



Dalton
Transactions

**Thermoelectric Properties of Zinc-Doped Cu₅Sn₂Se₇ and
Cu₅Sn₂Te₇**

Journal:	<i>Dalton Transactions</i>
Manuscript ID	DT-ART-02-2021-000615.R1
Article Type:	Paper
Date Submitted by the Author:	30-Mar-2021
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Thermoelectric Properties of Zinc-Doped $\text{Cu}_5\text{Sn}_2\text{Se}_7$ and $\text{Cu}_5\text{Sn}_2\text{Te}_7$ Cheryl Sturm,^a Leilane R. Macario,^a Takao Mori,^b and Holger Kleinke^{*a}Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

High-performance thermoelectric materials are currently being sought after to recycle waste heat. Copper chalcogenides in general are materials of great interest because of their naturally low thermal conductivity and readily modifiable electronic properties. The compounds $\text{Cu}_5\text{Sn}_2\text{Q}_7$ were previously reported to have metal-like properties, which is not a desirable characteristic for thermoelectric materials. The aim of this study was to reduce the carrier concentration of these materials by Zn-doping, and then investigate the electronic and thermoelectric properties of the doped materials in comparison to the undoped ones. The compounds were synthesized using both the traditional solid-state tube method and ball-milling. The crystal structures were characterized using powder X-ray diffraction, which confirmed that all materials crystallize in the monoclinic system with the space group $C2$. With the partial substitution of zinc for copper atoms, the compounds exhibited an overall improvement in their thermoelectric properties. Figure of merit values were determined to be 0.20 for $\text{Cu}_4\text{ZnSn}_2\text{Se}_7$ at 615 K and 0.05 for $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$ at 575 K.

1. Introduction

Research into thermoelectric (TE) devices as a method for waste heat recovery has received a lot of attention in the past few decades. Their high reliability, due to the absence of moving parts, scalability, and environmentally friendly materials has made TE devices sought after in many commercial and scientific settings.^{1,2} In short, TE materials have the capability of interchangeably converting heat into electricity and vice versa. The efficiency of these materials depends on the dimensionless figure of merit, zT , which is defined as $zT = \frac{S^2\sigma}{\kappa}T$, where S is the Seebeck coefficient (thermopower), σ is the electrical conductivity, T is the absolute temperature, and κ is the total thermal conductivity. High performance TE materials are optimized to have a large electrical conductivity and Seebeck coefficient, while the thermal conductivity ideally remains small.^{3–5} A zT of unity has been the benchmark value for advanced materials for decades; however in recent years this value has been exceeded - mostly through the implementation of nanostructuring.^{6,7}

To date, some of the best TE materials, such as Bi_2Te_3 ^{8,9} and PbTe ,^{10,11} contain toxic and expensive elements. Copper chalcogenides have been targeted as compounds of interest not only due to containing nontoxic and cheap elements, but also because of the high earth abundance of their elements, their relatively low thermal conductivity, and the ability to tune the

electrical properties.^{12,13} It is well known that copper chalcogenides with tetrahedral frameworks are good candidates for p -type thermoelectric materials.¹⁴ Due to the recent success of other copper chalcogenides, such as the chalcopyrites,^{15,16} colusites,^{17,18} and tetrahedrites,^{19,20} in which high figure of merit values have been obtained at moderate temperatures, we investigated the effects of Zn-doping on $\text{Cu}_5\text{Sn}_2\text{Se}_7$ ²² and $\text{Cu}_5\text{Sn}_2\text{Te}_7$,²³ which also adopt a supercell of sphalerite. It was predicted in 2016 that the hypothetical variant $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$ would exhibit semiconducting properties.²³ Of particular interest is how the selenides compare to the tellurides, as tellurium is scarce, expensive and toxic.

The ternary and quaternary Cu-based chalcogenides within the crystal family of $(\text{Cu},M)_5E_2Q_7$ (M = divalent transition metal; E = Si, Ge, Sn; Q = S, Se, Te) have seldom been reported in the literature. The earliest example was $\text{Cu}_4\text{NiSi}_2\text{S}_7$, described by Schäfer in 1980.²¹ The crystal structures and thermoelectric properties of the compounds $\text{Cu}_5\text{Sn}_2\text{Se}_7$ and $\text{Cu}_5\text{Sn}_2\text{Te}_7$ were reported in 2014²² and in 2016,²³ respectively. Both the selenide and telluride of $\text{Cu}_5\text{Sn}_2\text{Q}_7$ adopt a superstructure of the sphalerite structure, and crystallize in the $C2$ space group, isostructural with $\text{Cu}_4\text{NiSi}_2\text{S}_7$. All atoms are tetrahedrally coordinated, while Cu and Sn are surrounded by four Q atoms, the chalcogen atom is surrounded by three Cu atoms and one Sn atom (Figure 1).

