Synthesis, crystal structure and electrical properties of the tetrahedral quaternary chalcogenides
 $\text{CuM}_2\text{InTe}_4$ ($\text{M} = \text{Zn}, \text{Cd}$)

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Abstract

Quaternary chalcogenides form a large class of materials that continue to be of interest for energy-related applications. Certain compositions have recently been identified as possessing good thermoelectric properties however these materials typically have the kesterite structure type with limited variation in composition. In this study we report on the structural, optical and electrical properties of the quaternary chalcogenides $\text{CuZn}_2\text{InTe}_4$ and $\text{CuCd}_2\text{InTe}_4$ which crystallize in the modified zinc-blende crystal structure, and compare their properties with that of $\text{CuZn}_2\text{InSe}_4$. These p-type semiconductors have direct band gaps of about 1 eV resulting in relatively high Seebeck coefficient and resistivity values. This work expands on the research into quaternary chalcogenides with new compositions and structure types in order to further the fundamental investigation of multinary chalcogenides for potential thermoelectrics applications.

Keywords: Quaternary chalcogenides, thermoelectrics, electrical transport

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Introduction

Quaternary chalcogenides form a large class of materials generally composed of earth-abundant and nontoxic elements that are of interest for potential applications in solar-cell absorbers [1], photo catalysts for solar water splitting [2], and magneto-optic and magneto-ferroics [3, 4]. The crystal structure can accommodate a large number of different elements at different lattice sites thus allowing for relatively complex electronic and structural properties as compared to binary or ternary chalcogenide materials. This freedom and complexity has been exploited for different applications, for example, most recently several quaternary chalcogenides have been shown to be of interest for thermoelectrics applications [5-8]. Most of this work, however, has focused on a narrow range of compositions, with the kesterite or stannite crystal structures [9, 10]. New materials investigations with specific desirable properties is therefore of interest in the search for new thermoelectric materials.

In this study we investigate the optical and electrical properties of the quaternary chalcogenides $\text{CuCd}_2\text{InTe}_4$ and $\text{CuZn}_2\text{InTe}_4$ with the cubic modified zinc-blende crystal structure. This investigation is intended as part of the continuing effort to explore different quaternary chalcogenide structure types and compositions in an effort to understand their fundamental properties in order to investigate their potential for thermoelectrics applications.

Experimental

Polycrystalline $\text{CuCd}_2\text{InTe}_4$, $\text{CuZn}_2\text{InTe}_4$ and $\text{CuZn}_2\text{InSe}_4$ were prepared as follows. Cu Powder (99.9%, Alfa Aesar), Zn shot (1-6mm, 99.9999%, Alfa Aesar) or Cd shot (1-3mm, 99.9999%, Alfa Aesar), In ingots (99.9995%, Alfa Aesar), and Te powder (99.8%, Acros Organics) or Se powder (99.999%, Alfa Aesar) were loaded into silica ampoules with a nominal stoichiometry of

CuM_2InQ_4 ($\text{M} = \text{Zn, Cd; Q} = \text{Se, Te}$).¹ A conservative estimate of the uncertainty in the loaded compositions is about $\pm 0.01\%$. Each silica ampoule was put into a quartz tube and evacuated to 10^{-3} Torr before sealing. The elements were reacted at 973 K for 4 days. The furnace was then turned off and the reaction tubes cooled to room temperature. All specimens were ground into fine powders, cold pressed into pellets, and then sealed under vacuum for annealing. $\text{CuZn}_2\text{InSe}_4$ was annealed at 873 K for 21 days while the other two compositions were annealed at 723 K for 21 days. After annealing, the products were again ground into fine powders and sieved to 325 mesh ($< 50\mu\text{m}$) inside a N_2 glovebox before loading into graphite dies for hot pressing. Densification was carried out by hot pressing at 723 K for $\text{CuZn}_2\text{InSe}_4$, and 623 K for $\text{CuZn}_2\text{InTe}_4$ and $\text{CuCd}_2\text{InTe}_4$ with 150 MPa for 3 h under N_2 flow. The density of each hot pressed pellet was determined by measurement of the pellet dimensions and weight after polishing the surfaces. These measurements indicated that high-density polycrystalline specimens ($>92\%$) were obtained.

