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Origin of a simultaneous suppression of thermal conductivity and increase of electrical conductivity and Seebeck coefficient in disordered cubic $\text{Cu}_2\text{ZnSnS}_4$

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Abstract

The parameters governing the thermoelectric efficiency of a material, Seebeck coefficient, electrical and thermal conductivities, are correlated and their reciprocal interdependence typically prevents a simultaneous optimisation. Here, we present the case of disordered cubic kesterite $\text{Cu}_2\text{ZnSnS}_4$, a phase stabilized by structural disorder at low temperature. With respect to the ordered form, the introduction of disorder improves the three thermoelectric parameters at the same time. The origin of this peculiar behaviour lies in the localization of some Sn lone pair electrons, leading to “rattling” Sn ions. On one hand, these rattlers remarkably suppress thermal conductivity, dissipating lattice energy via optical phonons located below 1.5 THz; on the other, they form electron-deficient Sn-S bonds leading to a p-type doping-like effect and highly localized acceptor levels, simultaneously enhancing electrical conductivity and Seebeck coefficient. This phenomenon leads to a 3x reduced thermal conductivity and doubling of both electrical conductivity and Seebeck coefficient, resulting in a more than 20x increase in figure-of-merit, although still moderate in absolute terms.

I. INTRODUCTION

Thermoelectric (TE) materials, with the possibility of converting heat gradients into electricity, can substantially contribute to the global challenge for a reduced and more sustainable energy demand. But efficient TE energy harvesting and waste heat recovery require improved material performance. This is usually expressed by the thermoelectric figure of merit, $zT = \sigma S^2 T / k$, which combines three fundamental but conflicting characteristics: electrical conductivity (σ), Seebeck coefficient (S), and thermal conductivity (k), while T is the absolute temperature. TE research has recently led to a thriving of methods to improve zT : nanostructuring [1–3] reduces k_L (lattice component of k) without excessively penalizing electrical transport; chemical doping improves carrier concentration and conduction, though often to the expense of Seebeck coefficient; crystal and electronic structure engineering [4–8] mainly enhance the Seebeck coefficient. Many efforts were directed to promoting a phonon-glass electron-crystal behaviour, which aims at increasing the electrical and suppressing the thermal conductivity [9–11]. Nevertheless, the gain in conductivity, if

connected with an increased density of charge carriers, typically leads to a downturn of Seebeck coefficient. All in all, due to the conflicting interdependence of TE parameters, it has proved hard to improve σ , S , and to reduce k , simultaneously [12].

In this work, we present a physical mechanism capable of optimizing all three thermoelectric parameters at the same time. This is due to the introduction of structural disorder in the quaternary chalcogenide kesterite ($\text{Cu}_2\text{ZnSnS}_4$, CZTS), an earth-abundant, non-toxic, and low-cost material originally proposed for thin film photovoltaics [13,14]. In the attempt to generalize the concepts presented here, we compare its completely ordered (tetragonal) polymorph with its completely disordered (cubic) one. The low-temperature disordered cubic is a recently discovered phase [15,16] stabilized with high-energy mechanical alloying. The improvement of all the TE parameters obtained with the introduction of disorder has prompted us to investigate the underlying physical phenomenon. Even if the performance is moderate compared to actual commercial materials for end TE devices, this mechanism leads to the highest reported zT for undoped CZTS. Understanding the origin of this all-round improving phenomenon could open the path to applying similar strategies on other materials to potentially enhance all their TE properties.

II. METHODS

A. Synthesis

Nanocrystalline kesterite powder was produced via reactive mechanical alloying starting from stoichiometric precursors, as described elsewhere [7]. As-milled powder was cold pressed into 16 mm-diameter disks (~2 mm thickness) applying a load of 5 tons for 3 minutes. The disordered cubic sample was obtained after sintering in a dynamic atmosphere of Ar for 60 min at 160°C (ramp 20 K/min) followed by 20 min at 300°C (ramp 20 K/min up to 260°C and 10 K/min from 260°C to 300°C) and natural cooling down to room temperature. The ordered tetragonal sample was obtained with an identical procedure with temperatures being 300°C for the 60 min step (ramp 20 K/min) and 560°C for the 20 min step (ramp 20 K/min up to 520°C and 10 K/min from 520°C to 560°C).

B. Structural characterization (XRD, TEM) and thermal analyses

XRD patterns were collected on powder or disk samples at room temperature with $\text{Cu K}\alpha$ radiation generated at 40KV and 30 mA (Rigaku PMG diffractometer, graphite bent-crystal monochromator in the diffracted beam). Rietveld refinement of XRD data was performed with TOPAS 7 [17], with support of the macros based on Whole Powder Pattern Modelling [18] for crystallite size analysis [19]. Transmission Electron Microscopy (TEM) imaging, as well as Selected Area Electron Diffraction (SAED) and high-magnification Energy Dispersive X-ray analysis (EDX) have been performed with a HR-S/TEM instrument (ThermoFischer TALOS 200 s). XRD patterns in temperature were collected using a Panalytical X'Pert pro system equipped with an X'Celerator detector, over the range RT to 550°C, using a HTK1200N facility. The measurements were performed in He atmosphere with a gas pressure of 400 Torr at RT. For each temperature, the patterns were collected performing 10 repetitions on the same angular range (total time per temperature ~60 min with 3 min of equilibration time). Differential Scanning Calorimetry (DSC) was performed with an instrument DSC92 SETARAM on an as-milled powder sample sealed in a crucible under an atmosphere of Ar with 5% H₂ to hinder oxidation processes. Temperature scan from RT to 600°C with a ramp of 10 K/min.

C. Thermoelectric characterization

Absolute Seebeck coefficient was measured in 4-contact configuration and with Pt standard with a LINSEIS LSR-3 machine. Measurements have been performed under a static He atmosphere in the range RT-480K with heating rate of 10 K/min and a temperature gradient across the sample of approximately 10 K. Three measurement per temperature have been performed to calculate the mean and standard deviation, used in the plots as value and error bar. In addition, a declared instrumental accuracy of 7% should be considered.

Measurements over temperature have been repeated several times and on multiple samples to verify reproducibility. Further discussion on the repeatability of measurements in SN 10.

Carrier density and mobility have been measured with an MMR K-20 and an H-50 measurement systems. Results are obtained by a combined measurement of Hall effect and resistivity as a function of temperature. Resistivity is determined by the Van Der Pauw method using squared shaped samples with side 8 mm and thickness below 1 mm, providing an optimal geometrical ratio between surface and thickness. Hall effect measurements have been performed with a permanent-magnet field of 6270 ± 10 G. The currents for testing have been set to values below 10 mA to prevent any thermal change in the samples. All the measurements are performed in vacuum ($4\div 8$ mTorr) in the temperature range 300–450 K. A declared instrumental accuracy of 5% and 10% should be considered for Van der Pauw and hall measurements, respectively. Measurements have been repeated several times to verify reproducibility of results. Further discussion on the repeatability of measurements in SN 10 [20].

Thermal conductivity was calculated as $k = \alpha\rho Cp$, with α thermal diffusivity, ρ density and Cp specific heat. Thermal diffusivity measurements were performed with a laserflash Linseis LFA 500 under vacuum atmosphere on disk samples with a thickness of ~ 1.5 mm. A declared instrumental accuracy of 3% should be considered for thermal diffusivity. Density ρ was geometrically measured on disk samples and used for thermal conductivity calculations. The measurement with Archimede's method was also performed. Density results are discussed in SN 5 [20]. Specific heat measurements have been performed with a Thermal Analysis Q100 DSC instrument in modulated mode (MDSC). A modulation with period 120 s and semi-amplitude 0.5K was applied to isothermal measurements and used to extract the specific heat as a function of temperature. The samples were sealed in Ar atmosphere during the measurement. Discussion on the repeatability of measurements in SN 10 [20].

D. Ultraviolet-visible spectroscopy

The optical properties were investigated using a Perkin-Elmer spectrophotometer model LAMBDA 750, equipped with a 150 mm integrating sphere. Powder samples (ground disk samples) were dispersed in ethanol and sonicated for 1 h. The optical absorption spectra were collected in the wavelength range of 300–1000 nm with a step size of 0.5 nm. The Tauc plot was used to extrapolate the bandgap value, operating a linear fit in the range 2.2-2.8 eV.

