High thermoelectric performance of environmentally friendly sodium-doped Cu$_2$ZnSnS$_4$ single crystal: Evidence of valleytronics based strategy.

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Thermoelectrics (TEs) are an important class of technologies for harvesting electric power directly from heat sources. To design high performance TE materials, valleytronics has great theoretical potential to maximize a dimensionless figure of merit $ZT$ but has not yet been demonstrated experimentally. Pseudocubic structure approach based on valleytronics paves a new path to manipulate valley degeneracy and anisotropy with low thermal conductivity caused by short-range lattice distortion. Here, we report a record high $ZT = 1.6$ around 800 K, realized in totally environmentally benign Na-doped Cu$_2$ZnSnS$_4$ (CZTS) single crystal. The exceptional performance comes from a high power factor while maintaining intrinsically low thermal conductivity. The results demonstrate that valleytronics is a new strategy and direction in the TE field, which takes advantage of simple material nature tuning without complex techniques.
Many different strategies for improving the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is temperature, and $\kappa$ is the thermal conductivity, have been conducted for thermoelectric (TE) application. These concepts include, but are not limited to, phonon-glass electron-crystal\textsuperscript{1} or phonon-liquid electron-crystal\textsuperscript{2}, nanostructure modification by alloying and doping to reduce thermal conductivity or to enhance electrical properties by doping and alloying techniques\textsuperscript{3-8}, improvement of Seebeck coefficient by electronic density of states (DOS) distortion\textsuperscript{9}, the conduction (valence) band tuning\textsuperscript{10}, quantum confinement effects\textsuperscript{11}, and electron energy barrier filtering\textsuperscript{12}. Low thermal conductivity is possible by inducing nanostructure\textsuperscript{13, 14} and hierarchical architecture\textsuperscript{15, 16}. So far, the $ZT = 2.6$ for SnSe\textsuperscript{17} has been achieved by anisotropic properties\textsuperscript{18, 19}, multiple valence bands\textsuperscript{20, 21}, and three dimensional charge and two dimensional phonon transport\textsuperscript{22}. Nevertheless, for large-scale deployment of TE devices, TE materials will have to simultaneously fulfill tough requirements such as non-toxicity, non-scarcity and high efficiency. However, totally environmentally friendly TE materials by current strategies demonstrate far lower $ZT$ values than TE state-of-the-art such as 1.1 for SnS\textsuperscript{23}.

An unexplored approach for TE optimization is the emerging field of valleytronics. Valleytronics relies on the manipulation of the electronic band structure valley degree of freedom for functional materials to accomplish application needs. This idea was initially applied to new quantum computation devices to carry and store information\textsuperscript{24}. We unify traditional TE approaches into valley factors: the number of valleys contributing to electronic transport (valley degeneracy), the distortion of DOS (valley distortion), and the exact shape of valleys which can be expressed as the effective mass of carriers (valley anisotropy).
Pseudo-cubic approach of multinary compounds paves a path to manipulate the electronic band structure. The tetragonal I-III-VI$_2$ group chalcopyrite structure is analogous to a $1\times1\times2$ supercell expansion of the zinc-blende structure. It is easy for non-cubic structure to understand low symmetry with crystal-field splitting $\Delta$CF which leads to low valley degeneracy. This approach is that $\Delta$CF could be tuned to 0 when the crystal structure parameter $\eta$ is equal to 1 ($\eta = c/2a$, where $c$ and $a$ are lattice parameters for chalcopyrite), which means pseudo-cubic structure. This long-range cubic-like structure regains the valley degeneracy and maintains the localized short-range non-cubic lattice distortions.

Here, this novel pseudo-cubic approach based on valleytronics is applied to achieve a high $ZT$, environmentally friendly TE material. Single crystals are necessary for optimization of valley parameters, especially valley anisotropy. Typical TE materials have been polycrystalline because grain boundaries scatter phonons disproportionately more than they scatter electrons. This leads to a greater reduction in thermal conductivity than in electrical conductivity and therefore an overall increase in $ZT$ in the last few decades. A pseudo-cubic approach allows the ability to simultaneously optimize electrical and thermal transport properties by long- and short-range structure regions. We focus on the quaternary I$_2$-II-IV-VI$_4$ group compound p-type Cu$_2$ZnSnS$_4$ (CZTS), which has attracted much attention, mainly in the field of photovoltaic (PV) application.