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Electronic Supplementary Information (ESI) available: experimental X-ray patterns, refined unit cell parameters, EDX maps and data, electronic and lattice thermal conductivity curves. See DOI: 10.1039/x0xx00000x

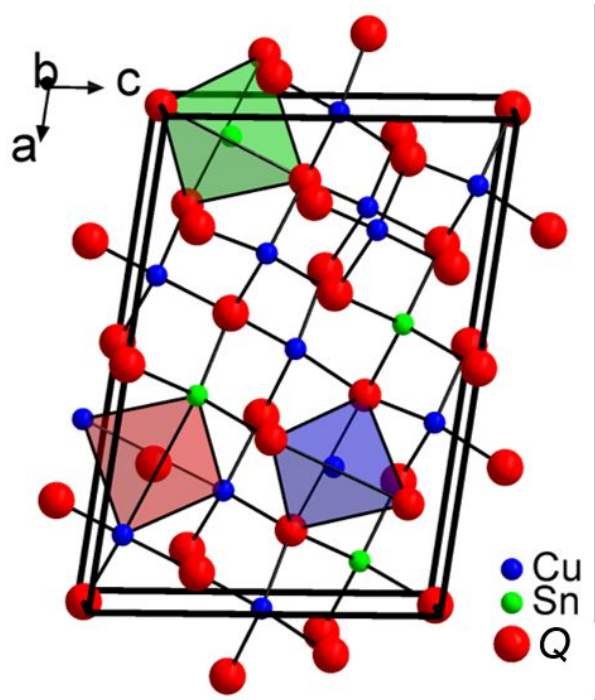


Fig. 1 Crystal structure of $\text{Cu}_5\text{Sn}_2\text{Q}_7$, highlighting the coordination tetrahedra.

Density functional theory (DFT) calculations on metal-like $\text{Cu}_5\text{Sn}_2\text{Te}_7$ ²³ revealed a band gap situated one electron per formula unit above the Fermi level. DFT calculations on $\text{Cu}_5\text{Sn}_2\text{Se}_7$ resulted in calculated zT values up to 0.1.²⁴ This article discusses the synthesis and thermoelectric properties of $\text{Cu}_5\text{Sn}_2\text{Q}_7$, doped with Zn in attempts to provide the additional electron to attain semiconducting properties.

2. Experimental

To synthesize all four compounds, the preparatory work was performed inside an argon-filled glove box, starting with stoichiometric amounts of Cu powder (99.5%, Alfa Aesar), Zn powder (99.9%, Alfa Aesar), Sn granules (99.9%, Aldrich), Se pellets (99.99%, Aldrich), and Te broken ingots (99.999%, Strem).

The compounds $\text{Cu}_5\text{Sn}_2\text{Se}_7$ and $\text{Cu}_4\text{ZnSn}_2\text{Se}_7$ were synthesized utilizing the traditional solid state tube method, in which the starting reagents were loaded in the desired stoichiometry into a fused silica tube, sealed under a dynamic vacuum of 2×10^{-3} mbar, and placed into a high temperature muffle furnace. The samples were heated to 1173 K for 24 hours, and then annealed at 873 K for one week.

The telluride $\text{Cu}_5\text{Sn}_2\text{Te}_7$ was also prepared via the solid state tube method. The starting reagents were heated to 923 K for four days and then cooled to room temperature. The resulting ingot was ground into a powder, placed again into a fused silica tube, evacuated, and heated to 673 K for 72 hours, with agitation applied every 24 hours, where the tubes were shaken manually while they remained in the furnace at 673 K.

Finally, $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$ was synthesized utilizing a planetary ball mill. Stoichiometric amounts of the elements were loaded into ball milling jars (lined with zirconia) along with 3 mm diameter zirconia balls, and a ball to powder ratio of approximately 10 : 1. The mill was run at 600 rpm for four hours. Based on powder X-ray diffractometer, the resulting mixture contained the target phase as well as some binary compounds, and was subsequently loaded into fused silica tubes, sealed under a dynamic vacuum and placed into a high temperature muffle furnace. The sample was heated to 673 K for 72 hours with intermittent agitation, which resulted in a pure product. Attempts to synthesize $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$ utilizing the traditional solid state tube method without prior ball milling failed to produce a phase pure sample.

