Tin-Substituted Chalcopyrite: An n-Type Sulfide with Enhanced Thermoelectric Performance

Sahil Tippireddy, Feridoon Azough, Vikram, Frances Towers Tompkins, Animesh Bhui, Robert Freer, Ricardo Grau-Crespo, Kanishka Biswas, Paz Vaqueiro, and Anthony V. Powell*

ABSTRACT: The dearth of n-type sulfides with thermoelectric performance comparable to that of their p-type analogues presents a problem in the fabrication of all-sulfide devices. Chalcopyrite (CuFeS2) offers a rare example of an n-type sulfide. Chemical substitution has been used to enhance the thermoelectric performance of chalcopyrite through preparation of Cu1−xSnxFeS2 (0 ≤ x ≤ 0.1). Substitution induces a high level of mass and strain field fluctuation, leading to lattice softening and enhanced point-defect scattering. Together with dislocations and twinning identified by transmission electron microscopy, this provides a mechanism for scattering phonons with a wide range of mean free paths. Substituted materials retain a large density-of-states effective mass and, hence, a high Seebeck coefficient. Combined with a high charge-carrier mobility and, thus, high electrical conductivity, a 3-fold improvement in power factor is achieved. Density functional theory (DFT) calculations reveal that substitution leads to the creation of small polarons, involving localized Fe2+ states, as confirmed by X-ray photoelectron spectroscopy. Small polaron formation limits the increase in carrier concentration to values that are lower than expected on electron-counting grounds. An improved power factor, coupled with substantial reductions (up to 40%) in lattice thermal conductivity, increases the maximum figure-of-merit by 300%, to zT ≈ 0.3 at 673 K for Cu0.96Sn0.04FeS2.

1. INTRODUCTION

Thermoelectric (TE) materials offer the ability to convert waste heat into useful electrical energy and are promising for a range of applications in the automotive, aerospace, manufacturing, energy, and electronic industries. The energy conversion efficiency of a thermoelectric material depends on a dimensionless quantity, the figure-of-merit, zT = S²σT/κ. For a high zT, the material should possess a high electrical conductivity (σ) and Seebeck coefficient (S), together with a low thermal conductivity (κ). The thermal conductivity comprises electronic (κₑ) and lattice (κₗ) components. However, obtaining a high zT is challenging due to the conflicting dependence of S, σ, and κ on the charge-carrier concentration. Using approaches such as doping, nanostructuring, band-structure engineering, and nanocompositing, high figures-of-merit have been achieved in many state-of-the-art thermoelectric materials including PbTe,SnSe, and Bi₂Te₃. However, these materials contain relatively toxic, expensive, and/or rare elements. The search for alternative materials containing relatively abundant and cheap elements has led to the identification of ternary and quaternary sulfides, some of which also exist as natural minerals, as promising candidates. However, while this has led to significant improvements in the figure-of-merit of p-type sulfides, there continues to be a dearth of n-type analogues with comparable performance.

Among the mineral-related sulfides, chalcopyrite, CuFeS₂, has been explored as a potential n-type candidate for thermoelectric applications in the mid-temperature (400 ≤ T/K ≤ 673) range. CuFeS₂ crystallizes in a tetragonal structure with space group: I42d (Figure 1), which can be considered as a superstructure of the cubic zinc-blende structure, where zinc is replaced by an ordered arrangement of copper and iron cations that occupy tetrahedral 4a and 4b sites, respectively. It exhibits an antiferromagnetic ground state (T_N = 823 K) in which the moments of iron cations in consecutive layers in the c-direction are aligned in an anti-parallel manner (Figure 1). Pristine CuFeS₂ possesses a high Seebeck coefficient (S ≈ −380 to −480 μV K⁻¹ at 300 K) as well as a relatively high electrical resistivity (ρ ≈ 0.25−0.4 mΩ m at this temperature), resulting in only a moderate power factor. Moreover, CuFeS₂ exhibits a high thermal conductivity (κ ≈ 7
to 9 W m⁻¹ K⁻¹ at 300 K).\textsuperscript{11,28–31} Efforts to improve electrical properties have focused on the substitution of Cu⁺ with higher-oxidation state transition-metal cations, including those of Mn, Co, Ni, Zn, Cd, and Pd,\textsuperscript{11,12,30,32} to adjust the carrier concentration and optimize the power factor. The introduction of substituents has also been found to be effective in reducing the lattice thermal conductivity, leading to an improvement in thermoelectric performance.\textsuperscript{11,12,30,32} Transition-metal substitution leads to a maximum figure-of-merit \( zT \approx 0.45 \) at 723 K\textsuperscript{33} for Cu₀.₉₈Ag₀.₁₂FeS₂, the highest achieved in sulfur-based chalcopyrite-related materials, while comparable performance has been reported for Cu₀.₇₅Cd₀.₂₅FeS₂ (\( zT = 0.39 \) at 723 K).\textsuperscript{12} However, Cd is toxic whereas Ag is expensive, thereby making these compositions unsuitable for large-scale production and applications.

Using density functional theory (DFT) calculations for CuFeS₂, Park et al.\textsuperscript{34} predicted that an optimum charge-carrier concentration of \( n \approx 6 \times 10^{21} \) to \( 8 \times 10^{21} \) cm⁻³ should lead to a high power factor (\( \gtrsim 1 \) mW m⁻¹ K⁻¹) and, thus, a high figure-of-merit (\( \sim 0.8 \) at 700 K for an average grain size of \( \sim 20 \) nm). However, CuFeS₂ typically has a charge-carrier concentration \( \sim 10^{19} \) cm⁻³, two orders of magnitude lower than the optimum value predicted in that study. In an effort to increase the charge-carrier concentration substantially and more closely approach this optimum carrier concentration, we have substituted copper with tin through the preparation of a series of materials with the general formula CuₓSnₓFeS₂ (0.0 \( \leq x \leq 0.1 \)). It has been reported that tin is present in the 4+ oxidation state in ternary and quaternary sulfides including CuₓSnₓS₄, CuₓSnₓSₓ, CuₓZnSnS₄, and CuₓFeSnS₄.\textsuperscript{35–38} Therefore, the substitution of Cu⁺ with Sn⁴⁺ potentially introduces more electrons per substituent than in the case of the previously-explored transition-metal substituents with a 2⁺ oxidation state. Moreover, tin is a relatively cheap and non-toxic element, thus making it a better candidate for large-scale thermoelectric applications. Our results demonstrate that while the 4⁺ substitution increases the charge-carrier concentration, the increase is lower than expected. Nevertheless, an optimized carrier concentration combined with a high density-of-states effective mass results in a significant increase in the power factor. The substitution also results in lattice softening and enhanced phonon scattering due to lattice strain and generation of point defects. The resulting reduction in thermal conductivity, coupled with improvements in the power factor, leads to an enhanced figure-of-merit at low levels of tin substitution. The comprehensive analysis of electronic and thermal transport properties of CuₓSnₓFeS₂ using a combination of theoretical calculations and experimental data that is reported here suggests an effective strategy to improve the thermoelectric properties of CuFeS₂.

2. METHODS

Materials of the general formula, CuₓSnₓFeS₂ (0.0 \( \leq x \leq 0.1 \)) were prepared by solid-state synthesis and consolidated by hot pressing. Mixtures of appropriate stoichiometric amounts of Cu (Sigma-Aldrich, 99.5%), Fe (Alfa Aesar, 99%), and Sn (Alfa Aesar, 99.8%) powders, together with S flakes (Sigma-Aldrich, 99.99%) were transferred to fused silica tubes, which were sealed under a vacuum (\( \sim 10^{-3} \) mbar). Reaction mixtures were heated to 723 K and held at this temperature for 150 h before being cooled slowly (0.4 K min⁻¹) to room temperature. The products were ground before re-firing in an evacuated fused silica tube at 1173 K for 48 h, followed by slow cooling (0.4 K min⁻¹) to room temperature. The products from the second firing were ground and hot-pressed at 873 K for 30 min under a pressure of 80 MPa to produce pellets for characterization and thermoelectric measurements. The densities of the pellets measured by the Archimedes method, using an AE Adam PW 184 balance, were >97% of the theoretical value.

