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Synthesis, crystal structure, and transport properties of Cu_2SnTe_3

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ABSTRACT

Polycrystalline Cu_2SnTe_3, a ternary chalcogenide forming in a cubic crystal structure, was synthesized by reaction of the constituent elements before annealing and densification by Spark Plasma Sintering. The structural and chemical analyses were investigated using powder X-ray diffraction and Rietveld refinement. Low temperature transport properties are reported and indicate that this cubic phase has metallic conduction and possessing relatively high thermal conductivity values with a relatively large lattice contribution. The results presented are intended to expand on the research into ternary chalcogenides in order to further advance the fundamental investigation of these materials as they continue to be of fundamental interest for potential energy-related applications.

1. Introduction

In addition to binary chalcogenides such as Bi_2Te_3 and PbTe [1], ternary [2–4] and quaternary chalcogenides [4–7] have recently attracted attention for potential photovoltaic applications, due to their low cost and high conversion efficiency solar cell devices. Furthermore, the intrinsically low thermal conductivity, κ, they often possess is attributed to their crystal structures, making them of interest as potential thermoelectric materials [8,9]. In the case of thermoelectric applications, these quaternary chalcogenides possess relatively wide band gaps, a property that is typically not of interest for thermoelectric applications [10]. However, the electrical properties can be modified by appropriate doping and/or variations in stoichiometry [9]. Certain compositions also display unique transport properties directly attributable to their structure and bonding [11,12], while others have been synthesized in nanocrystalline form in order to investigate nano-scale effects on their thermoelectric properties [13,14].

Most recently the synthesis and physical properties of new ternary and quaternary chalcogenides have been of intense interest, not only due to their fundamental properties but also for applied research towards energy-related applications [15–19]. All these compositions can be derived from zinc-blend structured binaries by cation sublattice substitution [20,21]. Here we report on the synthesis, structure and transport properties of Cu_2SnTe_3. Although substantial research has been reported on Se-based I_2-IV-VI_3 materials, for example Cu_2SnSe_3 as a material with potential for thermoelectric applications [22–24], little has been reported on Cu_2SnTe_3. In fact, the I_2-IV-VI_3 compositions have been reported to form in the monoclinic, tetragonal and cubic structure types [25–27], while the early work on this material system did not provide a description or evidence of the specific structure types for the compositions reported [28,29]. Our work focuses on the cubic phase of Cu_2SnTe_3, a material that has not been extensively investigated, with low temperature transport properties reported here for the first time.

2. Experimental section

Cubic Cu_2SnTe_3 was prepared by direct reaction of the high purity elements. Cu powder (99.99%, Alfa Aesar), Sn powder (99.99%, Alfa Aesar), and Te powder (99.8%, Acros Organics) were loaded into a silica ampoule in the nominal composition Cu_2SnTe_3 and sealed in a quartz tube under vacuum. The specimen was reacted in a resistive furnace at 973 K and held at this temperature for 7 days before it was air quenched to room temperature. It was then ground into fine powder, cold pressed into a pellet and annealed for 10 days at 673 K. The resulting pellet was ground into fine powder, sieved (~325 mesh) and loaded into a custom-designed WC die and punch assembly that was lined with graphite foil, in order to prevent reaction with the surrounding material, for densification by spark plasma sintering (SPS) at 573 K and 400 MPa for 30 min under vacuum. The maximum temperature for densification was evaluated by differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) using a TA Instruments Q600. A high-density polycrystalline (>98%) specimen was obtained from densification.

Powder X-ray diffraction (XRD) and Rietveld refinement was employed to examine the structure and chemical composition of the

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specimen. Powder XRD data was collected with a Bruker D8 Focus diffractometer in Bragg-Brentano geometry using Cu Kα radiation and a graphite monochromator. The Rietveld method was used for refinement utilizing GSASII [30]. The densified pellet was cut using a wire saw into a 2 mm × 2 mm x 5 mm parallelepiped for low temperature transport measurements. Temperature dependent four-probe resistivity (ρ) Seebeck coefficient (S) and steady-state thermal conductivity (κ) measurements from 12 K to 300 K were performed on a custom-built radiation shielded vacuum probe [31,32] with measurement uncertainties of 7%, 6%, and 8% for ρ, S, and κ measurements, respectively.