The phases and purity of each sample were analyzed using an INEL powder X-ray diffractometer with a position-sensitive detector and Cu $\text{K}\alpha_1$ radiation. The diffraction patterns were collected at room temperature in the 2θ range of 5° to 120° . No other side products were detected in the final products (Figure S1). The lattice parameters were refined using the Le Bail method²⁵ via the GSAS²⁶ suite of programs with the EXPGUI²⁷ interface, and yielded the expected minor changes when partially replacing Cu with Zn, and substantially larger cell parameters for the telluride, compared to the selenide (Table S1). Specifically, the a and b parameters increased both for the selenide and the telluride, while the c axis decreased more, resulting in an overall smaller unit cell upon Zn incorporation.

An EDX (energy dispersive analysis of X-rays) study was performed on the materials of nominal compositions $\text{Cu}_4\text{ZnSn}_2\text{Se}_7$ and $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$, utilizing a FEI Quanta Feg 250 ESEM under an acceleration voltage of 20 kV. The analyses showed both samples were homogenous, and the EDX mappings revealed that all four elements were distributed evenly throughout the scanned areas (Figures S2-3 and Tables S2-3).

The electronic structures of $\text{Cu}_5\text{Sn}_2\text{Te}_7$ and $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$ were calculated by employing the WIEN2k package, in which the full-potential linearized augmented plane wave (FP-LAPW) method was coupled with the density functional theory (DFT).^{28,29} The generalized gradient approximation (GGA) from Perdew, Burke and Ernzerhof (PBE) was utilized for the exchange and correlation energies.³⁰ Finally in order to obtain a more accurate band gap, the modified Becke-Johnson (mBJ)^{31,32} potential was applied. For self-consistent energy calculations, 234 independent k points were selected on a grid of $12 \times 6 \times 12$ points spread out evenly throughout the Brillouin zone in each case. The energy convergence for the self-consistent calculation was set to 10^{-4} Ry. Boltzmann transport properties were also calculated for $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$ using the BoltzTraP package³³ based on the results of the WIEN2k calculation.

Thermoelectric properties were determined after hot pressing the micro-crystalline samples under a 5% hydrogen and 95% argon atmosphere with an Oxy-Gon FR-210-30T-ASA-160-EVC hot-press furnace system, in a hardened graphite die with an inner diameter of 12.7 mm. The densification was done under 46 MPa for three hours, at 623 K for the selenides and at

563 K for the tellurides, which resulted in >95% of the theoretical densities, as determined via the Archimedes method. The resulting pellets had a diameter of 12.7 mm and a height of 2 mm.

The pellets were used to determine the thermal diffusivity in an argon filled TA Instruments DLF 1200 (University of Waterloo) and a nitrogen filled Netzsch LF467 (National Institute for Materials Science), both of which utilize a laser flash. The data were collected in steps of 50 K, using 1000 V, and were averaged over three shots at each temperature. The thermal conductivity, κ , was calculated from the equation $\kappa = \rho D C_p$, where ρ is the pellet's density, D , is the thermal diffusivity, and C_p is the heat capacity. The heat capacity was estimated using the Dulong-Petit law.³⁴

Afterwards, the pellets were cut into a rectangular bar with the dimensions of $10 \times 2 \times 2 \text{ mm}^3$, which were used to determine the electrical conductivity, σ , and the Seebeck coefficient, S , in an ULVAC-RIKO ZEM-3 system under helium. There, the data were also collected in steps of 50 K, and the Seebeck coefficient was determined at temperature gradients of 3 K, 4.5 K, and 6 K, and then averaged for each data point. The experimental errors were estimated to be $\pm 5\%$ for σ , $\pm 5\%$ for S , $\pm 5\%$ for κ , and $\pm 10\%$ for the figure of merit, zT .

3. Results and discussion

The density of states of $\text{Cu}_5\text{Sn}_2\text{Te}_7$ is depicted in Figure 2. The Fermi level cuts through the top of the valence band, composed of Cu- d and Te- p states. A narrow gap of 0.2 eV occurs about 0.5 eV above the Fermi level, predicting degenerate semiconducting properties for $\text{Cu}_5\text{Sn}_2\text{Te}_7$. Similar features were calculated for the isoelectronic and isostructural $\text{Cu}_5\text{Sn}_2\text{Se}_7$.²⁴

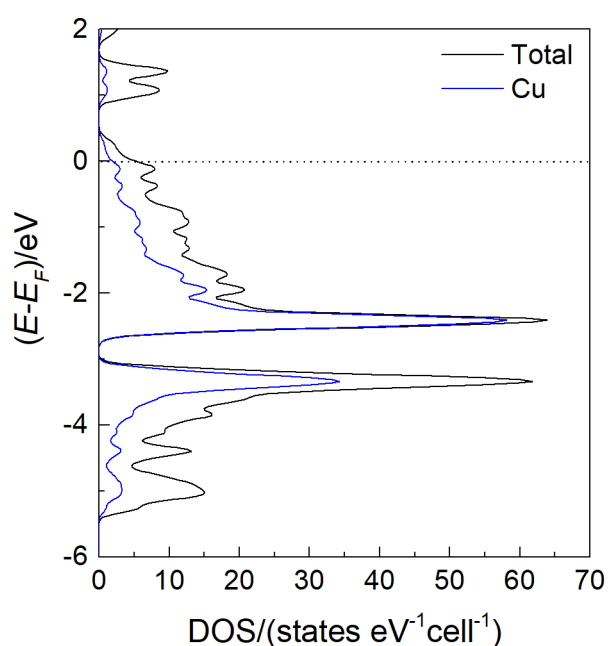


Fig. 2 Density of states of $\text{Cu}_5\text{Sn}_2\text{Te}_7$.

