Structural Modularization of Cu_2Te Leading to High Thermoelectric Performance near the Mott-Ioffe-Regel Limit

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Abstract

To date, thermoelectric materials research stays focused on optimizing the material's band edge details and disfavors low mobility. Here, we shift the paradigm from the band edge to the mobility edge, exploring high thermoelectricity near the border of band conduction and hopping. Through co-alloying iodine and sulfur, we modularize the plain crystal structure of liquid-like thermoelectric material Cu_2Te with mosaic nanodomains and the highly size mismatched S/Te sublattice that chemically quenches the Cu sublattice and drives the electronic states from itinerant to localized. A state-of-the-art figure of merit of 1.4 is obtained at 850 K for $\text{Cu}_2(\text{S}_{0.4}\text{I}_{0.1}\text{Te}_{0.5})$; and remarkably, it is achieved near the Mott-Ioffe-Regel limit unlike mainstream thermoelectric materials that are band conductors. Broadly, pairing structural modularization with the high performance near the Mott-Ioffe-Regel limit paves an important new path towards the rational design of high-performance thermoelectric materials.

Thermoelectric (TE) material-based energy conversion technology has attracted increasing global attention in virtue of the technical merits such as no moving parts, no greenhouse emission, noiseless, friendliness for miniaturization, and reliability.^{1–4} Based on the Seebeck and Peltier effects, thermoelectricity enables a direct energy conversion between temperature difference and electricity.^{5, 6} The performance of a TE material is primarily gauged by the material's figure of merit, $zT = S^2 T / \rho \kappa$, where S is the Seebeck coefficient, T is the absolute temperature, ρ is the electrical resistivity, and κ is the total thermal conductivity (consisting of the lattice thermal conductivity κ_L and the electronic thermal conductivity κ_E).

Main Text

Thermoelectric (TE) material-based energy conversion technology has attracted increasing global attention in virtue of the technical merits such as no moving parts, no greenhouse emission, noiseless, friendliness for miniaturization, and reliability.^{1–4} Based on the Seebeck and Peltier effects, thermoelectricity enables a direct energy conversion between temperature difference and electricity.^{5, 6} The performance of a TE material is primarily gauged by the material's figure of merit, $zT = S^2 T / \rho \kappa$, where S is the Seebeck coefficient, T is the absolute temperature, ρ is the electrical resistivity, and κ is the total thermal conductivity (consisting of the lattice thermal conductivity κ_L and the electronic thermal conductivity κ_E).

In view of the adversely inter-dependent S , ρ and κ , attaining high zT values entails hierarchical diverse structure-functional modules in the material. To this end, “hybrid crystal” or “structural modularity” is preferred in TE materials research as these complex materials are composed of building modules with distinct compositions and functions,^{7, 8} through which the adverse coupling of S , ρ and κ can be eased and tuned selectively. Layered cobalt oxides,⁹ filled skutterudites,¹⁰ and liquid-like TE materials¹¹ are good examples of hybrid crystals as they contain specific structural-functional modules such as the sublattices respectively undertaking charge conduction and phonon scattering.

The structural hybridity or modularity doesn't need to be native, extrinsic defects act as endowed structural-functional modules. For example, static point defects and mobile ions,¹¹⁻¹⁴ nanoscale lattice strains, and micro-scale grain boundaries jointly suppress the lattice thermal conductivity.¹⁵⁻¹⁷ Meanwhile, the doping induced resonant electronic states,¹⁸ the energy filtering effect at grain boundary,¹⁹ and the doping regulated carrier concentration optimization and band convergence enhance the electronic transport properties via optimizing the material's electron band structure, especially the details of band edge.^{20, 21} To date, the state-of-the-art TE materials are band conductors with decent carrier concentrations on the order of $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and above.

An important question follows directly, can we utilize doping to structurally modularize an otherwise plain crystal structure? Further, as structural modularization degrades the carrier mobility, a key ingredient of the TE quality factor,²² would such structurally modularized low-mobility materials be able to yield state-of-the-art TE performance? The answers are potentially paradigm shifting.