3. Results and discussion

The Rietveld refinement profile of the powder XRD data for Cu_2SnTe_3 is shown in Fig. 1, including the observed data, calculated data and difference. Table 1 contains the details of the refinement results and Table 2 shows the atomic coordinates and displacement parameters obtained. The cubic space group $F\bar{4}3m$ (No 216) was confirmed by our refinement and analyses. As indicated above, previous reports [25–27] on I_2-IV-VI_3 compositions indicate that monoclinic, tetragonal and cubic phases are possible; however, when investigating our XRD data additional reflections that should be present for non-cubic structure types were not observed therefore these phases were rejected. Our XRD data and refinement results clearly indicated the cubic phase, with no vacancies. Copper and Sn share the same crystallographic site, 4*a*, with an occupancy of 66% and 33%, respectively, and Te is located at the 4*c* crystallographic site. Small amounts of secondary phases were observed in our XRD data and thus refined and included in our refinement results.

Fig. 2 and 3 show the low temperature ρ and S data, respectively, from 12 to 300 K. Berger et al. [33] reported Cu_2SnTe_3 to be a p-type metal; however, only data above room temperature were reported. Our low temperature ρ data indicates metallic conduction, with ρ values increasing with increasing temperature for the entire temperature range, indicative of metallic behavior. This is in contrast to monoclinic Cu_2SnSe_3 that displays semiconducting properties and is of interest for potential thermoelectrics applications [22–24]. The magnitude of S is small and positive throughout the measured temperature range. The temperature dependence of S increases with increasing temperature up to 50 K where a change in slope (dS/dT) is observed, see Fig. 3. For metals such a temperature dependence may be due to phonon drag effects [34]. This may well be the case here as lower energy phonons, that contribute to the phonon-drag effect, are more readily scattered by higher energy heat-conducting phonons at elevated (>50 K) temperatures. One can estimate the Debye temperature (θ_D) from $T_p \approx \theta_D/5$, where T_p is the temperature region where the phonon-drag is dominant, resulting in an estimated θ_D value of 225 K for cubic Cu_2SnTe_3 [35].

The low temperature κ values are shown in Fig. 4. The data show that this material possesses relatively high κ values indicative of a covalently bonded material with a crystal structure of high symmetry, even though it contains heavy constituent elements. We estimate the electronic contribution to κ using the Wiedemann-Franz relation ($\kappa_e = L_0T/\rho$) with Lorenz number (L_0) taken to be 2.0 x 10^{-8} V^2/K^2 for heavily doped semiconductors [9,36]. Our estimate indicates that a large contribution to κ comes from the lattice component, κ_L, where $\kappa_L = \kappa - \kappa_e$, for example $\kappa_L \cong$ 83% of κ at room temperature. The contribution from κ_e is therefore insignificant compared with κ_L, as is the case for other materials with atypical metallic conduction [37].

4. Conclusion

Polycrystalline Cu_2SnTe_3 was synthesized and its structure and low temperature transport properties investigated. Our XRD data and refinements confirm the cubic crystal structure. Temperature-dependent electrical transport data show metallic behavior, however the change in slope of our temperature-dependence S data is attributed to the

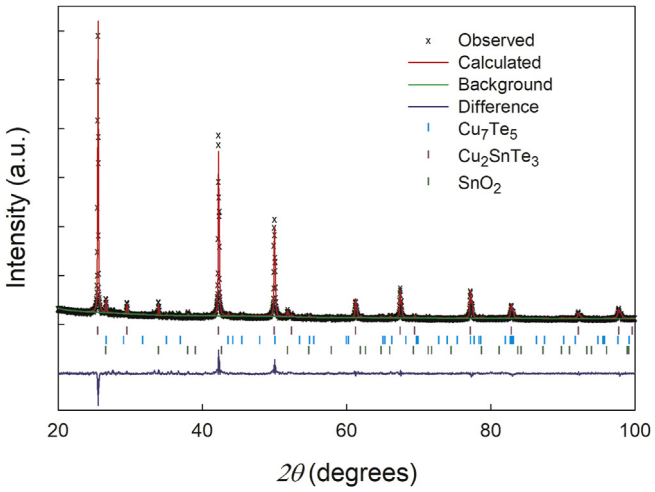

Fig. 1. Rietveld refinement results for Cn_2SnTe_3, including profile fit, profile difference, and profile residuals, with Bragg positions of each phase indicated. Also refined were SnO_2 and Cu_7Te_4 impurities, which were identified upon careful inspection and analyses of our XRD data and estimated to be 5.5% and 2.5%, respectively.

Table 1
Rietveld refinement results for Cu_2SnTe_3.

