maps of  $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{In}_{0.5}\text{Ga}_{0.5}\text{Te}_2$  obtained by Electron Probe Microanalysis (EPMA).



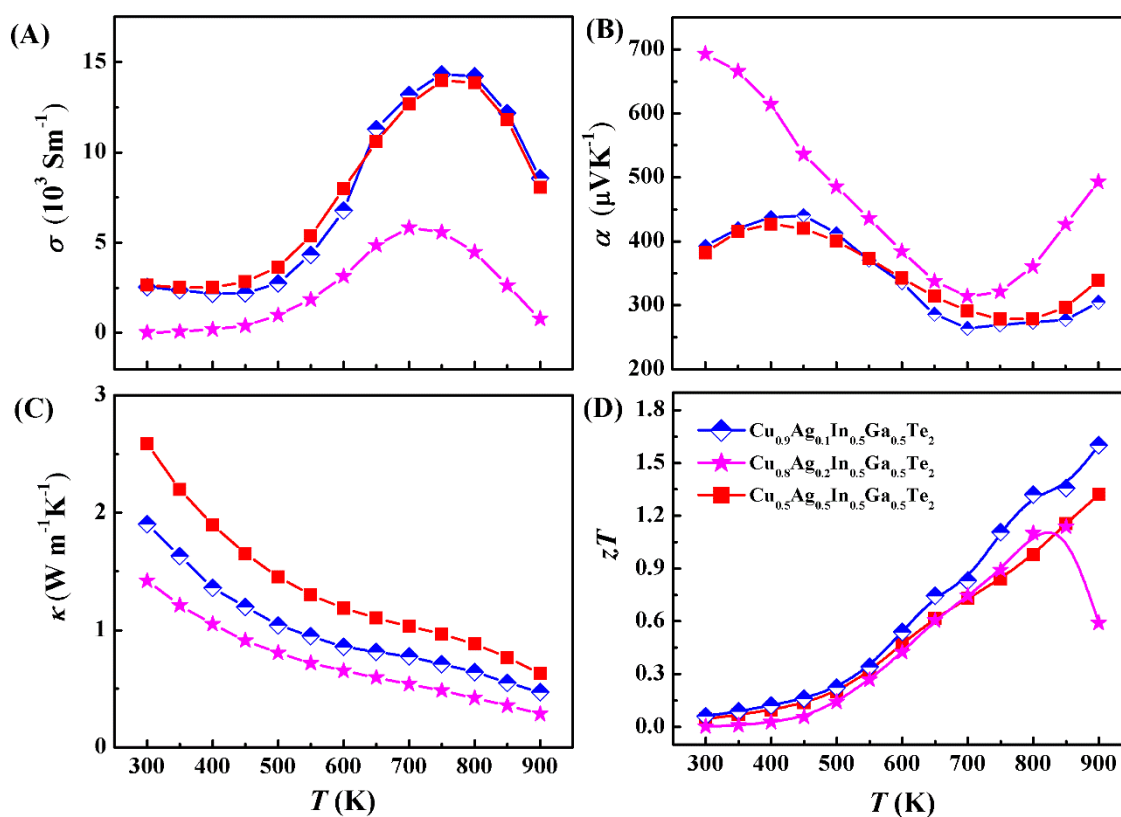
**Figure S5.** (A) Powder X-ray diffraction pattern of  $\text{Mn}_{0.25}\text{Ge}_{0.25}\text{Sn}_{0.25}\text{Pb}_{0.25}\text{Te}$ . (B) Elemental maps of  $\text{Mn}_{0.25}\text{Ge}_{0.25}\text{Sn}_{0.25}\text{Pb}_{0.25}\text{Te}$  obtained by Electron Probe Microanalysis (EPMA).