Here we present a case study in copper telluride (Cu_{2-x}Te), a liquid-like TE material known for its complex atomic order-disorder of Cu ions in a number of structural polymorphs.²³⁻²⁶ The nearly degenerate crystal structures make Cu_{2-x}Te a good material template to implement structural modularization and study the pertinent effects on the TE properties. Compared to other TE materials, doped copper tellurides have fairly high carrier concentrations in the range of $2 \sim 4 \times 10^{21} \text{ cm}^{-3}$, and the room temperature carrier mobilities are in the range of $15 \sim 30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,²³⁻²⁶ not far from the Mott-Ioffe-Regel limit.^{27, 28} Through co-alloying with iodine and sulfur, we structurally-functionally modularize Cu_{2-x}Te with (i) the atomic-scale aliovalent I dopants on the Te sites that act as effective donors to reduce the hole concentration and scatter the heat-carrying phonons at elevated temperatures; (ii) the highly size mismatched yet crystalline S/Te sublattice that chemically quenches the Cu sublattice and also drives the electronic states from itinerant to localized with increasing S content; and (iii) the mosaic nanodomains that joint force with other types of defects to suppress the thermal conductivity. A greatly enhanced Seebeck coefficient (260 mV K^{-1} at 850 K) and a record-high figure of merit (1.4 at 850 K) in $\text{Cu}_2\text{Te}_{0.5}\text{I}_{0.1}\text{S}_{0.4}$ (cf. **Figure 1a**) are attained near the Mott-Ioffe-Regel limit, which delimits band conduction and hopping, in contrast to the state-of-the-art TE materials that are well-established band conductors (cf. **Figure 1b**).

Figure 2a displays the room-temperature powder X-ray diffraction patterns (PXRD) of $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$ ($x = 0.0, 0.05, \text{ and } 0.1$) and $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$ ($y = 0.1, 0.2, 0.3, 0.4, \text{ and } 0.5$) samples. The crystal structure of pristine Cu_2Te tends to be structurally polymorphic, in accordance with literatures.^{24, 25} Upon doping I on the Te site (denoted by the x ratio), the XRD peaks are readily indexed to a hexagonal structure (space group P6₃/mmm). The maximum solubility of I in Cu_2Te is found to be around 10% (cf. **Figure S1**), below which I enters the Te site and serves as a substitutional point defect and also an effective donor. The lattice parameters remain unchanged upon I doping as the atomic size of I is close to that of Te (cf. **Figure 2b**). In the presence of I, further alloying S on the Te site (denoted by the y ratio), the (001) peak at $2\theta = 12^\circ$ gradually diminishes with increasing y value and finally disappears at $y \geq 0.3$, indicating the

structural transition from the space group $P6_3/mmm$ to $P6_3/mmc$. The linearly decreasing lattice parameter with increasing S ratio obeys the Vegard's law, agreeing with the substitution of S on the Te sites.

The solubility of S in Cu_2Te is much larger than that of I in Cu_2Te even though the atomic radius of I (1.40 Å) is closer to Te (1.40 Å) than that of S (1.00 Å). Notably, hump features are clearly detected in the XRD patterns of the samples with high S content ($x \geq 0.3$), pointing toward the presence of amorphous component in the relevant samples (cf. **Figure 2a**). Such observation is well consistent with our previous study that the Cu sublattice is chemically quenched into an amorphous state by the anionic S/Te sublattice with large atomic size mismatch.^{8, 45} The atom probe tomography (APT) analysis in **Figure 2c** confirms the homogeneity of all elements down to tens-of-nanometers scale. Furthermore, the imaging contrast variations of the atomically resolved high angle annular dark field (HAADF) image (cf. **Figure S2**) indicate the uniform distribution of Te, I, and S in the anionic framework. Cu ions are hard to discern due to the disordered nature. All these results unequivocally corroborate that I and S randomly substitute Te and exist as point defects.

Other than the aforementioned atomic scale defects and size mismatched S/Te sublattice, the I/S co-doped samples contain nanoscale mosaic microstructures and amorphous component on the Cu sublattice. **Figures 3b** shows the selected-area electron diffraction (SAED) pattern of the red circle area in **Figure 3a** along the [0001] zone axis. Closer scrutiny reveals that the diffraction patterns are not sharp dots but short arc-like Bragg streaks, a signature of diffuse diffraction and reminiscent of the SAED pattern of mosaic nanodomains with low-angle domain boundaries reported by He *et al.* in $\text{Cu}_2\text{Te}_{1-y}\text{S}_y$ samples.^{29, 46} This is further corroborated by the bright-field and dark-field images in **Figure 3c-f**. The nano-domains with low-angle boundaries lead to the formation of fluctuated imaging contrast in bright-field and dark-field images. The size of each domain is only around 10-30 nm, which plays a key role in scattering mid-to-long wavelength heat-carrying phonons. Besides, the diffraction rings in **Figure 3b** indicate the presence of amorphous component, i.e. glass-like Cu sublattice in $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$ in accordance with our XRD results.