The crystal structure of CZTS is kesterite, closely related to chalcopyrites. Our previous study reveals that $\eta$ value of CZTS is close to 1 from neutron diffraction measurement, which is ideally suited for a pseudo-cubic approach. High-quality large-size CZTS single crystals can be obtained to perform experimental thermoelectric measurements on bulk samples.
Electronic band structure of CZTS

Figure 1a shows the kesterite structure of CZTS, wherein the cation layers of Cu-Sn, Cu-Zn, Cu-Sn and Cu-Zn are alternated along the c-axis. In the Cu-Zn layer, the two atoms are easily disorderd leading to short-range distortion for low thermal conductivity. The experimental crystal structure parameter η value of CZTS is 0.997 (a = 5.455 Å and c = 10.880 Å), which minimizes the energy splitting parameter ΔCF. The utilization of a rational pseudo-cubic structure supports cubic-like degenerate electronic bands to be high power factor (PF) in Fig. 1b. The electronic band structure of CZTS was computed by density functional theory (DFT) and is shown in Fig. 1c. The spin-orbit interaction is included. Cubic-like valence band edges are observed as a result of the symmetry framework, which is highly degenerate at Γ point indicating an ideal character of pseudo-cubic structure. The band structure with direct bandgap can be observed. As is often the case, the DFT band gap is slightly smaller than the experimental value which we measured to be 1.6 eV for CZTS single crystal by using transient reflectivity measurements. The top of the valence band is split by the crystal field in Fig. 1d. Kesterite CZTS have Γ7+8 symmetry for the topmost (v1) and second (v2) valence bands and Γ5+6 symmetry for the third band (v3) where the single state is above the twofold degenerate state with ΔCF = 0.06 eV in the vicinity of Γ point. This theoretical result is in good agreement with a pseudo-cubic approach. Table 1 shows the anisotropic effective hole masses obtained directly from the band energy dispersion.

TE properties

In this study, we fabricated samples with different compositions including a stoichiometric Cu2ZnSnS4 (sample 1), Cu-poor Cu1.9ZnSnS4 (sample 2), Cu-poor Cu1.9ZnSnS4 with Na: 0.1 mol% doped (sample 3), and 0.04 mol% doped (sample 4) by Sn-solvent traveling heater method.
Sodium is known to benefit CZTS PV devices as an effective dopant for enhancement of electrical properties. Single crystals were cut in the transverse (⊥; perpendicular to the c-axis) and the longitudinal (∥; parallel to the c-axis) directions for thermoelectric measurements. The structural and compositional properties were investigated by powder X-ray diffraction (XRD), Raman spectroscopy, energy dispersive X-ray spectroscopy (EDX), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) in Supplementary Fig. 1 and Supplementary Tables 1-2.

The temperature dependent electrical and TE properties of CZTS single crystals from 300 K to 800 K are shown in Fig. 2 with the accuracy of TE measurements discussed in Supplementary Figs. 2-4. Consistent with our previous work on CZTS in PV devices, the electrical conductivity with a Cu-poor composition and Na-doping increased by approximately two orders of magnitude greater than the stoichiometric sample (Fig. 2a). We have reported that the carrier transport mechanism can be expressed by band conduction from valence band to defect level near room temperature. The conductivity data can be described quantitatively as typical thermal activation

\[
\sigma(T) = \sigma_B \exp\left(\frac{-E_A}{k_B T}\right),
\]