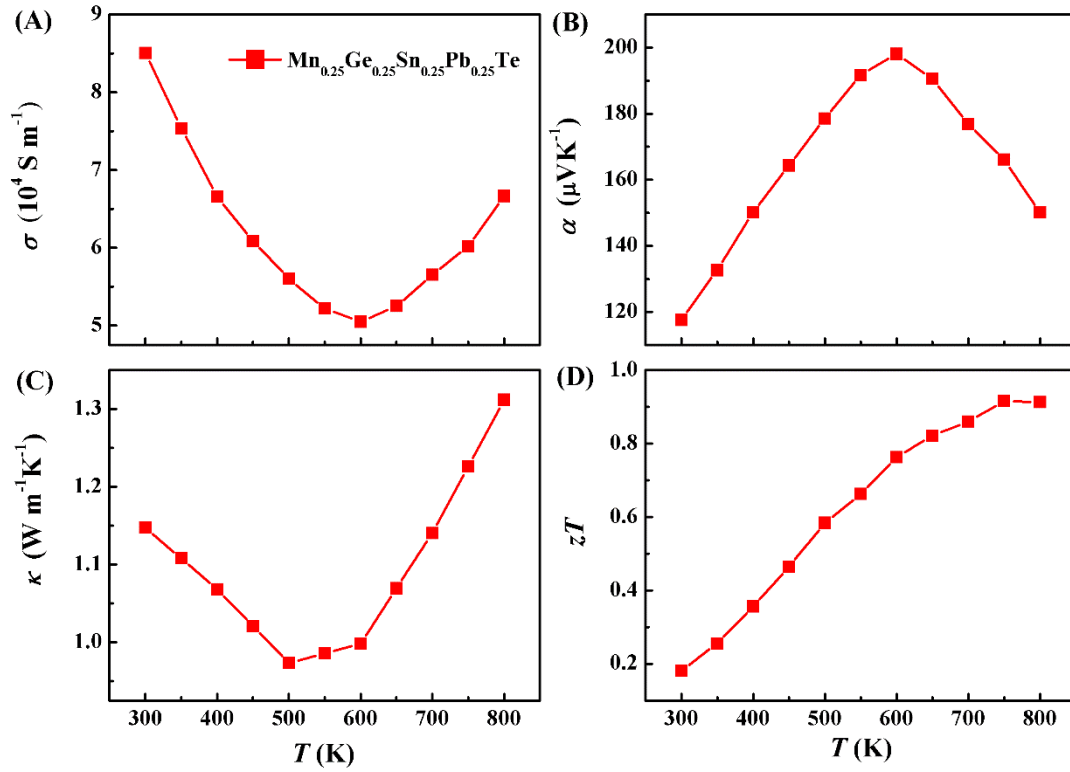
**Figure S6.** Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), thermal conductivity (C) and the thermoelectric figure of merit ( $zT$ ) (D) for  $\text{Cu}_2(\text{S}/\text{Se}/\text{Te})$ -based multi-component TE materials.

Author



**Figure S7.** Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), thermal conductivity (C) and the figure of merit ( $zT$ ) (D) for  $(\text{Cu}/\text{Ag})(\text{In}/\text{Ga})\text{Te}_2$ -based multi-component TE materials.