Substituting one Cu site (the Ni position in $\text{Cu}_4\text{NiSi}_2\text{S}_7$) with Zn results in the formula $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$, and moves the Fermi level into the band gap (Figure 3). Besides that shift, only minor changes occur between -2 eV and +2 eV around the Fermi level. With that, semiconducting properties are to be expected for the charge-balanced $(\text{Cu}^+)_4(\text{Zn}^{2+})(\text{Sn}^{4+})_2(\text{Te}^{2-})_7$.

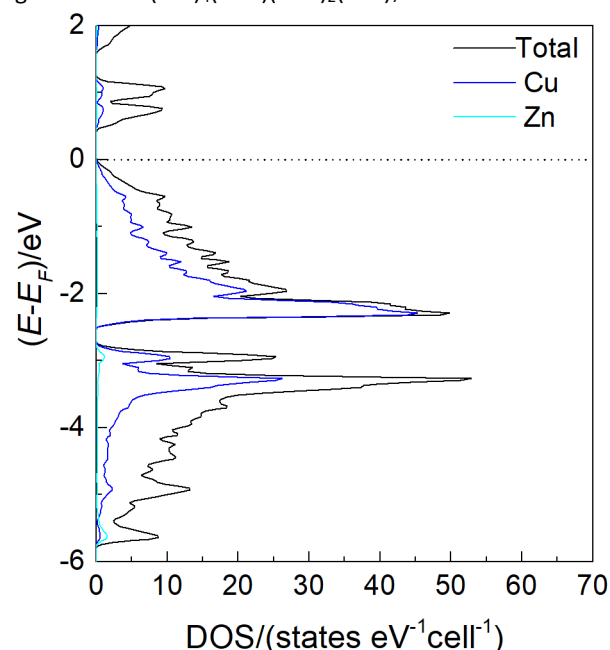


Fig. 3 Density of states of $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$.

The thermoelectric properties of the materials of nominal compositions $\text{Cu}_5\text{Sn}_2\text{Se}_7$ and $\text{Cu}_4\text{ZnSn}_2\text{Se}_7$ were studied in the temperature range of 300 K - 630 K, and of $\text{Cu}_5\text{Sn}_2\text{Te}_7$ and $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$ from 300 K - 575 K. The temperature dependence of the electrical conductivity is displayed in Figure 4. Due to the location of the Fermi level in the valence band, a large amount of charge carriers for both ternary (Zn-free) compounds was observed earlier, namely $\sim 3.0 \times 10^{21} \text{ cm}^{-3}$ and $\sim 1.4 \times 10^{21} \text{ cm}^{-3}$ at 300 K for the selenide²² and telluride,²³ respectively. Therefore, a decrease in the (high) electrical conductivity was expected for the ternaries with increasing temperature. This negative temperature dependence was indeed displayed, typical of heavily doped/degenerate semiconductors and metals, as the carrier concentration barely changes with temperature, and the charge carriers are more scattered with an increase in temperature, resulting in a decrease in carrier mobility. In the temperature range of 300 K - 630 K, electrical conductivity values of $8800 \text{ } \Omega^{-1}\text{cm}^{-1}$ - $3700 \text{ } \Omega^{-1}\text{cm}^{-1}$ were obtained for the selenide, while Fan et al. reported 24% lower electrical conductivity values within the same temperature range ($6700 \text{ } \Omega^{-1}\text{cm}^{-1}$ - $2900 \text{ } \Omega^{-1}\text{cm}^{-1}$).²² This is at least in part a consequence of their higher porosity as determined from the lower relative density of 92%, compared to our 96%. These values are significantly higher than in other known diamond-like structures, such as Cu_2SnSe_3 ($200 \text{ } \Omega^{-1}\text{cm}^{-1}$ - $100 \text{ } \Omega^{-1}\text{cm}^{-1}$), which also displayed the same negative temperature dependence.³⁵