where \(\sigma_B\) is pre-factor, \(E_A\) is the relevant activation energy associated with band conduction, and \(k_B\) is the Boltzmann constant. The conduction parameters are shown in Supplementary Table 3. The Fermi level lies around the top of the valence band because of typical thermal activation. Therefore, anisotropy of topmost \(v_1\) is dominant for electrical properties. The longitudinal \(m^\parallel_{v1}\) is smaller than the transverse \(m^\perp_{v1}\), which leads that conductivity along c-axis is higher than that along a-axis. First-principle calculations predict that the dominant shallow V\textsubscript{Cu} acceptor level under Cu-poor condition is at 20 meV above valence band maximum. Cu on Zn antisite defect (Cu\textsubscript{Zn}) becomes a dominant deep acceptor defect at 120 meV under near-stoichiometric and Cu-rich compositions. The lower \(E_A\) in Cu-poor compositions leads to higher
electrical conductivity values because of the increasing concentration of V\textsubscript{Cu} acceptor. In addition, Na-doping results in the improvement of compensation by suppression of dominant Zn on Cu antisite donor defect (Zn\textsubscript{Cu})\textsuperscript{29}. This donor defect may be inhibited by a finite Na substitution as neutral Na\textsubscript{Cu} defect, which is in good agreement with the lowest calculated formation energy of Na\textsubscript{Cu} by theoretical study\textsuperscript{31}. Therefore, the hole mobility and concentration can be enhanced by Na-doping simultaneously in Supplementary Table 3. The scattering process is discussed from temperature dependence of hole mobility in Supplementary Fig. 5.

The sign of the Seebeck coefficient, $S$, is always positive for all samples as expected for these p-type materials. The values of $S$ monotonically increase with increasing temperature because more holes are thermally activated to high energy states which leads to a higher average entropy of holes originated from valley degeneracy in Fig. 2b. Note that $S$ along $a$-axis is 10-20% higher than that of $c$-axis due to heavy effective hole mass from valley anisotropy. Lower $S$ values are observed in Cu-poor compositions and with increasing Na-doping because of the enhanced hole concentration in Table 1. So far, the reported $S$ values of stoichiometric CZTS bulk polycrystalline samples without doping range from 260 to 990 $\mu$V/K depending on hole concentration near 700 K\textsuperscript{32-34}. The temperature dependence of $PF$ is shown in Fig. 2c. The $PF$ value of sample 3 along $a$-axis at 800 K is $1.86 \times 10^{-3}$ W/mK\textsuperscript{2}, which is higher than $1.2 \times 10^{-3}$ W/mK\textsuperscript{2} of the state-of-the-art compound Cu\textsubscript{2}Se with $ZT = 2.6$ at 850 K\textsuperscript{3}. Our result reveals that high $S$ and $\sigma$ originated by valley degeneracy and anisotropy leads to high $PF$ value as totally environmentally TE material.

The temperature dependence of thermal conductivity, $\kappa$, is shown in Fig. 2d, which was calculated by the thermal diffusivity, $\lambda$, specific heat capacity, $C_p$, and density $D$. The thermal diffusivity and specific heat capacity dependence on temperature are shown in Supplementary Figs.
3b-3c. Weak anisotropy of thermal conductivity was observed which $\kappa_\perp$ indicates $\sim 3\%$ larger than $\kappa_\parallel$. The lattice thermal conductivity along $a$-axis is $\sim 5\%$ larger than that of $c$-axis in the kesterite structure from theoretical calculation based on the phonon Boltzmann transport$^{35}$. Weak anisotropy of thermal conductivity in this study is in good agreement with theoretical study$^{35}$. The thermal conductivity decreases with increasing temperature roughly according to a $T^{-1}$ relation for all samples. This temperature dependence suggests that the lattice thermal conductivity is primarily driven by phonon-phonon Umklapp scattering rather than intrinsic defects. If phonon scattering were driven by neutral dopant-induced, anti-site disorder, or alloy scattering then the scattering would be more uniform over the temperature range with very weak temperature dependence. Such thermal conductivity temperature dependence is typically observed in heavily defected materials such as yttria-stabilized zirconia$^{36}$. However, here the $T^{-1}$ temperature dependence characteristic of phonon-phonon scattering occurs when other mechanisms like neutral defect scattering are less important. In fact, literature examples exist where the thermal conductivity trend transitions from $T^{-1}$ to nearly temperature independent due to anti-site disorder or mixtures of point defects with Umklapp scattering$^{37,38}$. In this work, we see evidence that lattice scattering is impacted by the intrinsic complexity of the crystallographic structure. For example, consider the disorder between Cu and Zn by off-stoichiometric compositions and Na-doping. Even though these are single crystals which do not benefit from lattice thermal conductivity reduction due to grain boundary scattering, the values of $\kappa$ at 800 K are only between 0.94 to 1.7 W/mK. Such low values are only moderately higher than the other reported values of related polycrystalline quaternary compounds such as CZTSe and Cu$_2$CdSnSe$_4$$^{39,40}$. The ability to achieve such low thermal conductivity due to the intrinsic defects in this material while maintaining good electrical transport is an unexpected improvement which can be attributed to the single crystal
nature of these samples. Grain boundaries are typically known to present energy barriers of order 50-150 meV in polycrystalline chalcogenide semiconductors like CZTS\textsuperscript{41}. Recent literature points out that continued \( ZT \) enhancement due to lattice thermal conductivity reduction is fundamentally limited without a means whereby the \( PF \) is also enhanced\textsuperscript{42}. In light of this, the single crystal approach with a site-disordered material is promising.