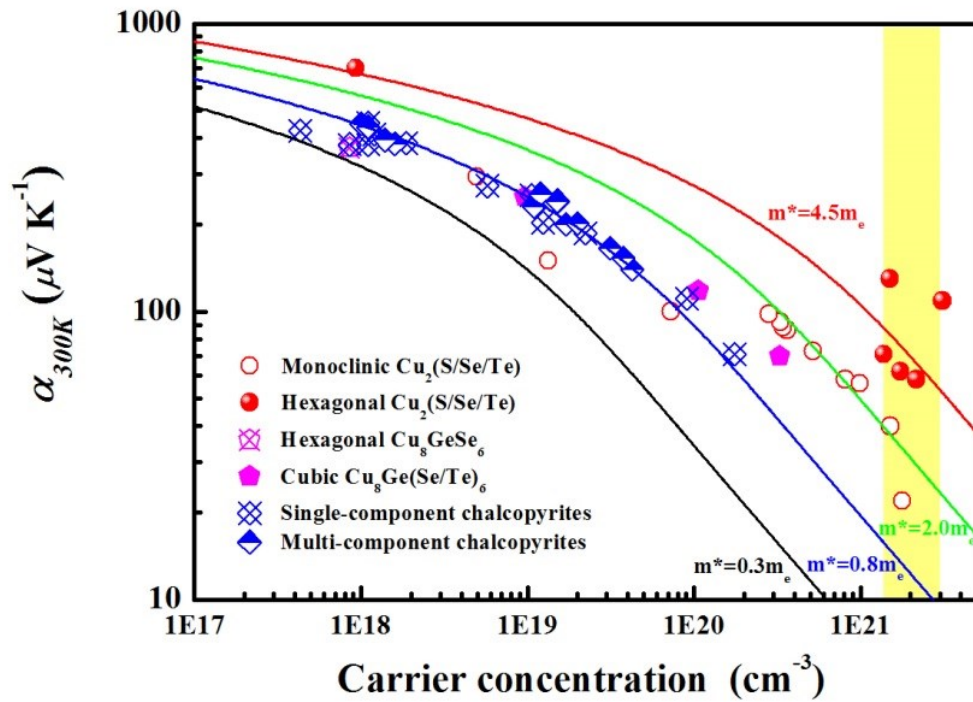
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**Figure S8.** Temperature dependence of the electrical conductivity (A), Seebeck coefficient (B), thermal conductivity (C) and the figure of merit ( $zT$ ) (D) for  $\text{Mn}_{0.25}\text{Ge}_{0.25}\text{Sn}_{0.25}\text{Pb}_{0.25}\text{Te}$  multi-component TE materials.

Author

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**Figure S9.** Hall carrier concentration dependence of room temperature Seebeck coefficient of  $\text{Cu}_2(\text{S/Se/Te})$ ,  $(\text{Cu/Ag})(\text{In/Ga})\text{Te}_2$ , and  $\text{Cu}_8\text{Ge}(\text{Se/Te})_6$ -based TE materials. The effective mass is estimated from the single parabolic band model.

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**Tables S1 to S4.**

**Table S1.** Internal strain energy ( $\Delta H_s$ ) arising from the atomic size mismatch, fluctuation of the internal ionic field energy ( $\Delta H_c$ ) from electron cloud redistribution,  $\Delta H_c/\Delta H_s$ , and the formation enthalpy ( $\Delta H$ ) for various binary TE solutions with equal atomic-ratio components.

Systems	$\Delta H_c$		$\Delta H_s$	$\Delta H_c/\Delta H_s$	$\Delta H$
	[J mol <sup>-1</sup> ]	[ $k_B T$ /f.u.]	[J mol <sup>-1</sup> ]		
PbSe-PbTe	316.7	0.13	5025.8	6.30%	5342.5
PbS-PbTe	40.3	0.02	12069.6	0.33%	12109.9
PbS-PbSe	-38.9	-0.02	1499.1	-2.59%	1460.2
CoSb <sub>3</sub> -IrSb <sub>3</sub>	440.5	0.18	3116.8	14.13%	3557.3
CoSb <sub>3</sub> -RhSb <sub>3</sub>	916.5	0.37	2487.0	36.85%	3403.5
CuInTe <sub>2</sub> -AgInTe <sub>2</sub>	13.8	<0.01	276.9	4.98%	290.7

**Table S2.** Space group, number of components ( $n$ ), average shear modulus ( $\bar{G}$ ), average effective lattice constant ( $\bar{R}^*$ ), and parameter  $\bar{\delta}$  for various systems of multi-component TE materials.

