Phase-engineered high-entropy metastable FCC Cu$_{2-y}$Ag$_y$(In$_x$Sn$_{1-x}$)Se$_2$S nanomaterials with high thermoelectric performance

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Crystal-phase engineering to create metastable polymorphs is an effective and powerful way to modulate the physicochemical properties and functions of semiconductor materials, but it has been rarely explored in thermoelectrics due to concerns over thermal stability. Herein, we develop a combined colloidal synthesis and sintering route to prepare nanostructured solids through ligand retention. Nano-scale control over the unconventional cubic-phase is realized in a high-entropy Cu$_{2-y}$Ag$_y$(In$_x$Sn$_{1-x}$)Se$_2$S (x = 0–0.25, y = 0, 0.07, 0.13) system by surface-ligand protection and size-driven phase stabilization. Different from the common monoclinic phase, the unconventional cubic-phase samples can optimize electrical and thermal properties through phase and entropy design. A high power factor (0.44 mW m$^{-1}$ K$^{-2}$), an ultralow thermal conductivity (0.25 W m$^{-1}$ K$^{-1}$) and a ZT value of 1.52 are achieved at 873 K for the cubic Cu$_{1.87}$Ag$_{0.13}$(In$_0.06$Sn$_{0.94}$)Se$_2$S nanostructured sample. This study highlights a new method for the synthesis of metastable phase high-entropy materials and gives insights into stabilizing the metastable phase through ligand retention in other research communities.

1. Introduction

Thermoelectric devices can directly convert waste heat into electrical power without hazardous emissions and moving parts and have become an attractive option for improving energy utilization in applications such as medical devices,$^1$ thermal management,$^2$ cooling$^{3,4}$ and thermocells.$^3$ In general, the energy conversion efficiency of a thermoelectric material is determined by the figure of merit, $ZT = S^2\sigma T/k_\text{tot}$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $k_\text{tot}$ is the total thermal conductivity, and $T$ is the working temperature. In the past few decades, several strategies such as band convergence,$^5$–$^9$ resonance level,$^{10}$–$^{11}$ introducing defects,$^{12}$–$^{13}$ and controlling grain size$^{14}$–$^{15}$ have been successfully developed to increase $ZT$. So far, TE materials have been thoroughly investigated, including SnSe,$^{16}$ GeTe,$^{17}$ carbon hybrids,$^{18}$ Cu$_2$Se$^{19}$ and organic thermoelectrics.$^{20}$ However, strong coupling between $S$, $\sigma$, and $k_\text{tot}$ remains a formidable challenge for further optimization of thermoelectric performance.

Phase engineering focuses on the synthesis of unconventional phases, phase transformations and phase-based heterostructures. In particular, preparation of unconventional phases in nanomaterials through carefully regulating reaction kinetics and/or thermodynamics endows them with distinctive properties.$^{21}$–$^{24}$ Meanwhile, this concept may also be developed in a coordinated way with other aspects, including composition, architecture, and dimensionality engineering, to realize a higher level of control over thermoelectric materials. Recently, high-entropy alloys (HEAs), in which multiple elements are utilized to occupy equivalent atomic sites resulting in increased configurational entropy, have provided a new means for improving the thermoelectric performance of materials.$^{25}$–$^{27}$ Based on the core effects of HEAs, a synergy of band structure engineering and all-scale hierarchical microstructures is well realized.$^{28}$–$^{30}$ However, the metastable-phase engineering of
high-entropy bulk thermoelectric materials remains a great challenge. According to the Gibbs free energy equation \(G = H - TS\), where \(T\) is temperature, \(S\) is entropy, and \(H\) is enthalpy), high mixing entropy at high temperature can effectively reduce the \(G\) of the alloy system and promote the formation of the solid solution phase of the alloy. Therefore, the traditional synthesis of high-entropy alloys mostly relies on the high temperature melting method, and metastable phases in high-entropy systems are hard to achieve.\(^{34}\) In contrast, phase engineering of nanomaterials may avoid high temperatures and pressures, because the molar Gibbs energy, the molar entropy and the molar enthalpy increase as the particle size decreases.\(^{31-33}\) In colloidal synthesis, the retained surface ligand can prevent grain growth and stabilize metastable phases through tuning the surface-related \(H\). On the basis of this, phase engineering of high entropy nanomaterials can be well realized by changing the reaction conditions such as the stoichiometric ratio of precursor to surfactant, and sintering conditions. Therefore, developing ligand-retention synthetic strategies for preparation of high-entropy nanostructured solids is of great importance but still remains unexplored.

\(\text{Cu}_2\text{SnSe}_3\) is a p-type semiconductor with a direct bandgap of 0.84 eV, which has attracted increasing attention in the thermoelectric community due to its compositionally tunable electronic structure and intrinsically low lattice thermal conductivity.\(^{34,35}\) Previous studies have shown that the thermoelectric properties of \(\text{Cu}_2\text{SnSe}_3\) can be improved by modulation doping, synergistic alloying and nanostructuring with second phases.\(^{34-38}\) For example, Li et al.\(^{34}\) showed that \((\text{Ag, In})\)-co-doping provides an effective solution to optimize the \(ZT\) of \(\text{Cu}_2\text{SnSe}_3\) to 1.42 at 823 K. Ming et al.\(^{35}\) achieved a record high \(ZT\) of 1.51 at 858 K for \(\text{Cu}_2\text{Sn}_{0.82}\text{In}_{0.18}\text{Se}_2\text{S}_{0.3}\) via alloying S and doping In. However, the structures of these materials are mostly monoclinic, while the cubic structure with high symmetry as a metastable phase is rarely obtained, as it requires thermodynamic control through specific synthetic conditions.

In this work, as shown in Scheme 1, we firstly adopt colloidal synthesis, performed at a low temperature for short reaction times, to obtain metastable wurtzite \(\text{Cu}_2\gamma\text{Ag}_x(\text{In}_y\text{Sn}_{1-x-y})\text{Se}_2\text{S}\) nanocrystals. Different from the monoclinic bulk materials in most of the literature,\(^{34,35,39-44}\) a series of multinary chalco-
genide nanostructured solids with a metastable cubic phase are obtained after spark plasma sintering (SPS). Here, oleylamine (OAm) and dodecanethiol (DDT) coated on nanoparticle surfaces could carbonize to protective amorphous carbon shells that can restrict the growth of nanoparticles and stabilize a metastable cubic phase of nanostructured solids. As a result, the cubic-phase, high-entropy \(\text{Cu}_{1.87}\text{Ag}_{0.13}(\text{In}_{0.06}\text{Sn}_{0.94})\text{Se}_2\text{S}\) nanomaterial achieves a high power factor (PF) of 0.44 mW m\(^{-1}\) K\(^{-2}\), an ultralow thermal conductivity of 0.25 W m\(^{-1}\) K\(^{-1}\), and a peak \(ZT\) of 1.52 at 873 K.

2. Results and discussion

2.1 Phase engineering through surface-ligand protection

\(\text{Cu}_2\text{SnSe}_3\), \(\text{Cu}_2\text{SnSe}_2\text{S}\), \(\text{Cu}_2\text{In}_{1-x-y}\text{Sn}_x\text{Se}_2\text{S}\), and \(\text{Cu}_2\gamma\text{Ag}_x(\text{In}_{0.06}\text{Sn}_{0.94})\text{Se}_2\text{S}\) \((y = 0, 0.07, 0.13)\) nanocrystals were synthesized by the reaction of metal chlorides and diphenyl diselenide/DDT/OAm solution as the precursors (see the Experimental section in the ESI† for details). X-ray diffraction (XRD) patterns (Fig. S1†) suggest that the as-synthesized nanocrystals have a wurtzite structure derived from \(\text{ZnSe}\), in which the cationic \(\text{Zn}^{2+}\) ions are substituted by \(\text{Cu}^+, \text{In}^{3+}, \) and \(\text{Sn}^{4+}\), and anionic \(\text{Se}^{2-}\) ions are partly substituted.