Powder X-ray diffraction of the final powdered product and hot-pressed samples was carried out using a Bruker D8 Advance diffractometer (Cu Kα₁: \( \lambda = 1.5405 \) Å), equipped with a LynxEye detector. Powder diffraction data for hot-pressed samples provided no evidence for preferred orientation. Rietveld analysis of the powder diffraction data was performed using FullProf software.\textsuperscript{39} X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Axis spectrometer using Al Kα (1486.6 eV) radiation. The spectra were calibrated with C 1s binding energy (B.E. = 284.8 eV), and a Shirley-type background was applied. The peaks were then deconvoluted and fitted with appropriate Lorenz/Gaussian functions using CasaXPS software.

Microstructural investigations were carried out using a SIRION FEI FEG-SEM followed by energy-dispersive X-ray spectroscopy (EDS) elemental point analysis and mapping using a TESCAN MIRA LEC FEG (SEM) equipped with an Oxford Instrument SDD energy dispersive detector. Electron backscatter diffraction (EBSD) data were collected using a TESCAN MIRA LC FEG scanning electron microscope (SEM) equipped with an Oxford Instrument SDD EDS detector and an Oxford Instrument Symmetry EBSD detector. Selected-area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) were performed using an FEI FACET (Tecnai G2, Hillsboro, OR) operating at 300 kV.

The electrical resistivity and Seebeck coefficient on consolidated materials were measured in a direction perpendicular to the pressing direction, over the temperature range 323 ≤ T ≤ 673 K. The electrical resistivity, Seebeck coefficient, and thermal conductivity were measured using a Netzsch LFA-447 NanoFlash instrument (323 ≤ T ≤ 573 K) and an Anter Flashline-3000 system (573 ≤ T ≤ 673 K). The thermal conductivity was determined from the diffusivity data using, \( \kappa = \alpha C_p d \), where \( \alpha \) denotes the thermal diffusivity, \( C_p \) is the specific heat capacity, and \( d \) is the sample density. The Dulong–Petit equation was used to calculate the specific heat capacity, \( C_p = 0.52 \) J g⁻¹ K⁻¹. The uncertainties for electrical resistivity, Seebeck coefficient, and thermal conductivity are 2, 2, and 10%, respectively. Considering the combined uncertainties of all the measurements, the uncertainty in the calculation of figure-of-merit (\( zT \)) is estimated to be ca. 15%. An Epoch 650 Ultrasonic Flaw Detector (Olympus) with a transducer frequency of 5 MHz was used for the longitudinal (\( v_l \)) and transverse (\( v_t \)) sound velocity measurements at room temperature using disc-shaped consolidated samples.
All the DFT calculations were carried out using the VASP code \textsuperscript{40–42} with a projected augmented-wave basis \textsuperscript{43} and the generalized gradient approximation (GGA) exchange-correlation functional of Perdew–Burke–Ernzerhof (PBE).\textsuperscript{44} In order to account for the strong correlations of the Fe 3d electrons, the Hubbard correction method (GGA + U) was used with the formulation of Dudarev et al.\textsuperscript{45} implemented in VASP and an \textit{U}_{\text{eff}} of 3 eV. The zero-damping DFT-D3 method of Grimme\textsuperscript{46} was employed to account for long-range dispersion forces, bringing the lattice parameters in close agreement with the experimentally reported values. A converged plane wave cutoff of 385 eV was used in all the calculations. The tetrahedron method with Blöchl corrections\textsuperscript{47} was used to calculate the electronic density of states (DOS). Cell volume, shape and atomic positions for all the structures were fully relaxed using a conjugate gradient algorithm until the forces on each atom fell below 10\textsuperscript{−4} eV Å\textsuperscript{−1}. A fully converged automated \textit{T}-centered \textit{k}-point mesh was used to define the Brillouin zone. Spin-polarized calculations were performed to include the Fe magnetic moments with antiferromagnetic ordering in CuFeS\textsubscript{2} (which was found to be more stable than the ferromagnetic ordering by 0.58 eV per primitive unit cell). The Fe atoms are in a high-spin configuration with a moment of 3.59\textit{μ}\textsubscript{B}, in close agreement with the experimental value of 3.67\textit{μ}\textsubscript{B} determined using neutron diffraction, and with reported theoretical values of 3.62–3.89\textit{μ}\textsubscript{B}.\textsuperscript{48–49} The tetragonal CuFeS\textsubscript{2} in space group \textit{I\textit{4}1\textit{a}} was simulated using the optimized lattice parameters \textit{a} = \textit{b} = 5.27 Å and \textit{c} = 10.41 Å, which are in good agreement with previous theoretical reports\textsuperscript{44} and the lattice parameters obtained experimentally in the current study. The harmonic and anharmonic force constants were calculated via the machine-learning regression algorithms implemented in the hiPhive package\textsuperscript{50} using settings optimized in a previous study\textsuperscript{41} of the thermal conductivities of chalcopyrite-structured semiconductors. The force constants were used to calculate the lattice thermal conductivity using the ShengBTE code.\textsuperscript{50}

In the case of Sn-substituted CuFeS\textsubscript{2}, the small polaron formation scenario where neighboring Fe\textsuperscript{3+} is reduced to Fe\textsuperscript{2+} was simulated by modifying the geometric environment around the substitution site to make it suitable to a reduced Fe species.\textsuperscript{53} To do this, we pre-relaxed the configuration after substituting the neighboring Fe atom by an atom that adopts a 2+ state and with a similar ionic radius as Fe\textsuperscript{2+} (we used Zn\textsuperscript{2+}), which is then replaced again by Fe, and the configuration is re-relaxed. The reduction of Fe species was then confirmed by Bader charge analysis.\textsuperscript{54,55}

3. RESULTS AND DISCUSSION

Powder X-ray diffraction data (Figure 2) for Cu\textsubscript{1−}\textit{x}Sn\textsubscript{\textit{x}}FeS\textsubscript{2} (0 ≤ \textit{x} ≤ 0.1) can be indexed on the basis of a tetragonal unit cell, confirming the presence of a chalcopyrite-related phase throughout the composition range. The low levels of tin incorporation, coupled with the similar X-ray scattering powers of copper and iron, make it impossible to establish unambiguously the location of the incorporated tin cations, and therefore, all structural refinements were performed on the basis that tin substitutes at the copper (4\textit{a}) sites (Figure 3).

No reflections arising from secondary phases are observed up to a composition with \textit{x} = 0.04. However, materials with higher tin contents (\textit{x} ≥ 0.05) exhibit reflections assignable to a cubic phase identified as CuFeS\textsubscript{3} (isocubanite), which adopts a structure consisting of a ccp array of anions with a statistical distribution of Cu and Fe cations on half of the tetrahedral sites (Figure S1a). The intensity of the peaks arising from CuFeS\textsubscript{3} increases with increasing tin concentration (Figure S1b), with volume fractions determined by Rietveld analysis increasing from 8 vol % at \textit{x} = 0.05 to 32 vol % at \textit{x} = 0.1. The compositional variation of lattice parameters evaluated from Rietveld analysis (Figure 3) reveals that the \textit{a} (≡\textit{b}) and \textit{c} lattice parameters increase almost monotonically with increasing tin content, whereas the \textit{c}-parameter saturates at \textit{x} = 0.05 before decreasing at higher tin contents. This suggests a solubility limit of ca. 4–5 at % of tin, with further increases in tin content resulting in the formation of CuFeS\textsubscript{3}.

The electrical resistivity (\(\rho\)) of unsubstituted CuFeS\textsubscript{2} (Figure 4a) is ca. 0.31 mΩ m at 323 K and shows a metallic \(\rho\)\((\text{T})\) dependence. The Seebeck coefficient of CuFeS\textsubscript{2} is negative (Figure 4b), consistent with electrons as the majority charge carriers and the n-type nature of CuFeS\textsubscript{2}.