Powder X-ray diffraction (XRD) data were collected with a Bruker D8 Focus diffractometer in Bragg–Brentano geometry using $\text{Cu K}\alpha$ radiation and a graphite monochromator and refined employing the Rietveld method using the GSAS suite of program [11]. Energy dispersive X-ray analysis (EDS) of the hot-pressed pellets was performed with an Oxford INCA X-Sight 7582M (INCA software) equipped scanning electron microscope (SEM, JEOL JSM-6390LV). The average atomic ratios were calculated from at least 5 data sets obtained from random positions of

¹ Certain commercial equipment, instrumentation, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of

Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

the hot-pressed pellet for each specimen. Optical diffuse absorbance measurements were performed at room temperature using a JASCO V-670 UV-Vis double beam Spectrophotometer equipped with a 60 mm diameter integrating sphere. The pulverized powder for each specimen was pressed between two quartz glass slides. Absorbance data were collected over the 200 to 2500 nm wavelength range and the optical band gap was determined as the intersection point between the energy axis at the absorption offset and the line extrapolated from the linear portion of the absorption edge. The densified polycrystalline pellets were cut into parallelepipeds of dimensions 2mm x 2mm x 11mm for high temperature Seebeck coefficient, S , and electrical resistivity, ρ , measurements using a custom-designed and constructed apparatus at NIST (expanded uncertainty of 1.5% and 1.1% for S and ρ , respectively) [12]. In addition, parallelepipeds of dimensions 0.5 mm $\times$ 2 mm $\times$ 5 mm were cut for four probe Hall measurements and data was collected at multiple positive and negative magnetic fields in order to eliminate voltage probe misalignment effects.

Results and Discussion

Figure 1 shows the observed and calculated XRD patterns and the difference profiles for each specimen. The crystallographic details are given in Table 1. The refinement results indicate that all three specimens have the cubic zinc-blende structure with $F\bar{4}3m$ space group and 4 formula units per unit cell, consistent with a random arrangement of the cations on the cation position of the zinc blende structure. The lattice constants for all three compounds are in agreement with those reported previously [13]. There are two crystallographic sites in the structure [14] with the

Zn and S atoms located at the crystallographic $4a$ and $4c$ sites, respectively. Each site is surrounded by four different atoms in a tetrahedral geometry. The crystal structural relationship between ZnS and CuM_2InQ_4 ($\text{M} = \text{Zn, Cd}$; $\text{Q} = \text{Se, Te}$) can be understood by cross substitution of cations to obtain higher order materials [15]. $(\text{Zn}^{2+})_4$ in ZnS replaced by three different metals having different oxidation states $(\text{Cu}^{1+}(\text{M}^{2+})_2\text{In}^{3+})$ at the crystallographic $4a$ site to satisfy charge balance. EDS semi-quantitative analyses on the densified pellet suggest that the elemental ratio ($\text{Cu}:\text{M}:\text{In}:\text{Q}$) in these compounds is 1:2:1:4. Figure 2 shows the SEM and EDS elemental mapping image of a hot-pressed rectangular piece of $\text{CuZn}_2\text{InSe}_4$ as representative of our analysis. EDS analysis indicated that each element was uniformly distributed, as expected based on the XRD and refinement results.

The UV-Vis diffuse absorbance spectra are shown in Figure 3 and include $\text{CuZn}_2\text{InSe}_4$ in order to compare with our tellurium compositions. From these data values for the optical band gaps of the three compositions, $\text{CuCd}_2\text{InTe}_4$, $\text{CuZn}_2\text{InTe}_4$ and $\text{CuZn}_2\text{InSe}_4$, are 0.85, 1.05 and 1.10 eV, respectively. The sharp absorption onset for all three specimens implies that all have a direct optical band gap. Photoconductivity studies conducted by Anedda et al. [16] indicated the band gaps of $\text{Cu}_x\text{Ag}_{1-x}\text{Cd}_2\text{InTe}_4$ to be approximately 1 eV, in general agreement with our measurements. These results also indicate that the band gaps of quaternary chalcogenides are similar to those of $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ [17, 18], two materials with the kesterite structure type.