Taken together, the outstanding electrical properties with relatively low thermal conductivity of sample 3 resulted an totally environmentally friendly TE material with TE figure of merit of up to \( ZT = 1.6 \) at 800 K (Fig. 3). This value is comparable to the highest \( ZT \) reported for other relating quaternary materials in Supplementary Table 5. The combined uncertainty of all measurements involved in the calculation of \( ZT \) leads to an estimated uncertainty near 30%. Our approach reveals that TE valleytronics concept is comparable with phonon-liquid electron-crystal concept discovering non-toxic earth-abundant Cu\textsubscript{2-x}S with \( ZT = 1.7 \) at 1000 K\textsuperscript{43}.

**Intrinsic cation fluctuation for low thermal conductivity**

Intrinsically disordered structures, such as CZTS where the Cu and Zn cations can exchange site occupancy with little energy cost, lead to low thermal conductivity. Single crystals provide an exceptional opportunity to control and quantify the degree of this fluctuation by simply controlling single crystal cooling rates. The cation fluctuation in CZTS was studied by scanning transmission microscopy (STEM) and EDX relating to structure and chemical composition. Fig. 4a shows a STEM-based image that was subsequently chemically mapped using EDX with the point-resolved Cu-K, Zn-K, Sn-L, and S-K emission lines at micrometer scale. At low magnifications of \( \times11000 \) corresponding to the micrometer scale the composition ratio was in good agreement with the expected stoichiometry sample 1 (Cu:Zn:Sn:S = 24.6:13.0:12.2:50.2). Considering the
correlations in elemental composition, we computed and compiled the Cu/Zn, Cu/Sn, and Zn/Sn maps to discuss the compositional fluctuation at the 50 nm scale length in Fig. 4b. These cation fluctuations, which are effective for phonon scattering, were observed at high magnification in all CZTS single crystals grown by gentle cooling. Note that the spatial compositional fluctuations of amplitude are larger for sample 1 (ranging 2.0×10^{19} \text{ cm}^{-3}) than for sample 4 (ranging 5.0×10^{20} \text{ cm}^{-3}) calculated by difference in composition, which coincides with the observed trends in thermal conductivity where sample 4 has the lowest thermal conductivity. Based on these chemical maps, we suggest that there are presumably distinct nanoscale regions in CZTS where this material is at least partially disordered. This suggestion is supported by compositional inhomogeneties at nanoscale from entropy-driven cation clustering expected from the motif-based model^{44}. However, the origin of this behavior still remains unclear. Even so, we believe that cation fluctuation is influenced by the native phase space in which CZTS can form S-Cu$_3$Sn and S-CuSnZn$_2$ motifs$^{44}$.

**Enhancement of electrical and TE properties**

Admittance spectroscopy (AS) measurements were used to characterize the defect levels and concentrations in samples. Figure 5a shows an Arrhenius plot to verify the defect levels, which were extracted from inflection points from the AS curves in Figs. 5b-d. All parameters for AS measurement are shown in Supplementary Table 3. The activation energy, $E(\omega)$, were obtained from the slope of the Arrhenius plot, $\ln(\omega_0/T^2)$ versus $1/T$, where $\omega_0$ is the inflection point of the capacitance versus frequency. The shallow acceptor level becomes lower in the Cu-poor composition from 100 meV to 65 meV because the dominant acceptor is $V_{\text{Cu}}$. The Na-doping in Cu-deficient compositions results in two orders of magnitude higher hole concentration compared to stiochiometric compositions because there is a reduction in the degree of compensation$^{29}$. The
dual advantages of lower thermal activation energy and higher hole concentration dramatically improve electrical properties by tuning composition and doping.