Despite the metallic \(\rho\)\((\text{T})\) dependence, the Seebeck coefficient is high (\(S \approx -430 \mu V/K\) at 323 K) and almost constant up to 573 K. This value is consistent with previous literature reports. However, as is clear from Table S2, there are wide variations in the electrical-transport properties of CuFeS\textsubscript{2}, with Seebeck coefficients in the range of −320 to −500 \(\mu V/K\) having been reported. These variations are likely to be associated with slight compositional variations arising from differences in synthesis and processing conditions. The marked decrease in Seebeck coefficient at higher temperatures may be associated with the thermal activation of the minority charge carriers. The low concentration of the minority carriers (holes) results in a low hole contribution to the conductivity, but the hole contribution to the Seebeck coefficient is increased at low carrier contents. The presence of magnetic ions may also
influence the $S(T)$ dependence at higher temperatures as the magnetic ordering transition at ca. 800 K is approached, resulting in significant changes in band structure. The metal-like $\rho(T)$ behavior, coupled with a large Seebeck coefficient and high electrical resistivity, indicates degenerate semiconductor behavior and is consistent with previous reports for synthetic CuFeS$_2$.

The electrical resistivity falls markedly on the partial replacement of copper with tin. For example, the electrical resistivity at 323 K is reduced by 50% on the introduction of just 2 at. % of tin in Cu$_{0.98}$Sn$_{0.02}$FeS$_2$. The electrical resistivity continues to fall at higher tin contents, although the changes become less pronounced. While pristine CuFeS$_2$ exhibits a sharp decrease in the Seebeck coefficient at ca. 573 K, in contrast, tin-substitution results in a much weaker $S(T)$ dependence and appears to decrease the effect of bipolar conduction. For a composition with $x = 0.02$, the Seebeck coefficient falls to ca. $-340 \text{ nV/K}$ at 323 K; a 20% reduction from that of pure CuFeS$_2$, while the electrical resistivity shows an almost 50% reduction at the same temperature. Hence, low levels of tin substitution ($x \leq 0.04$) appear to be more effective in reducing the electrical resistivity compared to the Seebeck coefficient, which contributes to relatively high power factors (Figure 4c).

Materials with higher levels of tin incorporation contain increasing amounts of the isocubanite (CuFe$_2$S$_3$) phase as evidenced by X-ray diffraction. Since the electrical resistivity of isocubanite is an order of magnitude lower ($\rho \approx 0.01 \text{ m}$$\Omega$ m at 323 K $\leq T/K \leq 723$) than that of the Cu$_{1-x}$Sn$_x$FeS$_2$ phases, it has an increasingly marked impact on electrical transport properties, effectively decreasing the overall electrical resistivity and significantly modifying its temperature dependence.

The end-member CuFeS$_2$ exhibits a power factor (PF) ca. 0.6 mW m$^{-1}$ K$^{-2}$ at 323 K that falls to 0.24 mW m$^{-1}$ K$^{-2}$ at 673 K, which is primarily due to the decrease in the Seebeck coefficient. At high temperatures, the highest maximum PF $\approx 0.7$ mW m$^{-1}$ K$^{-2}$ at 673 K was achieved for the $x = 0.03$ and 0.04 samples. However, the weak $S(T)$ dependence shown by the tin-substituted materials results in a much flatter temperature dependence of the power factors, while the magnitude of the power factor is increased. For compositions with $x > 0.05$, although the power factor increases slightly with temperature, the values remain low throughout the measured temperature range.

Room-temperature Hall effect measurements (Table S3) for Cu$_{1-x}$Sn$_x$FeS$_2$ ($0.0 \leq x \leq 0.1$) presented in Figure 5a reveal that the charge-carrier concentration of the end-member phase, CuFeS$_2$, is relatively high ($n = 1.4(2) \times 10^{19}$ cm$^{-3}$), suggesting the existence of defects in the stoichiometric phase, with a mobility, $\mu$, of $15(3)$ cm$^2$ V$^{-1}$ s$^{-1}$. The mobility shows a marked increase on tin substitution, after which it retains a constant value up to $x = 0.05$, before increasing further at higher levels of substitution. The partial replacement of formally Cu$^+$ with Sn$^{4+}$ leads to an increase in the carrier concentration, as expected. However, a maximum carrier concentration of $n = 3.5(3) \times 10^{19}$ cm$^{-3}$ is reached at Cu$_{0.99}$Sn$_{0.01}$FeS$_2$, with the value of carrier concentration decreasing at higher levels of substitution. The maximum carrier concentration achieved was much lower than expected on the basis of electron counting (e.g., ca. $2 \times 10^{21}$ cm$^{-3}$ for each increment of 0.05 in $x$). To the best of our knowledge, the carrier mobility of isocubanite has not been reported. However, the lower reported resistivity and Seebeck coefficient of this phase suggests that the mobility is appreciably higher than that of chalcopyrite: a view that is supported by the DFT calculations of Barbier et al.$^{57,58}$ Therefore, the presence of appreciable amounts of isocubanite at $x > 0.05$ may contribute to the observed marked increase in the charge-carrier mobility at higher levels of tin substitution. Similar increases in mobility on introduction of a higher mobility phase have been reported in nanocomposites of thermoelectrics.$^{34,59-61}$ Carrier scattering due to the presence of a secondary phases becomes significant only when the average mean free path of the carriers is comparable to the dimensions of the secondary phase. DFT calculations$^{34}$ show that the average mean free path of the carriers in CuFeS$_2$ is $<1$ nm, which is much lower than the size of the inclusions of isocubanite (of the order of microns), observed by SEM (Figure S4). Hence, the carrier scattering due to isocubanite is likely to have a small impact on electrical transport.

**Figure 4.** (a) Electrical resistivity ($\rho$), (b) Seebeck coefficient ($S$), and (c) power factor (PF) of Cu$_{1-x}$Sn$_x$FeS$_2$ ($0.0 \leq x \leq 0.1$) samples as a function of temperature.
transport properties, given the much higher carrier mobility of this secondary phase.

DFT simulations have been performed in an effort to understand the electrical transport behavior of CuFeS₂. Electronic structure calculations (Figure 6a) reveal that the conduction band of CuFeS₂ consists primarily of contributions from sulfur 3p and iron 3d states, while the valence band in the region of the Fermi level (E_F) is principally composed of copper 3d and sulfur 3p states. There is strong hybridization between the Cu d-states and S p-states as evidenced by the similarity in the partial density of states (DOS) for these states, which is consistent with a strongly covalent Cu−S interaction (Figure 6b). Fe d-states are mostly localized as low-lying valence-band states as well as near-edge conduction-band states, indicating a high degree of ionicity in the Fe−S interaction. The n-type behavior of CuFeS₂ identified above implies the presence of intrinsic sulfur vacancies, which serve to move E_F into the conduction band, and suggests that the band structure in the region of the conduction band edge plays a key role in determining the transport properties of CuFeS₂. Although there is a clear conduction band minimum (CBM) at the N point, electron pockets exist at the Σ and Z points with energies only 0.04 and 0.06 eV above the CBM, respectively, while the electron pocket at the X point is 0.09 eV higher than the CBM. The close proximity of these electron pockets leads to a high band degeneracy near the CBM. Band degeneracy is known to enhance the Seebeck coefficients even at low carrier concentrations.62−64 Combined with the relatively flat nature of the band at the CBM (implying high electron effective mass), this results in the high Seebeck coefficient of pristine CuFeS₂ (Figure 4b).

DFT calculations also provide insight into the origin of the lower-than-expected increase in carrier concentration on substitution of copper by tin noted above. In particular, the possibility of formation of an Fe^{3+}−e⁻ bound state (small polaron), corresponding to a reduction of Fe^{3+} to Fe^{2+}, was investigated. Given the limitations of the X-ray diffraction analysis noted above, substitution of tin at both the copper (4a) and iron (4b) sites was considered. For each mode of substitution, calculations were performed for each of the two possible scenarios: (i) the Fe atom adjacent to the Sn atom is allowed to remain in the Fe^{3+} state (without polaron formation) and (ii) the same Fe atom is “forced” to be in the Fe^{2+} state (with polaron formation). Examination of the ground state energies suggests that in the case of incorporation of Sn at the Cu’ site, the polaronic solution is 0.36 eV lower in energy than the non-polaronic solution, i.e., a partial reduction of Fe^{3+} to Fe^{2+} is favored. On the other hand, for Sn substitution at the Fe^{3+} site, the polaronic solution is less stable than the non-polaronic solution by 1.61 eV. This analysis
suggests that polaron formation, which results from substitution of tin at the copper site, may be responsible for the lower-than-expected carrier concentration on substitution. Partial reduction of iron, to form a localized Fe$^{2+}$ state effectively reduces the free carrier concentration and leads to a smaller increase in carrier concentration upon tin substitution (at $x \leq 0.05$) than expected on the basis of replacement of Cu$^+$ by Sn$^{4+}$.

