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Influence of doping and solid solution formation on the thermoelectric properties of chalcopyrite semiconductors

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ABSTRACT

We have investigated the influence of zinc doping on the thermoelectric properties of $CuInTe_2$–$CuGaTe_2$ solid solution alloys. Undoped end-member compounds display typical p-type semiconducting behavior, with a negative temperature coefficient of resistivity and large Seebeck coefficient. With zinc substituting for indium or gallium, the hole concentration is increased and the electrical transport behavior evolves into that of a degenerate semiconductor, with both electrical resistivity and Seebeck coefficient increasing with temperature up to the highest temperature measured. For undoped samples the thermoelectric power factor is maximized close to 750 K, while in doped specimens the maximum occurs at much lower temperature. Substitution of gallium for indium induces significant phonon scattering and thermal conductivity reduction below 500 K. The dimensionless figure of merit rises to above unity over a range of compositions in these chalcopyrite compounds, with optimized samples reaching a figure of merit of 1.3.

1. Introduction

Thermoelectric power generation, with its ability to convert heat directly into electricity, offers the promise of enhanced efficiency for power generation at both large and small scales, from automobiles and power plants, to interstellar space propulsion. However, low device performance and high material cost have relegated it largely to niche applications. The performance of a thermoelectric material is typically characterized by zT, the dimensionless figure of merit, which is given by $zT = S^2\sigma T\kappa^{-1}$, where S is the Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity and T is temperature. Traditionally, thermoelectric materials have possessed zT values on the order of or less than unity, limiting device conversion efficiency to significantly less than 10%.

In the last two decades, however, there has been a significant resurgence in thermoelectric materials research as new concepts, synthesis strategies, and understanding have steadily pushed zT values ever higher. In particular, materials based on traditional Pb chalcogenide semiconductors, but modified to include nanostructured second phases, have undergone significant recent development. By taking advantage of a number of new approaches, including the combination of defects across length scales to scatter a wide range of phonons [1], "endotaxial" nanostructuring [2], band convergence and band engineering [3–7], anharmonicity [8–10], and resonant bonding [11] the dimensionless figure of merit has been raised to values in excess of 2.5 at high temperatures. At the same time, workers have realized that the low abundance of some elements, such as Te, and the toxicity of others, such as Pb, may place a limitation on the application of thermoelectric materials containing these elements. Recent work has sought enhanced thermoelectric performance on inexpensive and earth-abundant materials such as Mg_2Si-based compounds [12–15], organic conductors [16], inorganic–organic perovskites [17] and even materials based on natural minerals such as tetrahedrite [18–21] and earth-abundant copper sulfide [22], which offer quite good thermoelectric performance at a potentially greatly reduced cost.

The success in finding good thermoelectric performance in compounds based on natural minerals has led us to consider other potential mineral families that may provide such behavior. While tetrahedrites, of nominal composition $Cu_{12-x}Zn_xSb_4S_{13}$, are the most abundant sulfosalts in the world and a minor ore of copper, the most common copper mineral is chalcopyrite, $CuFeS_2$. This particular compound is just one of many isostructural compounds known generally as chalcopyrites, many of which have undergone development as photovoltaic materials. Given the wide range of compositions available in this family, and the corresponding wide range of energy band gaps, their potential application as thermoelectric materials deserves some scrutiny, and even the question

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of whether natural mineral chalcopyrite itself may, as in the case of tetrahedrite, serve as a source material for low-cost thermoelectrics. Indeed, Mori et al. recently reported upon their investigations of the thermoelectric properties of $CuFeS_2$ [23], while others have explored the influence of lattice defects [24] and nanostructure [25] on thermoelectricity in chalcopyrites.

As in the case of tetrahedrites, before an investigation of the natural mineral itself as source thermoelectric material can be successfully carried out, it is desirable to study the thermoelectric properties of samples produced under ideal conditions in the laboratory, in order to assess the range of capability with respect to thermoelectric behavior of this family of compounds. In fact, some experimental studies in this area have already been reported. Recent work on tellurium-based chalcopyrite materials, for instance, has shown much promise, with reported zT values in excess of unity for both $CuInTe_2$ [26] and $CuGaTe_2$ [27]. These very promising values for the figure of merit were obtained in the nominally pure ternary compounds without the use of doping to optimize the electronic properties or of solid solutions to reduce the lattice thermal conductivity. In the present work, therefore, we have undertaken an investigation of the synthesis and thermoelectric properties of $Cu[In_{1-x}Ga_x]_{1-y}Zn_yTe_2$ $(0 \leqslant x \leqslant 1;\ 0 \leqslant y \leqslant 0.15)$. Nominally divalent Zn could act as either a donor on the nominally monovalent Cu site or as an acceptor on the nominally trivalent [In, Ga]. Here, we adjust the composition to provide for the latter case, and we show that indeed Zn is a p-type dopant in these compounds with capability of modifying the electrical properties. Meanwhile, we also explore the formation of solid solutions by substitution of In for Ga in order to reduce the lattice thermal conductivity of the material. These two effects act synergistically to increase zT of optimized composition to values close to 1.3 at 850 K.