![Scheme 1](https://example.com/scheme1.png)

Scheme 1. (a) The monoclinic \(\text{Cu}_2\text{SnSe}_3\)-based bulk materials reported in most of the literature\(^{34,35,39-42}\) are obtained via the high temperature melting method. (b) Synthetic methods of the metastable wurtzite structure \(\text{Cu}_2\gamma\text{Ag}_x(\text{In}_y\text{Sn}_{1-x-y})\text{Se}_2\text{S}\) nanocrystals and metastable cubic \(\text{Cu}_2\gamma\text{Ag}_x(\text{In}_y\text{Sn}_{1-x-y})\text{Se}_2\text{S}\) nanostructured solids.
by S²⁻. As a representative, the powder XRD pattern of Cu₃-InSnSe₃S₂ nanocrystals was analyzed by the Rietveld refinement method (Fig. S1b†), in which the crystal structure fitted well to the wurtzite structure with space group P6₃mc (186) and the lattice parameters are listed in Table S1.† When Ag element is alloyed in Cu₂₋yAgₓ(In₀.06Sn₀.94)Se₂S (y = 0.07 and 0.13), a small fraction of the second phase, CuAgS, is observed in the samples (Fig. S1a†). To characterize the thermoelectric properties of the dense materials compacted from these nanoparticles, the purified nanocrystals were sintered by SPS and characterized by XRD, as shown in Fig. 1a. The main peaks of SPSed-Cu₂SnSe₃ match well with the cubic phase Cu₂SnSe₃ (PDF# 65-4145). The peaks shift to high angle after alloying S into the anionic site and/or doping In into the cationic site, indicating the shrinkage of lattice parameters. Interestingly, when the amount of indium increases to a certain amount, SPSed-Cu₂In₀.06Sn₀.94Se₂S and SPSed-Cu₁InSnSe₂S nanostructured solids have a tetragonal structure (space group I42m) without impurities, and this tetragonal unit cell can be approximately depicted as a 1×1×2 supercell of cubic Cu₂SnSe₃ (Fig. 1a and Table S1†). After Ag alloying, SPSed-Cu₁₋ₓAgₓ(In₀.06Sn₀.94)Se₂S shows a cubic structure (Fig. 1c). Due to the larger ionic radius of Ag⁺ (1.26 Å) compared to that of Cu⁺ (0.96 Å), the diffraction peaks shift toward the low-angle direction with respect to cubic SPSed-Cu₂In₀.06Sn₀.94Se₂S (Fig. 1a) due to an expansion of the lattice. The cubic Cu₁₋ₓSe phase still exists as a second phase in samples and disappears upon increasing In content and/or alloying Ag. In addition, according to the classical theory of grain growth, the Zener pinning effect caused by the introduction of a second phase could inhibit grain growth to some extent.

From a synthetic perspective, a high-entropy system, Cu₂₋yAgₓ(In₀.06Sn₁₋x)Se₂S (x = 0–0.25, y = 0, 0.07, 0.13), with two metastable phases (wurtzite nanocrystals and cubic nanostructured solids) is obtained, which is hard to realize in their bulk counterparts. Formation energies of the cubic and monoclinic-phase Cu₂SnSe₃, Cu₂SnSe₂S, Cu₁In₀.06Sn₀.94Se₂S, and Cu₁₋ₓAgₓ(In₀.06Sn₀.94)Se₂S, and tetragonal-phase Cu₁InSnSe₂S are calculated by density functional theory (DFT). Indeed, all monoclinic crystals show lower formation energy than the metastable cubic phase (Table S2†). The colloidal synthetic strategy for monodisperse multinary chalcogenide nanocrystals and the following SPS process are the key factors for the retention of the metastable phase. As shown in Fig. 1f, FTIR spectrometry was performed to verify the surface ligand of OAm in a solution-synthesized Cu₁.87Ag₁.13(In₀.06Sn₀.94)Se₂S sample. The presence of the OAm molecule is indicated by the symmetric and asymmetric stretching vibrations of –NH₂ at 3430.74 cm⁻¹, the bending vibrations of C–C and –NH₂ bonds.
at 1626.72 cm\(^{-1}\), and the bending vibration of the C–N bond at 1109.88 cm\(^{-1}\). During the nanocrystal consolidation process, OAm as a surfactant capping agent at the surface of colloidal nanoparticles can decrease the surface free energy of nano-crystals, simultaneously acting as a controllable molecular solder,\(^*\) which might have a dominant effect that restricts the growth of nanoparticles and stabilizes the metastable phase.\(^{46–49}\) Detailed evidence is shown in SEM and TEM images (Fig. 6b and 9a and S9, and the EDS element map of SPSed-Cu\(_{1.87}\)Ag\(_{0.13}\)(In\(_{0.06}\)Sn\(_{0.94}\))Se\(_2\)S confirms the existence of carbon after sintering (Fig. 1g). In addition, the contents of hydrogen (0.05 wt%) and carbon (1.15 wt%) were measured in the SPSed-Cu\(_{1.87}\)Ag\(_{0.13}\)(In\(_{0.06}\)Sn\(_{0.94}\))Se\(_2\)S sample, and the results indicate that some of the surface ligands were converted into a mixture of organic hydrocarbons between nanograins of nanostructured solids during the sintering process (Fig. S9c). Based on size reduction, metastable cubic nanostructured solids during the sintering process (Fig. S9c). Based on size reduction, metastable cubic nanostructured solids with low entropy effects, which is different from the strategy for stabilizing the cubic crystal nucleus due to its higher reactively. Then highly active diphenyl diselenide (PhSeSePh) rapidly decomposes at high temperatures a perfect local element enrichment is observed (Fig. S3c, S4c, S6b, S7b and S11d). For nanostructured solids, Fig. S9a and S11e show the HAADF-STEM images of a Cu\(_3\)InSnSe\(_3\)S nanocrystals show hexagonal structures with an average size of 10 (±2) nm (Fig. S4a and b and S5a). Elemental mapping measurement was performed to identify the presence of Cu, Ag, In, Sn, Se, and S elements in nanoparticles of Cu\(_2\)SnSe\(_3\), Cu\(_2\)SnSe\(_2\)S, SPSed-Cu\(_2\)SnSe\(_3\), SPSed-Cu\(_2\)SnSe\(_2\)S, and SPSed-Cu\(_{1.87}\)Ag\(_{0.13}\)(In\(_{0.06}\)Sn\(_{0.94}\))Se\(_2\)S. All elements in the samples show homogeneous distributions, and no significant local element enrichment is observed (Fig. S3c, S4c, S6b, S7b and S11d). For nanostructured solids, Fig. S9a and b† show the scanning electron microscopy (SEM) surface micrographs of SPSed-Cu\(_{2}\)In\(_{0.06}\)Sn\(_{0.94}\)Se\(_2\)S and SPSed-Cu\(_{1.87}\)Ag\(_{0.13}\)(In\(_{0.06}\)Sn\(_{0.94}\))Se\(_2\)S pellets. A slight grain growth of nanoparticles can be observed during the sintering process and the final average grain sizes are 63.06 (±30) and 131.98 (±50) nm for SPSed-Cu\(_{2}\)In\(_{0.06}\)Sn\(_{0.94}\)Se\(_2\)S and SPSed-Cu\(_{1.87}\)Ag\(_{0.13}\)(In\(_{0.06}\)Sn\(_{0.94}\))Se\(_2\)S, respectively. Fig. S10a and d and S11e† show the high-resolution TEM (HRTEM) images of the SPSed-Cu\(_2\)SnSe\(_3\)S, SPSed-Cu\(_2\)SnSe\(_2\)S, and SPSed-Cu\(_{1.87}\)Ag\(_{0.13}\)(In\(_{0.06}\)Sn\(_{0.94}\))Se\(_2\)S samples. The inverse fast Fourier transform (IFFT) images (Fig. S10b and e and S11f) clearly show the highly dense dislocation arrays. In order to investigate the strain fields from distorted lattices caused by the strong mismatch of the atomic radius, geometric phase analysis (GPA) was performed based on IFFT images to calculate the strains. As shown in Fig. S10c and f and S11e,† strong strain distribution fluctuations can be observed in the SPSed samples, which should strongly affect the thermal transport process.

In order to understand the local and long-range structures of the as-obtained nanostructured solids, an X-ray pair distribution function (X-PDF) analysis was performed. The corresponding Rietveld results are shown in Fig. 1d and e, and S1d and e.† It is evident that the global X-PDF structures of simulated structure models provide good descriptions of all the samples, demonstrating the overall crystallographic structure. The peaks with chemical bonding information in the diagrams labeled by letters can be well assigned to the atomic pair distances of the samples (Table S3†). As shown in Fig. 1e and S1e,† the residual curve (green curve) of the cubic model establishes much smoother characteristics in the large range from 10 Å to 30 Å, demonstrating long-range highly crystalline structures. In contrast, the local bonding interactions (5–10 Å) deviate significantly from the simulated profile for the cubic model, as observed from the asymmetric peaks and large fluctuations in the green line. Such a phenomenon is an indication of the local structural distortion with the unbalanced long and short bond lengths. The coexistence of the high-symmetry long-range structure and distorted local structure could be an example of ideal thermoelectric materials based on the ‘phonon-glass, electron-crystal’ concept that could lead to high electrical conductivity and low thermal conductivity and finally achieve a high ZT value.\(^{50,51}\)