NO.	Systems	Space group	$n$	$\bar{G}$ [GPa]	$\bar{R}^*$ [Å]	$\bar{\delta}$ [GPa·Å <sup>3</sup> ]
1	TiCoSb-ZrCoSb-HfCoSb	<i>Fm</i> -3m	3	76	6.01	1.85
2	CoSb <sub>3</sub> -RhSb <sub>3</sub> -IrSb <sub>3</sub>	<i>I</i> m-3 (LT) <i>P</i> 2 <sub>1</sub> / <i>c</i> , <i>C</i> 2/ <i>c</i> ;	3	63	9.18	2.14
3	Cu <sub>2</sub> S-Cu <sub>2</sub> Se-Cu <sub>2</sub> Te	(MT) <i>P</i> 6 <sub>3</sub> / <i>m</i> mc; (HT) <i>F</i> m-3m	3	26	5.91	2.39
4	ZnTe-CdTe-HgTe	<i>F</i> -43m	3	16	6.35	2.40
5	TiNiSn-ZrNiSn-HfNiSn	<i>F</i> -43m	3	90	6.04	2.45
6	CuGaTe <sub>2</sub> -CuInTe <sub>2</sub> -AgGaTe <sub>2</sub> -AgInTe <sub>2</sub>	<i>I</i> -42d	4	22	8.71	3.12
7	MnTe-GeTe-SnTe-PbTe	<i>F</i> m-3m	4	19	6.18	3.36
8	PbS-PbSe-PbTe	<i>F</i> m-3m	3	27	6.19	4.57
9	AlSb-GaSb-InSb	<i>F</i> -43m	3	53	6.25	7.01

**Table S3.** Seebeck coefficient ( $\alpha$ ), electrical conductivity ( $\sigma$ ), thermal conductivity ( $\kappa$ ), carrier concentration ( $p$ ) at 300 K, and the maximum TE figure of merit at corresponded temperatures ( $(zT)_{max}$ ) of various single component and multi-component TE materials.

Compositions	$\alpha$ [ $\mu\text{V K}^{-1}$ ]	$\sigma$ [ $\text{S m}^{-1}$ ]	$\kappa$ [ $\text{Wm}^{-1}\text{K}^{-1}$ ]	$P$ [ $\text{cm}^{-3}$ ]	$(zT)_{max}$
$\text{Cu}_{1.92}\text{S}^{[10]}$	40	$4.10 \times 10^4$	1.06	$2.50 \times 10^{21}$	0.57
$\text{Cu}_{1.9}\text{Se}$	40	$3.48 \times 10^5$	2.16	$1.51 \times 10^{21}$	0.43
$\text{Cu}_2\text{Te}^{11}$	25	$4.10 \times 10^5$	2.08	$1.78 \times 10^{21}$	0.56
$\text{Cu}_2\text{Se}_{0.8}\text{Te}_{0.2}$	44	$1.32 \times 10^5$	1.37	$1.10 \times 10^{21}$	0.80
$\text{Cu}_2\text{Se}_{0.5}\text{Te}_{0.5}$	40	$1.20 \times 10^5$	1.03	$1.12 \times 10^{21}$	1.11
$\text{Cu}_2\text{S}_{0.50}\text{Te}_{0.50}^{[12]}$	58	$3.13 \times 10^4$	0.52	$2.17 \times 10^{21}$	2.10
$\text{Cu}_2\text{S}_{0.52}\text{Te}_{0.48}^{[12]}$	62	$2.77 \times 10^4$	0.48	$1.74 \times 10^{21}$	1.83
$\text{Cu}_2\text{S}_{0.54}\text{Te}_{0.46}^{[12]}$	71	$1.92 \times 10^4$	0.41	$1.37 \times 10^{21}$	1.70
$\text{Cu}_{1.94}\text{S}_{0.5}\text{Se}_{0.5}$	87	$2.27 \times 10^4$	0.67	$1.34 \times 10^{21}$	2.23
$\text{Cu}_2\text{S}_{1/3}\text{Se}_{1/3}\text{Te}_{1/3}$	130	$7.87 \times 10^3$	0.35	$1.50 \times 10^{21}$	1.32
$\text{Cu}_{1.95}\text{Ag}_{0.05}\text{S}_{1/3}\text{Se}_{1/3}\text{Te}_{1/3}$	109	$1.19 \times 10^4$	0.39	$3.01 \times 10^{21}$	1.92
$\text{CuInTe}_2^{13}$	204	$9.70 \times 10^3$	6.03	$1.24 \times 10^{19}$	1.02
$\text{Cu}_{0.99}\text{GaTe}_2^{[14]}$	263	$1.59 \times 10^4$	7.80	$1.22 \times 10^{19}$	0.70
$\text{Cu}_{0.99}\text{In}_{0.5}\text{Ga}_{0.5}\text{Te}_2^{[14]}$	202	$2.54 \times 10^4$	3.50	$1.59 \times 10^{19}$	0.82
$\text{Cu}_{0.88}\text{Ag}_{0.1}\text{InTe}_2^{[15]}$	201	$1.35 \times 10^4$	2.84	$1.70 \times 10^{19}$	1.09
$\text{Cu}_{0.75}\text{Ag}_{0.2}\text{InTe}_2^{[15]}$	231	$7.10 \times 10^3$	1.84	$1.11 \times 10^{19}$	1.24
$\text{Cu}_{0.88}\text{Ag}_{0.1}\text{InTe}_2^{[15]}$	211	$1.42 \times 10^4$	2.90	$2.00 \times 10^{19}$	0.68
$\text{Cu}_{0.75}\text{Ag}_{0.2}\text{InTe}_2^{[15]}$	242	$8.20 \times 10^3$	1.95	$1.52 \times 10^{19}$	0.77
$\text{Cu}_{0.9}\text{Ag}_{0.1}\text{In}_{0.5}\text{Ga}_{0.5}\text{Te}_2$	382	$2.63 \times 10^3$	2.58	$1.75 \times 10^{18}$	1.32