Using the charge-carrier concentration ($n$) determined from Hall measurements, Pisarenko plots were constructed for materials with compositions in the range $0.0 \leq x \leq 0.04$ (Figure 5b). Materials with higher tin contents were not analyzed in this way owing to the presence of significant amounts of an impurity phase, as identified from powder X-ray diffraction. The end-member CuFeS$_2$ phase exhibits a density-of-states (DOS) effective mass, $m^*_n = 2.6$ $m_e$, in good agreement with previously reported$^{30,33,56}$ values of $m^*_n = 2.2$ to 2.5 $m_e$. The high DOS effective mass contributes to the high Seebeck coefficient and is also consistent with the results of DFT calculations discussed above, where the conduction band was shown to contain multiple pockets with a flat band near the conduction band edge. Tin substitution leads to only a slight decrease in the DOS effective mass to $m^*_n = 2.2$ $m_e$ in Cu$_{0.98}$Sn$_{0.02}$FeS$_2$. This relatively high value is maintained at low Seebeck coefficient and electrical conductivity, enabling optimum performance to be realized at lower doping levels. This is in agreement with the suggestion of Park et al.$^{34}$ that high mobility affords a better compromise between Seebeck coefficient and electrical conductivity, enabling optimum performance to be realized at lower doping levels.

X-ray photoelectron spectroscopy (XPS) provides support for the presence of iron in mixed oxidation states, resulting from tin substitution, as predicted by the DFT calculations. Data for the end-member phase, CuFeS$_2$, and for Cu$_{0.96}$Sn$_{0.04}$FeS$_2$ exhibit peaks due to Cu$^+$ (Figure 7a), Fe$^{3+}$, and Sn$^{4+}$. Partial reduction of iron, to form a localized Fe$^{2+}$ state, may be responsible for the lower-than-expected carrier concentration on substitution. This enables a relatively high value of the Seebeck coefficient, albeit reduced from that of the end-member phase, to be maintained for levels of tin incorporation of $x \leq 0.04$. Above this value, the isocubanite impurity, which has a much lower Seebeck coefficient ($S = -65$ to $-75$ $\mu$V K$^{-1}$ at $323 \leq T/K \leq 723$), significantly reduces the measured Seebeck coefficient of Cu$_{1-x}$Sn$_x$FeS$_2$ ($0.05 \leq x \leq 0.1$). Therefore, although it has been predicted$^{34}$ that very high charge-carrier concentrations (ca. $10^{21}$ cm$^{-3}$) are required for high electrical performance, when combined with a high DOS effective mass and carrier mobility, comparable power factors can be achieved at significantly lower carrier concentrations (ca. $10^{19}$ cm$^{-3}$).

\[ S = \frac{8\pi^2k_BT}{3eh^2}m^*_n\left(\frac{\pi}{3n}\right)^{2/3} \]

(1)

where $m^*_n$, $n$, $e$, $k_B$, and $h$ denote the density-of-states effective mass, charge-carrier concentration, electronic charge, Boltzmann constant, and Planck’s constant, respectively. For compositions in the range $0.02 \leq x \leq 0.04$, the DOS effective mass (numerator) is effectively constant, but the charge-carrier concentration (denominator) increases with increasing tin content, resulting in a decrease of the Seebeck coefficient with $x$. The polaron formation induced by tin substitution reduces the carrier concentration from that expected at a given level of substitution. This enables a relatively high value of the Seebeck coefficient, albeit reduced from that of the end-member phase, to be maintained for levels of tin incorporation of $x \leq 0.04$. Above this value, the isocubanite impurity, which has a much lower Seebeck coefficient ($S = -65$ to $-75$ $\mu$V K$^{-1}$ at $323 \leq T/K \leq 723$), significantly reduces the measured Seebeck coefficient of Cu$_{1-x}$Sn$_x$FeS$_2$ ($0.05 \leq x \leq 0.1$). Therefore, although it has been predicted$^{34}$ that very high charge-carrier concentrations (ca. $10^{21}$ cm$^{-3}$) are required for high electrical performance, when combined with a high DOS effective mass and carrier mobility, comparable power factors can be achieved at significantly lower carrier concentrations (ca. $10^{19}$ cm$^{-3}$).

X-ray photoelectron spectroscopy (XPS) provides support for the presence of iron in mixed oxidation states, resulting from tin substitution, as predicted by the DFT calculations. Data for the end-member phase, CuFeS$_2$, and for Cu$_{0.96}$Sn$_{0.04}$FeS$_2$ exhibit peaks due to Cu$^+$ (Figure 7a), Fe$^{3+}$, and Sn$^{4+}$. Partial reduction of iron, to form a localized Fe$^{2+}$ state, may be responsible for the lower-than-expected carrier concentration on substitution. This enables a relatively high value of the Seebeck coefficient, albeit reduced from that of the end-member phase, to be maintained for levels of tin incorporation of $x \leq 0.04$. Above this value, the isocubanite impurity, which has a much lower Seebeck coefficient ($S = -65$ to $-75$ $\mu$V K$^{-1}$ at $323 \leq T/K \leq 723$), significantly reduces the measured Seebeck coefficient of Cu$_{1-x}$Sn$_x$FeS$_2$ ($0.05 \leq x \leq 0.1$). Therefore, although it has been predicted$^{34}$ that very high charge-carrier concentrations (ca. $10^{21}$ cm$^{-3}$) are required for high electrical performance, when combined with a high DOS effective mass and carrier mobility, comparable power factors can be achieved at significantly lower carrier concentrations (ca. $10^{19}$ cm$^{-3}$).
(Figure 7bd), and S\(^{2-}\) (Figure 7ce), consistent with the reported formal oxidation states of CuFeS\(_2\)\(^{11,33,65,66}\) (Table S4). The deconvoluted tin XPS spectrum for Cu\(_{0.96}\)Sn\(_{0.04}\)FeS\(_2\) (Figure 7f) exhibits a 3d\(_{5/2}\) peak corresponding to Sn\(^{4+}\). This supports our assertion that tin is incorporated in the 4+ oxidation state, in common with a number of ternary and quaternary sulﬁdes including Cu\(_2\)SnS\(_3\), Cu\(_2\)Sn\(_2\)S\(_6\), Cu\(_2\)FeSnS\(_4\), and Cu\(_2\)ZnSnS\(_4\)\(^3\(^{-}\)\)\(^{38}\) However, in both spectra, a broad weak feature that can be assigned to the persulﬁde species, S\(_2\)\(^{2-}\), is present, together with a second weak feature associated with Fe\(^{3+}\). These peaks may be associated with the presence of trace amounts of Cu\(_5\)FeS\(_4\) (bornite) are also discernible in the SEM images for Cu\(_1\)Sn\(_{0.04}\)FeS\(_2\) for 0.0 ≤ x ≤ 0.04 (Figure 8) and for x > 0.04 (Figures S3 and S4).

![Scanning electron microscopy (SEM) images of Cu\(_{1-x}\)Sn\(_x\)FeS\(_2\) for 0.0 ≤ x ≤ 0.04 (Figure 8) and for x > 0.04 (Figures S3 and S4)](https://example.com)

Figure 8. Scanning electron microscopy (SEM) images of Cu\(_{1-x}\)Sn\(_x\)FeS\(_2\) for 0.0 ≤ x ≤ 0.04 (Figure 8) and for x > 0.04 (Figures S3 and S4).