2.2 Microstructure and composition

The microstructures of the as-synthesized samples were comprehensively characterized. First, the hexagonal (wurtzite) structure of Cu\(_2\)SnSe\(_3\) is confirmed with an average size of around 30 (±10) nm by transmission electron microscopy (TEM) (Fig. S3a and b†). Then, thiol is added to the reaction system as the S source and surfactant capping agent, which can passivate the crystalline facets of the wurtzite nanocrystals, and thus realize size control. As a result, the synthesized Cu\(_2\)SnSe\(_3\) and Cu\(_2\)InSnSe\(_3\) nanocrystals show hexagonal structures with an average size of 10 (±2) nm (Fig. S4a and b and S5a†). Elemental mapping measurement was performed to identify the presence of Cu, Ag, In, Sn, Se, and S elements in nanoparticles of Cu\(_2\)SnSe\(_3\), Cu\(_2\)SnSe\(_2\)S, SPSed-Cu\(_2\)SnSe\(_3\), SPSed-Cu\(_2\)SnSe\(_2\)S, and SPSed-Cu\(_{1.87}\)Ag\(_{0.13}\)(In\(_{0.06}\)Sn\(_{0.94}\))Se\(_2\)S. All elements in the samples show homogeneous distributions, and no significant local element enrichment is observed (Fig. S3c, S4c, S6b, S7b and S11d). For nanostructured solids, Fig. S9a and b† show the scanning electron microscopy (SEM) surface micrographs of SPSed-Cu\(_{2}\)In\(_{0.06}\)Sn\(_{0.94}\)Se\(_2\)S and SPSed-Cu\(_{1.87}\)Ag\(_{0.13}\)(In\(_{0.06}\)Sn\(_{0.94}\))Se\(_2\)S pellets. A slight grain growth of nanoparticles can be observed during the sintering process and the final average grain sizes are 63.06 (±30) and 131.98 (±50) nm for SPSed-Cu\(_{2}\)In\(_{0.06}\)Sn\(_{0.94}\)Se\(_2\)S and SPSed-Cu\(_{1.87}\)Ag\(_{0.13}\)(In\(_{0.06}\)Sn\(_{0.94}\))Se\(_2\)S, respectively. Fig. S10a and d and S11e† show the high-resolution TEM (HRTEM) images of the SPSed-Cu\(_2\)SnSe\(_3\)S, SPSed-Cu\(_2\)SnSe\(_2\)S, and SPSed-Cu\(_{1.87}\)Ag\(_{0.13}\)(In\(_{0.06}\)Sn\(_{0.94}\))Se\(_2\)S samples. The inverse fast Fourier transform (IFFT) images (Fig. S10b and e and S11f) clearly show the highly dense dislocation arrays. In order to investigate the strain fields from distorted lattices caused by the strong mismatch of the atomic radius, geometric phase analysis (GPA) was performed based on IFFT images to calculate the strains. As shown in Fig. S10c and f and S11e,† strong strain distribution fluctuations can be observed in the SPSed samples, which should strongly affect the thermal transport process.

To further verify the single-phase and high-entropy configuration in the as-synthesized Cu\(_2\)InSnSe\(_2\)S and SPSed-Cu\(_2\)InSnSe\(_3\)S, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was conducted. Fig. 2a and e show the HAADF-STEM images of a Cu\(_2\)InSnSe\(_2\)S nanoparticle and SPSed-Cu\(_2\)InSnSe\(_2\)S nanostructured solid viewed along the [001] and [110] zone axes, respectively. The atomic models of the hexagonal structure and tetragonal structure are in good agreement with the experimental images, indicating the consistency of the atomic lattices and positions of all atoms (Fig. 2b and f). As shown in Fig. 2d, all elements are distributed in the nanoparticle, and Cu and S are a little bit aggregated in the center of the particle. From our results and some literature reports,\(^{52,53}\) we believe that the copper thiolate in solution could preferentially decompose into a Cu\(_2\)S–S crystal nucleus due to its higher reactively. Then highly active diphenyl diselenide (PhSeSePh) rapidly decomposes at high temperatures after injection and triggers the growth of nanocrystals, in which Se, Sn and In atoms gradually diffuse into the Cu\(_2\)S crystal nucleus simultaneously with the epitaxial growth and matura-
the EDS mapping of the SPSed-Cu₃InSnSe₃S₂ sample demonstrates that the distribution of all elements is homogeneous in the nanostructured solid.

Atom probe tomography (APT) analysis provides the mapping of three-dimensional microstructural and compositional information with sub-nanometer spatial accuracy and elemental sensitivity in the range of tens of ppm, which can provide solid evidence that these elements are indeed homogeneously distributed in the nanostructured solid at the atomic scale. The 3D atomic maps and the nearest-neighbor (NN) atomic distribution of SPSed-Cu₂In₀.₀⁹Sn₀.⁹₁Se₂S are shown in Fig. 2i and S14, respectively. The measured NN atomic distance histograms of each element completely overlap with the calculated curves (Fig. S14) without deviating from the randomized Gaussian peak, revealing the homogeneous distribution of the Cu, In, Sn, Se, and S elements. The homogeneous and disordered distribution of all the elements on the macroscale, nanoscale, and atomic-scale confirms that the as-synthesized nanostructured solid is a high-entropy multinary metal chalcogenide.

2.3 Electronic and phononic band structures
To gain insight into the evolution of electronic states in the conventional monoclinic structure and metastable cubic structure, DFT calculations were performed. Fig. 3a and b show the electronic band structures of monoclinic and cubic Cu₁.₈⁷Ag₀.₁₃(In₀.₀₆Sn₀.₉₄)Se₂S, respectively. Those of Cu₂SnSe₃, Cu₂SnSe₂S, and Cu₂In₀.₀₆Sn₀.₹₄Se₂S are shown in Fig. S15. The monoclinic and cubic Cu₂SnSe₃ are direct-band-gap semiconductors with band gaps (E_g) of 0.12 and 0.11 eV, respectively (Fig. S15a and b). E_g can be effectively enlarged by alloying S into the anionic site of Cu₂SnSe₃ (Fig. S15c and d). In-Doped Cu₂SnSe₂S pushes the Fermi level (E_F) deep into the multiple bands and turns Cu₂In₀.₀₆Sn₀.₹₄Se₂S into a highly degenerate
semiconductor (Fig. S15e and ff), which thus increases channels for electrical transport. From the valence bands near the Fermi level that are highlighted by the red circles in Fig. 3a and b and S15, we find that the top three valence bands at the Γ point of the monoclinic structure display band splitting while the cubic structure is degenerate. The cubic phase with high degeneracy can lead to more energy valleys participating in electrical transport.13

To gain insight into phonon and thermal properties, we calculated the phonon dispersion relations of monoclinic and cubic Cu$_2$SnSe$_3$ based on DFT, as shown in Fig. 3c and d. The monoclinic phase has 12 atoms in a primitive cell and thus 36 phonon branches (Fig. S16a†). The cubic phase has a zinc blende structure, in which Cu and Sn randomly occupy the cation sites with a ratio of 2:1, and Se occupies the anion sites (Fig. S16b†). We used the virtual crystal approximation (VCA) to calculate the phonon dispersion of the cubic phase. Under VCA, the cubic phase has a primitive cell that consists of 2 atoms – a virtual atom, made of 2/3 Cu and 1/3 Sn, and a Se atom. The phonon dispersion of the cubic phase does not show any imaginary frequency, indicating that the structure is locally stable. The maximum frequency of the cubic phase is larger than that of the monoclinic phase, indicating that the cubic phase may have stronger bonds. The phonon group velocity, especially for the longitudinal acoustic (LA) branch, of the cubic phase is much larger than that of the monoclinic phase (Fig. S16†). The volumetric heat capacity of the cubic phase is slightly larger than that of the monoclinic phase (Fig. S16†), partially because the cubic phase has higher symmetry and packing density. Based on phonon kinetic theory, the lattice thermal conductivity is $k_\text{L} = 1/3c\nu^2\tau$, in which $c$ is the heat capacity, $\nu$ is the group velocity, and $\tau$ is the phonon relaxation time. Since the cubic phase has larger $c$ and $\nu$ than the monoclinic phase, its $\tau$ must be much smaller, in order to have similar or lower $k_\text{L}$. This inference indicates that the disorder and distortion induced by Cu/Sn alloying that was not considered in the VCA in the cubic phase must be strong and induce severe phonon scattering. Additionally, grain boundaries, dislocations, Ag and S alloying and In doping further reduce the phonon relaxation time.