E. NIS measurements

Nuclear Inelastic Scattering (NIS) measurements were performed at the Dynamics beamline P01 at PETRAIII (DESY, Hamburg) using ^{119}Sn nuclear resonance. A high-resolution monochromator provided an energy bandwidth of 1.4 meV at 23.9 keV. The measurements were carried out on samples with natural enrichment of ^{119}Sn (8.6%), inserted into a closed cycle He cryostat and kept at 43K. The low temperature was chosen to suppress multi-phonon contributions in the inelastic scattering signal, which make difficult the extraction of the one-phonon scattering term and projected vibrational density of states. The nuclear resonance signal was separated in time from electronic X-ray fluorescence and measured using a Si avalanche photodiode detector.

F. DFT and DFPT calculations

The *ab initio* electronic structure calculations have been performed using the plane wave basis set implemented in the Vienna *ab initio* simulation package (VASP) [21,22]. The electron-exchange correlation functional was approximated using the Perdew–Burke–Ernzerhof (PBE) [23] form of the generalized gradient approximation (GGA). All calculations were performed with an energy cutoff of 300 eV. The tetragonal ordered and cubic disordered structures were modelled with 16 and 64 atom supercells, respectively. For the latter, to try to better simulate disorder in the real case, three different configurations were modelled

randomly assigning the cation site to Cu, Zn or Sn, respecting the overall stoichiometry (2:1:1). Results for the additional configurations, both of DFT and DFPT, are reported in SN 7 and 11 [20]. The geometry was optimized with an $8 \times 8 \times 8$ and $4 \times 4 \times 4$ Monkhorst Pack (MP) k-mesh, respectively for the ordered and disordered cells, centered at the Γ point, with Gaussian charge smearing in the order of 0.01 eV. The electronic degrees of freedom were relaxed until the change in the total free energy and energy eigenvalues were both smaller than 10^{-6} eV. The bands were calculated along a high-symmetry path in the irreducible Brillouin zone obtained using the SeeK-path [24] tool, while the electronic density of states (DOS) was obtained using a dense $12 \times 12 \times 12$ MP k-mesh for the 16-atom supercell and an $8 \times 8 \times 8$ MP k-mesh for the 64-atom supercells. The ELF and charge densities are visualized using the VESTA [25] visualization tool.

The vibrational properties are obtained using the dynamical matrix calculated using density functional perturbation theory (DFPT). The PhonoPy code [26] is then used to diagonalize the dynamical matrix to calculate the inter-atomic force constants, from which the phonon dispersion relations and vibrational density of states are calculated.

III. RESULTS AND DISCUSSION

A. Structural: the low-temperature disordered cubic kesterite phase

The stable crystallographic structure of kesterite is the ordered tetragonal (space group $I-4$, Figure 1a). The structural complexity of this quaternary chalcogenide frequently causes the occurrence of several types of structural defects. The most common one is the Cu_{Zn} substitutional, which is believed to be the cause of the p-type nature of kesterite and possesses the lowest formation energy among the possible defects [27–29]. Indeed, above 533 K the ordered tetragonal polymorph evolves into a disordered tetragonal (space group $I-42m$, Figure 1b) through the reversible order-disorder phase transition [7,30–32], involving a mixed and random occupation of Cu and Zn cations in the $4d$ Wyckoff positions (whereas in the ordered the $2c$ site is occupied by Cu and the $2d$ by Zn) [7,30].

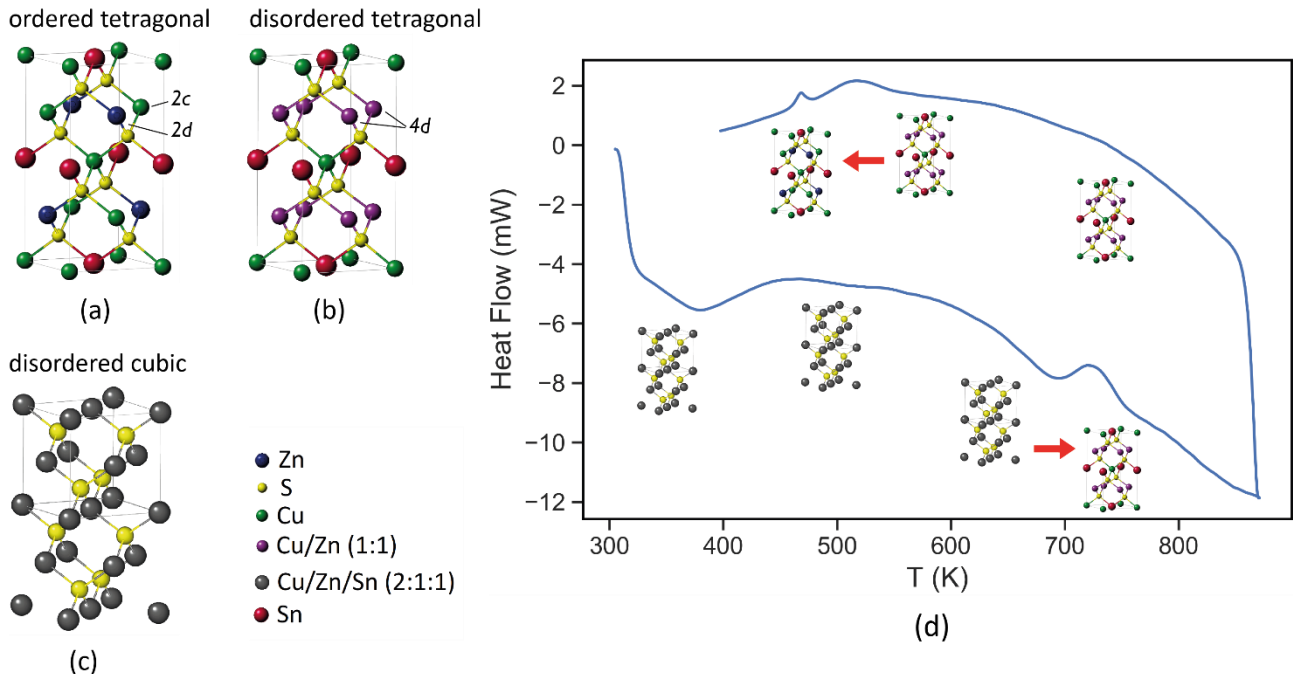


FIG 1. The different crystal structures of kesterite: a) tetragonal ordered $I-4$, for the sample sintered at 560°C below the order-disorder transition temperature of 533 K, b) tetragonal disordered $I-42m$, above the order-disorder transition, and c) cubic $F-43m$ (ZnS -like), found for the ball-milled powder and for samples sintered up to 300°C . In panel d) a DSC measurement for an as-milled powder sample can be seen, showing the phase evolutions in temperature. On heating, kesterite is cubic $F-43m$ up to around 650 K, where it transitions to tetragonal disordered $I-42m$, the polymorph that is stable at that temperature. On cooling, around 533 K disordered tetragonal kesterite transitions to ordered tetragonal $I-4$, as the transformation is reversible.