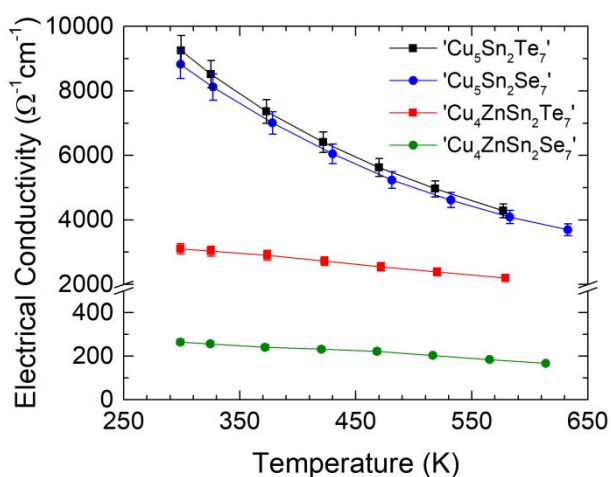


Fig. 4 Temperature dependence of the electrical conductivity of 'Cu₅Sn₂Te₇' and 'Cu₄ZnSn₂Te₇' with 5% error bars.

As anticipated, a dramatic decrease of the electrical conductivity occurred with the introduction of Zn. Much lower values of 265 Ω⁻¹cm⁻¹ - 170 Ω⁻¹cm⁻¹ were observed from 300 K to 630 K. The electrical conductivity values of Cu₄ZnSn₂Se₇ are also lower than those of the kesterite Cu₂ZnSnSe₄ (σ = 500 Ω⁻¹cm⁻¹ - 266 Ω⁻¹cm⁻¹ from 340 K - 630 K),³⁶ while higher than in case of Cu₂SnSe₃. Typically, advanced TE materials exhibit electrical conductivity values between 400 Ω⁻¹cm⁻¹ and 2000 Ω⁻¹cm⁻¹.^{37,38}

Similarly, the electrical conductivity of Cu₅Sn₂Te₇ experienced a three-fold decrease from 9200 Ω⁻¹cm⁻¹ to 3100 Ω⁻¹cm⁻¹ at 300 K after the introduction of Zn. Our room temperature results on the ternary telluride are in qualitative agreement with the (low temperature) data from Adhikary et al. who reported an electrical conductivity of 9800 Ω⁻¹cm⁻¹ at 300 K.²³ At 575 K, there was a roughly 50% reduction of the electrical conductivity with the inclusion of Zn, with values of 4300 Ω⁻¹cm⁻¹ and 2200 Ω⁻¹cm⁻¹, respectively. The same negative temperature dependence is observed for the kesterite Cu₂CdSnTe₄, but with higher electrical conductivity values (σ = 2500 Ω⁻¹cm⁻¹ at 300 K to 1300 Ω⁻¹cm⁻¹ at 600 K).³⁹ As such a dependence is indicative of extrinsic semiconductors, all of the above-mentioned materials have defects, likely Cu atom deficiencies, that contribute to itinerant charge carriers. These conductivity values are also significantly higher than those of the chalcopyrite CuInTe₂ (σ = 22 Ω⁻¹cm⁻¹ at 300 K to 70 Ω⁻¹cm⁻¹ at 600 K), which does exhibit the positive temperature trend expected for intrinsic semiconductors.⁴⁰

The temperature dependence of the Seebeck coefficient is displayed in Figure 5. For all compounds, there is an increase in the thermopower with an increase in temperature, which is typical behavior for both degenerate and extrinsic semiconductors. The Seebeck coefficient for Cu₅Sn₂Se₇ was found to be +16 μV K⁻¹ - +40 μV K⁻¹ within the temperature range of 300 K - 630 K. These results are in good agreement with Fan et al., who reported values of +20 μV K⁻¹ - +43 μV K⁻¹.²² The intended and desired overall increase in the Seebeck coefficient was observed with the introduction of Zn, resulting in +80 μV K⁻¹ - +165 μV K⁻¹. The Zn doped sample has values comparable

to Cu₂ZnSnSe₄ (S = +50 μV K⁻¹ - +110 μV K⁻¹ from 340 K - 630 K)³⁶ as well as Cu₂SnSe₃ (S = +90 μV K⁻¹ - +150 μV K⁻¹ from 300 K - 600 K).³⁵ The positive sign of the Seebeck coefficient is indicative of dominant *p*-type character, which is typical for Cu chalcogenides, in accord with the postulated, common Cu defects. One such example is Cu₂S, in which Zhao et al. found extrinsic semiconducting behavior from 400 K - 650 K, which was a result of Cu deficiencies.⁴¹ The latter Seebeck values are in the desired range for thermoelectric materials, whereas *p*-type materials with S < +50 μV K⁻¹ need further enhancements.