2.4 Thermoelectric properties

2.4.1. Sulfur alloying at the anionic site. Fig. S19† shows the thermoelectric properties of Cu$_2$SnSe$_3$ and Cu$_2$SnSe$_2$S in the temperature range of 323–873 K. It is found that S-alloying leads to a clear decrease in electrical conductivity ($\sigma$) (Fig. S19a†). The positive Seebeck coefficient ($S$) (Fig. S19b†) indicates that the major charge carrier is holes. The $S$ values of Cu$_2$SnSe$_3$ and Cu$_2$SnSe$_2$S increase with rising temperature. Specifically, $S$ increases from 28.15 $\mu$V K$^{-1}$ for Cu$_2$SnSe$_3$ to 133.62 $\mu$V K$^{-1}$ for Cu$_2$SnSe$_2$S at 323 K by partial replacement of Se with S. Despite the enhanced Seebeck coefficient, the power factor (PF) of Cu$_2$SnSe$_3$ (0.37 mW m$^{-1}$ K$^{-2}$ at 873 K) is smaller than that of Cu$_2$SnSe$_2$ (0.58 mW m$^{-1}$ K$^{-2}$ at 873 K) (Fig. S19c†) because of the lower electrical conductivity. Cu$_2$SnSe$_3$ has a low thermal conductivity ($k_\text{tot}$) of 0.43 W m$^{-1}$ K$^{-1}$, which is about 47% lower than that of non-alloyed Cu$_2$SnSe$_3$ (Fig. S19d†), indicating the role of S alloying in reducing $k$. This result may be caused by the distortion and diminished uniformity of the lattice structure, as well as the coexistence of the minor secondary phase of Cu$_1$8Se, which enhances the scattering of phonons. Since the large decrease in $k_\text{tot}$ overwhelms the decreased PF, the $ZT$ value of the Cu$_2$SnSe$_2$S nanostructured solid is 0.75 at 873 K, higher than that of Cu$_2$SnSe$_3$ (Fig. S19e†).

2.4.2. Ag and In alloying at the cationic site. Fig. 4a depicts the temperature dependence of $\sigma$ of Cu$_{2-x}$Ag$_x$(In$_{0.5}$Sn$_{1-x}$)Se$_2$S ($x = 0, 0.05, 0.06, 0.25, y = 0, 0.07, 0.13$), which show complex dependence on the $x$ and $y$ values. Ag alloying can increase $\sigma$ from 7.06 $\times$ 10$^3$ S m$^{-1}$ for Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S to 19.18 $\times$ 10$^3$ S m$^{-1}$ for Cu$_{1.93}$Ag$_{0.07}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S at 873 K. Fig. 4b shows $S$ of Cu$_{2-x}$Ag$_x$(In$_{0.5}$Sn$_{1-x}$)Se$_2$S for different values of $x$ and $y$. $S$ increases with increasing temperature in the range of 323–723 K and then decreases slightly in the high-temperature zone, which may be ascribed to the thermal excitation of minority carriers. Moreover, with an increase in the amount of In, $S$ is boosted from 197 $\mu$V K$^{-1}$ for Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S to 298 $\mu$V K$^{-1}$ for Cu$_2$In$_{0.25}$Sn$_{0.75}$Se$_2$S at 873 K. Fig. 4d shows the $k_\text{tot}$ of Cu$_{2-x}$Ag$_x$(In$_{0.5}$Sn$_{1-x}$)Se$_2$S. A significant reduction in $k_\text{tot}$ upon doping In at the Sn site and/or alloying Ag at the Cu site is found, demonstrating the important role of entropy effects.

2.4.3. High crystallographic symmetry leads to high Seebeck coefficient and power factor. In order to understand the electrical transport, effective mass analysis by the Pisarenko plot was done, as shown in Fig. 5a. Compared with the largest $m_\text{eff} = 3.1 m_e$ ($m_e$ is the free electron mass) in the monoclinic phase of Cu$_2$SnSe$_2$, Cu$_2$SnSe$_2$S, and Cu$_{2-x}$Ag$_x$(In$_{0.5}$Sn$_{1-x}$)In$_2$Se$_3$ reported by Ming et al.15 and Li et al.14 the enhancement in symmetry increases the effective mass to 4.0$m_e$ in our cubic Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S sample, yielding a large Seebeck coefficient. As shown in Fig. 4c, the PF further increases via Ag alloying in the whole investigated temperature range. The maximum PF values of 0.45 and 0.44 mW m$^{-1}$ K$^{-2}$ are obtained at 873 K for...
Cu$_1$$_{1.93}$Ag$_{0.07}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S and Cu$_1$$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S, respectively.

2.4.4. Unique crystal structure and nanostructures lead to ultralow thermal conductivity. The temperature-dependent total ($k_{\text{tot}}$) and lattice ($k_{\text{lat}}$) thermal conductivity for all the samples decline with increasing temperature in the whole investigated temperature range, as exhibited in Fig. 4d and e. The $k_{\text{lat}}$ is calculated by $k_{\text{lat}} = k_{\text{tot}} - k_{e}$, in which $k_{e}$ is electronic thermal conductivity and is estimated using the Wiedemann–Franz law, i.e., $k_{e} = L\sigma T$, where $L$ is the Lorentz factor, calculated based on the single parabolic band (SPB) assumption. The $k_{\text{tot}}$ and $k_{\text{lat}}$ gradually decrease with In doping, but increase with more In content doping, which should be attributed to the reduction of secondary phase and the decrease of atomic disorder resulting from the transition to the tetragonal phase. Furthermore, the substitution of Ag on the Cu site further decreases the $k_{\text{tot}}$ and $k_{\text{lat}}$ down to 0.25 and 0.13 W m$^{-1}$ K$^{-1}$ respectively at 873 K for the Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S sample due to the enhanced scattering of phonons resulting from the distortion and diminished uniformity of the lattice structure, which is comparable to some reported materials with extremely low $k$, such as AgSbTe$_2$, Bi$_4$O$_4$SeCl$_2$ (ref. 56) and TlCuSe.$^{57}$ Compared to the thermal conductivity reported in Cu$_2$SnSe$_3$-based systems in the literature,$^{34-36,39}$ our value is relatively low, as shown in Fig. 5c.

The ultralow $k_{\text{lat}}$ of the as-synthesized samples can be attributed to the following three reasons. First, the intrinsic crystal structure of Cu$_2$SnSe$_3$-based materials leads to low phonon thermal conductivity. More specifically, the Cu–Se bond constructs a conductive framework for controlling hole
transport, and cationic doping is allowed to adjust the carrier concentration. Such structural characteristics are similar to those of phonon glass electron crystal (PGEC) compounds, which can be confirmed by low-temperature $C_p$ measurement (Fig. S22†). The plot of $C_p$ vs. $T$ can be fitted by a Debye model combined with three Einstein modes (black line, the detailed calculation is shown in the ESI†), which illustrates that the contribution to $C_p$ at low temperature is dominated by low-energy optical modes resulting from the weakly bound Cu or Ag-rattlers (Einstein oscillators) that suppress lattice thermal conductivity ($k_{lat}$). Second, the configurational entropy in a material increases through doping and alloying (Fig. S23†). Based on the Boltzmann hypothesis, the configurational entropy ($\Delta S$) is given by:

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

where $k_B$ is the Boltzmann constant, $\Omega$ is the atomic occupation probability, $n$ is the number of substituted components, $x_i$ is the mole content of the $i$th component, and $N_A$ is Avogadro's number. Among the various components, the possibility of each element having the same lattice size and different atomic size and electronegativity results in lattice distortion, which can be confirmed by the PDF result in Fig. 1e. Short-range disordered structure of multi-component high-entropy materials caused by severe lattice distortion can strongly scatter heat-carrying phonons, reducing the material's lattice thermal conductivity down to its theoretical minimum value. Third, the nano-sized grain effects (boundary scattering) and multidimensional defects (i.e., minor secondary phase of Cu$_{1.8}$Se, point defects, dislocations, and strain fields) (Fig. 5b) induce severe phonon scattering and efficiently reduce the lattice thermal conductivity. Additionally, the amorphous carbon formed by carbonization of ligands after SPS could result in the reduction of thermal conductivity $k$ due to the large interfacial thermal resistance ($R_k$) resulting from the high dissimilarity in density, sound velocity, and phonon density of states between carbon and the semiconductor matrix.

Fig. 5f shows the temperature dependence of $ZT$ values for Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S. Owing to the high PF and low thermal conductivity, Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S shows the maximum $ZT$ of 1.52 at 873 K. Compared to the $ZT$ values reported in Cu$_2$SnSe$_3$-based systems in the literature, our value is essentially record-high, as shown in Fig. 5d. Compared with the...
lat and carrier mobility ($\mu_\text{H}$) at ~300 K in the monoclinic-phase Cu$_{2}$Sn$_{0.8}$In$_{0.2}$Se$_{2.7}$S$_{0.3}$ and Cu$_{1.85}$Ag$_{0.15}$Sn$_{0.9}$In$_{0.1}$Se$_{3}$ reported by Ming et al.$^{35}$ and Li et al.$^{34}$, a relatively low $k_\text{lat}$ and $\mu_\text{H}$ (Table S5†) are obtained in our cubic Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S sample due to the nano-grain size, which enhances the grain boundary scattering for the charge carrier. The ultralow $k_\text{lat}$ can compensate for the deterioration in electrical conductivity, which can be understood from the quality factor,$^{65}$

$$\beta = \frac{\mu_\text{H} k_\text{lat}}{m_\text{d}^*/m_\text{e}^{3/2}}$$

(Table S5†), taking into account the $k_\text{lat}$ and $\mu_\text{H}$ in the numerator and denominator, respectively.