This reveals a matrix, identiﬁed by EDS as the primary chalcopyrite phase, together with a small amount of a secondary FeS\(_2\) phase in all compositions. The FeS\(_2\) impurity can be considered to be the origin of the XPS features assignable to Fe\(^{2+}\) and S\(_2\)\(^{2-}\) in the end-member phase. At higher magniﬁcation (Figure S3), trace amounts of CuFeS\(_2\) (bornite) are also discernible in the SEM data, although the formation of this phase is suppressed on substitution by tin. The secondary phases, FeS\(_2\) and CuFeS\(_3\), are present in too low an amount to be detectable by powder X-ray diffraction. For compositions in the range 0.02 ≤ x ≤ 0.04, the amount and distribution of the FeS\(_2\) impurity is reduced substantially compared to that in the end-member (x = 0) phase, as was also evidenced in the reduced intensity of the S\(_2\)\(^{2-}\) peak in the XPS data for the material with a composition corresponding to x = 0.04. This strongly suggests that the increase in the signal from Fe\(^{2+}\) in the XPS spectra of the tin-substituted phase is due to the reduction of a fraction of the Fe\(^{3+}\) in the main chalcopyrite phase. For compositions with higher tin contents (x ≥ 0.05), the SEM data show large amounts of a CuFeS\(_3\) (isocubanite) type phase (Figure S4), consistent with the powder X-ray diffraction data, in addition to the FeS\(_2\) secondary phase, while in x ≥ 0.08 samples, bornite is also evident at the periphery of the isocubanite phase (Figure S4). Tin substitution has no signiﬁcant impact on the morphology for compositions of x ≤ 0.04 but at higher levels of substitution (x ≥ 0.05), a high concentration of microcracks and pores are observed. The compositions of the primary chalcopyrite-type phase in the series Cu\(_{1-x}\)Sn\(_x\)FeS\(_2\) were determined from EDS data (Table S5). The experimentally determined compositions are broadly in line with the nominal compositions. The slight Cu excess may be a consequence of the overlap of the K\(_\alpha\) and L\(_\alpha\) characteristic lines of Cu and Fe (from both the main CuFeS\(_2\) and secondary FeS\(_2\) phases), while the tin content agrees well with the nominal values.

The thermal conductivity of the end-member phase, CuFeS\(_2\), is relatively high (ca. 6.7 W m\(^{-1}\) K\(^{-1}\) at 323 K), similar to reported values of ~6.5–8 W m\(^{-1}\) K\(^{-1}\) (at 323 K)\(^{11,12,30,35,67}\), but is substantially reduced on substitution of copper by tin (Figure 9a). The electronic contribution to the thermal conductivity (details of the calculation of κ\(_e\)) is typically 1–10% (for 0.0 ≤ x ≤ 0.04 at 673 K) of the total thermal conductivity. Therefore, the thermal conductivity of materials in the series Cu\(_{1-x}\)Sn\(_x\)FeS\(_2\) is mainly due to the lattice contribution (κ\(_L\)), and the reduction of 20–40% in the observed thermal conductivity.

![Figure 9. (a) Total (κ), (b) electronic (κ\(_e\)), and lattice (κ\(_L\)) thermal conductivities of Cu\(_{1-x}\)Sn\(_x\)FeS\(_2\) (0.0 ≤ x ≤ 0.1) samples as a function of temperature.](https://example.com)

Figure 9. (a) Total (κ), (b) electronic (κ\(_e\)), and lattice (κ\(_L\)) thermal conductivities of Cu\(_{1-x}\)Sn\(_x\)FeS\(_2\) (0.0 ≤ x ≤ 0.1) samples as a function of temperature.
for substituted phases over the range $0.02 \leq x \leq 0.04$, is primarily due to a reduction in $\kappa_L$ (Figure 9b).

Sound velocity measurements (Table 1) were conducted for $\text{Cu}_{1-x}\text{Sn}_x\text{FeS}_2$ with compositions corresponding to $x = 0, 0.02,$ and $0.04$. In common with previously reported values, the end-member phase, $\text{CuFeS}_2$, exhibits a high mean sound velocity ($v_m$) of $2831 \text{ m s}^{-1}$, accounting for the high measured lattice thermal conductivity, $\kappa_L$. On tin substitution, the mean sound velocity is markedly reduced, which is reflected in the significant reduction of $\kappa_L$ for the tin-substituted materials (Figure 9b). The Debye temperature and elastic modulus, derived from the sound velocity measurements (details of the calculation are provided in the Supporting Information), show corresponding reductions on substitution of copper with tin.

Calculation of the phonon dispersion (Figure 10a) and phonon density-of-states (PDOS) for $\text{CuFeS}_2$ (Figure 10b) reveal that the majority of the low frequency (<3 THz) heat-carrying acoustic phonon modes lie below 8–12 meV. The average group velocity of these acoustic modes is relatively high (3448 m s$^{-1}$ along $\Gamma - X$ and 3400 m s$^{-1}$ along $\Gamma - Z$) and is responsible for the high mean sound velocity and lattice component of the thermal conductivity. It can be seen from Figure 10b that copper vibrations are the biggest contributor to the acoustic phonons. The low-energy optical modes with frequencies in the range of 4 to 6 THz arise from both Cu and Fe atoms vibrating inside their tetrahedra with almost fixed S positions, whereas the high-frequency (8–11 THz) optical modes are dominated by the motion of S atoms, involving considerable bond stretching.

The frequency dependence of the phonon mean free paths reveal that at 300 K, the majority of the transverse and longitudinal acoustic modes have a mean free path between 50 and 500 nm (Figure 10c). At 700 K, the mean free paths reduce to $\sim 20$–200 nm. We have calculated the effect of nanoparticle and/or grain boundary size on $\kappa_L$ (Figure 10d). This calculation was performed by imposing a cut-off on the mean free path of the phonons. Phonons with a longer mean free path than the cut-off are considered to be scattered, leading to a reduction in $\kappa_L$. At 300 K, a small population of phonons can be scattered effectively for a nanoparticle/grain boundary size of $\sim 500$–600 nm, reducing $\kappa_L$ by ca. 20%. However, the particle size required for a given relative decrease of $\kappa_L$ reduces with increasing temperature. For example, at 700 K, the same 20% reduction would require a nanoparticle/grain boundary size of $\sim 200$ nm. Therefore, in order to achieve the 20 to 40% reduction of $\kappa_L$ at higher temperatures, which is observed experimentally (Figure 9b) for $\text{Cu}_{1-x}\text{Sn}_x\text{FeS}_2$ ($0.02 \leq x \leq 0.04$) samples, the nanoparticle/grain boundary size should be <100 nm.

Table 1. Various Physical Parameters for $\text{Cu}_{1-x}\text{Sn}_x\text{FeS}_2$ ($x = 0, 0.02$ and 0.04) Samples Showing the Longitudinal ($v_L$), Transverse ($v_T$), Average ($v_{av}$), and Mean ($v_m$) Sound Velocities, Young’s ($E$) and Shear ($G$) Moduli, and Debye Temperature ($\theta_D$)

| sample | $v_L$ (m/s) | $v_T$ (m/s) | $v_{av}$ (m/s) | $v_m$ (m/s) | $E$ (Gpa) | $G$ (Gpa) | $\theta_D$ (K) |
|--------|------------|------------|----------------|------------|-----------|-----------|---------------|
| $x = 0$ | 4720       | 2536       | 3264           | 2831       | 69.9      | 26.94     | 319           |
| $x = 0.02$ | 3850      | 2245       | 2780           | 2490       | 50.59     | 20.36     | 280           |
| $x = 0.04$ | 3500      | 2150       | 2600           | 2372       | 45.03     | 18.81     | 267           |

Figure 10. The phonon (a) dispersion curve and (b) DOS of $\text{CuFeS}_2$. (c) The mean free path (MFP) of optical (O), transverse acoustic (TA) and longitudinal acoustic (LA) phonon modes at 300 and 700 K. (d) The accumulated percentage of lattice thermal conductivity ($\kappa_L$) as a function of mean free path cut-off at different temperatures.
High-resolution transmission electron microscopy (HRTEM) was used to investigate the micro- and nanostructural features of Cu$_{0.96}$Sn$_{0.04}$FeS$_2$ that may have an impact on the mean free path of heat-carrying acoustic phonons. The [110] zone HRTEM image (Figure 11a) of the chalcopyrite phase in Cu$_{0.96}$Sn$_{0.04}$FeS$_2$ shows uniform atomic ordering with no short-/long-range disordered domains. The selected area electron diffraction (SAED) pattern confirming the tetragonal structure of chalcopyrite. Therefore, the cubic zinc-blende structure in which twinning of the {111} plane is a typical feature and occurs frequently. Therefore, the superstructures of cubic phases (of which chalcopyrite is one example), with the $c/a$ ratio approaching 2, exhibit similar twinning since the [112] plane of CuFeS$_2$ is analogous to the [111] plane of the zinc-blende. In the case of Cu$_{0.96}$Sn$_{0.04}$FeS$_2$, $c/a = 1.976$, and therefore, twinning is to be expected. These dislocations and twinning features are on the length scale of 10–50 nm and, hence, on the basis of the calculations discussed above, are expected to scatter acoustic phonons. Electron backscattering diffraction (EBSD) data for Cu$_{0.96}$Sn$_{0.04}$FeS$_2$ reveals a multiscale grain size distribution (Figure S5) with grain sizes ranging from one to several microns. However, our calculations suggest that since these grains have much larger sizes than the mean free path of the acoustic phonons, they are unlikely to have significant impact in reducing the lattice thermal conductivity.