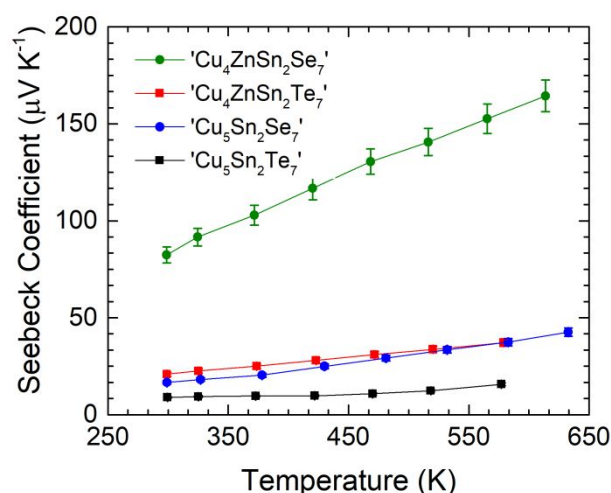


Fig. 5 Temperature dependence of the Seebeck coefficient of 'Cu₅Sn₂Te₇' and 'Cu₄ZnSn₂Te₇' with 5% error bars.

At 300 K, we found a Seebeck coefficient of +9 μV K⁻¹ for Cu₅Sn₂Te₇, in qualitative agreement with the earlier published value of +6 μV K⁻¹.²³ With the inclusion of Zn, the Seebeck coefficient experienced an over two-fold improvement at 300 K, from +9 μV K⁻¹ (Cu₅Sn₂Te₇) to +21 μV K⁻¹ (Cu₄ZnSn₂Te₇). At 575 K, a maximum of +37 μV K⁻¹ was obtained for Cu₄ZnSn₂Te₇. Even with the inclusion of Zn, the thermopower values are still significantly lower than those of Cu₂CdSnTe₄ (S = +60 μV K⁻¹ at 600 K)³⁹ and CuInTe₂ (S = +250 μV K⁻¹ at 600 K).⁴⁰

The increase of the Seebeck coefficient can be attributed to the decrease in carrier concentration with the introduction of Zn, as the carrier concentration is almost inversely proportional to the thermopower.⁴² The Seebeck coefficient for degenerate semiconductors can be expressed via $S = \frac{8\pi^2 k_B^2}{3eh^2} m^* \left(\frac{\pi}{3n}\right)^{2/3}$, where k_B is the Boltzmann constant, e is the charge of an electron, m^* is the average effective mass, and T is the temperature. Boltzmann transport calculations were carried out on Cu₄ZnSn₂Te₇, which revealed Seebeck coefficients in excess of +300 μV K⁻¹ in the vicinity of the Fermi level (Figure 6). There is thus a possibility that such high values could be experimentally obtained, if for example the apparent Cu atom defects could be minimized, or more Zn could be introduced.

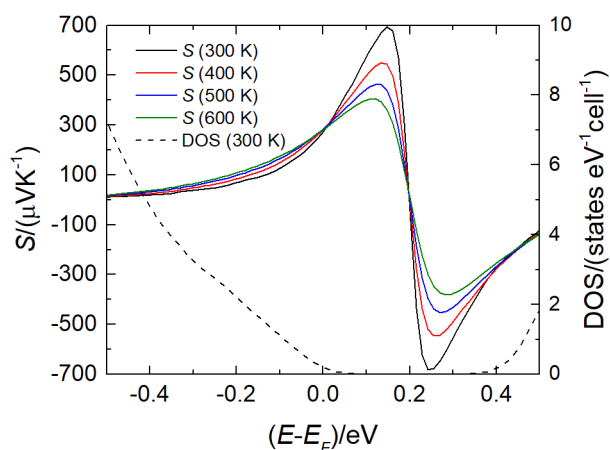


Fig. 6 Calculated Seebeck coefficient and density of states relative to the Fermi energy for $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$.

An overall, desired decrease in the thermal conductivity was also observed with the introduction of Zn for both the selenide and the telluride (Figure 7). The reduction in the thermal conductivity is a direct consequence from decreasing the electrical conductivity. The thermal conductivity is a summation of two components: electrical (κ_e) and lattice (κ_L) (Figure S4). The electrical component of the thermal conductivity can be derived using the Wiedemann-Franz law, $\kappa_e = L \sigma T$ (where L is the Lorenz number). Due to all samples investigated here displaying extrinsic semiconducting-behavior, the Lorenz number was estimated by using the equation $L = \left(1.5 + \exp\left[\frac{-|S|}{116 \mu\text{V K}^{-1}}\right]\right) 10^{-8} \text{ V}^2 \text{ K}^{-2}$.⁴³ The lattice component can then be estimated by subtracting the electrical component from the total thermal conductivity.