Nominal Composition	Cu_2SnTe_3.
Space Group	$F\bar{4}3m$
a (Å)	6.0484(6)
V ($Å^3$)	221.27(6)
Radiation	Graphite Monochromated CuKα (1.54056 A)
Dcalc. (g/cm3)	6.28(4)
2θ range (deg.)	20–100
Step Width (deg.)	0.025
wR_p, R_p	0.0768, 0.0607
Goodness of Fit	1.55

Table 2
Atomic coordinates and displacement parameters.

Atoms	x (Å)	y (Å)	z (Å)	Uiso (Å2)	Occupancy	multiplicity
Cu	0	0	0	0.0103(3)	0.66	4
Sn	0	0	0	0.0250(0)	0.33	4
Te	0.25	0.25	0.25	0.0196(8)	1	4

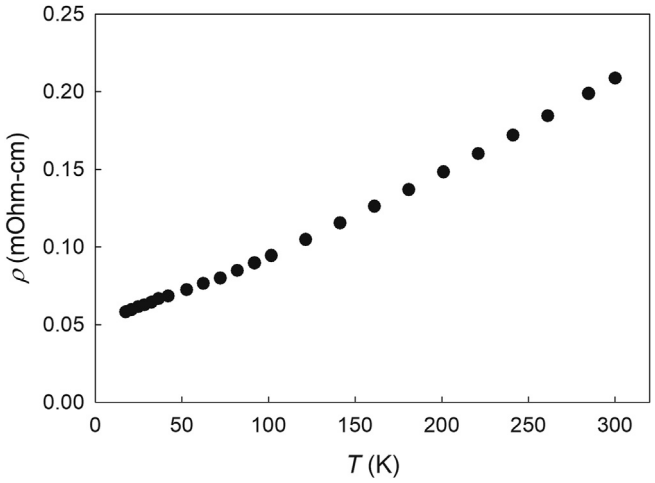

Fig. 2. Temperature dependent S for Cn_2SnTe_3.

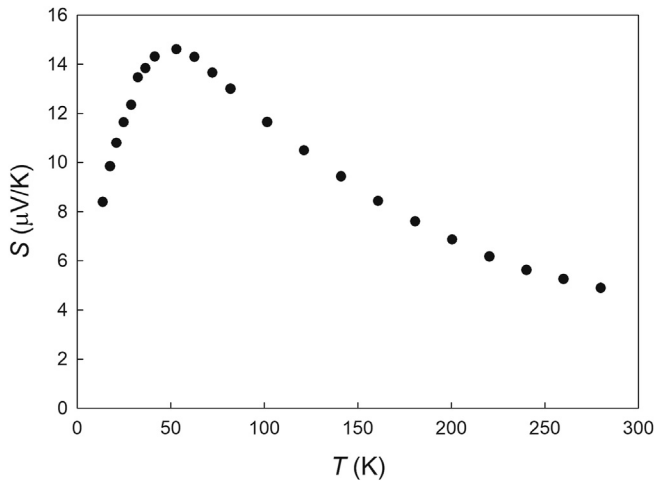

Fig. 3. Temperature dependent ρ of Cn_2SnTe_3.

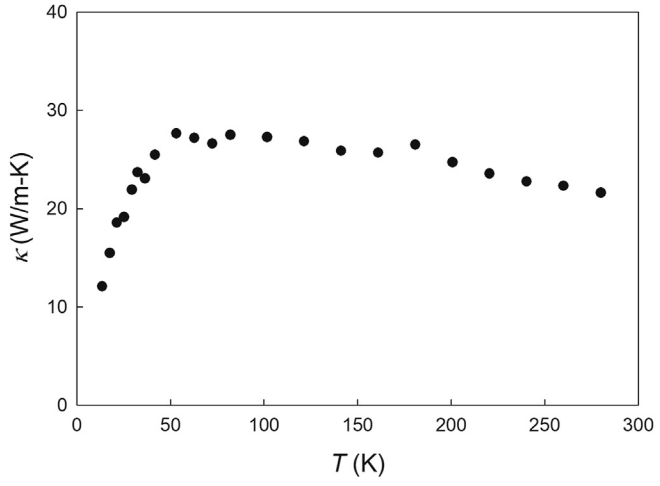

Fig. 4. Temperature dependent κ for Cn_2SnTe_3.

phonon-drag effect. We estimate θ_D to be 225 K from the temperature region where phonon-drag is dominant. The main contribution to κ is from the lattice. These results build on the current research into ternary chalcogenides as they continue to be of interest for energy-related applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Noha Alzahrani: Formal analysis, Data curation. **Dean Hobbis:** Data curation. **George S. Nolas:** Conceptualization.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jssc.2020.121566.

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