Temperature dependent S and ρ from 300 to 650 K are shown in the Figures 4a and 4b, respectively. Polycrystalline $\text{CuZn}_2\text{InSe}_4$ was highly resistive, higher than what our instrument can measure, with $S \approx 400 \mu\text{V/K}$ at room temperature. The positive S values for both

CuZn₂InTe₄ and CuCd₂InTe₄ throughout the measured temperature range imply that holes are the majority carriers. The ρ and S values for CuCd₂InTe₄ increase with increasing temperature up to about 550 K at which point they decrease with increasing temperature. For the case of CuZn₂InTe₄ ρ and S plateau at 600 K. The weak temperature dependence of ρ for CuZn₂InTe₄ may indicate a smaller activation energy for this material than that estimated by our UV-Vis measurements and suggests conduction originating from donor states. Room temperature hall measurements indicate p -type conduction with room temperature carrier concentrations, p , of $3.7 \times 10^{19} \text{ cm}^{-3}$ and $7.4 \times 10^{18} \text{ cm}^{-3}$ for CuZn₂InTe₄ and CuCd₂InTe₄, respectively, and corresponding room temperature Hall mobilities of $9.1 \text{ cm}^2/\text{V-sec}$ for CuZn₂InTe₄ and $6.0 \text{ cm}^2/\text{V-sec}$ for CuCd₂InTe₄; the mobility for CuCd₂InTe₄ is in good agreement with a previously reported study [19].

In the single parabolic band model, [20]

$$S = \frac{k_B}{e} \left(\frac{(2+t)F_{1+t}(\eta)}{(1+t)F_t(\eta)} - \eta \right)$$

and

$$p = \frac{4\pi(2m_e k_B T)^{3/2}}{h^3} \left(\frac{m^*}{m_e} \right)^{3/2} F_{1/2}(\eta)$$

where $\eta (=E_F/k_B T)$ with E_F being the Fermi energy) is the reduced Fermi energy, t is the exponent of the energy dependence of the electron mean free path, F_t is the Fermi integral and m_e is the mass of the free electron and m^* is the effective mass. In the case of acoustic phonon scattering from lattice vibrations $t = 0$ while for ionized impurity scattering $t = 2$. Used the intermediate value of $t = 1$ to accommodate both lattice vibrations and impurity scattering, [21] we estimate

m^* to be $0.6 m_e$ for $\text{CuZn}_2\text{InTe}_4$ and $0.7 m_e$ for $\text{CuCd}_2\text{InTe}_4$. Similar values for m^* were reported for quaternary stannites and kesterites, $\text{Cu}_2\text{ZnSnS}_4$ ($0.84 m_e$) and $\text{Cu}_2\text{ZnSnSe}_4$ ($0.66 m_e$) for example; [22] however, m^* for p-type stannite $\text{Cu}_2\text{ZnGeSe}_4$ was reported to be $1.2 m_e$ with a Hall mobility of $\sim 3 \text{ cm}^2/\text{V}\cdot\text{sec}$. [23] This is a factor of two lower than that of $\text{CuZn}_2\text{InTe}_4$, as expected for this low m^* materials. The power factor $S^2\sigma$ [24] for $\text{CuCd}_2\text{InTe}_4$ and $\text{CuZn}_2\text{InTe}_4$ is shown in Figure 4c. $S^2\sigma$ for $\text{CuZn}_2\text{InTe}_4$ is higher than that of $\text{CuCd}_2\text{InTe}_4$, a factor of 2 larger than that of $\text{Cu}_2\text{CdSnSe}_4$, and similar to that of $\text{Cu}_2\text{Cd}_{0.9}\text{Mn}_{0.1}\text{SnSe}_4$ [25]. It may be possible to increase $S^2\sigma$ in these materials by doping [26] or increasing the Cu content on the 4a site, as is the case for $\text{Cu}_2\text{ZnSnSe}_4$ [8]. Another possibility is substitutional doping for Zn/Cd across the compositional range. This may also affect the band structure of these materials, thereby changing their electrical properties.