The interplay between the I dopants and S dopants has an interesting effect on the carrier concentration. Doping iodine into Cu_2Te , the hole concentration (p) is decreased from $(2-3) \times 10^{21} \text{ cm}^{-3}$ to $1.3 \times 10^{21} \text{ cm}^{-3}$ for $\text{Cu}_2\text{Te}_{0.9}\text{I}_{0.1}$ (cf. **Figure 4a** and **Figure S3a**) as iodine acts as a donor. With further alloying S in the I-doped $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$, the hole concentrations are barely changed. This is somewhat a surprise as the early study showed that the p was gradually reduced with increasing S alloying content when S is solely alloyed in $\text{Cu}_2\text{Te}_{1-y}\text{S}_y$ (cf. **Figure 4a**).^{45, 47} To probe the interplay between iodine doping and sulfur doping, we performed defect formation energy (E_v) calculations to find out what occurs upon S alloying with or without I doping. A $2 \times 2 \times 2$ Cu_2Te supercell containing 48 atoms (i.e. $\text{Cu}_{32}\text{Te}_{16}$) was used to simulate the alloyed system (cf. **Figure 4b**). The Cu vacancy (V_{Cu}) formation energy (E_v) for $\text{Cu}_{32}\text{Te}_{16}$ (i.e. Cu_2Te) is around 0.08 eV (cf. **Figure 4c**). Substituting Te by S, the E_v of V_{Cu} is increased to 0.18-0.29 eV, and thus

the formation of V_{Cu} is substantially suppressed. Using extrinsic point defects to regulate the formation energy and thus the concentration of native point defects is a routine to tune the electrical properties of narrow bandgap semiconductors by isoelectronic doping.^{20, 48} The change of E_v of V_{Cu} explains the observed reduction of p in S alloyed $\text{Cu}_2\text{Te}_{1-y}\text{S}_y$. Substituting Te by I, the E_v values for V_{Cu1} , V_{Cu2} , and V_{Cu4} are substantially enhanced but the E_v for the Cu bonded to I, namely, V_{Cu3} , is reduced to negative. It is hard to conclude on the trend of the total Cu vacancy concentration upon iodine doping. Nonetheless, the overall carrier concentration should be somewhat reduced as iodine dopants serve as donors. Co-alloying Cu_2Te with both S and I, the variations of E_v of V_{Cu} are found to be similar to those of sole I-doping (cf. **Figure 4c**). With regard to the net carrier concentration variation, S alloying seems to play a minor role on the formation of V_{Cu} in the presence of I. As a result, the carrier concentration is expected to be barely changed in $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$ with increasing S content, agreeing with what we experimentally observed (cf. **Figure 4a**).

Figure 4d shows the room temperature carrier mobility (μ) of $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$, $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$, and $\text{Cu}_2\text{Te}_{1-y}\text{S}_y$ as a function of I/S content. Upon doping I, the μ of Cu_2Te is largely suppressed due to the enhanced ionized-impurity scattering. When alloying S in $\text{Cu}_2\text{Te}_{0.9}\text{I}_{0.1}$ while fixing the I ratio at 0.1, the μ is further reduced by nearly one order of magnitude. The minimum μ at room temperature of the $y = 0.4$ sample is only $0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is lower than the Mott-Ioffe-Regel (MIR) limit ($1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^{27, 28} Though we were unable to measure the carrier mobility above room temperature due to general technical restrictions and the already ultralow mobility values, the mobility values of the high S-ratio samples are expected to be near, if not lower than, the MIR limit at temperatures where these samples attain their maximum zT values. By contrast, the state-of-the-art TE materials are featured by well-established band conduction with the carrier mobilities on the order of $10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and above. The μ of $y \leq 0.3$ samples exhibit weak temperature dependence, in contrast, the μ of $y = 0.4$ sample exhibits a slight yet clear positive slope with increasing temperature from 25 K to 300 K (cf. **Figure S3b**). Since the I content stays the same in the samples studied, ionized impurity scattering alone can't be the cause of the positive slope of μ vs T for the $y = 0.4$ sample. The high magnitude on the order of 10^{21} cm^{-3} and the weak temperature dependence of the carrier concentration (**Figure S3a**) exclude the Mott localization and band gap opening as the main cause of the S-content driven resistivity and Seebeck coefficient behavior changeovers shown in **Figure 4a** and **4b**.