The Seebeck coefficient of CZTS single crystal along $a$-axis is large, for example as Na: 0.1 mol% sample 3, 290 $\mu$V/K at 300 K and 347 $\mu$V/K at 800 K. As mentioned above, we suggested that it is possible to tune DOS by the formation of $V_{Cu}$ in Cu-deficient samples and Na-doping. The energetic defect DOS is obtained by converting frequency into energy by using equations (1) and (2)\textsuperscript{45}.

$$E(\omega) = k_B T \cdot \ln \left( \frac{2\zeta T^2}{\omega} \right) \quad (1)$$

$$N_t(E(\omega)) = -\frac{V_{bi}}{W_d} \cdot \frac{dC}{d\omega} \cdot \frac{\omega}{k_B T} \quad (2)$$

Where $N_t$ is integrated defect density, $\zeta$ is pre-exponential factor comprising all temperature independent terms, $V_{bi}$ is built-in potential, $W_d$ is depletion width. $V_{bi}$ and $W_d$ are extracted from capacitance-voltage measurement. Figure 5e reveals DOS of dominant acceptor levels extracted from AS data. The enhancement of DOS with shallow acceptor and Na-doping relating to TE properties can be observed. Considering the impact of Na on DOS in CZTS, perhaps low compensation, we present the DOS for the Na-dopant substitution on Cu by DFT calculation in Supplementary Fig. 7. There are no significant increase in DOS by Na$_{Cu}$ defect, on the other hand the effective masses for each valence band are slightly larger than stoichiometric CZTS. Other possible Na impact on DOS is the increasing of Na substitution on Zn site (Na$_{Zn}$) shallow acceptor defect which is low formation energy next to Na$_{Cu}$\textsuperscript{31}. We experimentally demonstrate that DOS in CZTS can be improved by Cu-deficit and Na-doping for high TE performance.
Conclusions

In this study, our focus was to first achieve competitive ZT values for kesterite CZTS as totally environmentally friendly TE material by novel pseudo-cubic approach based on valleytronics. The value of $ZT = 1.6$ at 800 K in high-quality p-type CZTS single crystals is remarkable and due primarily to high degeneracy at valence band edge (valley degeneracy), the anisotropy of effective mass (valley anisotropy) and localized lattice distortin. Several insights (a)-(c) for a high $ZT$ quaternary compound can be highlighted from this study as follows: (a) high $PF$ value $1.9 \times 10^{-3}$ W/mK$^2$ at 800 K was obtained by tuning valley parameters, (b) the intrinsic local cation anti-site disorder and cation fluctuation results in a low thermal conductivity of $\sim 0.94$ W/mK at 800 K even for single crystal samples, (c) Cu-deficient composition and Na-doping lead to high electrical and TE properties due to $V_{\text{Cu}}$ and Na related shallow acceptor defects. Compared to other high performance TE materials, our results for CZTS demonstrate that a high $ZT$ can be realized in an intrinsic structure, as single crystal, with simple tuning by composition and doping without complex nanostructuring. This is the evidence that valleytronics have a potential to produce intrinsic TE material compared with state-of-the-art concepts. We expect the discovery of high TE performance for CZTS could attract great attention within the waste heat recovery industry due to the totally environmentally friendly combination of elements that are low cost, non-toxic, and earth-abundant.

Methods

Single crystal growth. CZTS single crystals were grown by Sn-solvent traveling heater method (THM) at 40 °C/cm axial temperature gradient, a growth temperature at 850 °C, at a growth speed of 4 mm/day. The details are explained in Supplementary Information. A conical quartz ampoule
was coated with carbon to avoid solution adhesion. The detailed composition of the crystals was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; SII NanoTechnology SPS3520UV). Samples were dissolved into a mixed acid containing HNO$_3$ and HCl.

**Sample preparation before characterization.** Grown crystals were cut with a diamond blade and polished mechanically with 0.01 μm Al$_2$O$_3$ powder and then etched with a HCl solution for 5 minutes to remove saw and polishing damage. The electrical and TE measurements were carried out along the c-axis in Supplementary Fig. 1c.