When obtained with mechanical alloying in high-energy conditions starting from elemental precursors, the level of structural disorder is so high that the crystal structure is better described by a cubic symmetry. We put forward that atoms arrange in a cubic $F-43m$ structure similar to that of sphalerite ZnS, where the Zn site is occupied by all the kesterite cations (Figure 1c). X-Ray Diffraction (XRD) and Selected Area Electron Diffraction (SAED) on the as-milled powder both support this statement, as the patterns show reflections of a cubic structure only (Figure 2a). After cold pressing the powder into a disk sample and annealing at 300°C, the XRD-peak and SAED-ring positions do not change (Figure 2b), suggesting that the cubic crystal structure is preserved. Tetragonal kesterite forms instead after a heat treatment at 560°C, as pointed out by the superstructure reflections visible in the XRD and SAED patterns of Figure 2c. Allegedly the cubic phase, stable at low temperature, transitions to the tetragonal on heating, when the structural defects reduce owing to the

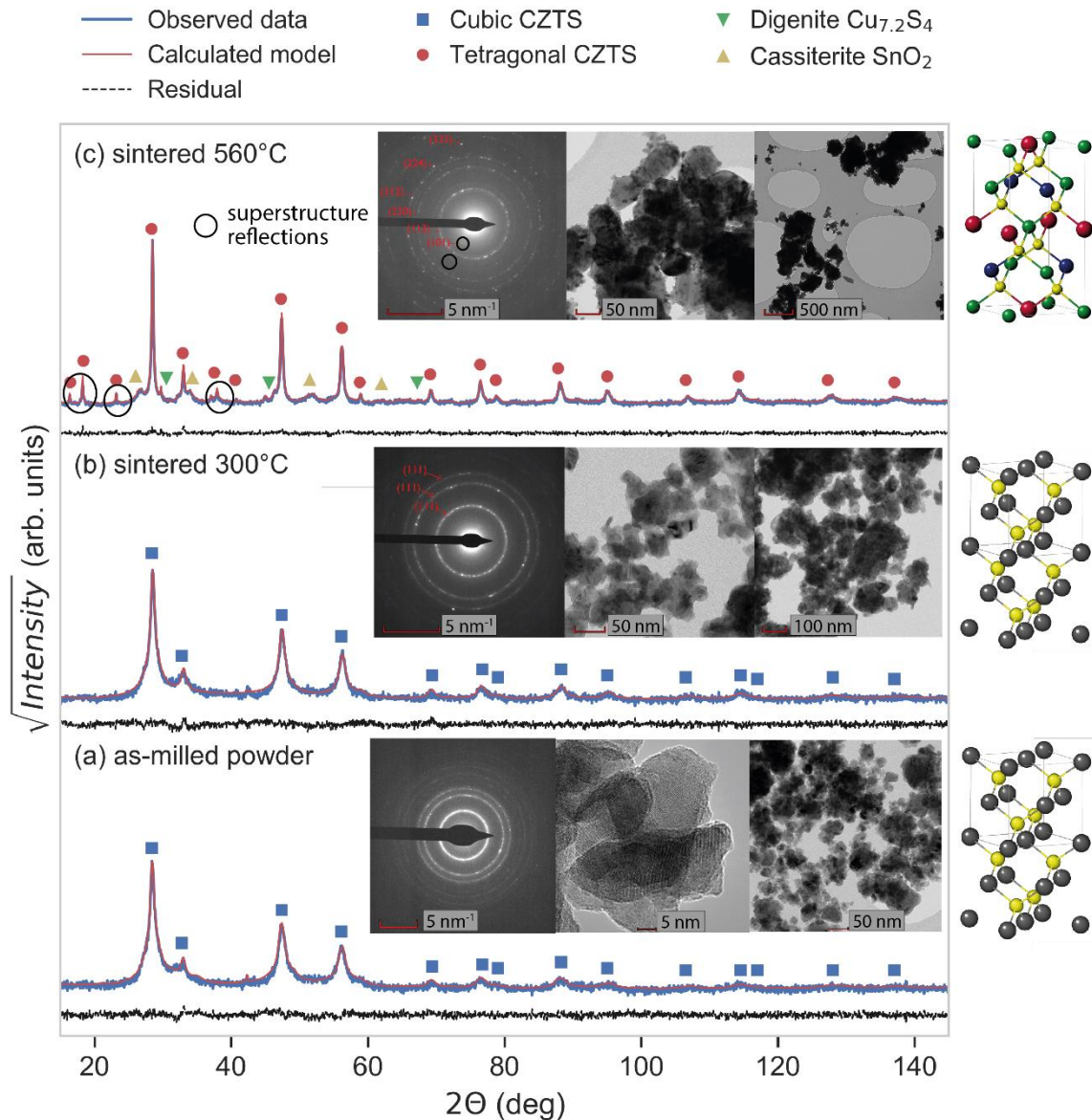


FIG 2. XRD patterns with phase identification, as well as TEM imaging and SAED, with plane indexing, for a) the as-milled powder, b) sample sintered at 300°C, both with a disordered cubic kesterite crystal structure, and c) sample sintered at 560°C, presenting a tetragonal structure with distinctive superstructure reflections both in the XRD and SAED patterns. The result of the Rietveld refinement modelling made with TOPAS 7 is visible as well as experimental data (blue points), modelled data (solid red line) and difference (solid black line). Part of panel c is reproduced with permission from ref 6. Copyright 2019 MDPI.

activation of cation diffusion. From Differential Scanning Calorimetry (DSC) thermal analyses on as-milled powder (Figure 1d), we locate the cubic-to-tetragonal phase transition close to 650 K. The same critical temperature is detected with XRD measurements in temperature (see Supplemental Note SN 1 [20]). At this

temperature and above, kesterite is known to be stable in the disordered tetragonal form, so it is understood that the Sn and S lattice participates the most in this structural rearrangement. Due to the reversibility of the order-disorder transition [7], the tetragonal ordered form appears at around 533 K during the slow cooling down to ambient temperature, when the XRD pattern reveals the tetragonal nature of CZTS.

By cross-comparing Rietveld refinements of XRD data, Transmission Electron Microscopy (TEM) imaging and Energy Dispersive X-ray analysis (EDX) data (see SN 2 [20]), it is possible to assess that sintering at 560°C develops tetragonal kesterite as well as minor fractions of secondary phases, mainly consisting in SnO₂ and Cu_{7.2}S₄ (Figure 2c, see also SN 3 [20]). Both for the as-milled powder and the sample sintered at 300°C (Figures 2a and 2b), instead, an almost pure CZTS phase is found with significantly reduced levels of oxidation and secondary phases. All the samples display nanometric domains (quantitative estimations in SN 3 [20]), a feature deemed beneficial for thermoelectricity as it selectively suppresses thermal over electrical conductivity, due to different scattering from the grain boundary region. XRD powder pattern refinements reveal that in the cubic sample the Debye-Waller coefficients for the cation site are comparatively higher, refined as 1.7(3) Å² with respect to an average of 0.75(7) Å² for the tetragonal sample. Large values of these coefficients (proportional to the atomic mean square displacement (MSD) in the crystal structure) can accommodate an effect of high cation disorder, as well as of softer bonds with a wider spectrum of vibrational modes.

B. Suppressed thermal conduction along with a gain in electrical conductivity and thermopower

The disordered cubic sample shows a remarkable reduction in thermal conductivity (Figure 3a), with room temperature values less than one third of the ordered tetragonal counterpart. It also displays an almost flat curve, a feature that points to temperature-independent mechanisms. Experimental values for the cubic sample are in the order of 0.2 W/(mK) for temperatures between 300 K - 650 K, significantly below the ultra-low limit of high-performance TE materials, typically set as 0.5 W/(mK) [1]. Both the samples present comparable values of density (see SN 4 [20]), so we exclude density-related origins. The smaller domain size of the cubic sample plays a role in this suppression through an increased phonon scattering from the grain boundary area. On top of this, we can reasonably assert that part of the suppression achieved with the cubic is due to the underlying structural disorder. Indeed, when measured in a higher temperature range (Figure 3a, solid orange curve) the cubic sample displays a sudden increase in thermal conductivity around 650 K (see SN 5 [20]), coinciding with the cubic-to-tetragonal transition observed by thermal analyses (Figure 1d) and XRD measurements in temperature (SN 1 [20]).