The reproducibility of thermoelectric performance for Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S is provided in Fig. S24.$^\dagger$ Besides, the thermal stability is a critical concern for metastable phases in the thermoelectric community. Thus, the XRD patterns of SPSed-Cu$_2$In$_{0.05}$Sn$_{0.95}$Se$_2$S before testing and after the 3rd electrical test were measured, and no change in phase structure is found (Fig. 6a). Additionally, after measuring the electrical properties three times, the SPSed-Cu$_2$In$_{0.05}$Sn$_{0.95}$Se$_2$S sample could still maintain the same grain size (Fig. 6b and c). The electrical performance was re-measured three times for Cu$_2$In$_{0.05}$Sn$_{0.95}$Se$_2$S and shows no deterioration (Fig. 6d–f).

### 3. Conclusions

In summary, we have successfully synthesized a high-entropy system, Cu$_{2-y}$Ag$_y$(In$_x$Sn$_{1-x}$)Se$_2$S ($x = 0–0.25$, $y = 0$, 0.07, 0.13), by adopting a hot-injection strategy and characterized the thermoelectric properties of dense materials compacted from those nanoparticles. We propose a new synthetic route for compacting nanocrystals without eliminating long organic ligands and subsequently obtain a series of high-entropy multinary chalcogenide nanocrystals with a metastable cubic phase induced by size-driven structural stabilization. Through phase and entropy design, a high power factor ($0.44$ mW m$^{-1}$ K$^{-2}$) and an ultralow thermal conductivity ($0.25$ W m$^{-1}$ K$^{-1}$) are achieved at 873 K for the Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S sample. A high $ZT$ of 1.52 is achieved which is about 204% higher than that of pristine Cu$_2$SnSe$_3$. This work provides a new strategy for stabilizing the metastable phase through ligand retention induced small size and may have broader application in various fields such as photocatalysis, electronic devices, and photovoltaics.

### Data availability

Chemicals, preparation of Cu$_2$SnSe$_3$, Cu$_2$SnSe$_2$S, Cu$_2$In$_{1-y}$Sn$_y$Se$_2$S, Cu$_2$In$_{0.1}$Sn$_{0.9}$Se$_2$S, Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S nanocrystals, spark plasma sintering, characterization, measurement of thermoelectric properties, DFT calculation, formation energy calculation, the calculation details of Lorentz factor ($L$) and density of states effective mass ($m^*_e$) via single parabolic band (SPB) model, the calculation details of heat capacity $C_V$ via the Debye–3 Einstein model, crystal structure characterization,
microstructure and composition, electronic and phononic band structures and thermoelectric properties are available in the ESL.†

Author contributions


Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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References

Electronic Supporting Information

Phase-Engineered High-Entropy Metastable FCC Cu$_{2.5}$Ag$_{0.5}$(In$_x$Sn$_{1-x}$)Se$_2$S Nanomaterials with High Thermoelectric Performance

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Experimental Procedures

Chemicals. Oleylamine (OAm, 80~90%) and 1-dodecanethiol (DDT, 98%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Tin chloride dehydrate (SnCl$_2$·2H$_2$O, 99.99%), indium chloride (InCl$_3$, 99.99%) and copper chloride (CuCl, 99.95%) were obtained from Aladdin Reagent Co. Ltd. Diphenyl diselenide (97%) was purchased from Energy Chemical. Silver nitrate (AgNO$_3$) and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd and Nanjing Chemical Reagent Co., Ltd. All chemicals were directly used without any purifying treatments.

Preparation of Cu$_2$SnSe$_3$ nanocrystals. Solution A: Diphenyl diselenide/OAm solution was prepared by dissolving diphenyl diselenide (2.3410 g, 7.5 mmol) in OAm (30 mL) at room temperature through sonicallyating for about 15 minutes. Solution B: CuCl (0.8910 g, 9 mmol), SnCl$_2$·2H$_2$O (0.6770 g, 3 mmol) and OAm (120 mL) were mixed in a 500 mL three-neck flask. The mixture was degassed at room temperature for several minutes followed by purging with N$_2$ under magnetic stirring. Subsequently, the mixture was heated to 230 °C, and solution A was rapidly injected into the mixture. Finally, the mixture was heated to 240 °C and held for 30 min. After being cooled to room temperature naturally, the products were washed with ethanol and dried under a vacuum.

Preparation of Cu$_2$SnSe$_2$S nanocrystals. All the steps and parameters are the same as the preparation of Cu$_2$SnSe$_3$, except for the addition of DDT (15 mL) in Solution B.

Preparation of Cu$_2$In$_x$Sn$_{1-x}$Se$_2$S and Cu$_3$InSnSe$_3$S$_2$ nanocrystals. All the steps and parameters are the same as the preparation of Cu$_2$SnSe$_2$S, except for the addition of InCl$_3$ (3x mmol) in Solution B and the corresponding decrease in SnCl$_2$·2H$_2$O amount.

Preparation of Cu$_{2-y}$Ag$_y$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S nanocrystals. All the steps and parameters are the same as the preparation of Cu$_2$In$_x$Sn$_{1-x}$Se$_2$S, except for the addition of AgNO$_3$ and the corresponding decrease in CuCl amount.

Spark Plasma Sintering. The dense bulk matrixes compacted from nanocrystals were prepared by spark plasma sintering (SPS) system (LABOX-110, Sinter Land) at 673 K with an axial compressive stress of 50 MPa for 10 min under vacuum. The obtained pellets were then cut into a 3 × 3 × 10 mm$^3$ rectangular bar and into a $\bigcirc$10 × 1.5 mm disk.

Characterization. Synchrotron X-ray diffraction data were measured at BL17b in an energy state of 20 keV (0.62 Å). The pair distribution function G(r), correction, background subtraction, and sample absorption were completed by employing PDFgetX. Structure refinements were accomplished by using PDFgui. The crystalline phase of the samples was measured by powder X-ray diffraction (XRD; D8 ADVANCE, Bruker, Germany) with Cu Kα radiation (λ = 1.5418
Å) at a voltage of 40 kV and current of 40 mA. The microstructure of nanomaterials was investigated by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM), taken by a Talos F200s transmission electron microscope operated at 200 kV. Elemental mapping images were acquired at the same instrument. Energy dispersive spectroscopy (EDS; JEOL JSM-6700F) was used for chemical composition analysis under an acceleration voltage of 10 kV. Atomic-resolution scanning transmission electron microscopy (STEM) images and energy-dispersive spectrometry (EDS) maps were acquired on an FEI-Titan Cubed Themis G2 300. STEM high angle annular dark field (STEM-HAADF) images were taken using an annular-type detector. The microstructure of the SPSed-samples pellets was characterized by a scanning electron microscope (SEM; FEI Scios 2 HiVac). X-ray photoelectron spectroscopy (XPS) was recorded by a PHI5000 Versa Probe system (ULVAC-PHI, Japan) with the monochromatic Al Kα line as the X-ray source. Atomic-scale composition analysis was conducted using atom probe tomography (APT). APT measurements were performed on a local electrode atom probe (LEAP4000X Si, CAMECA) by applying 10-ps, 10-pJ ultraviolet (wavelength = 355 nm) laser pulses with a detection rate of 1 ion per 100 pulses on average, a pulse repetition rate of 200 kHz at a base temperature of 40 K, and an ion flight path of 160 mm. The corresponding 3D reconstructions and data analysis were processed using the IVASTM 3.8.0. Oxygen nitrogen hydrogen analyzer (ONH836) and carbon-sulfur analyzer (USA, LECO, CS844) were used for measurement of hydrogen and carbon concentrations in sintered nanomaterials.

Measurement of thermoelectric properties. The electrical conductivity and Seebeck coefficient were measured simultaneously by the static direct current method and four-probe method (CTA-3S, CRYALL). The measuring uncertainty of σ and S was ~ 5%. The thermal conductivity was calculated by $κ = C_p \cdot ρ \cdot D$, in which the specific heat at constant pressure ($C_p$) was obtained by using a differential scanning calorimetry thermalanalyzer (DSC 404 F3, NETZSCH), the pellet density ($ρ$) was calculated by Archimedes method and the thermal diffusivity ($D$) was measured using the laser flash method (Discovery Xeon Flash, TA Instrument). The measurement uncertainty of thermal conductivity $κ$ was estimated to be within 10%, and thus the combined uncertainty for all measurements involved in ZT determination is below 20%. Charge carrier concentration ($n_H$) and Hall mobility ($μ_H$) were determined from the Hall coefficient ($R_H$) measurement using the Van der Pauw method under a reversible magnetic field of 1.5 T (Lake Shore 8400 Series, Model 8404, USA), and from $n_H = 1/ɛR_H$ and $μ_H = σR_H$, respectively. Low-temperature constant-pressure heat capacities ($C_p$) were measured using a Quantum Design Physical Properties Measurement System (QD-PPMS) with logarithmic T
spacings over 2 – 250 K repeating three times at each temperature point. Thermogravimetric analysis (TGA) was carried out on a thermal gravimetric analyzer (TGA 5500).

