Synthesis, Preparation, and Thermoelectric Properties of Synthetic Mineral Sulfides

Jace Waybright, 2018 CNF iREU Intern

Physics Major, South Dakota State University, Brookings, SD

REU Program: 2018 Cornell NanoScale Facility International Research Experience for Undergraduates (CNF iREU) Program at the National Institute of Material Science (NIMS), Tsukuba, Ibaraki, Japan

CNF iREU Principal Investigator: Takao Mori, National Institute for Materials Science

CNF iREU Mentor: Gabin Guélou and Naohito Tsujii, National Institute for Materials Science

Primary Source of CNF iREU Funding: National Science Foundation under Grant No. OISE-1559368

Contact: jace.waybright@jacks.sdstate.edu, mori.takao@nims.go.jp, guelou.gabin@nims.go.jp

Website: http://www.cnf.cornell.edu/cnf_2018reu.html (this report will not be available online until Spring 2019)

Abstract:

Thermoelectric generators offer a means of recovering waste heat in the form of electrical energy and have potential applications in the automobile and industrial sectors. In this study, two promising materials, chalcopyrite ($CuFeS_2$) and paracostibite (CoSbS), were studied by systematic synthesis and analysis. Chalcopyrite thin films were synthesized using magnetron sputtering onto glass and silicon substrates. Bulk paracostibite samples were synthesized by reacting high purity elements in a furnace followed by spark plasma sintering (SPS) to conduct phase boundary mapping on sulfur and study the effects of adding excess Te. Paracostibite samples with varied sulfur content retained their thermoelectric properties apart from the sample with 5% sulfur deficiency, which had significantly worse properties. Excess Te past simple substitution led to significant improvement in thermoelectric efficiency.

Introduction:

Thermoelectric effects describe the direct conversion that takes place between temperature differences and electric potential in a conducting material. The effects can be applied via thermoelectric generators and refrigerators using n-type and p-type doped materials. The efficiency of thermoelectric materials is characterized by a figure of merit, $ZT = \frac{S^2 \sigma T}{\kappa}$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature, and κ is the thermal conductivity. A $ZT \approx 1$ is highly sought after, however optimization is difficult due to close relationships that lie between electrical and thermal properties [1].

Chalcopyrite is a thermoelectric material which has been studied in bulk for its attractive electrical properties [2]. Our goal was to synthesize thin films in hope of decreasing the lattice thermal conductivity. Paracostibite is a mineral whose recent experiments have suggested that Te doping improves electrical properties by increasing charge carrier concentration [3]. Our goal was to conduct phase boundary mapping on sulfur due to its strong tendency to volatize away during synthesis. We would also like to study paracostibite synthesized with excess Te in hope of forming pores to decrease the thermal conductivity [4].

Research Summary:

Magnetron sputtering was used to grow four chalcopyrite films on silicon and glass substrates. The sputtering system power was set to 60W for 3.5h using a previously synthesized chalcopyrite target. X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray microscopy (EDX) were used to identify the structure and elemental composition of the films.

Bulk paracostibite samples, $CoSb_{0.96}Te_{0.04}S_x$ (x = 0.95, 0.98, 1, 1.02, 1.05) and $CoSb_{0.96}Te_{0.04}S(Te_y)$ (y = 0.14, 0.28) were synthesized by reacting high purity elements in sealed quartz tubes placed in a furnace for two firings. During the first firing, samples were heated to 300°C in 3h, held for 24h, then heated to 650°C in 6h, held for 48h, and cooled to room temperature in 10h. During the second firing, samples were heated to 650°C in 10h, held for 48h, and cooled in 10h. Next, the samples were ground into a powder, sieved to 100 μm, and placed in SPS to increase sample density and remove excess Te to promote the formation of pores. SPS conditions included heating to 650°C in 7min, holding for 15min, and cooling for another 7min. Additionally, the samples with excess Te were annealed by heating to 650°C in 10h, holding for 24h, and cooling for 9h. The structure and composition of the samples were measured using XRD as well as SEM-EDX for y = 0.28. Electrical properties were measured using a Seebeck coefficient / electrical resistivity measurement system (Ulvac ZEM-2) and the thermal conductivity was measured using laser flash analysis (Netzsch LFA-457). The single parabolic band (SPB) model was used to approximate the Lorentz number L to calculate the lattice thermal conductivity κ_L from the Wiedemann-Franz relation, $\kappa_L = \kappa - L\sigma T$ [5-6].

Results and Conclusions:

Chalcopyrite films grown on glass substrates were found to have poor adhesion to the surface. Films grown on silicon substrates displayed a homogeneous surface although its stoichiometry, $Cu_{0.25}Fe_{0.78}S_2$, was far from chalcopyrite and consistent with Cu doped pyrite. An SEM image of the silicon substrate film is shown in Figure 1.