In order to understand the mechanism behind the reduced lattice thermal conductivity in tin-substituted samples, the Debye–Callaway model$^{69,70}$ was fitted to the experimentally measured thermal conductivities. According to this model, the lattice thermal conductivity can be written as

$$\kappa_L = \frac{k_B}{2\pi^2 v_m} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\tau_c^{-1}(e^x - 1)^2} dx$$

where $x = \hbar \omega/k_B T$, $k_B$ is the Boltzmann’s constant, $\hbar$ is the reduced Plank’s constant, $\omega$ is the phonon frequency, $v_m$ is the mean sound velocity, $\theta_D$ is the Debye temperature, and $\tau_c^{-1}$ is the total phonon relaxation rate given by

$$\tau_c^{-1} = \tau_B^{-1} + \tau_D^{-1} + \tau_U^{-1} = \frac{v_m}{L} + A\omega^4 + B\omega^2T e^{-\omega_0/3T}$$

which considers contributions from grain boundary ($\tau_B^{-1}$), point defect ($\tau_D^{-1}$), and phonon–phonon Umklapp ($\tau_U^{-1}$) scattering processes. In eq 3, $L$ is the average grain size, and $A$ and $B$ are the fitting parameters, which, respectively, are a measure of the contributions of the point defect and Umklapp scattering processes. The fitted parameters (Table 2) reveal that while the Umklapp contribution shows little change with increasing levels of tin substitution, the point defect scattering contribution increases significantly. Since copper cations within the CuS$_4$ tetrahedral network are primarily responsible for the heat-carrying acoustic modes (vide supra), the substitution by tin, which has a higher mass and larger atomic radius, can lead to significant local disorder and, therefore, point defect scattering of these acoustic modes. The effect of this disorder can be quantified by formulating the coefficient, $A_\Gamma$, in terms of the following expression:

$$A = \frac{\Omega_0}{4\pi v_m^3} \Gamma$$

where, $\Omega_0$ is the volume of the primitive unit cell and $\Gamma$ is the scattering parameter. Using the model of Slack$^{71}$ and Abeles$^{72}$ the scattering parameter $\Gamma$ can be written as $\Gamma = \Gamma_M + \Gamma_S$, $\Gamma_M$ is the scattering parameter due to the presence of point defects, and $\Gamma_S$ is the scattering parameter due to the presence of Umklapp processes.

### Table 2. Extracted Scattering Parameters from the Debye–Callaway Model for Cu$_{1-x}$Sn$_x$FeS$_2$ ($x = 0, 0.02$ and $0.04$) Samples

| sample | $L$ (μm) | $A$ ($\times 10^{15}$ s$^{-3}$) | $B$ ($\times 10^{15}$ s$^{-3}$) | $\Gamma$ ($\times 10^{-3}$) | $\Gamma_M$ ($\times 10^{-5}$) | $\Gamma_S$ ($\times 10^{-3}$) | $\epsilon$ |
|--------|----------|-------------------------------|-------------------------------|---------------------------|-----------------------------|-----------------------------|------|
| $x = 0$ | 12.1     | 2                             | 6                             | 10.86                     | 7.08                        | 3.78                        | 68   |
| $x = 0.02$ | 9.9      | 10.24                         | 6.2                           |                           |                             |                             |      |
| $x = 0.04$ | 5.4      | 43.66                         | 6                             | 39.91                     | 13.88                       | 26.03                       | 242  |

Figure 11. (a) Transmission electron microscopy (TEM) images of the Sn-substituted Cu$_{0.96}$Sn$_{0.04}$FeS$_2$ with the selected area electron diffraction (SAED) pattern confirming the tetragonal structure of chalcopyrite. (b) High-resolution TEM images showing dislocations and twinning of the [112] planes.
where $\Gamma_M$ and $\Gamma_S$ are the scattering parameters for mass-difference and strain field fluctuations, respectively, given by

$$\Gamma_M = \sum_{i=1}^{n} \varepsilon_i \frac{M_i^2 f_i^2}{M} \frac{1}{J_i f_i^4 (M_i - M_i^f)^2}$$

and

$$\Gamma_S = \sum_{i=1}^{n} \varepsilon_i \frac{M_i^2 f_i^2}{M} \frac{1}{J_i f_i^4 (\varepsilon_i - \varepsilon_i^f)^2}$$

where $\bar{M}_i = \sum f_i^k M_i^k$, $\bar{r}_i = \sum f_i^k r_i^k$, and $\bar{M} = \sum \bar{M}_i$. Here, $n$ is the number of crystallographic sub-lattices which is 3 for CuFeS$_2$ and $\varepsilon_i$ is the degeneracy of each site in the primitive unit cell ($\varepsilon_1 = \varepsilon_2 = 1$, $\varepsilon_3 = 2$ corresponding to Cu, Fe, and S sites, respectively). $M_i$ and $\bar{r}_i$ denote the average mass and radius of the atoms on the $i^{th}$ sublattice, respectively. $M_i^f$ and $f_i^k$ are the atomic mass and fractional occupation of the $k^{th}$ atom on the $i^{th}$ sublattice, respectively. $\bar{M}$ is the total average atomic mass of the compound. Finally, $\varepsilon$ is a phenomenological adjustable parameter that was evaluated from fitting eq 2 to the experimental $\kappa_i$. For Cu$_{1-x}$Sn$_x$FeS$_2$ samples, on the basis of tin substitution occurring at the copper site, as established above, the total scattering parameter can be thus written as

$$\Gamma = \frac{1}{4} \frac{M_{Cu}}{M} x(1-x) \left( \frac{M_{Cu} - M_{Sn}}{M_{Cu}} \right)^2 + \varepsilon \left( \frac{r_{Cu} - r_{Sn}}{\bar{r}_{Cu}} \right)^2$$

The extracted scattering parameters from substituting the coefficient A in eq 2 and fitting the expression to the experimental $\kappa_i$ are shown in Table 2, where it can be seen that both the mass and strain field fluctuation scattering increase with an increase in the tin content. In previous work with transition metals, such as zinc substitution at the copper site, it was found that only the strain field fluctuation contributes to the reduction in the lattice thermal conductivity because of the similar atomic masses of Zn and Cu. However, tin having a much higher atomic mass (118.7 amu) compared to Cu (63.5 amu) also introduces a considerable contribution from mass-difference fluctuation scattering. Interestingly, at a low level of tin substitution ($x = 0.02$), the scattering is dominated by the mass-fluctuation term ($\Gamma_M$) but for $x \approx 0.04$, the strain field ($\Gamma_S$) scattering term becomes much larger compared to $\Gamma_M$: Clearly, higher levels of tin substitution induce a significant strain in the lattice.