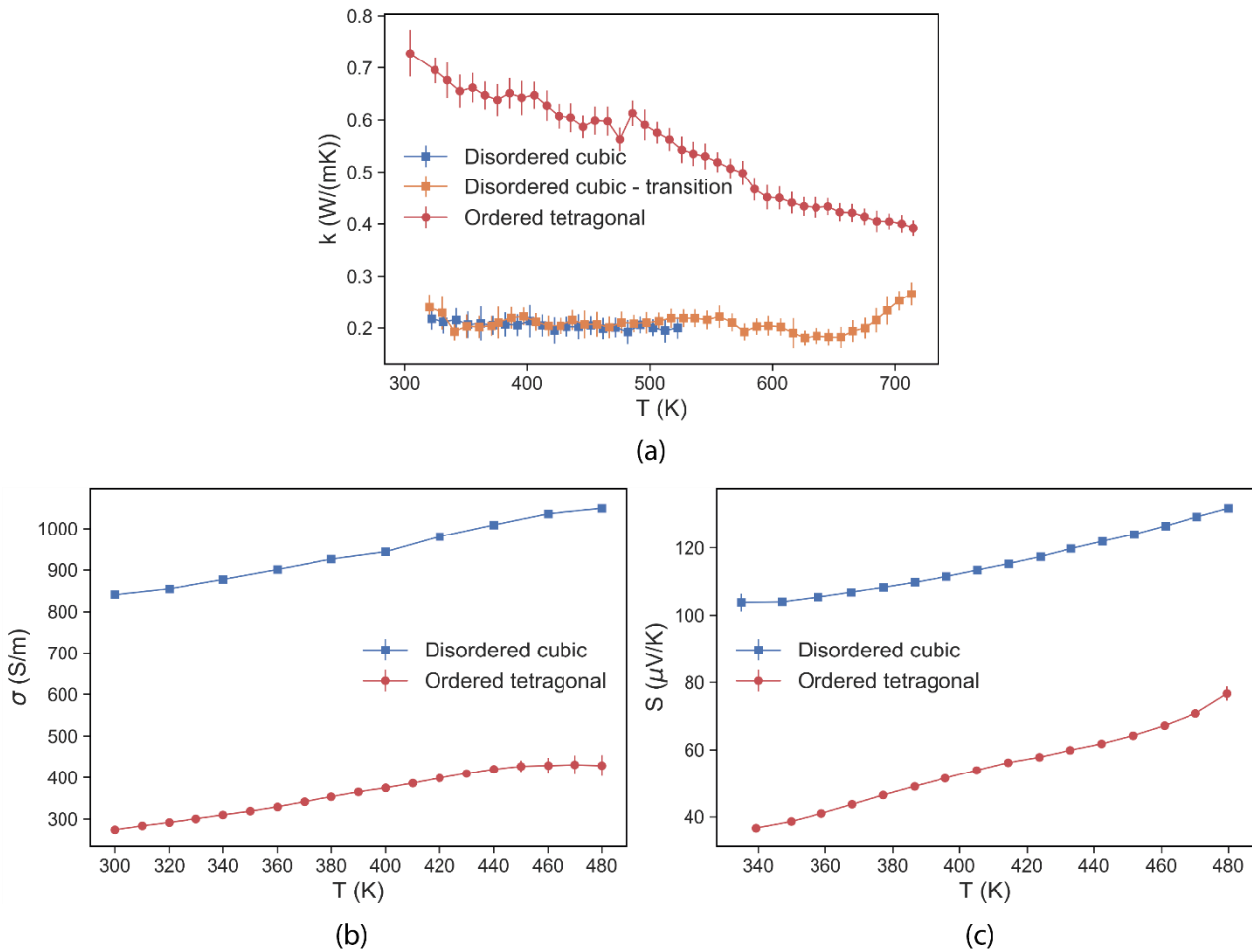


FIG 3. Thermal conductivity (a), electrical conductivity (b) and absolute Seebeck coefficient (c) as a function of temperature measured for a disordered cubic and an ordered tetragonal CZTS sample.

In order to confirm and understand the structural origins of the reduced thermal conductivity in the cubic polymorph, the vibrational properties were calculated *ab initio* from density functional perturbation theory (DFPT). By plotting the vibrational density of states (VDOS) as a function of frequency, we observe more available vibrational modes in the high-frequency region (around 5.5-7 THz) of cubic CZTS (Figure 4d), compared to tetragonal (Figure 4c), with a significantly reduced gap between higher and lower frequency modes. These are optical modes and therefore are less effective in carrying heat. They can instead promote Umklapp or diffusive phonon-phonon scattering, leading to a lower thermal conductivity in general. Nevertheless, Umklapp processes increase with temperature, while the low values of thermal conductivity

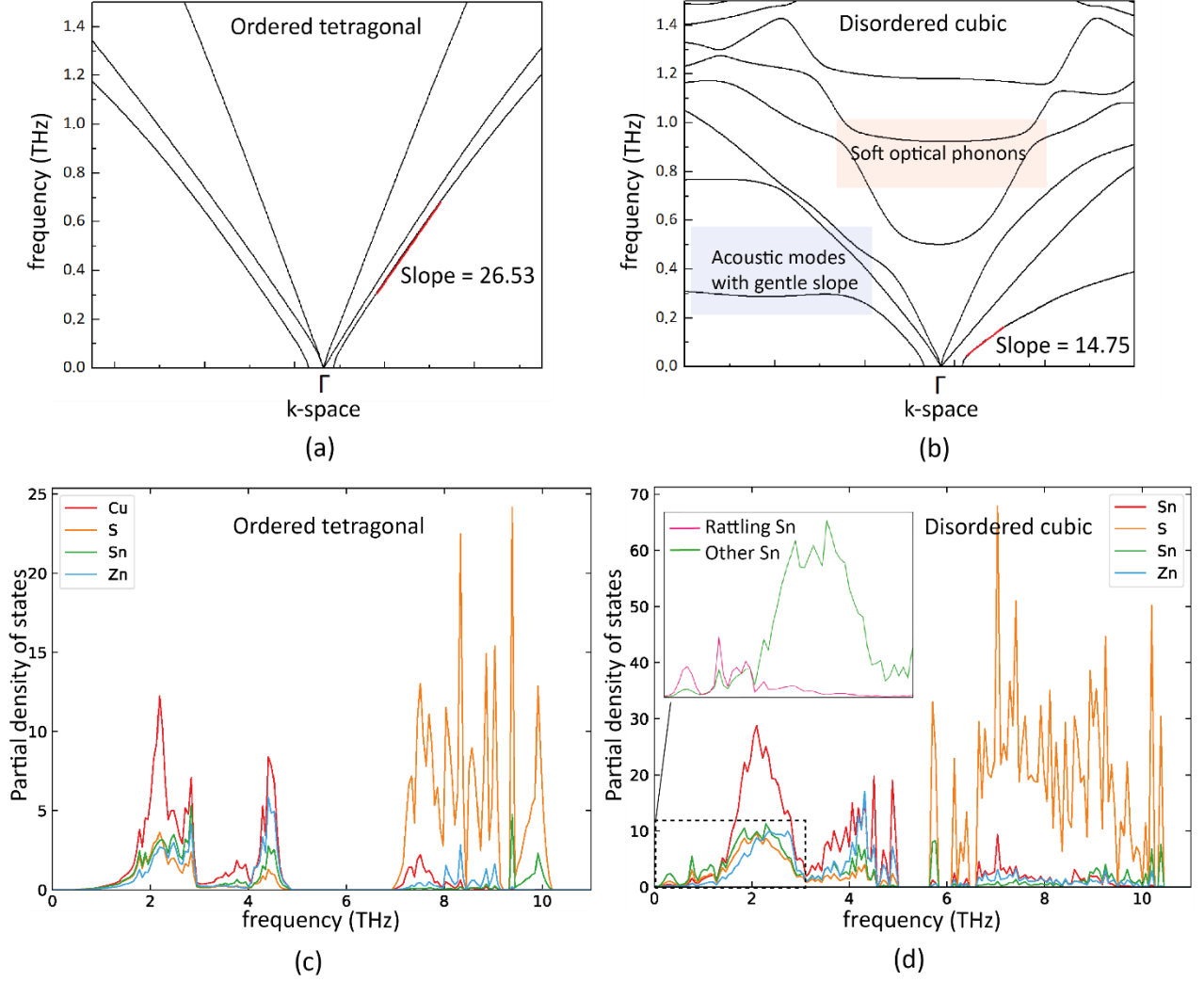


FIG 4. Phonon dispersion relations for the ordered tetragonal (a) and a disordered cubic (b) supercell. Vibrational density of states with contributions from individual atoms for an ordered tetragonal (c) and a disordered cubic (d). The inset in panel d, commented later on in the text, represents the projected VDOS of two different types of Sn: a “rattling” one (Sn7) and all the others.

for cubic CZTS remain almost constant over a wide range in temperature. This suggests an additional, temperature-independent contribution to the low thermal conductivity observed in cubic CZTS. Comparing the phonon dispersion relation in the two polymorphs (Figure 4a and 4b), it is evident that the long-wavelength acoustic modes in cubic CZTS have a lower slope than the tetragonal polymorph. This indicates a lower group velocity for phonon wave packets with consequent lowering of the thermal conductivity. More significantly, the acoustic modes in cubic CZTS have a lower frequency cut-off (< 1.1 THz) [33], with several optical phonon modes in the low frequency (long wavelength) region below 1.5 THz (~ 50 cm^{-1}). Thermal energy is then dissipated through the activation of these low-frequency optical modes which, by virtue of representing out-of-phase vibrations of ions, do not participate in the conduction of heat. This explanation is supported by recent reports in the literature [34,35] showing that these soft optical phonon modes are the primary mechanism for reduced thermal conductivity in certain ternary and quaternary chalcogenides.