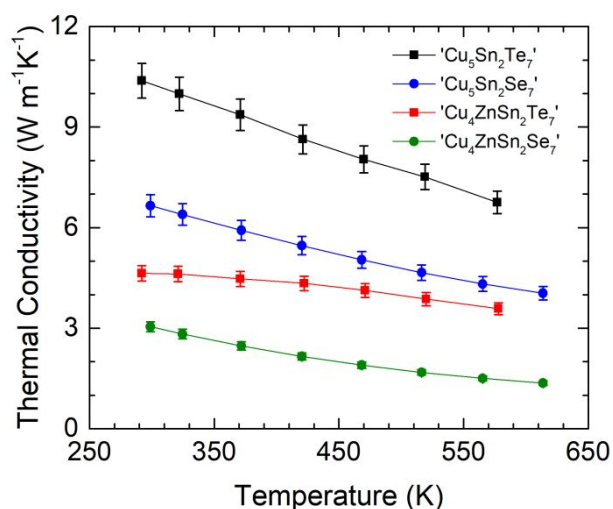


Fig. 7 Temperature dependence of the thermal conductivity of ' $\text{Cu}_5\text{Sn}_2\text{Q}_7$ ' and ' $\text{Cu}_4\text{ZnSn}_2\text{Q}_7$ ' with 5% error bars.

The thermal conductivity values obtained for $\text{Cu}_5\text{Sn}_2\text{Se}_7$ are $6.7 \text{ W m}^{-1}\text{K}^{-1}$ - $4.0 \text{ W m}^{-1}\text{K}^{-1}$ from 300 K - 630 K (which qualitatively match Fan et al. with values of $5.3 \text{ W m}^{-1}\text{K}^{-1}$ - $3.5 \text{ W m}^{-1}\text{K}^{-1}$ within the same temperature range²²). In accord with its lower electrical conductivity, $\text{Cu}_4\text{ZnSn}_2\text{Se}_7$ had lower thermal

conductivity values of $3.0 \text{ W m}^{-1}\text{K}^{-1}$ - $1.4 \text{ W m}^{-1}\text{K}^{-1}$. Again, these values are quite comparable to $\text{Cu}_2\text{ZnSnSe}_4$ ($\kappa = 1.9 \text{ W m}^{-1}\text{K}^{-1}$ - $1.1 \text{ W m}^{-1}\text{K}^{-1}$),³⁶ but higher than those of Cu_2SnSe_3 ($\kappa = 1.5 \text{ W m}^{-1}\text{K}^{-1}$ - $0.7 \text{ W m}^{-1}\text{K}^{-1}$ between 300 K and 600 K).³⁵ The thermal conductivity values for $\text{Cu}_4\text{ZnSn}_2\text{Se}_7$ are somewhat on the high side, as many of the state of the art thermoelectric materials and Cu chalcogenides have κ values below $1 \text{ W m}^{-1}\text{K}^{-1}$.^{37,41,44}

The telluride $\text{Cu}_5\text{Sn}_2\text{Te}_7$ also displayed thermal conductivity values higher than that of the sample containing Zn ($\kappa = 10 \text{ W m}^{-1}\text{K}^{-1}$ - $6.8 \text{ W m}^{-1}\text{K}^{-1}$ versus $4.6 \text{ W m}^{-1}\text{K}^{-1}$ - $3.6 \text{ W m}^{-1}\text{K}^{-1}$, respectively, in the range of 300 K - 575 K). The room temperature thermal conductivity result for $\text{Cu}_5\text{Sn}_2\text{Te}_7$ is in reasonable agreement with Adhikary et al. ($15 \text{ W m}^{-1}\text{K}^{-1}$).²³ The thermal conductivity values of $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$ are comparable to $\text{Cu}_2\text{CdSnTe}_4$ ($5.0 \text{ W m}^{-1}\text{K}^{-1}$ - $2.0 \text{ W m}^{-1}\text{K}^{-1}$)³⁹ and CuInTe_2 ($6.0 \text{ W m}^{-1}\text{K}^{-1}$ - $2.5 \text{ W m}^{-1}\text{K}^{-1}$)⁴⁰ within the same temperature range. Although substantial improvements were made with the addition of Zn, the thermal conductivity values are still too high for a thermoelectric material. We obtained lattice thermal conductivity values of $2.9 \text{ W m}^{-1}\text{K}^{-1}$ for $\text{Cu}_4\text{ZnSn}_2\text{Se}_7$ and $2.5 \text{ W m}^{-1}\text{K}^{-1}$ for $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$ at room temperature.