**DFT calculation.**

**Electronic band structures:** All calculations were performed within the first-principles density functional theory (DFT) formalism as implemented in the Vienna Ab-initio Simulation Package (VASP). The structural optimizations and self-consistent calculations were carried out using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation exchange functional plus the effective Hubbard $U$ of the Dudarev et al’s approach. In this work, the on-site effective $U = 10 \text{ eV}$ was introduced to describe the localization characteristic of copper’s 3d block. The cutoff energy was set to 500 eV and the energy conversion criterion of $1 \times 10^{-6} \text{ eV}$ per atom was used for the calculation of the electronic band structure. In the structural optimization, we constrained the cell parameters onto the experimental data and optimized the atomic coordinates until the Hellman-Feynman forces fell below $10^{-3} \text{ eV/Å}$.

**Phonon band structures:** The phonon band structure, group velocity, specific heat, density of states are calculated by using Phonopy and VASP. The plane-wave energy cutoff is 500 eV. The energy convergence threshold is $10^{-8} \text{ eV}$ per atom. The cubic Cu$_2$SnSe$_3$, under virtual crystal approximation, has 2 atoms per primitive cell. The monoclinic Cu$_2$SnSe$_3$ has 12 atoms per primitive cell. In the primitive cell relaxations, we use $10^{-6}$ and $10^{-4} \text{ eV/Å}$ for the force convergence threshold for the cubic and monoclinic Cu$_2$SnSe$_3$, respectively. The k-mesh during the primitive cell relaxations are 16×16×16 and 9×9×9 for the cubic and monoclinic Cu$_2$SnSe$_3$, respectively. 4×4×4 and 3×3×3 supercells are used for the calculation of phonon dispersion for cubic and monoclinic Cu$_2$SnSe$_3$, respectively. The k-mesh used in the supercell calculations is 3×3×3.

**Formation Energy Calculation.** In general, the formation energy for a compound is calculated by using the equation given below:

$$\Delta H_f = E_{tot} - \sum_i \mu_i x_i$$  \hspace{1cm} (S1)

where $E_{tot}$ is the DFT total energy of the compound, $\mu_i$ is the chemical potential of element $i$, and $x_i$ is the quantity of element $i$ in the compound.

The calculation details of Lorentz factor (L) and density of states effective mass ($m^*_d$) via single parabolic band (SPB) model. In the case of electron scattering by the acoustical vibrations of the lattice atoms, the Lorenz number can be expressed as:

$$L = \left(\frac{k_B}{e}\right)^2 \frac{3F_0(\eta)F_2(\eta) - 4F_0^2(\eta)}{F_0^2(\eta)}$$  \hspace{1cm} (S2)
Assuming the acoustic scattering for all investigated samples is prominent (\( \lambda = 0 \)), the \( m_d^* \) can be acquired from the experimental data \( S \) and \( p \) by using the following equations:

\[
S = \frac{k_B}{e} \left[ \frac{\lambda + 2}{\lambda + 1} F_{\lambda + 1}(\eta) - \eta \right] \tag{S3}
\]

\[
m_d^* = \frac{\hbar^2}{2k_B T} \left( \frac{p}{4\pi^2 F_{1/2}(\eta)} \right)^{2/3} \tag{S4}
\]

\[
F_j(\eta) = \int_0^\infty \frac{x^j}{1 - e^{x-\eta}} dx \tag{S5}
\]

where \( F_j(\eta) \) is the Fermi integral of order \( j \), \( \eta \) is the reduced Fermi level \( E_f / k_B T \) and \( \hbar \) is the Planck constant.

The calculation details of heat capacity \( C_p \) via the Debye-3 Einstein model. The plot of \( C_p \) vs \( T \) could be well fitted to a sum of Debye and Einstein models ranging from 100-200 K as the following equation\(^8\)-\(^10\):

\[
C_{ph}(T) = 9R \sum_{i=1}^3 a_i \frac{x_D^3}{n-1} x_D^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx + 3R \sum_{i=1}^3 \left| a_i \frac{x_{E_i}^2 e^{x_{E_i}}}{(e^{x_{E_i}} - 1)^2} \right| \tag{S6}
\]

where \( x_D = \theta_D / T \), \( x_E = \theta_E / T \), and \( \theta_D \), \( \theta_E \) are the Debye and Einstein temperatures, respectively. The constant \( R \) is the molar gas constant. The parameter \( n \) is the number of atoms per molecular formula. The letters are adjustable, and the subscript \( i \) represents the degeneracy of the multiple optical branches. The various fitting parameters are listed in Table S4.
Results and Discussion

1. Crystal structure characterization

As shown in Fig. S1, for Cu$_2$SnSe$_3$, Cu$_2$SnSe$_2$S, Cu$_2$In$_x$Sn$_{1-x}$Se$_2$S ($x=0.06, 0.14, 0.25$), the peak at 26.8° can be indexed to the (111) plane of the cubic structure of Cu$_{1.8}$Se phase, which indicates the existence of a small quantity of the second phase. And we can observe that Cu$_{1.8}$Se phase disappeared when the amount of In increased, and finally Cu$_2$In$_{0.4}$Sn$_{0.6}$Se$_2$S and Cu$_3$InSnSe$_3$S nanocrystals without the second phase were obtained. This phenomenon demonstrates that the main reason of the formation of Cu$_{1.8}$Se second phase is feed ratio of metal salts. When the amount of In is small, excess Se will reacted with Cu to obtain Cu$_{1.8}$Se.

![Fig. S1](image_url) (a) Powder X-ray diffraction (PXRD) patterns of solution-synthesized samples. Rietveld refinement results of (b) solution-synthesized Cu$_3$InSnSe$_3$S$_2$ and (c) SPSed-Cu$_2$SnSe$_3$. PDF fit to G(r) function at the range of 5-30 Å by using the hexagonal model for (d) solution-synthesized Cu$_3$InSnSe$_3$S$_2$ and cubic model for (e) SPSed-Cu$_2$SnSe$_3$.

Table S1. The cell parameters of solution-synthesized and SPSed-samples from Rietveld refinement data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Solution-synthesized Cu$_3$InSnSe$_3$S$_2$</th>
<th>SPSed-Cu$_2$SnSe$_3$</th>
<th>SPSed-Cu$_3$InSnSe$_3$S$_2$</th>
<th>SPSed-Cu$<em>{1.93}$Ag$</em>{0.07}$(In$<em>{0.06}$Sn$</em>{0.94}$)Se$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>space group</td>
<td>P6$_3$mc</td>
<td>Fm-3m</td>
<td>I-42m</td>
<td>Fm-3m</td>
</tr>
<tr>
<td>a</td>
<td>3.982 Å</td>
<td>5.6636 Å</td>
<td>5.6378 Å</td>
<td>5.6421 Å</td>
</tr>
<tr>
<td>b</td>
<td>3.982 Å</td>
<td>5.6636 Å</td>
<td>5.6378 Å</td>
<td>5.6421 Å</td>
</tr>
<tr>
<td>c</td>
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<td>11.2620 Å</td>
<td>5.6421 Å</td>
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<td>90°</td>
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<td>90°</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>120°</td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
</tr>
</tbody>
</table>
As demonstrated in Fig. S2, metastable wurtzite Cu$_2$SnSe$_3$ nanocrystals with uniform size and morphology is firstly synthesized via colloid synthesis. Then S is incorporated into the anionic site and Ag, In are alloyed at the cationic site through well controlling the balance of precursors reactivity in colloidal synthesis. Subsequently, based on size reduction and entropy optimization engineering of our solution-synthesized nanocrystals, a series of high-entropy multinary chalcogenides nanostructured solid with metastable cubic phase are obtained, which is different from the conventional monoclinic phase synthesized via solid-state synthesis, as exemplified by melting. Besides, when the amount of indium increases to a certain amount, SPSed-Cu$_2$In$_{0.4}$Sn$_{0.6}$Se$_2$S and SPSed-Cu$_3$InSnSe$_3$S$_2$ nanostructured solid have a tetragonal structure (space group I-42m), and this tetragonal unit cell can be approximately depicted as a 1x1x2 supercell of cubic Cu$_2$SnSe$_3$.