Hence, the phonon-assisted hopping mechanism is a plausible scenario, and the reduction of μ is mainly ascribed to the S-alloying induced disorder and Anderson localization.^{45, 49-51} The electronic conduction is dominated by hopping conduction (band conduction) when the Fermi level is in localized state (extended state).⁵² With increasing S content, the degree of disorder is increased, the electron transport behavior is thus driven from itinerant conduction to hopping conduction, leading to a large reduction of μ . On the other hand, the electronic conduction of a material governed by a mobility edge is expected to have strong TE response, i.e., large Seebeck coefficient, on the insulating side of the mobility edge.⁵³ Indeed, the room temperature Seebeck coefficients of the S-alloyed samples studied herein are in the

range of 40-120 $\mu\text{V K}^{-1}$ (cf. **Figure 4e**) at high carrier concentrations on the order of 10^{21} cm^{-3} (cf. **Figure 4a**), which is hard to explain by band conduction and points towards hopping conduction.

The Seebeck coefficient S is significantly enhanced upon I doping and/or S alloying. Specifically, a maximum S of 119 $\mu\text{V K}^{-1}$ at room temperature is obtained for $\text{Cu}_2\text{Te}_{0.4}\text{I}_{0.1}\text{S}_{0.5}$, which is four times larger than that of Cu_2Te and three times higher than that of S-free $\text{Cu}_2\text{Te}_{0.9}\text{I}_{0.1}$ (cf. **Figure 4e**). **Figure 4f** shows the Seebeck coefficient as a function of carrier concentration at room temperature for $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$, $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$, and $\text{Cu}_2\text{Te}_{1-y}\text{S}_y$. Though the electronic conduction in the sample studied is complex, the Pisarenko plot gives some insights into the microscopic conduction mechanism. Specifically, the data of I-doped samples lie around the Pisarenko plot with effective mass of $2.1 m_0$ suggesting that I doping shifts the Fermi level without obviously altering the band structure. In contrast, the S-alloyed samples clearly show much larger Seebeck coefficient than the calculated Pisarenko plot. For $\text{Cu}_2\text{Te}_{1-y}\text{S}_y$, the Seebeck coefficient S are improved by nearly three times while the carrier concentration is reduced to half the value of Cu_2Te . For the $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$ samples, the Seebeck coefficients S are also significantly increased after alloying S although the carrier concentrations are barely changed. This is quite unusual since such large enhancement of S at comparable p has only been reported in several cases such as the existence of resonant states,^{18, 54} band convergence/ overlapping,⁵⁵⁻⁵⁸ or electron critical scattering.⁵⁹ Here, we attribute the enhanced S to the disorder-induced electronic localization,^{52, 60} which qualitatively alters the nature of the wavefunction and the conduction mechanism. For amorphous materials or complex crystalline systems with large disorder, the Seebeck coefficient is intimately related to the enthalpy barrier of carrier hopping between neighbor localized states.^{52, 61} With increasing S content, the disorder strength is gradually increased, resulting in larger enthalpy barriers and thus higher Seebeck coefficients.