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$\text{Cu}_{0.8}\text{Ag}_{0.2}\text{In}_{0.5}\text{Ga}_{0.5}\text{Te}_2$	392	$2.55 \times 10^3$	1.90	$1.90 \times 10^{18}$	1.60
$\text{Cu}_{0.5}\text{Ag}_{0.5}\text{In}_{0.5}\text{Ga}_{0.5}\text{Te}_2$	693	$2.54 \times 10^1$	1.42	-	1.13
$\text{Mn}_{0.25}\text{Ge}_{0.25}\text{Sn}_{0.25}\text{Pb}_{0.25}\text{Te}$	118	$4.98 \times 10^4$	1.15	-	0.91
$\text{Cu}_8\text{GeSe}_6$	235	$3.23 \times 10^0$	0.31	$8.48 \times 10^{17}$	0.54
$\text{Cu}_8\text{GeSe}_{5.7}\text{Te}_{0.3}$	284	$1.52 \times 10^2$	0.29	$9.56 \times 10^{18}$	0.71
$\text{Cu}_8\text{GeSe}_{5.4}\text{Te}_{0.6}$	104	$1.35 \times 10^4$	0.51	$1.06 \times 10^{20}$	0.89
$\text{Cu}_{7.6}\text{Ag}_{0.4}\text{GeSe}_{5.1}\text{Te}_{0.9}$	88	$3.57 \times 10^4$	0.41	$4.38 \times 10^{20}$	1.07

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**Table S4.** Space group, shear modulus ( $G$ ), lattice parameters ( $a$  and  $c$ ), unit cell volume ( $V_{cell}$ ), number of formula units ( $Z$ ) in one unit cell for typical TE materials from the ICSD database.