**Fig. S2** Crystal structures for synthesized and SPSed-Cu$_2$SnSe$_3$, Cu$_2$SnSe$_2$S, Cu$_2$In$_{x}$Sn$_{1-x}$Se$_2$S ($x=0.02-0.25$), Cu$_2$In$_{0.4}$Sn$_{0.6}$Se$_2$S, Cu$_3$InSnSe$_3$S$_2$ and Cu$_{2+y}$Ag$_y$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S ($y=0.07, 0.13$).
Table S2. Calculated formation energy ($\Delta H_f$) for different phase structures via DFT using the Vienna ab initio simulation package (VASP).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Monoclinic ($\text{eV\ atom}^{-1}$)</th>
<th>Cubic ($\text{eV\ atom}^{-1}$)</th>
<th>Tetragonal ($\text{eV\ atom}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPSed-Cu$_2$SnSe$_3$</td>
<td>-2.4564</td>
<td>-2.4529</td>
<td>/</td>
</tr>
<tr>
<td>SPSed-Cu$_2$SnSe$_2$S</td>
<td>-2.5603</td>
<td>-2.5519</td>
<td>/</td>
</tr>
<tr>
<td>SPSed-Cu$<em>2$In$</em>{0.06}$Sn$_{0.94}$Se$_3$</td>
<td>-2.5523</td>
<td>-2.5435</td>
<td>/</td>
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<tr>
<td>SPSed-Cu$_3$InSnSe$_3$S$_2$</td>
<td>-3.3915</td>
<td>-3.3863</td>
<td>-3.3994</td>
</tr>
<tr>
<td>SPSed-Cu$<em>1.87$Ag$</em>{0.13}$In$<em>{0.06}$Sn$</em>{0.94}$Se$_2$S</td>
<td>-2.5816</td>
<td>-2.5730</td>
<td>/</td>
</tr>
</tbody>
</table>

Table S3. Table peaks assignment to the atomic pair in SPSed-Cu$_2$SnSe$_3$, solution-synthesized Cu$_3$InSnSe$_3$S$_2$, SPSed-Cu$_3$InSnSe$_3$S$_2$ and SPSed-Cu$_{1.93}$Ag$_{0.07}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S, respectively.

SPSed-Cu$_2$SnSe$_3$:

<table>
<thead>
<tr>
<th>label</th>
<th>atomic pair</th>
<th>atomic pair distances(Å)</th>
</tr>
</thead>
<tbody>
<tr>
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SPSed-Cu$_{1.93}$Ag$_{0.07}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S:

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2. Microstructure and composition

Fig. S3 (a) Low-magnification TEM image, (b) HRTEM image, (c) EDS elemental mapping images of solution-synthesized Cu₂SnSe₃.
Fig. S4 (a) Low-magnification TEM image, (b) HRTEM image, (c) EDS elemental mapping images of solution-synthesized Cu₂SnSe₂S.
Fig. S5 (a) Low-magnification TEM image of solution-synthesized Cu₃InSnSe₅S₂ and (b) SEM micrograph of SPSed-Cu₃InSnSe₅S₂ sample.
Fig. S6 (a) Low-magnification TEM image and (b) EDS elemental mapping images of SPSed-Cu₂SnSe₃.

Fig. S7 (a) Low-magnification TEM image and (b) EDS elemental mapping images of SPSed-Cu₂SnSe₂S.
Fig. S8 The SEM/EDS mapping of SPSed-Cu$_3$InSnSe$_3$S$_2$.

Fig. S9 SEM micrographs of (a) SPSed-Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S and (b) SPSed-Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S pellets. (c) The TEM image of SPSed-Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S, exhibiting the organic hydrocarbons between nanocrystals of nanosructured solids during sintering process.
**Fig. S10** HRTEM images of the dislocations in (a) SPSed-Cu$_2$SnSe$_3$ and (d) SPSed-Cu$_2$SnSe$_2$S samples. (b and e) The corresponding inverse FFT (IFFT) images of boxed region in (a) and (d), inset is the enlarged view of boxed region. (c and f) The corresponding strain mappings of (b) and (e), showing the dislocations cores with the high intensity.
Fig. S11 HRTEM image of the dislocations in (a) SPSed-Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S sample, inset is the corresponding FFT along the [121] zone axis. (b) The corresponding inverse FFT (IFFT) image of boxed region in (a), inset is the enlarged view of boxed region. (c) The corresponding strain mapping of (b), showing the dislocations cores with high intensity. (d) EDS elemental mapping images of SPSed-Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S sample.
EDS analysis was used to quantify the elemental composition of solution-synthesized and SPSed-samples, as shown in Fig. S10. The EDS result of Cu$_2$SnSe$_3$ is shown in Fig. S10a, indicating that the atomic ratio of Cu: Sn: Se is 2.24: 1: 3.24. Then DDT was added as a sulfur source to prepare Cu$_2$SnSe$_2$S. The EDS spectra of Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S and SPSed-Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S are shown in Figs. S10c and f, proving the successful incorporation of In. And the composition of as-synthesized nanocrystals remains unchanged after the sintering process. Additionally, the In content in the nanocrystals increases almost linearly with increasing In content in the precursors. When a 1:1 ratio of SnCl$_2$·2H$_2$O to InCl$_3$ was used for the synthesis, the atom ratio of Cu: In: Sn: Se: S is around 3:1:1:3:2, which further verifies that the resulting products are Cu$_3$InSnSe$_3$S$_2$.

Fig. S12 EDS results of (a) solution-synthesized Cu$_2$SnSe$_3$, (b) solution-synthesized Cu$_2$SnSe$_2$S, (c) solution-synthesized Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S, (d) solution-synthesized Cu$_2$In$_{0.14}$Sn$_{0.86}$Se$_2$S, (e) solution-synthesized Cu$_3$InSnSe$_3$S$_2$ and (f) SPSed-Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S.
X-ray photoelectron spectroscopy (XPS) was performed to disclose the valence states of each element on the surface in the solution-synthesized Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S and SPSed-Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S, as shown in Fig. S11. No peaks of other elements than Cu, In, Sn, Se, S, C, and O are observed in XPS survey spectrum, which agrees well with the EDS results. The dual peaks of Cu 2p for Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S at 932.0 eV and 951.8 eV with a separation of 19.8 eV reveal the presence of Cu with a valence of +1, and no satellite peak caused by Cu with +2 valence is found.$^{11-13}$ It is worth mentioning that the valence state of Cu changed before and after sintering. The binding energy of SPSed-Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S at the Cu 2p region could be divided into four peaks. The peaks located at 932.3 eV and 952.3 eV are associated with Cu$^+$ 2p$_{3/2}$ and 2p$_{1/2}$, respectively, and the peaks located at 934.5 eV and 954.7 eV are assigned to Cu$^{2+}$ 2p$_{3/2}$ and 2p$_{1/2}$, respectively.$^{14}$ The In 3d peaks of Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S and SPSed-Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S at 444.6 eV and 452 eV can be assigned to In with a valence of +3.$^{11-13}$ The peaks of Sn 3d for Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S and SPSed-Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S at 486.3 eV and 494.7 eV are characteristic for Sn with a valence of +4.$^{11-13}$ The Se 3d peak at 54 eV for Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S and SPSed-Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S correspond to Se with a valence of -2.$^{15,16}$ In addition, we can find that another peak located at 58.8 eV for Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S was attributed to Se substance,$^{14}$ demonstrating excessive Se in raw materials. However, the Se substance peak disappears after sintering, indicating that part of Se volatilizes or reacts with Cu to form Cu$_{1.8}$Se during the sintering process, which explains the existence of Cu$^{2+}$ in the SPSed-sample. The corresponding peaks for the S 2p$_{3/2}$ and 2p$_{1/2}$ orbitals of bivalent sulfide ions (S$^{2-}$) are observed at 160.5 and 165.4 eV of Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S and SPSed-Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S, respectively.$^{12}$

![XPS spectra](image_url)
Fig. S14 Nearest-neighbor atomic distribution histograms of Cu, In, Sn, Se, S for SPSed-Cu$_2$In$_{0.09}$Sn$_{0.91}$Se$_2$S. The navy-blue line represents the calculated curves assuming all elements are homogeneously and randomly distributed in the material.
3. Electronic and phononic band structures

Fig. S15 The electronic energy band structures for (a) monoclinic Cu$_2$SnSe$_3$, (b) cubic Cu$_2$SnSe$_3$, (c) monoclinic Cu$_2$SnSe$_2$S, (d) cubic Cu$_2$SnSe$_2$S, (e) monoclinic Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S and (f) cubic Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S.
Fig. S16 The crystal structures of (a) monoclinic and (b) cubic Cu$_2$SnSe$_3$. (c) The phonon group velocity comparison and (d) the phonon heat capacity comparison between monoclinic and cubic Cu$_2$SnSe$_3$.