**DFT calculation.** First-principle calculations were performed using the plane-wave basis projector augmented wave (PAW)$^{46}$ method and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)$^{47}$ implemented in Vienna *Ab initio* Simulation Package (VASP)$^{48, 49}$. The planewave basis-set cutoff was set to 300 eV and spin polarization was considered. We used the PAW potentials which treat Cu (3d$^{10}$ 4s$^1$), Zn (3d$^{10}$ 4s$^2$), Sn (4d$^{10}$ 5s$^2$ 5p$^2$), S (3s$^2$ 3p$^4$), and Na (2p$^6$ 3s$^1$) explicitly as valence electrons and the rest as core electrons. We adopted the effective Hubbard $U$ values of 5.2 eV for Cu, 6.5 eV for Zn, and 3.5 eV for Sn. Atomic positions and the unit cell parameters were relaxed until the forces on all atoms become less than 2.0$x$10$^{-2}$ eV/Å. A Na-doped model with the concentration of 6.25% was constructed by substituting a Na atom for a Cu site within a 2×2×1 supercell of the conventional unit cell. The substitution for Cu 2a site was considered because the energy was lower than that for Cu 2c site. The Brillouin zones were sampled with 4×4×2 and 2×2×2 Monkhorst–Pack k-point meshes for the unit cell and 2×2×1 supercell, respectively. For electronic DOS, the 2×2×1 supercell and finer Γ-centered k-point mesh of 4×4×4 were used for both pristine and Na-doped CZTS models. For electronic band structure, a conventional unit cell instead of a primitive cell was intentionally used.
for the ease of analyzing anisotropic effective masses along the \( a \) and \( c \) directions. The band unfolding for the Na-doped supercell were performed using Band UP code\(^5\).

**Characterization.** The structural properties were analyzed by powder X-ray diffraction (XRD; Panalytical X’ Pert PRO) and Raman spectroscopy (HORIBA T64000). XRD measurement was operated under 40 kV and 40 mA using a Cu-K\( \alpha \) radiation source. A 514 nm Ar\(^+\) laser was used in the Raman measurements and focused on the sample by an objective lens with a numerical aperture of 0.55. The laser power on the sample was 100 mW. The spectra were calibrated based on 520 cm\(^{-1}\) of Si peak.

The disorder structure in stoichiometric CZTS single crystal was performed by STEM (JEOL 2800) operated at 200 kV using two simultaneous solid-state EDX detectors. The spectral image acquisition was performed over a series of consecutive sub-second frames with drift correction between frames with a total acquisition time of less than 20 min. The EDX data were processed using Thermo-Scientific Image Analysis software. The X-ray emission spectra captured were quantified after subtracting the background and each of elements. The analytical certainty associated with EDX profiling is within 0.5 at.\%.

The electrical conductivity \( \sigma \) and Seebeck coefficient \( S \) were measured simultaneously in a helium atmosphere at 300-800 K using a commercial system (ZEM3; ADVANCE RIKO) on the samples with the dimension of about 2 mm\( \times \)2 mm\( \times \)10 mm. Thermal conductivity \( \kappa \) was calculated based on the equation: \( \kappa = \lambda C_p D \), where \( \lambda \) is the thermal diffusivity, \( C_p \) is the specific heat capacity, and \( D \) is the density. The thermal diffusivity was measured by laser flash method (Netzsch; LFA457) on the rectangular samples with 8 mm\( \times \)8 mm\( \times \)1 mm coated with a thin layer of graphite to minimize errors from the emissivity of the material. The specific heat capacity was measured by differential scanning calorimetry (DSC; Rigaku Thermo plus EVO2 DSCvesta) on
the samples with 3 mm×3 mm×3 mm. The mass of all samples is unchanged after measurements by using Thermogravimetric analysis (TGA) in Supplementary Fig. 7. The density values between 4.4-4.5 g/cm³ were measured using the Archimedes method at room temperature.

The hole concentration \( p \) and mobility \( \mu \) were measured by temperature dependence of Hall effect (TOYO; ResiTest8300) performed in a 0.45 T magnetic field in the van der Pauw geometry under a helium atmosphere at 20-800 K. For Hall measurements, Au contacts, each with a diameter of 1 mm and thickness of 200-300 nm, were evaporated onto the corners of each CZTS bulk single crystal with the dimension of 5 mm×5 mm×0.8 mm.