In terms of electronic properties, the disordered cubic sample exhibits an improvement in both electrical conductivity σ and absolute Seebeck coefficient S (also addressed as thermopower), visible in Figure 3b-3c, a coupling that is considered quite unusual in TE materials [36]. The electronic density of states (DOS, Figure 5d), from *ab initio* calculations, reveals the presence of sharp valence-type mid-gap levels at and above the Fermi energy. These are thought to arise from crystal disorder, as they are not present in the DOS of the tetragonal structure. Similar trap-states have been reported by Walsh et. Al [37] in tetragonal kesterite with

introduced defects. These levels can act as acceptor states within the gap region, generating holes in the valence band, without a corresponding production of conduction electrons. Experimental observations do indeed show a considerably higher p-type carrier concentration for the cubic sample, (in the order of 10^{19} cm^{-3} compared to $1\text{-}2 \cdot 10^{17} \text{ cm}^{-3}$ of the tetragonal sample, Figure 5c), thus explaining the higher electrical conductivity. This hypothesis is further supported by absorption spectroscopy measurements (see SN 6 [20]), which do not show significant differences between the bandgap values of the two samples, suggesting that the improvement in carrier concentration is not connected with a reduction of the gap. Indeed, this is measured as 1.56 eV for the ordered tetragonal polymorph, in accordance with literature reports [38–40], and as 1.53 eV for the disordered cubic polymorph. The bandgaps observed in the DFT band structures (Figure 5a-5b) do not match with the experimental results. This is expected as the generalized gradient approximation (GGA) of the exchange-correlation functional is known to strongly underestimate the band gap [32,41]. Although the DFT representation in Figure 5b can be somewhat misleading, it is to be remembered that above the acceptor states the actual bandgap is not narrow, measured in the range of 1.53 eV. We believe this is the reason why the carrier density, although increased, is not as high as typical narrow bandgap semiconductors.

Nevertheless, a higher carrier concentration is expected to have a negative impact on thermopower, as expressed by Mott's equation (Equation 1) [42], but the opposite is observed for cubic CZTS.

$$S \approx \frac{\pi^2}{3} \left(\frac{k_B^2 T}{q} \right) \left[\frac{1}{n} \frac{\partial [f(E) \text{DOS}(E)]}{\partial E} + \frac{1}{\mu} \frac{\partial \mu}{\partial E} \right]_{E=E_F} *$$

It is to be noticed that the electronic bands corresponding to these mid-gap states are rather flat, implying a high effective mass of carriers. The effect on the DOS is an increased steepness at the top of the valence band

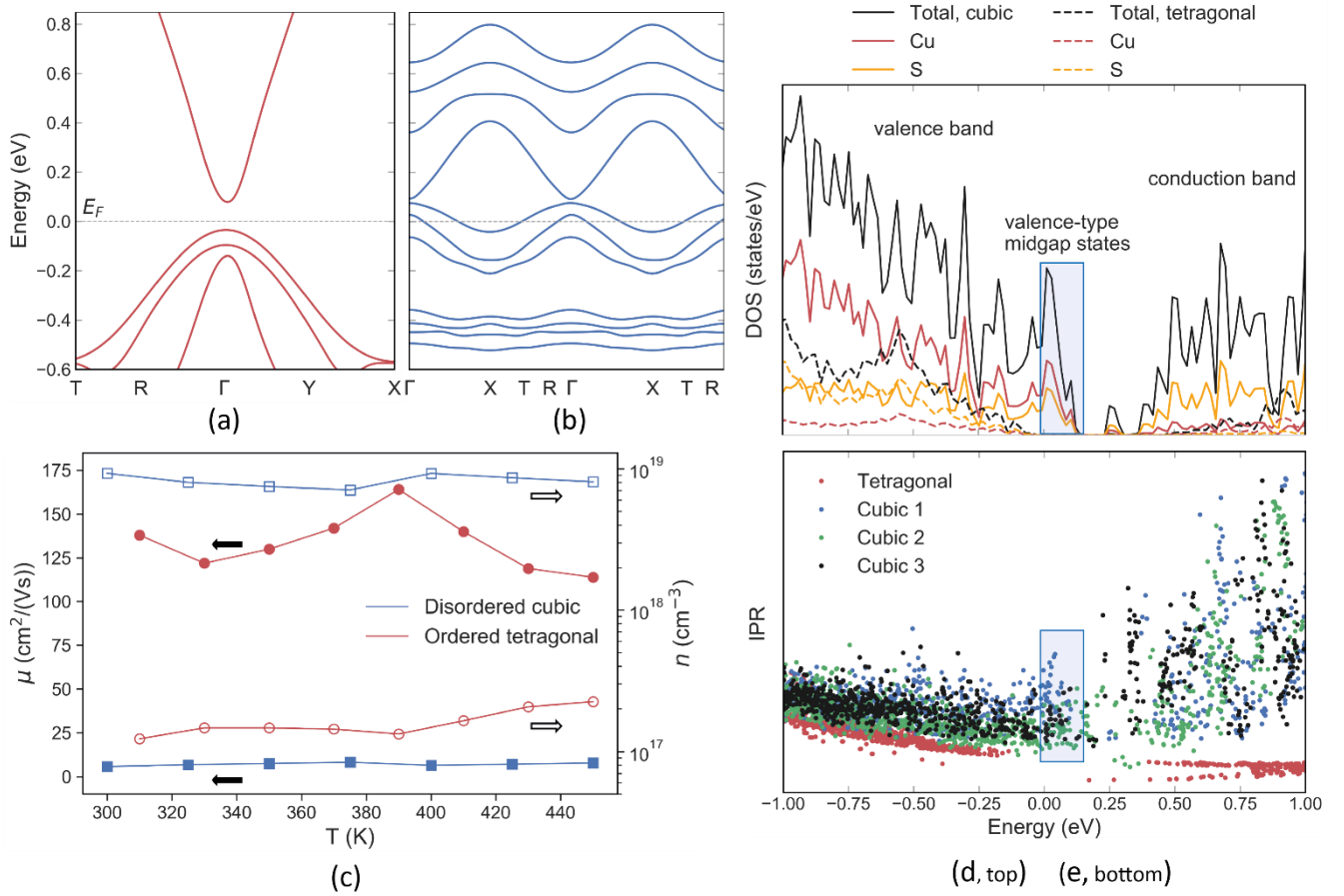


FIG 5. Electronic band structures for the ordered tetragonal $I-4$ (a) and a disordered cubic $F-43m$ (b) kesterite supercell. (c) Experimental measurements of carrier concentration n and mobility μ for the two samples. Electronic density of states DOS (d) calculated for a disordered cubic and an ordered tetragonal supercell, with partial density of states showing the individual contributions of Cu and S atoms. In panel (e) is the inverse participation ratio IPR , calculated for the ordered tetragonal supercell and three different configurations of disordered cubic supercells. Panels d) and e), where the mid-gap state region is highlighted in blue, show highly localized valence-type states in the bandgap, deemed responsible for the improved electronic behaviour of disordered cubic kesterite.