The reduced elastic moduli and Debye temperature (derived from the sound velocity data shown in Table 1) in the tin-substituted materials compared to CuFeS$_2$ further confirm that the local strain fluctuation caused by tin results in a significant lattice softening. Comparing the $\Gamma$ values of Cu$_{0.95}$Sn$_{0.05}$FeS$_2$ determined in the present study with those obtained at similar levels of substitution (24 at %) of Zn$^{15}$ and Cd$^{14}$ at the Cu site reveals that the total scattering parameter is much larger in the present case as both $\Gamma_M$ and $\Gamma_S$ have significant contributions. These point defects, combined with a small contribution from the dislocations and twinning faults, observed in the HRTEM data result in effective scattering of phonons over a wide range of the acoustic phonon spectrum. For higher levels of substitution ($x \geq 0.05$), $\kappa_i$ decreases further through a combination of these effects and the increased amount of impurity phases. The thermal conductivity of isocubanite, identified by powder X-ray diffraction, is somewhat lower than that of chalcopyrite ($\kappa_i \approx 3.6$ to 2.5 W m$^{-1}$K$^{-1}$ over the range 323 $\leq$ T/K $\leq$ 673) $^{52}$, and therefore contributes to the reduction in thermal conductivity of the more highly substituted materials. Moreover, for materials with $x > 0.05$, the microstructure consists of a high concentration of pores and microcracks. The combination of these factors produces strong phonon scattering for compositions with $x \geq 0.05$ samples, the lowest lattice thermal conductivity ($\kappa_i \approx 1.45$ W m$^{-1}$K$^{-1}$ at 673 K) being observed for the $x = 0.1$ composition.

The relatively low maximum thermoelectric figure-of-merit ($\varphi T \approx 0.08$ at 673 K) of the end-member phase CuFeS$_2$ (Figure 12) is due to a combination of a high electrical resistivity and a high lattice thermal conductivity. However, the almost 3-fold increase in power factor at low levels of tin substitution, principally due to the combination of an optimum charge-carrier concentration and high DOS effective mass ($m_0^*$), coupled with marked reductions in thermal conductivity, leads to a significant increase in the figure-of-merit. The maximum figure-of-merit of $\varphi T \approx 0.3$ achieved at 673 K in Cu$_{0.95}$Sn$_{0.05}$FeS$_2$ is more than 3 times higher than that of the end-member CuFeS$_2$ and is larger than that of the majority of the previously reported substituted CuFeS$_2$ phases. $^{11,28,30,52,56}$ As noted previously, the thermoelectric performance of n-type sulﬁdes is inferior to that of their p-type counterparts. Achieving high performance in n-type analogues is of paramount importance for the construction of an all-sulﬁde TE device containing chemically compatible components. The maximum figure-of-merit reported in this work compares favorably with previous reports of n-type sulﬁdes (Figure 13). Moreover, the level of performance in the chalcopyrite-derived phase reported here is achieved in a material containing cheap and abundant elements. This offers clear advantages over materials containing rarer elements such as silver, which outweigh the slightly higher performance of the latter.
4. CONCLUSIONS

The impact on the structural, electronic, and thermoelectric properties of CuFeS₂ of substitution of copper by tin has been investigated using a range of experimental and computational methods. The solubility limit of Sn was found to be ca. 4 at. %, beyond which an isocubanite secondary phase is observed. While it is not possible to establish the mode of substitution directly by powder X-ray diffraction, the combination of DFT calculations and XPS measurements indirectly support the interpretation that tin preferentially replaces copper at the 4a sites. The DFT calculations reveal that substitution of Cu⁺ by Sn⁺ leads to small polaron formation. This arises from the partial reduction of Fe³⁺ to form localized Fe²⁺ states, which is consistent with the reduction of iron that is observed by XPS. In contrast, DFT predicts that replacement of Fe by Sn would not result in Fe reduction and would therefore be inconsistent with the XPS results.

Polaron formation leads to a lower-than-expected increase in the charge-carrier concentration. Nevertheless, the charge-carrier concentration of CuFeS₂ is still increased through substitution with tin. While this is reduced from the 3 electrons per substituent that would be expected on the basis of formal charges, the increase in charge-carrier concentration results in a reduction in electrical resistivity. Significantly, this occurs with the retention of a high density-of-states effective mass, which results in a relatively high Seebeck coefficient being maintained. This combination of a low resistivity and high Seebeck coefficient results in a high power-factor (ca. 0.7 mW m⁻¹ K⁻² for Cu₀.⁹₆Sn₀.₀₄FeS₂ at 673 K) at modest levels of substitution. This demonstrates the effectiveness of relatively small changes in carrier concentration, similar to that reported for a number of chalcogenide systems.³³,⁷⁹−⁸¹ Furthermore, the power factor shows a very weak temperature dependence. The nearly flat PF(T) response may be an attractive feature for device performance.

Tin substitution also leads to lattice softening and enhanced phonon scattering due to both mass and strain field fluctuations. This, in combination with dislocations and twinning faults, results in a substantial reduction in the lattice thermal conductivity, demonstrating the effectiveness of tin substitution as a promising strategy to increase the phonon scattering across different length scales and improve the thermoelectric performance. On the basis of the calculated accumulated percentage of lattice thermal conductivity (κₐ) as a function of mean free path (Figure 10d), increasing phonon scattering, particularly for those with mean free paths in the range 50–500 nm, is a key element in the design of new high-performance n-type chalcopyrite materials. In the present work, we have shown that the reductions in thermal conductivity achieved through lattice softening, together with the high power factor, results in a maximum figure-of-merit zT = 0.3 at 673 K for Cu₀.⁹₆Sn₀.₀₄FeS₂. This represents a more than 3-fold increase over that of the parent phase, suggesting that Cu₁−ₓSnₓFeS₂ materials may indeed hold promise as candidates for thermoelectric applications in the mid-temperature range.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.2c00637.

Crystal structure of isocubanite secondary phase and XRD patterns of Sn substituted Cu₁−ₓSnₓFeS₂ (x = 0.05–0.1) showing an increase in isocubanite peaks with x; comparison of the Seebeck coefficient of pristine CuFeS₂ with that of the literature; lattice parameters and room-temperature Hall measurement data of Cu₁−ₓSnₓFeS₂ (0.0 ≤ x ≤ 0.1); Pisarenko plots of Sn substituted Cu₁−ₓSnₓFeS₂ (0.0 ≤ x ≤ 0.04) samples (present work) and that of other substituted CuFeS₂ phases in the literature; XPS binding energies and corresponding oxidation states of individual elements in pristine CuFeS₂ and Sn-substituted Cu₀.₉₆Sn₀.₀₄FeS₂; SEM images of Cu₁−ₓSnₓFeS₂ (0.0 ≤ x ≤ 0.1) showing the various secondary phases; EBSD compositions of the main phase in all the samples; EBSD results for Cu₀.₉₆Sn₀.₀₄FeS₂; calculation details of the Lorenz number, mean and average sound velocities, shear and Young’s moduli, and Debye temperature (PDF)

AUTHOR INFORMATION

Corresponding Author

Anthony V. Powell — Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6DX, United Kingdom; orcid.org/0000-0002-9650-1568; Email: a.v.powell@reading.ac.uk

Authors

Sahil Tippireddy — Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6DX, United Kingdom
Feridoon Azough — Department of Materials, University of Manchester, Manchester M13 9PL, United Kingdom
Vikram — Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6DX, United Kingdom; orcid.org/0000-0002-5734-6905
Frances Towers Tompkins — Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6DX, United Kingdom
Animesh Bhuil — New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India
Robert Freer — Department of Materials, University of Manchester, Manchester M13 9PL, United Kingdom; orcid.org/0000-0003-1100-8975
Ricardo Grau-Crespo — Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6DX, United Kingdom; orcid.org/0000-0001-8845-1719

Figure 13. A comparison of the thermoelectric figure-of-merit (zT) at 673 K of potential n-type sulfide-based materials.¹⁵,³³,⁶⁷,⁷³–⁷⁸
Kanishka Biswas — New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India; orcid.org/0000-0001-9119-2455
Paz Vaqueiro — Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6DX, United Kingdom; orcid.org/0000-0001-7545-6262

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chemmater.2c00637

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The present work was carried out as part of the UKRI Global Challenges Research Fund (GCRF) project supported by EPSRC, UK (grant no. EP/T020040/1). The authors would like to acknowledge the Chemical Analysis Facility (CAF) at the University of Reading, Reading, UK and the national XPS facility at Harwell Campus, Didcot, UK. The work was also supported by the Henry Royce Institute for Advanced Materials funded through EPSRC grants EP/R00661X/1, EP/S019367/1, EP/P025021/1, and EP/P025498/1. We appreciate the support from X-ray facilities in Department of Materials in the University of Manchester. For the computational part, this work made use of ARCHER, the UK’s national high-performance computing service, via the UK’s HPC Materials Chemistry Consortium, which is funded by EPSRC (EP/R029431), and the Yong supercomputer via the UK’s Materials and Molecular Modeling Hub, which is also partially funded by EPSRC (EP/T022213/1).