Compounds	Space group	$G$ [GPa]	Lattice parameter		$V_{cell}$ [Å <sup>3</sup> ]	$Z$
			$a$ [Å]	$c$ [Å]		
PbS	<i>Fm-3m</i>	30	5.996	-	215	4
PbSe	<i>Fm-3m</i>	27	6.140	-	231	4
PbTe	<i>Fm-3m</i>	23	6.440	-	268	4
Bi <sub>2</sub> Te <sub>3</sub> <sup>a)</sup>	<i>R-3m</i>	52	4.390	30.480	-	3
Sb <sub>2</sub> Te <sub>3</sub> <sup>a)</sup>	<i>R-3m</i>	-	4.260	30.400	-	3
Bi <sub>2</sub> Se <sub>3</sub> <sup>a)</sup>	<i>R-3m</i>	-	4.130	28.600	-	3
SnTe	<i>Fm-3m</i>	10	6.310	-	251	4
GeTe	<i>Fm-3m</i>	25	5.985	-	214	4
MnTe	<i>Fm-3m</i>	-	5.980	-	214	4
CoSb <sub>3</sub>	<i>Im-3</i>	56	9.034	-	737	8
RhSb <sub>3</sub>	<i>Im-3</i>	63	9.242	-	786	8
IrSb <sub>3</sub>	<i>Im-3</i>	70	9.253	-	792	8
CuInTe <sub>2</sub>	<i>I-42d</i>	19	6.194	12.416	476	4
AgInTe <sub>2</sub>	<i>I-42d</i>	14	6.401	12.613	515	4
CuGaTe <sub>2</sub>	<i>I-42d</i>	26	6.024	11.929	432	4
AgGaTe <sub>2</sub>	<i>I-42d</i>	28	6.296	11.990	475	4
ZnTe	<i>F-43m</i>	20	6.104	-	227	4
CdTe	<i>F-43m</i>	18.3	6.481	-	272	4
HgTe	<i>F-43m</i>	8.9	6.461	-	270	4
Cu <sub>2</sub> S	(HT) <i>Fm-3m</i> <sup>b)</sup>	17.8 <sup>c)</sup>	5.762	-	191	4
Cu <sub>2</sub> Se	(HT) <i>Fm-3m</i> <sup>b)</sup>	36.3 <sup>c)</sup>	5.871	-	202	4
Cu <sub>2</sub> Te	(HT) <i>Fm-3m</i> <sup>b)</sup>	25 <sup>c)</sup>	6.114	-	228	4
AlSb	<i>F-43m</i>	58	6.135	-	231	4
GaSb	<i>F-43m</i>	56	6.118	-	229	4
InSb	<i>F-43m</i>	46	6.487	-	273	4
TiNiSn	<i>Fm-3m</i>	76	5.921	-	208	4

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ZrNiSn	Fm-3m	-	6.113	-	228	4
HfNiSn	Fm-3m	-	6.084	-	225	4
TiCoSb	Fm-3m	90.5	5.913	-	207	4
ZrCoSb	Fm-3m	-	6.068	-	223	4
HfCoSb	Fm-3m	-	6.040	-	220	4
SrZn <sub>2</sub> Sb <sub>2</sub>	P-3m1	-	4.500	7.716	135	1
CaZn <sub>2</sub> Sb <sub>2</sub>	P-3m1	-	4.441	7.464	127	1
EuZn <sub>2</sub> Sb <sub>2</sub>	P-3m1	25	4.480	7.601	133	1
YbZn <sub>2</sub> Sb <sub>2</sub>	P-3m1	-	4.446	7.426	127	1

a) For Bi<sub>2</sub>Te<sub>3</sub>-based materials, a supercell with lattice parameters of ( $4a^* \times 4b^* \times c^*$ ) is used, where  $a^*$ ,  $b^*$ , and  $c^*$  are the lattice parameters of a conventional unit cell;

b) The lattice parameters of high temperature cubic structure are used<sup>[16,17]</sup>;

c) Shear modulus is calculated based on the reported acoustic velocity<sup>[11,18]</sup>.

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