The figure of merit curve of $\text{Cu}_5\text{Sn}_2\text{Se}_7$ nicely resembles the one calculated in 2016.²⁴ The figure of merit doubled for the Zn containing selenide, from 0.10 to 0.20 at 630 K (Figure 8), and is higher than that of $\text{Cu}_2\text{ZnSnSe}_4$ (maximum zT of 0.16 at 630 K),³⁶ but significantly lower than Cu_2SnSe_3 , which attained a maximum zT of 0.95 at 800 K.³⁵ This could be attributed to Cu_2SnSe_3 having a much larger Seebeck coefficient as well as lower thermal conductivity values.

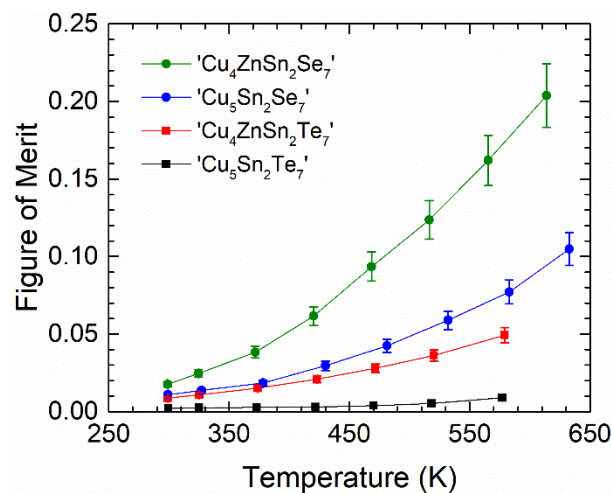


Fig. 8 Temperature dependence of the figure of merit of ' $\text{Cu}_5\text{Sn}_2\text{Q}_7$ ' and ' $\text{Cu}_4\text{ZnSn}_2\text{Q}_7$ ' with 10% error bars.

The quaternary telluride experienced a five-fold improvement in the figure of merit after incorporation of Zn, with a maximum of 0.05 for $\text{Cu}_4\text{ZnSn}_2\text{Te}_7$ at 575 K, whereas the corresponding zT for $\text{Cu}_5\text{Sn}_2\text{Te}_7$ was 0.009. For comparison, the maximum figure of merit value reported for $\text{Cu}_2\text{CdSnTe}_4$ was 0.12 at 510 K,³⁹ and 0.60 at 850 K for CuInTe_2 .⁴⁰

Conclusions

By doping both the selenide and telluride materials with Zn, the carrier concentration decreased, resulting in an overall decrease in the electrical conductivity, which had values that are comparable to some of the stannites and kesterites. Although substantial improvements were made, especially in case of the less toxic selenide, high zT values (closer to unity) were not possible due to low Seebeck coefficient and relatively high thermal conductivity values. It can be predicted based on our Boltzmann calculations that with the introduction of more Zn, higher thermopower values would be possible, but at the cost of a decrease in the electrical conductivity. Furthermore, due to the diamond-like structures, as well as the lack of heavy atoms for mass fluctuations, the lattice components of the thermal conductivity with $2.5 \text{ W m}^{-1}\text{K}^{-1}$ – $2.9 \text{ W m}^{-1}\text{K}^{-1}$ at 300 K need to be improved as well.

The tetrahedrites with their high zT values are considered to include some of the best tellurium-free copper chalcogenide TE materials in the mid temperature range. This is due to their complex frameworks and heavy atoms, which increases phonon scattering which reduces the thermal conductivity, while retaining a high electrical conductivity and thermopower values. One such example is $\text{Cu}_{11}\text{MnSb}_4\text{S}_{13}$, whose electrical conductivity and Seebeck coefficient were comparable to those of $\text{Cu}_4\text{ZnSn}_2\text{Se}_7$ ($\sigma = 200 \text{ } \Omega^{-1}\text{cm}^{-1}$, $S = 125 \text{ } \mu\text{V K}^{-1}$ at 575 K), however the thermal conductivity was very low ($\kappa = 0.30 \text{ W m}^{-1}\text{K}^{-1}$ at 575 K), which culminated in a high zT of 1.1 at 575 K.³⁷ Future work on the materials presented here could include attempts in which mass fluctuations are introduced, or nanostructuring in order to further reduce the thermal conductivity of these compounds.

Author contributions

Cheryl Sturm: conceptualization, data curation, formal analysis; investigation, visualization, writing – original draft; Leilane R. Macario: formal analysis; Takao Mori: data curation, formal analysis, writing – review & editing; Holger Kleinke: conceptualization, funding acquisition, supervision, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Authors appreciate the financial support from the Natural Sciences and Engineering Research Council of Canada in form of a Discovery Grant (RGPIN-2015-04584). TM acknowledges support from JSPS KAKENHI JP16H06441 and JST Mirai JPMJMI19A1, CREST JPMJCR19Q4.

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