and an enhanced asymmetry with respect to the conduction band. All these features are in accordance with the reduced carrier mobility, experimentally measured to be more than one order of magnitude below tetragonal CZTS (Figure 5c) and with the enhancement of Seebeck coefficient (see Mott's equation 1). In principle, electrical conductivity should be degraded by this low mobility, so it is quite surprising to find such a decoupling of Seebeck coefficient and electrical conductivity trends. A similar occurrence has been occasionally reported for systems where the grain boundary generated a potential barrier for carriers promoting energy filtering effects [43,44]. We do not exclude that phenomena of this kind could contribute to the decoupling, although we do not see particular reasons why the grain boundary region of the cubic and tetragonal sample should differ significantly. Alternatively, behaviours of this kind often relate to the mechanism of band degeneracy (tendency of electronic bands to converge within an energy range of $\sim 2k_B T$), that can selectively promote the thermopower without penalizing carrier conduction. [4,6–8,36,45] However, band convergence does not seem to play a significant role in this case, as little difference is observed in the spacing of bands between the two structures (Figure 5a-5b), with the top three bands being separated by more than $2 k_B T$. We therefore put forward that the mid-gap states exert a strong influence in decoupling electrical conductivity and Seebeck coefficient. In fact, the addition of these acceptor states increases the carrier density (and conductivity). At the same time, these correspond to flatter bands carrying heavy holes and thus improving the Seebeck coefficient. In other words, these states are seen to be highly localized in energy as also confirmed by the calculated inverse participation ratio IPR , see Figure 5e). This leads to a higher localization of charge carriers (or, alternatively, slowly propagating carriers, because of the

low dispersion of the band), a feature known for improving thermopower. [5]

The calculated power factor PF (Figure 6a) is unsurprisingly higher for the disordered cubic sample, of almost one order of magnitude at 480K. Combined with the added benefit of a highly suppressed thermal conductivity, this leads to a remarkable improvement in the figure of merit zT , more than twenty times larger at 480K for the disordered sample (Figure 6b). Although this value is moderate compared to materials used in highly-efficient TEs, it is the highest reported zT for an undoped CZTS.

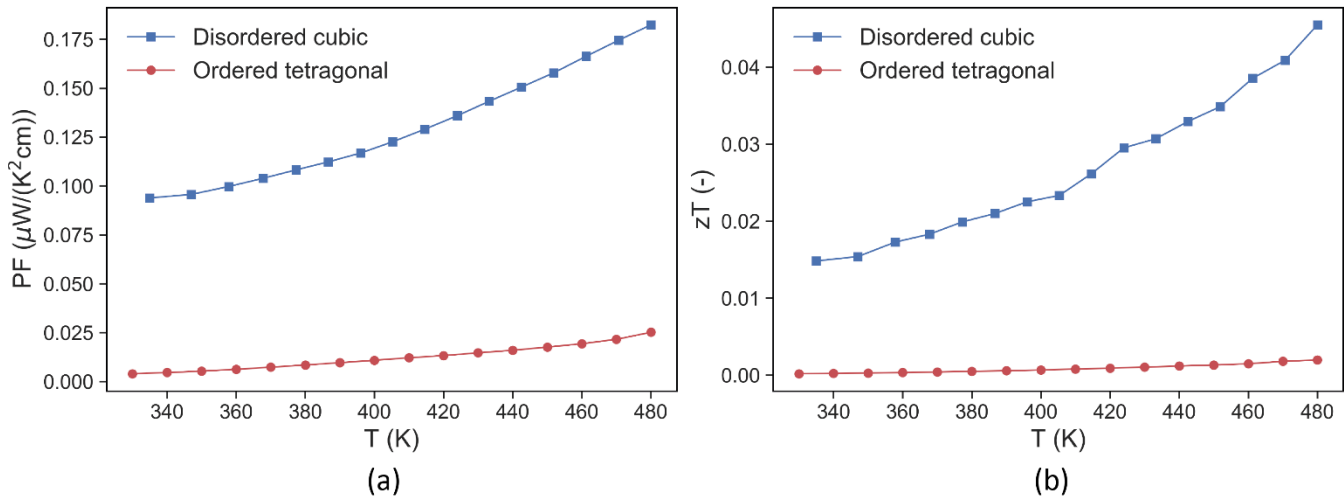


FIG 6. Power Factor PF (a) and thermoelectric figure of merit zT (b) as a function of temperature measured for a disordered cubic and an ordered tetragonal CZTS sample. A cumulative standard deviation of $\sim 3\%$ should be considered for PF , and ~ 12 for zT .

C. Nature of bonding and disorder in CZTS

The origin of this peculiar behaviour of disordered cubic CZTS, better performing in terms of both thermal and electronic properties, can ultimately be traced down to the nature of chemical bonding. To understand the charge distribution within the lattice, we calculate the electron localization function (ELF) [46], a measure of the degree of charge localization in a given volume in space (ELF cross-sections, Figure 7, other views and 3D animation of ELF isosurfaces in SN 7 and Supplementary Video SV 1 [20]), along with charge density (Figure 8, SN 8 and SV 2 [20]). These reveal that cation disorder in the cubic structure leads to different degrees of localization for the $5s^2$ lone pair, for different Sn atoms (see Sn7 and Sn4, Figure 7a). From the partial charge density of the Sn s electrons (Figure 8a and S8a), we observe that Sn in general forms tetrahedral sp^3 hybridized bonds with S in both the cubic and tetragonal polymorphs. This is in agreement with reports of the Sn-S bond being generally covalent in nature, with Sn in a +4 oxidation state [47].

However, in the case of cubic CZTS, the highly disordered crystal structure gives rise to a correspondingly inhomogeneous crystal field. This in turn leads to a strong localization of the s^2 lone pair in some Sn atoms, as seen around atom Sn7 in Figure 8a. These lone pairs form a separate nonbonding orbital, with reduced contribution to the bonding sp^3 orbitals, resulting in electron-poor bonds between Sn7 and its coordinating S atoms. From the partial charge density distribution, we attribute to these Sn atoms an approximate oxidation state of +2, in line with theoretical predictions in recent literature [47]. The presence of these atypical Sn atoms then naturally gives rise to inhomogeneity in bonding within the crystal structure. In the presence of thermal vibrations, the movement of atoms brings the lone pair in proximity to orbitals of electrons from neighbouring atoms. The induced overlap of these non-interacting electrons gives rise to a repulsive force [48], resulting in a rattling of the Sn7 type atoms within a cage formed by the coordinating S