■ REFERENCES

(1) Freer, R.; Powell, A. V. Realising the Potential of Thermoelectric Technology: A Roadmap. J. Mater. Chem. C 2020, 8, 441–463.
(2) He, J.; Tritt, T. M. Advances in Thermoelectric Materials Research: Looking Back and Moving Forward. Science 2017, 357, 1369.
(3) Wei, J.; Yang, L.; Ma, Z.; Song, P.; Zhang, M.; Ma, J.; Yang, F.; Wang, X. Review of Current High-ZT Thermoelectric Materials. J. Mater. Sci. 2020, 55, 12642–12704.
(4) Zhao, L. D.; Wu, H. J.; Hao, S. Q.; Wu, C. L.; Zhou, X. Y.; Biswas, K.; He, J. Q.; Hogan, T. P.; Uhler, C.; Wolverton, C.; Dravid, V. P.; Kanatzidis, M. G. All-Scale Hierarchical Thermoelectrics: MgTe in PbTe Facilitates Valence Band Convergence and Suppresses Bipolar Thermal Transport for High Performance. Energy Environ. Sci. 2013, 6, 3346–3355.
(5) Wu, Y.; Chen, Z.; Nan, P.; Xiong, F.; Lin, S.; Zhang, X.; Chen, Y.; Chen, L.; Ge, B.; Pei, Y. Lattice Strain Advances Thermoelectrics. Joule 2019, 3, 1276–1288.
(6) Chang, C.; Wu, M.; He, D.; Pei, Y.; Wu, C. F.; Wu, X.; Yu, H.; Zhu, F.; Wang, K.; Chen, Y.; Huang, L.; Li, J. F.; He, J.; Zhao, L. D. 3D Charge and 2D Phonon Transports Leading to High Out-of-Plane ZT in n-Type SnSe Crystals. Science 2018, 360, 778–783.
(7) Qin, B.; Wang, D.; He, W.; Zhang, Y.; Wu, H.; Pennycook, S. J.; Zhao, L. D. Realizing High Thermoelectric Performance through Inelastic Neutron Scattering. J. Mater. Chem. C 2019, 141, 1141–1149.
(8) Zhang, C.; de la Mata, M.; Li, Z.; Belarde, F. J.; Arbiol, J.; Khor, K. A.; Poletti, D.; Zhu, B.; Yan, Q.; Xiong, Q. Enhanced Thermoelectric Performance of Solution-Derived Bismuth Telluride Based Nanocomposites via Liquid-Phase Sintering. Nano Energy 2016, 30, 630–638.
(9) Shin, W. H.; Roh, J. W.; Ryu, B.; Chang, H. J.; Kim, H. S.; Lee, S.; Seo, W. S.; Ahn, K. Enhancing Thermoelectric Performances of Bismuth Antimony Telluride via Synergistic Combination of Multi-
(66) Ghahremaninezhad, A.; Dixon, D. G.; Asselin, E. Electrochemical and XPS Analysis of Chalcopyrite (CuFeS₂) Dissolution in Sulfuric Acid Solution. *Electrochim. Acta* 2013, 87, 97−112.

(67) Li, Y.; Zhang, T.; Qin, Y.; Day, T.; Jeffrey Snyder, G.; Shi, X.; Chen, L. Thermoelectric Transport Properties of Diamond-like Cu₄Fe₃S₉ Tetrahedral Compounds. *J. Appl. Phys.* 2014, 116, 203705.

(68) Murr, L. E.; Lerner, S. L. Transmission Electron Microscopic Study of Defect Structure in Natural Chalcopyrite (CuFeS₂). *J. Mater. Sci.* 1977, 12, 1349−1354.

(69) Callaway, J. Model for Lattice Thermal Conductivity at Low Temperatures. *Phys. Rev.* 1959, 113, 1046−1051.

(70) Callaway, J.; von Bayer, H. C. Effect of Point Imperfections on Lattice Thermal Conductivity. *Phys. Rev.* 1960, 120, 1149−1154.

(71) Slack, G. A. Effect of Isotopes on Low-Temperature Thermal Conductivity. *Phys. Rev.* 1957, 105, 829.

(72) Abeles, B. Lattice Thermal Conductivity of Disordered Semiconductor Alloys at High Temperatures. *Phys. Rev.* 1963, 131, 1906−1911.

(73) Hashikuni, K.; Suekuni, K.; Watanabe, K.; Bouyrie, Y.; Ohta, M.; Ohtaki, M.; Takabatake, T. Carrier Concentration Tuning in Thermoelectric Thiospinel Cu₂CoTi₃S₈ by Oxidative Extraction of Copper. *J. Solid State Chem.* 2018, 259, 5−10.

(74) Zhang, D.; Zhang, B.; Zhou, Z.; Peng, K.; Wu, H.; Wang, H.; Wang, G.; Han, G.; Wang, G.; Zhou, X.; Lu, X. Ultralow Lattice Thermal Conductivity of Cubic CuFeS₂ Induced by Atomic Disorder. *Chem. Mater.* 2021, 33, 9795−9802.

(75) Ge, B.; Lee, H.; Zhou, C.; Lu, W.; Hu, J.; Yang, J.; Cho, S.-P.; Qiao, G.; Shi, Z.; Chung, I. Exceptionally Low Thermal Conductivity Realized in the Chalcopyrite CuFeS₂ via Atomic-Level Lattice Engineering. *Nano Energy* 2022, 94, 106941.

(76) Guilmeau, E.; Barbier, T.; Maignan, A.; Chateigner, D. Thermoelectric Anisotropy and Texture of Intercalated TiS₂. *Appl. Phys. Lett.* 2017, 111, 133903.

(77) Rathore, E.; Juneja, R.; Culver, S. P.; Minafra, N.; Singh, A. K.; Zeier, W. G.; Biswas, K. Origin of Ultralow Thermal Conductivity in n-Type Cubic Bulk AgBiS₂: Soft Ag Vibrations and Local Structural Distortion Induced by the Bi 6s² Lone Pair. *Chem. Mater.* 2019, 31, 2106−2113.

(78) Chmielowski, R.; Pérez, D.; Bera, C.; Opahle, I.; Xie, W.; Jacob, S.; Capet, F.; Roussel, P.; Weidenkaff, A.; Madsen, G. K. H.; Denieler, G. Theoretical and Experimental Investigations of the Thermoelectric Properties of Bi₃S₆. *J. Appl. Phys.* 2015, 117, 125103.

(79) Wang, L.; Ying, P.; Deng, Y.; Zhou, H.; Du, Z.; Cui, J. Site Occupations of Zn in AgInSe₂-Based Chalcopyrites Responsible for Modified Structures and Significantly Improved Thermoelectric Performance. *RSC Adv.* 2014, 4, 33897−33904.

(80) Ohta, M.; Chung, D. Y.; Kunii, M.; Kanatzidis, M. G. Low Lattice Thermal Conductivity in Pb₇Bi₈Se₁₄, Pb₇Bi₅S₂₀ and PbBi₃S₇: Promising Thermoelectric Materials in the Cannizzarite, Lillianite, and Galenobismuthite Homologous Series. *J. Mater. Chem. A* 2014, 2, 20048−20058.

(81) Song, Q.; Qin, P.; Zhao, K.; Deng, T.; Shi, X.; Chen, L. Crystal Structure and Thermoelectric Properties of Cu₃Fe₃MnSnSe₄: Diamond-like Chalcogenides. *ACS Appl. Energy Mater.* 2020, 3, 2137−2146.