The TE properties of $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$ and $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$ as a function of temperature are plotted in **Figure 5**. Both electrical resistivity (ρ) and Seebeck coefficient (S) are significantly increased with an increasing amount of I and S content. The ρ for pristine Cu_2Te is on the order of $10^{-6} \Omega \text{ m}$, which is enhanced by nearly two orders of magnitude, reaching $(1-3) \times 10^{-4} \Omega \text{ m}$ in $\text{Cu}_2\text{Te}_{0.4}\text{I}_{0.1}\text{S}_{0.5}$. With increasing values of ρ , the temperature coefficient of resistivity (TCR) gradually turns from positive in Cu_2Te to negative in $\text{Cu}_2\text{Te}_{0.4}\text{I}_{0.1}\text{S}_{0.5}$ (**Figure 5a** and **Figure S3c**). The change of sign of TCR is reminiscent of the Mooij correlation,⁶² which is typically related with the incipient Anderson localization in highly disordered metals.⁶³ Furthermore, the low temperature electrical resistivities of $\text{Cu}_2\text{Te}_{0.5}\text{I}_{0.1}\text{S}_{0.4}$ and $\text{Cu}_2\text{Te}_{0.4}\text{I}_{0.1}\text{S}_{0.5}$ follow the relation $\ln \rho$ vs. $T^{-1/4}$ (**Figure S4**),⁵² which is also a signature of variable-range hopping conduction for disordered systems. The maximum S for pristine Cu_2Te is only 74 mV K^{-1} , which is improved to 102 mV K^{-1} for $\text{Cu}_2\text{Te}_{0.9}\text{I}_{0.1}$, and further enhanced to 260 mV K^{-1} for $\text{Cu}_2\text{Te}_{0.4}\text{I}_{0.1}\text{S}_{0.5}$ (**Figure 5a**). Note this value is the highest Seebeck coefficient reported in Cu_2Te -based materials. The positive sign of Seebeck coefficients and the positive sign of Hall coefficients indicate that holes are the majority charge carrier. The power factor (PF) is slightly improved when the S alloying content y is lower than 0.3;

however, with further increasing y , the PF is gradually decreased. Specifically, a maximum PF of $8.7 \mu\text{W cm}^{-1} \text{ K}^{-2}$ is obtained for $\text{Cu}_2\text{Te}_{0.6}\text{I}_{0.1}\text{S}_{0.3}$ at 850 K.

Figure 5d displays the total thermal conductivity (κ) as a function of temperature for $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$ and $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$. Most samples exhibit complex temperature dependencies of κ from 300 to 850 K due to the existence of multiple structural transformations.^{23, 24} Notably, κ is significantly reduced with increasing I and S content, which largely stems from the decreased electronic contribution to thermal transport. The lowest κ of $0.3 \text{ W m}^{-1} \text{ K}^{-1}$ is achieved in $\text{Cu}_2\text{Te}_{0.5}\text{I}_{0.1}\text{S}_{0.4}$, which is only one ninth of that of Cu_2Te . The lattice thermal conductivity (κ_L) for $\text{Cu}_2\text{Te}_{1-x-y}\text{I}_x\text{S}_y$ is only $0.27 \text{ W m}^{-1} \text{ K}^{-1}$ at both low and high temperatures (cf. **Figure S5**), approaching the amorphous limit. The low κ_L is attributed to the strong phonon scattering by the as formed hierarchical structural modularity and/or the emerging quasi-particles such as propagons, diffusons, and locons instead of the phonons in the strict sense.⁶⁴

Benefiting from the improved PF and reduced κ , the TE figures of merit zT are greatly enhanced over the entire temperature range studied (cf. **Figure 5e**). Specifically, a record-high zT of ~ 1.4 at 850 K is achieved in $\text{Cu}_2\text{Te}_{0.5}\text{I}_{0.1}\text{S}_{0.4}$, an improvement of $\sim 370\%$ over that of the pristine Cu_2Te ($zT = 0.29$). This zT value is not only much higher than the literature data of Cu_2Te -based TE materials (cf. **Figure 5f**) but also attained near the MIR limit in contrast to most other state-of-the-art TE materials that are band conductors (cf. **Figure 1b**).

In summary, we devise an effective method to integrate the structural-functional modules in the liquid-like TE material Cu_2Te . The aliovalent I dopants in the Te-sites not only stabilize hexagonal structure at room temperature but also act as donors to substantially reduce the hole concentration otherwise too high. Meanwhile, the introduction of isovalent S dopants induces sublattice-level distortions and Anderson localization, which enables a great enhancement of Seebeck coefficient and an ultralow lattice thermal conductivity. Near the Mott-Ioffe-Regel limit where the carrier mobility is exceptionally low, a state-of-the-art zT of 1.4 is achieved at 850 K in $\text{Cu}_2\text{Te}_{0.5}\text{I}_{0.1}\text{S}_{0.4}$, in contrast to the state-of-the-art TE thermoelectric materials that are well-established band conductors. The doping induced hierarchical structural modularity and the discovery of high zT values near the MIR limit in copper tellurides thus present a case of paradigm shift from the band edge to the mobility edge in TE materials research.