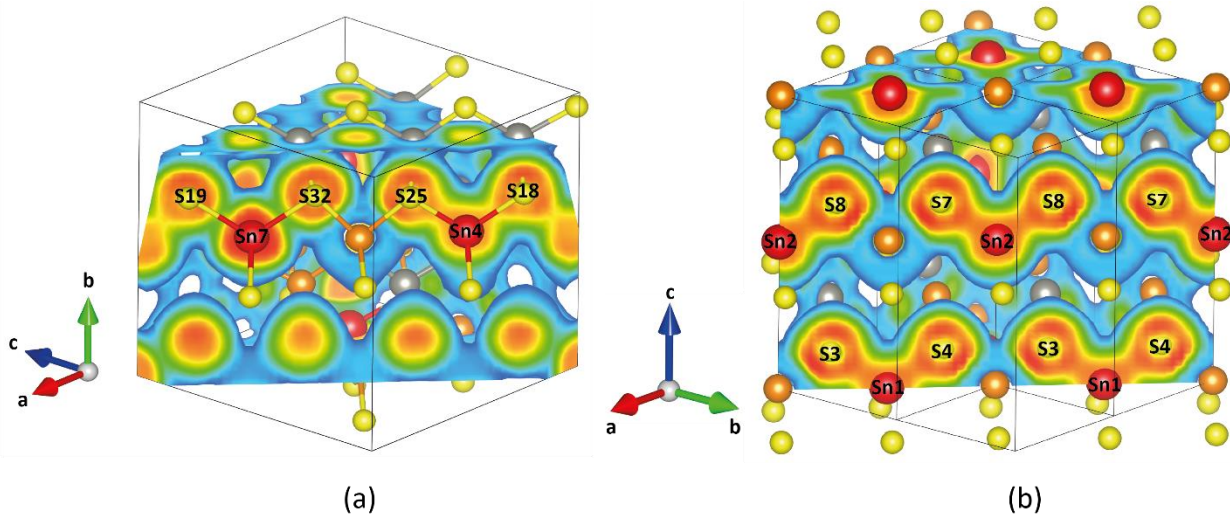


FIG 7. Electron Localization Function (ELF) for a disordered cubic (a) and an ordered tetragonal (b) kesterite supercell, where the latter, for visualization purposes, is composed of four copies of the cell used in calculations. Sections along a plane including some Sn-S bonds are shown, with colour indicating the likelihood to find an electron close to a reference electron at a given point in space. As visible, in the tetragonal cell (b) Sn atoms form all-similar bonds with sulphur atoms with a high level of electron sharing. In the cubic cell, some Sn atoms behave similarly as in the tetragonal structure (Sn4) while some others behave differently (Sn7) with a significantly higher retention of lone pairs. This is believed to be the cause of the ultra-low thermal conductivity measured for the cubic samples, through an enhancement of phonon scattering caused by the rattling of this type of Sn atoms.

atoms. The rattling mechanism, consisting in the spring-like vibration of an atomic specie that contributes in dissipating phonon transport, has long been known to be responsible for reduced lattice thermal conductivity in binary and ternary compounds [35,49] including chalcogenides [50,51]. However, the type of rattling observed here would be different from the generally reported specie-wide rattling, as just a fraction of Sn ions shows this behaviour. By looking closely at the atom-projected VDOS (Figure 4c-4d), we observe that while Cu ions generally dominate the vibrational modes in the low-frequency/long-wavelength region, it is in fact Sn which dominates in the frequency range between 1 – 1.5 THz, the region of the low-lying optical modes in the phonon dispersion. Furthermore, by calculating the VDOS projected over individual Sn ions (Figure 9a), it is clear that the rattling Sn7 ion contributes the most to the formation of the long wavelength optical vibrations.

To gain further insights into vibrational properties, Nuclear Inelastic Scattering (NIS) measurements were performed at low temperature (43K) on a disordered cubic and an ordered tetragonal sample. Experiments were carried out at the Dynamics beamline P01 at PETRAIII (DESY, Hamburg) using a Mössbauer-active isotope, ^{119}Sn , and, therefore, are representative of the vibrational behaviour of Sn. This is a particularly favourable condition to validate our DFPT calculations, showing that Sn dominates the total VDOS below 1.5 THz (see Figure 4d), where the proposed rattling mechanism manifests. The Sn projected VDOS in Figure 9b (and Figure 9b for reduced range) show characteristic features of cation disorder for the cubic sample, with a broadening of the vibrational modes, especially visible at high energy (~ 4.8 THz and ~ 11.1 THz). NIS results also point out a higher MSD (see SN 9 [20]), in agreement with XRD, showing a higher Debye-Waller coefficient for cations in the cubic phase. An even more direct indication of disorder is the softening of the acoustic modes in the cubic sample, clearly seen in the reduced VDOS (VDOS/E^2) (Figure 9d) as an enhancement of the low energy part. Disorder is typically connected with a lower sound velocity v and, indeed, the ratio of mean sound velocities (see SN 9 [20]) $v_{\text{cubic}}/v_{\text{tetragonal}} = 0.86$ is in the order of that obtained for the acoustic modes in the phonon dispersion relations (0.66, Figure 4a-b, see SN 9 [20]). But a lower sound velocity alone cannot explain the large suppression of thermal conductivity observed for the cubic sample. We put forward that the rattling Sn atoms are decisive in the reduction of thermal conductivity. Nevertheless, we expect a mild overall contribution from the weakly-bound Sn atoms in the experimental Sn

VDOS curve. Figure 9c shows the theoretical Sn projected VDOS for three configurations of disordered cubic supercells, compared with that of the ordered tetragonal. The mild peaks below 1.5 THz in the cubic Sn VDOS curves are ascribed to rattling Sn ions, their positions varying somewhat for the different configurations (see Figure 9a and SN 11 [20]). Therefore, considering the rare occurrence of rattling atoms, estimated as 8-15 % of total Sn atoms, the overall contribution of rattling is limited to a small enhancement of the experimental Sn VDOS in the energy range between 0.5 and 1.5 THz (Figure 9b). These weakly-bound atoms also contribute to the enhancement of the reduced Sn VDOS for the cubic sample (Figure 9d). We thus assert that the introduction of disorder, which we connect with an increase of the rattling phenomenon, is responsible for the marked suppression of thermal conductivity observed in the cubic polymorph with respect to the stable tetragonal CZTS.

For what concerns the effect on electronic properties, the presence of the electron-deficient Sn-S bonds leads to a transfer in charge from Cu d states close to the Fermi surface (within 0.5 eV). These electrons move in to fill the charge deficiency, as shown in Figure 8b, where the partial charge density of one of the Cu d states is localized around the rattling Sn atom. This process generates free holes in a way analogous to p-type doping, as evidenced by the increased carrier concentration. The presence of the strongly localized s^2 electrons in the rattling Sn atoms thus gives rise to the localized acceptor states above the Fermi energy, thereby explaining the observed improvement in electrical conductivity despite the lower mobility of charge carriers. Thus, by closely analysing the electronic structure of cubic CZTS we can ultimately attribute the considerable improvement in thermoelectric properties of this polymorph to the increased localization of Sn lone pairs, resulting from higher disorder and randomness compared to the tetragonal polymorph. This leads both to a suppression in thermal conduction, as well as to an enhancement of electrical conductivity without penalizing the Seebeck coefficient, which is actually increased by the strongly localized states in the DOS.

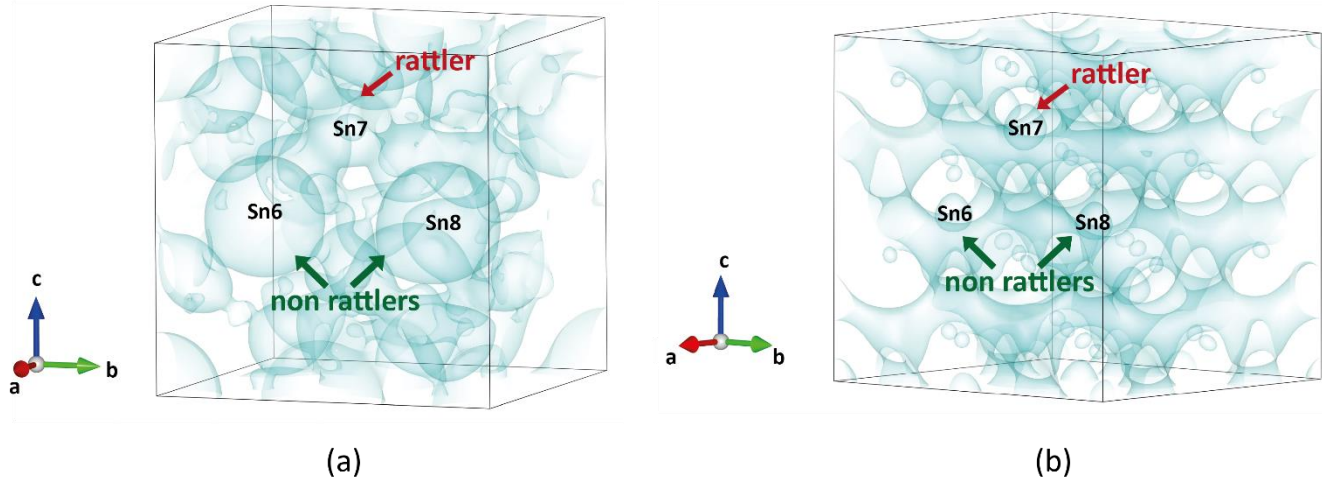


FIG 8. Partial charge density isosurfaces for a disordered cubic supercell. Picture (a) selectively shows the isosurface corresponding to Sn s electrons while picture (b) is representative of Cu d electrons. As visible, Sn s electrons of the rattling type ions (Sn7 in this case) tend to present a charge density distribution with a different shape, more slender and with a smaller radius, while the charge distribution of Cu d electrons surrounding the rattling Sn has a larger radius. This bonding inhomogeneity is shown to cause both a suppression of thermal conductivity, via promoting the rattling of these Sn atoms, and an improvement of carrier concentration, as the delocalization of Cu- d electrons can behave like a doping agent.