2. Materials and methods

Samples were synthesized by reacting raw starting elements (Alfa Aesar): Cu, In, Ga (99.999% each) and Zn, Te (99.9999%). Materials were weighed in stoichiometric amounts and placed in quartz ampoules, which were subsequently evacuated to less than 10^{-5} Torr and sealed with a methane–oxygen torch. Sealed ampoules were then suspended in a vertical tube furnace and heated at a rate of 1 °C min^{-1} to a temperature of 900 °C, where they were soaked for 24 h. Samples were then cooled at a rate of 1 °C min^{-1} to 600 °C, and held for another 24 h, after which they were quenched in water. The resulting ingots were then placed in an argon filled stainless steel SPEX vial and ball-milled for one hour on a SPEX Sample Prep Mixer/Mill 8000 M. The resultant powder was hot-pressed in an argon atmosphere at 90 MPa and 475 °C for 15 min. Although the ingots were fragile and contained cracks, the hot pressed specimens were high density (92% using the Archimedes method) and mechanically robust, making them suitable for transport measurements.

X-ray diffraction was performed on a Rigaku Miniflex II at room temperature, and patterns were indexed using the Jade 9 software package and database. From 80 K to 350 K the Seebeck coefficient, electrical resistivity, and thermal conductivity were measured with a standard 4-probe steady-state technique in a liquid nitrogen flow cryostat; details of this measurement setup can be found in a previous publication [28]. From 350 to 900 K the Seebeck coefficient and electrical resistivity measurements were performed on an Ulvac ZEM-3 system in an argon atmosphere. Thermal diffusivity measurements in this temperature range were obtained on a Netzsch LFA 457, and were combined with the measured densities and specific heat (Dulong-Petit values) to yield thermal conductivity values. Hall measurements were performed from 80 to 300 K, with a field strength ranging over ±1.5 T. Carrier concentration was determined using a single band model and assuming a Hall factor of unity. We estimate an uncertainty in resistivity, Hall, and Seebeck coefficient of 5% and that in thermal conductivity of 10%. The use of two different techniques at low and high temperature induces a slight discontinuity in the data at 350 K that is within the measurement uncertainty.

3. Results and discussion

3.1. XRD and lattice parameters

The X-ray diffraction patterns (Fig. 1) for all samples exhibit only a single phase indexing to the chalcopyrite crystal structure. We find that the two lattice parameters a and c characterizing this crystal structure display a linear shift with composition, as expected from Vegard's law. We do observe a fluctuation in the ratio c/a from 1.99 to 1.97 in moving from $CuInTe_2$ to $CuGaTe_2$, consistent with the published values of 2.00 [26] and 1.98 [27]. The deviation of the c/a from a value of 2.0 is due to a slight distortion of the tetrahedral arrangement around the Te atom due to the two different bond lengths (Cu-Te and In/Ga-Te). The observed XRD patterns match very well with published studies on their structure, and we conclude that our samples are all single phase chalcopyrite with little or no presence of impurity phases [29].

3.2. Electrical properties

We first studied the influence of Zn doping on the pure end member compound $CuInTe_2$. As expected, with increasing Zn we observe a decrease in electrical resistivity (Fig. 2a), as well as a decrease in Seebeck coefficient (Fig. 2b). The thermoelectric power factor $S^2\sigma$ was found to be optimized at a doping level of 1%. The addition of 1% zinc on the indium atomic site resulted in an increase in room temperature hole concentration from 5.6×10^{17} cm^{-3} to 3.4×10^{19} cm^{-3} for $CuInTe_2$, while for $CuGaTe_2$ an increase of 1.4×10^{18} to 6.2×10^{19} cm^{-3} was found. Along with the increase in carrier concentration, we see a decrease in electrical resistivity of up to two orders of magnitude at room temperature, and a change from a typical semiconductor temperature dependence, to an increasing electrical resistivity as a function of temperature, characteristic of that of a degenerately doped semiconductor. These factors confirm that the zinc is primarily located on the indium lattice site and is acting as a p-type dopant.

Subsequent to this doping study on $CuInTe_2$, we investigated the influence of Ga substitution for In in both undoped samples and samples doped at the optimum level of 1% Zn. For the undoped series, although the magnitudes differ from sample to sample, we find that the resistivity (Fig. 3a) maintains a semiconducting nature throughout the solid solution, while the Seebeck coefficient (Fig. 3b) peaks near approximately 400 K for all samples in the solid-solution. Due to the similar band gaps of the end components, we would expect this behavior [26,27]. For the undoped samples, the power factor peaks (Fig. 3c) near 750 K, with $CuGaTe_2$ having the highest value at 12 $\mu W\ cm^{-1}\ K^{-2}$, and decreases with increasing amount of indium, to 8 $\mu W\ cm^{-1}\ K^{-2}$ for $CuInTe_2$. While the values for electrical resistivity and Seebeck coefficient vary from those published, the resulting power factor is in agreement. This is expected, as Liu et al. [26] showed that annealing time can vary the electrical properties, but ultimately not the zT of the

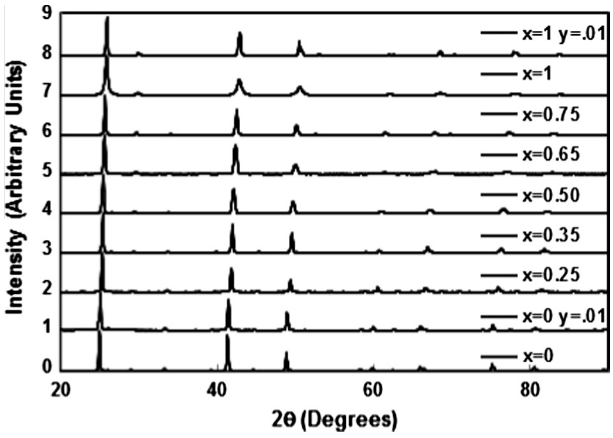

Fig. 1. X-ray powder diffraction patterns for $CuIn_{1-x}Ga_xTe_2$ and doped end members of the solid solution.