Conclusion

Polycrystalline quaternary chalcogenides $\text{CuZn}_2\text{InTe}_4$ and $\text{CuCd}_2\text{InTe}_4$ were synthesized and their structure, electrical and optical properties were investigated and compared with that of $\text{CuZn}_2\text{InSe}_4$. All three compounds possess a zinc-blende type structure with space group $F\bar{4}3m$ (# 216). The $\text{CuZn}_2\text{InSe}_4$ compound has the largest band gap (1.10 eV) and a very high resistivity, beyond the measurement capabilities of the instrument used. Doping studies may lead to higher $S^2\sigma$ values and may help elucidate their potential for thermoelectric applications. Moreover, the optical band gaps of these materials suggest that they may also be of interest for further study for photovoltaics applications.

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Table1: EDS and XRD Refinement results for the three compositions prepared for this study

Refined Composition	CuZn ₂ InSe ₄	CuZn ₂ InTe ₄	CuCd ₂ InTe ₄
EDS Composition	Cu _{1.0(3)} Zn _{2.0(2)} In _{1.0(1)} Se _{3.7(3)}	Cu _{1.0(4)} Zn _{2.0(6)} In _{1.0(3)} Te _{3.9(4)}	Cu _{0.9(4)} Cd _{2.0(2)} In _{1.0(1)} Te _{3.9(3)}
Space Group, Z		$F\bar{4}3m$ (#216), 4	
Lattice constant (Å)	5.73157(5)	6.15203 (9)	6.34257(4)
Volume (Å ³)	188.288	232.839	255.151
Radiation	Graphite monochromated CuK α (1.54056 Å)		
D _{cal.} (g/cm ³)	5.512	5.845	5.946
2 θ range (deg.)	15-100	10-100	10-100
Step width (deg.)	0.01	0.02	0.02
Reduced χ^2	5.841	4.216	3.155
R _p , wR _p	0.0438, 0.0606	0.0353, 0.0479	0.0324, 0.0418
U _{iso} (Å ²) for Cu/Cd/Zn/In	0.03339	0.02553	0.03023
U _{iso} (Å ²) for Se/Te	0.02709	0.02329	0.03162

Atomic positions: Cu/Zn/Cd/In, 4a (0, 0, 0); Se/Te, 4c (0.25, 0.25, 0.25)

Figure Captions

Figure 1 Rietveld refinement results for (a) $\text{CuZn}_2\text{InSe}_4$, (b) $\text{CuZn}_2\text{InTe}_4$ and (c) $\text{CuCd}_2\text{InTe}_4$ including profile fit, profile difference and profile residuals. Figure 1d shows the projected crystal structure of CuM_2InQ_4 along the crystallographic c -axis.

Figure 2 (a) SEM and (b) EDS elemental mapping images of hot-pressed $\text{CuZn}_2\text{InSe}_4$ as an example of the analyses employed for all three specimens.

Figure 3 UV-Vis data for $\text{CuZn}_2\text{InSe}_4$ (green), $\text{CuZn}_2\text{InTe}_4$ (red) and $\text{CuCd}_2\text{InTe}_4$ (blue).

Figure 4 Temperature dependent (a) S , (b) ρ and (c) $S^2\sigma$ data for $\text{CuZn}_2\text{InTe}_4$ (up triangle) and $\text{CuCd}_2\text{InTe}_4$ (down triangle).

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Figure1

Figure2

Figure 3

Figure 4

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Synthesis, crystal structure and electrical properties of the tetrahedral quaternary chalcogenides $\text{CuM}_2\text{InTe}_4$ ($\text{M} = \text{Zn}, \text{Cd}$)

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The structural, optical and electrical properties of the quaternary chalcogenides $\text{CuZn}_2\text{InTe}_4$ and $\text{CuCd}_2\text{InTe}_4$ are reported for the first time. The unique crystal structure allows for relatively good electrical transports and therefore potential for thermoelectric applications.