Admittance spectroscopy measurements were carried out in the temperature of 120-300 K under dark condition with a LCR meter (HP 4284A), which applied an AC voltage of 50 mV by varying the frequencies from 100 Hz to 1 MHz. Schottky diode structures of 1 mm diameter Al Schottky contact/CZTS (5 mm×5 mm×1 mm)/Au Ohmic back contact were fabricated by evaporation. The thickness of contacts was 300-400 nm.

**Data availability**

The data that support the findings of this study are available from the authors on reasonable request.

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Author contributions

A.N. and K.N. designed, conducted the all experiments and prepared the manuscript. K.Y. and M.A.S helped in single crystal growth and electrical measurements. T.M. conducted theoretical
calculation. T.D.S. helped in thermoelectric measurements. All authors contributed to the
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Additional information

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Figure 1 Pseudo-cubic approach based on valleytronics in TE CZTS material. 

Conventional unit cell of the kesterite structure having b, pseudo-cubic structure by the crystal structure parameter \( \eta (c/2a) \approx 1 \). c, Electronic band structure of kesterite structure of CZTS along the two symmetry directions (100) and (001). d, The top of the valence band is split into the topmost \( (v_1) \) and second \( (v_2) \) bands with \( \Gamma_{7+8} \) symmetry and the third band \( (v_3) \) with \( \Gamma_{5+6} \) symmetry where the single state is above the twofold degenerate state with the energy splitting parameter \( \Delta CF = 0.06 \) eV in the vicinity of \( \Gamma \) point. Dashed line denote the Fermi energy.
Figure 2 TE characterization of CZTS single crystals. Temperature dependence of a, electrical conductivity $\sigma$ fitted by $\sigma(T) = \sigma_B \exp(-E_A/k_B T)$; b, Seebeck coefficient $S$; c, power factor $PF$; and d, thermal conductivity $\kappa$. Lines are roughly following to a $T^{-1}$ relation. Measurements are carried out in the transverse (⊥; perpendicular to the $c$-axis) and the longitudinal (‖; parallel to the $c$-axis) directions.
Figure 3 Temperature dependence of the dimensionless figure of merit $ZT$ for different compositional CZTS single crystals. The insets are a typical CZTS ingot and samples cutting along the (100) and (001) planes.
Figure 4 The cation fluctuation by high-resolution STEM image. a, STEM-based EDX mapping images of stoichiometric sample 1 at micrometer scale. Stoichiometric Cu:Zn:Sn:S = 24.6:13.0:12.2:50.2 could be observed, and there is local compositional non-uniformity in large scale. b, Elemental correlations for Cu/Zn, Cu/Sn, and Zn/Sn at nanometer scale. Considering stoichiometric ratio of Cu/Zn = 2, Cu/Sn = 2, and Zn/Sn = 1, the large cation fluctuation with spatial compositional amplitude less than 0.5 at.% could be observed in samples 1-3 at high magnification.
Figure 5 The defect level and DOS of CZTS single crystals extracted by AS measurement as a function of temperature. a, Arrhenius plot of $\omega_0/T^2$, $\omega_0$ being the angular emission frequency of the inflection points. b-d, Temperature dependence of AS spectra of each sample. e, $N_t$ calculated from AS measurement for different compositional samples. The defect level and DOS values are shallower and higher with Cu-poor and Na-doping, respectively. Associated integrated $N_t$ is calculated based on Gaussian fitting. No anisotropy of defect properties can be observed.
Table 1 Anisotropy of the effective hole masses ($m_n$ for $n = v_1, v_2, $ and $v_3$ in Fig. 1) in CZTS. $m_e$ is electron mass. The transverse $\perp$ masses are determined from the energy dispersions in (100) direction, and the longitudinal $\parallel$ masses are determined from the dispersions in (001) direction.

| $m_{v_1}^{\perp}[m_e]$ | $m_{v_1}^{\parallel}[m_e]$ | $m_{v_2}^{\perp}[m_e]$ | $m_{v_2}^{\parallel}[m_e]$ | $m_{v_3}^{\perp}[m_e]$ | $m_{v_3}^{\parallel}[m_e]$ |
|------------------------|-------------------------|------------------------|------------------------|------------------------|------------------------|
| 0.77                   | 0.17                    | 0.78                   | 0.76                   | 0.16                   | 0.76                   |