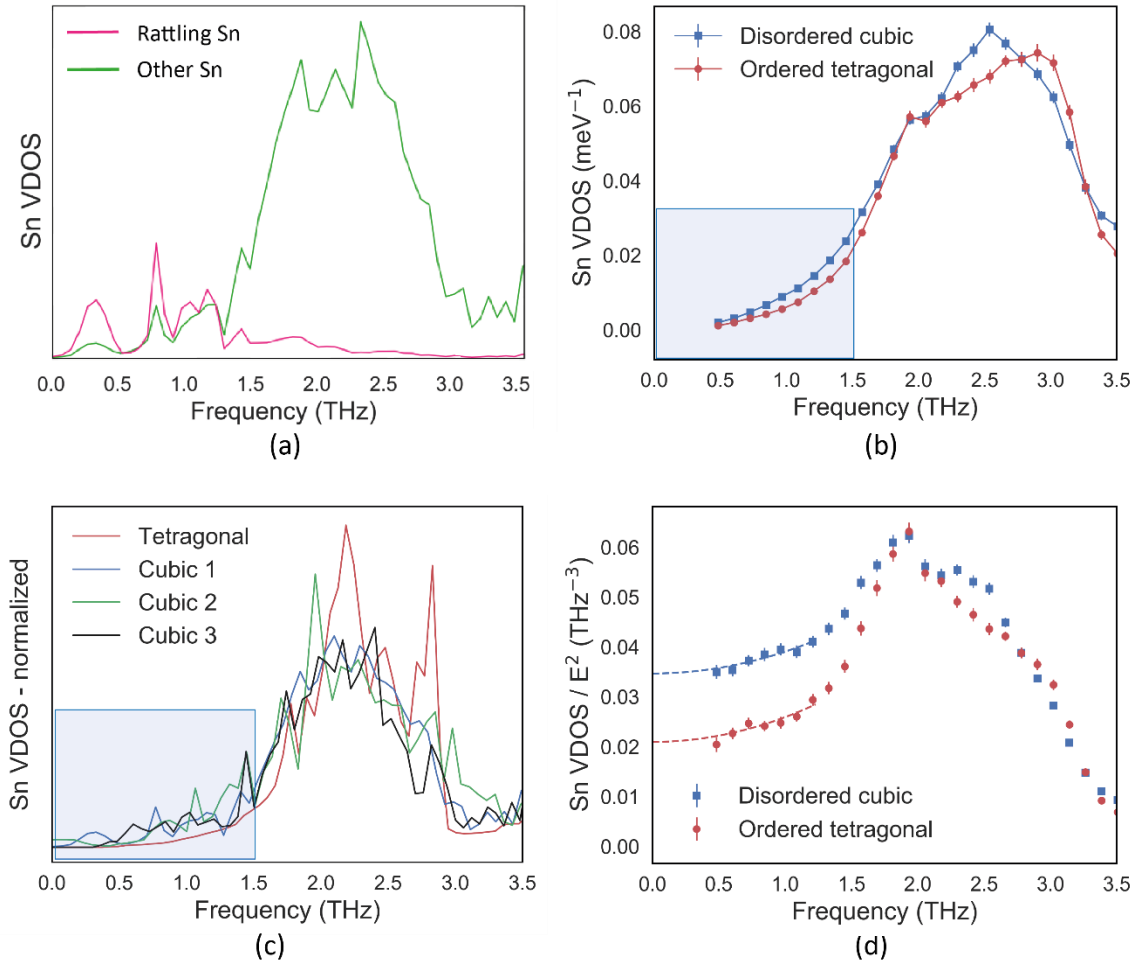


FIG 9. (a) Theoretical projected VDOS of two different types of Sn: a “rattling” one (Sn7) and the others. (b) Experimental measurement of the ^{119}Sn projected vibrational density of states for a disordered cubic and an ordered tetragonal sample obtained with Nuclear Inelastic Scattering (NIS). (c) Theoretical Sn projected phonon density of states calculated for three different configurations of disordered cubic supercells and for the ordered tetragonal cell. Panel a corresponds to the curve labelled as Cubic 1. Values are normalized per atom. In the highlighted region it is possible to observe some peaks for the cubic cells corresponding to Sn atoms of the rattling type. Experimental results in (b) could be compatible with DFPT calculations and the rattling interpretation. (d) Reduced ^{119}Sn projected VDOS (divided by E^2) for two samples. The dashed lines show a parabolic fit in the range 0.5-1.23 THz to extrapolate the Debye level value at $E=0$, used to obtain the mean sound velocity (see SN for explanation).

IV. CONCLUSION

Disordered cubic is a recently discovered polymorph of kesterite, characterized by complete randomness in the occupation of the cation sites. In comparison to the generally reported ordered tetragonal phase, we demonstrate how the introduction of disorder leads to a significant change in Sn-S bonding. This leads to an optimization of all the thermoelectric properties, suppressing thermal conductivity with a concomitant enhancement of electrical conductivity and Seebeck coefficient, a rather uncommon occurrence in thermoelectricity.

The high density of defects in the cubic polymorph promotes the localization of lone pair electrons in some Sn atoms, which turn into rattlers. These ions suppress thermal conductivity, dissipating lattice energy via low-frequency optical phonon modes. At the same time, they cause a charge deficiency in some Sn-S bonds that turns out to improve the electronic properties. This Sn charge deficiency is compensated by Cu electrons

which in turn generate holes. This gives rise to a p-type doping-like effect, improving electrical conductivity, and to highly-localized acceptor states, responsible for the enhancement in Seebeck coefficient. The unveiled physical mechanism reveals that a single phenomenon connected with structural disorder can provide a concurrent optimization of electronic and thermal properties.

While this mechanism qualitatively accounts very well for the observed properties, we do not exclude the possibility that other mechanisms provide an additional contribution to this simultaneous optimization. As such, further investigation is proposed for the future, with particular attention to microstructural and surface effects.

Comparing cubic to tetragonal, we report a 3x reduced thermal conductivity together with a doubling in both electrical conductivity and Seebeck coefficient, resulting in a more than 20x increase in figure-of-merit. This emergent paradigm has the potential to be extended to other materials for achieving an all-round improvement of TE performance.

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AUTHOR CONTRIBUTIONS

E.I. contributed with sample preparation, structural and thermoelectric characterization, data interpretation and discussion, main draft preparation. B.M. contributed with DFT and DFPT calculations, data interpretation and discussion, main draft preparation. C.F. contributed with Hall and Van der Pauw measurements, data interpretation and discussion, reviewing and editing of the draft. N.A. contributed with absorption spectroscopy measurements. I. S., S.S. and R.E. contributed with Nuclear Inelastic Scattering measurements and interpretation, reviewing of the draft. N.M.P. contributed with funding acquisition and reviewing of the draft. P.S. contributed with conceptualization of the work, funding acquisition, structural characterization, data interpretation and discussion, reviewing and editing of the draft and supervision of the work.

COMPETING INTERESTS

The authors declare no conflict of interests.

REFERENCES AND FOOTNOTES

*Mott's equation [42], expressed in a convenient form for this dissertation, where k_B is the Boltzmann constant, T is the absolute temperature, q is the electron charge, n and μ are respectively the carrier density and mobility, while $f(E)$ and $DOS(E)$ are the Fermi function and the density of states calculated at energy E , equal to the Fermi energy E_F . Notice that the Seebeck coefficient is inversely proportional to the carrier density and mobility, while it scales with the derivative of DOS .

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