Experimental Section

Synthesis. Polycrystalline $\text{Cu}_2\text{Te}_{1-x-y}\text{I}_x\text{S}_y$ samples were synthesized by a melting-annealing method followed by spark plasma sintering. High-purity raw materials of Cu (Sigma Aldrich, 99.999%), Te (Sigma Aldrich, 99.999%), CuI (Sigma Aldrich, 99.9%), and S (Sigma Aldrich, 99.999%) were weighed according to the nominal compositions of $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$ ($x = 0.05, 0.1, 0.12$, and 0.15) and $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$ ($y = 0.1, 0.2, 0.3, 0.4$, and 0.5) and then put inside a pyrolytic boron nitride crucible that sealed in evacuated quartz tubes. The loaded tubes were flame-sealed and then heated to 1403 K in 12 h, soaked at this temperature for 12 h, cooled to 923 K in 50 h, annealed at 923 K for 4 days, and subsequently cooled to room temperature by

turning off the furnace power. After removing the copper precipitate on the surface, the obtained ingots were hand-ground into fine powders and then densified using a spark plasma sintering (Sumitomo SPS-2040) apparatus at 773-823 K under a pressure of 60-65 MPa. Boron nitride was sprayed on the carbon foils and the inner walls of the graphite die to prevent currents from going through the samples causing undesired ionic migration. Finally, highly dense (>97% of theoretical density) disk-shaped pellets were obtained.

Characterization. Room-temperature powder XRD characterization was performed using Rigaku Rint 2000 diffractometer equipped with a Cu-K $_{\alpha}$ source. Rietveld refinement was performed to calculate the lattice parameters using FULLPROF software. The sample compositions were estimated using energy dispersive X-ray analysis (EDS, Horiba 250) that equipped in field emission scanning electron microscopy (FESEM, Magellan-400). Atom-probe tomography (APT) analysis was performed in a Cameca Instruments (LEAP 5000 XR) by applying a DC voltage of 2-4 kV and laser pulse energy of 3 pJ. 20 million ions were collected by the APT with a 50 K measurement temperature and a detection rate of 1%. The needled-sharped samples for the APT analysis were prepared using the standard lift-out procedure by a focused ion beam lift-off methodology (Helios, Nanolab 600). Aberration-corrected scanning transmission electron microscopy (STEM) investigation was conducted on a probe-corrected Hitachi® HF5000 operating at 200kV. The electrical conductivity (σ) and Seebeck coefficient (S) were simultaneously measured by the ULVAC ZEM-3 apparatus. The thermal diffusivity (D) was measured via the laser flash technique with a Netzsch LFA-457. The specific heat (C_p) was estimated by using the Dulong-Petit law. The pellet density (d) was measured by the Archimedes method. The total thermal conductivity (κ) was calculated from the equation $\kappa = d \cdot C_p \cdot D$. The Hall coefficient (R_H) was measured using PPMS-9 with magnetic field swept from -3 to 3 T. The Hall carrier concentration (p) and mobility (μ) were calculated by $p = 1/eR_H$ and $\mu = \sigma R_H$, respectively.

Defect formation energy calculations: The calculations were performed within the framework of density functional theory (DFT) with projector-augmented wave (PAW) method, as implemented in the Vienna Ab Initio Simulation Package (VASP).⁶⁵ The cutoff energy of the plane wave was set at 500 eV. The energy convergence criterion was chosen to be 1×10^{-5} eV per unit cell. A 2×2×2 Cu₂Te supercell containing 48 atoms was used in all DFT calculations. The Brillouin zone integration was sampled using Monkhorst-Pack grids⁶⁶ with a 9×9×9 k-point mesh. The E_v of a Cu vacancy (V_{Cu}) is calculated according to the equation

$$E_v = E_{tot,V_{Cu}} + E_{Cu} - E_{tot} \quad ,$$

where E_{tot} and $E_{tot,V_{Cu}}$ are the cohesive energies of the supercell before and after the introduction of a Cu vacancy, respectively; E_{Cu} is the cohesive energy of copper with fcc crystal structure.

Declarations

Conflicts of interest

There are no conflicts to declare.