4. Thermoelectric properties

Fig. S17 Temperature dependence of specific heat capacity $C_p$ for SPSed-Cu$_2$In$_{0.05}$Sn$_{0.95}$Se$_2$S.
Fig. S18 Thermal gravimetric analysis (TGA) of SPSed-Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S and SPSed-Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S from 50 °C to 600 °C with nitrogen protection. The weight losses of both samples are less than 1%.

Fig. S19 Temperature dependence of (a) electrical conductivity $\sigma$; (b) Seebeck coefficient $S$, (c) power factor $PF$, (d) total thermal conductivity $\kappa_{tot}$ and (e) ZT values for Cu$_2$SnSe$_3$ and Cu$_2$SnSe$_2$S.
Fig. S20 shows the thermoelectric properties of \( \text{Cu}_2\text{In}_{0.02}\text{Sn}_{0.98}\text{Se}_2\text{S} \), \( \text{Cu}_2\text{In}_{0.14}\text{Sn}_{0.86}\text{Se}_2\text{S} \), \( \text{Cu}_2\text{In}_{0.4}\text{Sn}_{0.6}\text{Se}_2\text{S} \) and \( \text{Cu}_3\text{InSnSe}_3\text{S}_2 \) in the temperature range of 323-873 K. It is found that with a large increase of In content, the electrical conductivity \( \sigma \) decreases sharply (Fig. S20a) and the \( S \) value increases (Fig. S20b). Specifically, \( \sigma \) decreases from \( 7.89\times10^3 \) S m\(^{-1}\) for \( \text{Cu}_2\text{In}_{0.02}\text{Sn}_{0.98}\text{Se}_2\text{S} \) to \( 1.38\times10^3 \) S m\(^{-1}\) for \( \text{Cu}_3\text{InSnSe}_3\text{S}_2 \) at 873 K, \( S \) increases from 225.38 \( \mu \)V K\(^{-1}\) for \( \text{Cu}_2\text{In}_{0.02}\text{Sn}_{0.98}\text{Se}_2\text{S} \) to 288.84 \( \mu \)V K\(^{-1}\) for \( \text{Cu}_3\text{InSnSe}_3\text{S}_2 \) at 873 K. Despite the enhanced Seebeck coefficient, the power factor (\( PF \)) of \( \text{Cu}_3\text{InSnSe}_3\text{S}_2 \) (0.11 mW m\(^{-1}\) K\(^{-2}\) at 873 K) is smaller than that of \( \text{Cu}_2\text{In}_{0.02}\text{Sn}_{0.98}\text{Se}_2\text{S} \) (0.40 mW m\(^{-1}\) K\(^{-2}\) at 873 K) (Fig. S20c) because of the lower electrical conductivity. Although the thermal conductivity decreases with the increase of In content, the ZT value of \( \text{Cu}_3\text{InSnSe}_3\text{S}_2 \) sample is not increased.

Fig. S20 Temperature dependence of (a) electrical conductivity \( \sigma \); (b) Seebeck coefficient \( S \), (c) power factor \( PF \), (d) total thermal conductivity \( k_{\text{tot}} \) and (e) ZT values for \( \text{Cu}_2\text{In}_{0.02}\text{Sn}_{0.98}\text{Se}_2\text{S} \), \( \text{Cu}_2\text{In}_{0.14}\text{Sn}_{0.86}\text{Se}_2\text{S} \), \( \text{Cu}_2\text{In}_{0.4}\text{Sn}_{0.6}\text{Se}_2\text{S} \) and \( \text{Cu}_3\text{InSnSe}_3\text{S}_2 \).
The weighted mobility $\mu_w$ of $\text{Cu}_{2-y}\text{Ag}_{y}(\text{In}_x\text{Sn}_{1-x})\text{Se}_2\text{S}$ ($x=0, 0.05, 0.06, 0.25, y=0, 0.07, 0.13$) was calculated from the measured electrical conductivity $\sigma$ and Seebeck coefficient $S$ according to the formula

$$\mu_w = 331 \frac{cm^2}{Vs} \left(\frac{m\Omega cm}{\rho} \right) \left( \frac{T}{300 \, K} \right)^{-\frac{3}{2}} \left[ \frac{\exp\left(\frac{|S|}{k_B} - 2\right)}{1 + \exp\left(-5\frac{|S|}{k_B} - 1\right)} \right] + \frac{3 \frac{|S|}{e^2 k_B}}{1 + \exp\left[\frac{|S|}{k_B} - 1\right]} \right]^{17}. $$

As shown in Fig. S21a, the weighted mobility of the samples is not high and decreases with temperature before 723 K because of phonon scattering. The enhancement on $\mu_w$ is especially significant near room temperature as the In doping and when the temperature reaches 773 K, the weighted mobility $\mu_w$ of $\text{Cu}_{2-y}\text{Ag}_{y}(\text{In}_x\text{Sn}_{1-x})\text{Se}_2\text{S}$ ($x=0, 0.05, 0.06, 0.25, y=0, 0.07, 0.13$) is improved. Benefitting from the improved $\mu_w$ values, as well as the decreasing value of $\kappa_L$, the $ZT$ value was enhanced after In-doping and Ag-alloying, which can be confirmed by the enhancement of thermoelectric quality factor $B$ via doping In and alloying Ag (Fig. S21b). The quality factor $B$ is designed to estimate the optimal thermoelectric performance for specified materials and proportional to the weighted mobility divided by the lattice thermal conductivity $\mu_w/\kappa_L$ according to the formula $B = \frac{(k_B)^3}{8\pi e} \frac{2}{h^3} \frac{8\pi e(2m_e k_B T)^{3/2}}{3 h^3} \frac{\mu_w}{\kappa_L T}$.  

![Fig. S21](image-url)

Fig. S21 (a) The weighted mobility $\mu_w$ and (b) Quality factor $B$ as a function of temperature of $\text{Cu}_{2-y}\text{Ag}_{y}(\text{In}_x\text{Sn}_{1-x})\text{Se}_2\text{S}$ ($x=0, 0.05, 0.06, 0.25, y=0, 0.07, 0.13$) samples.
**Fig. S22** The experimental $C_p$ with respect to $T$ at low temperature fitted by a combination of Debye and three Einstein models. Red dots illustrate the experimental heat capacity plotted as $C_p$ versus $T$ for (a) SPSed-Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S, (b) SPSed-Cu$_2$In$_{0.14}$Sn$_{0.86}$Se$_2$S and (c) SPSed-Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S. Obviously, the data can be fitted only with the Debye–3 Einstein model rather than the Debye model.

**Fig. S23** Calculated configurational entropy $\Delta S$ and lattice thermal conductivities ($\kappa_{Lat}$) for Cu$_2$SnSe$_2$S, Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S, Cu$_{1.93}$Ag$_{0.07}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S and Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S.
Fig. S24 Data repeatability of (a) electrical conductivity $\sigma$, (b) Seebeck coefficient $S$, (c) total thermal conductivity $\kappa_{tot}$ and (d) $ZT$ values for Cu$_{1.87}$Ag$_{0.13}$(In$_{0.06}$Sn$_{0.94}$)Se$_2$S.

Table S4. Fitting parameters for modelling $C_p$ vs. $T$ plot given in Fig. S18 in the main text.

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<td>$\theta_{e2}$ (K)</td>
<td>4.02 K</td>
</tr>
<tr>
<td>$\theta_{e3}$ (K)</td>
<td>100 K</td>
</tr>
<tr>
<td>$\theta_0$ (K)</td>
<td>359.19 K</td>
</tr>
</tbody>
</table>
Table S5. Comparison between the Present and Literature-Reported Properties of Cu$_2$SnSe$_3$-based materials.

| Sample description | Synthesis strategy | Phase structure | $\kappa_{\text{tot}}$ [W/mK] | $\mu_H$ [cm$^2$/V·s] | $\langle\mu_h\rangle$ [10$^{-4}$ m$^2$kV$^{-1}$s$^{-1}$] | ZT$^{|a|}$ |
|--------------------|-------------------|-----------------|-----------------|----------------|-----------------|----------|
| this work, Cu$_2$In$_{0.06}$Sn$_{0.94}$Se$_2$S | colloidal synthesis | cubic | 0.68 | 1.75 | 0.21 | 0.07 |
| Ming, Cu$_2$Sn$_{0.82}$In$_{0.18}$Se$_2.7$S$_{0.3}$ | melting | monoclinic | 1.32 | 7.80 | 0.26 | 0.04 |
| Li, Cu$_{1.85}$Ag$_{0.15}$Sn$_{0.9}$In$_{0.1}$Se$_3$ | ball milling | monoclinic | 1.30$^{|b|}$ | 5.23 | 0.17 | 0.06 |

[a] All the values are measured at ~300 K. [b] Calculated from $\kappa_{\text{tot}} = \kappa_{\text{el}} - \kappa_{\text{ph}}$.

References in the supporting information