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Figures

Figure 1

(a) TE figure of merit zT as a function of Seebeck coefficient at 850 K for the $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$, $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$, and $\text{Cu}_2\text{Te}_{1-y}\text{S}_y$ series. The grey symbols denote the literature data of doped, composited and nanostructured Cu_2Te -based materials.^{25, 26, 29-33} The dashed line is guide to the eyes. The four different functional modules are illustrated in the inset. (b) Maximal z values as a function of the room temperature carrier mobility for a number of representative TE materials.^{11, 16, 34-44} The green region at around $1.3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ denotes the Mott-Ioffe-Regel (MIR) limit. High z values are achieved near the MIR limit in the present work. The carrier mobility for $\text{Cu}_2\text{Te}_{0.4}\text{I}_{0.1}\text{S}_{0.5}$ is too low to be reliably measured, and the corresponding z value is not the highest among the samples studied, so the red dashed line bends downward at the lower side of the carrier mobility.

Figure 2

(a) Room temperature powder X-ray diffraction patterns for $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$ and $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$. (b) Room temperature lattice parameters (a and c) as a function of I content (x) and S content (y). The lattice parameters are markedly decreased with increasing S content due to the much smaller atomic radius of S than that of Te. The crystal structures of hexagonal Cu_2Te ($\text{P6}_3/\text{mmc}$) and hexagonal Cu_2S structure ($\text{P6}_3/\text{mmc}$) are illustrated in the insets. (c) Elemental mapping obtained by three-dimensional atom probe tomography (APT) analysis for $\text{Cu}_2\text{Te}_{0.5}\text{I}_{0.1}\text{S}_{0.4}$.

Figure 3

Transmission electron microscopy (TEM) analyses of the mosaic microstructures in $\text{Cu}_2\text{Te}_{0.6}\text{I}_{0.1}\text{S}_{0.3}$. (a) Bright-field image of an ultra-thin sectioned sample. (b) Electron diffraction pattern of the red circle area in (a). (c) Bright-field image. (d, e, f) Dark-field images obtained using the diffraction spots 1, 2 and 3 in (a), respectively.

Figure 4

(a) Carrier concentration (p) as a function of I content (x) or S content (y) for $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$, $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$, and $\text{Cu}_2\text{Te}_{1-y}\text{S}_y$ at 300 K. (b) The crystal structure used for DFT calculations of copper vacancy formation energy. (c) Calculated copper vacancy formation energy in $\text{Cu}_{32}\text{Te}_{16}$, $\text{Cu}_{32}\text{Te}_{15}\text{S}$, $\text{Cu}_{32}\text{Te}_{15}\text{I}$, and $\text{Cu}_{32}\text{Te}_{14}\text{IS}$. (d) Carrier mobility (μ) as a function of I content (x) or S content (y) for $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$, $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$, and $\text{Cu}_2\text{Te}_{1-y}\text{S}_y$ at 300 K. The inset shows a schematic of the localized electronic states and extended electronic states. The red dashed line denotes the Mott-Ioffe-Regel (MIR) limit.^{27, 28} (e) Seebeck coefficient (S) as a function of I content (x) or S content (y) for $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$, $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$, and $\text{Cu}_2\text{Te}_{1-y}\text{S}_y$ at 300 K. (f) Seebeck coefficient (S) as a function of carrier concentration (p) at 300 K.

The carrier concentration of $\text{Cu}_2\text{Te}_{0.4}\text{I}_{0.1}\text{S}_{0.5}$ is hard to measure because of localized electronic states. Here the p of $\text{Cu}_2\text{Te}_{0.4}\text{I}_{0.1}\text{S}_{0.5}$ (grey sphere) is assumed to be the same as that of $\text{Cu}_2\text{Te}_{0.5}\text{I}_{0.1}\text{S}_{0.4}$. The dashed lines are the calculated Pisarenko plots based on a single parabolic band (SPB) model.²⁰ The reported S vs. p experimental data of $\text{Cu}_2\text{Te}_{1-y}\text{Sy}$ and $\text{Cu}_2\text{Te}_{0.5+x}\text{S}_{0.5-x}$ are included for comparison.^{29, 45}

Figure 5

Temperature dependent TE properties for $\text{Cu}_2\text{Te}_{1-x-y}\text{I}_x\text{S}_y$. (a) electrical resistivity ρ , (b) Seebeck coefficient S , (c) power factor PF , (d) thermal conductivity κ , (e) TE figure of merit zT . The open and filled symbols refer to the data of I-doping $\text{Cu}_2\text{Te}_{1-x}\text{I}_x$ and S-alloying $\text{Cu}_2\text{Te}_{0.9-y}\text{I}_{0.1}\text{S}_y$ samples, respectively. (f) Comparison of zT values for several reported Cu_2Te -based TE materials.^{20, 25, 26, 29-33}

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