Paracostibite samples with varied sulfur content retained most of their properties except for x = 0.95. This sample had a higher electrical resistivity and thermal conductivity resulting in a significantly lower figure of merit. The *ZT* calculations for the series are shown in Figure 2. It can be concluded that adding small excess amounts of sulfur to paracostibite samples is an effective method of preventing the detrimental effects of sulfur deficiency.

Measurements on paracostibite samples with excess Te indicated a major improvement in thermoelectric efficiency. The electrical resistivity and lattice thermal conductivity were decreased, resulting in a nearly 100% increase in *ZT* for y = 0.28, shown in Figure 3. XRD and SEM-EDX measurements suggest that improvement was a combination of point defect scattering from Te substitution, compositing effect from secondary phases, and micro sized pores. Figure 4 shows an SEM image of y = 0.28. With a *ZT* closer to 1, Te doped paracostibite is becoming a more attractive material that will require further study.

Future Work:

Chalcopyrite thin films will be further investigated using a set of newly synthesized targets ($Cu_{0.97}Zn_{0.03}FeS_2$, $Cu_{1.8}S$, FeS, Cu) to closely control film stoichiometry. Paracostibite with excess Te will also be studied by altering SPS and annealing conditions to observe their effect on the formation of pores.

Acknowledgements:

I would like to thank my PI Dr. Takao Mori, my mentors Dr. Gabin Guélou and Dr. Naohito Tsujii, as well as Dr. Lynn Rathbun and the CNF iREU Program. The program was supported by the National Science Foundation under award OISE-1559368.

References:

[1] Tritt, T. M. (2011). Thermal conductivity: Theory, properties, and applications. New York: Springer.

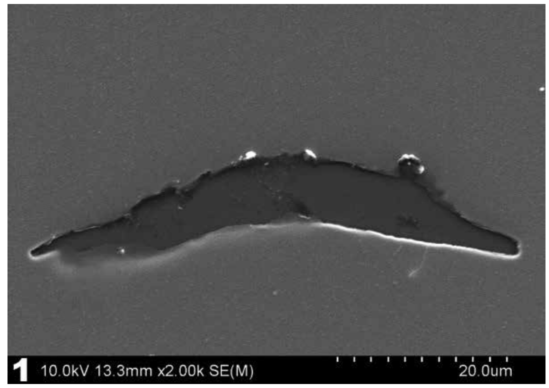
[2] N. Tsujii and T. Mori (2013). Appl. Phys. Express 6043001.

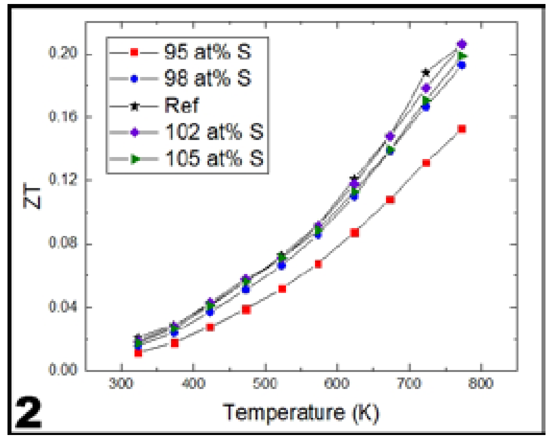
[3] Chmielowski, et al. (2016). Journal of Materials Chemistry C, 4(15), 3094-3100.

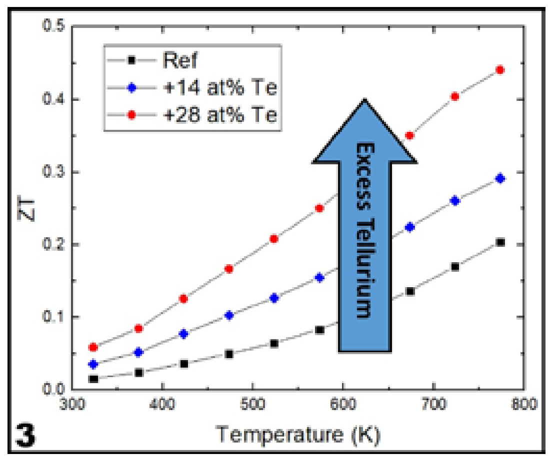
[4] Khan, et al. (2017). Nano Energy, 31, 2211-2855.

[5] B. Abeles, Phys. Rev., 1963, 131, 1906.

[6] G. A. Slack Phys. Rev., 1957, 105, 829.







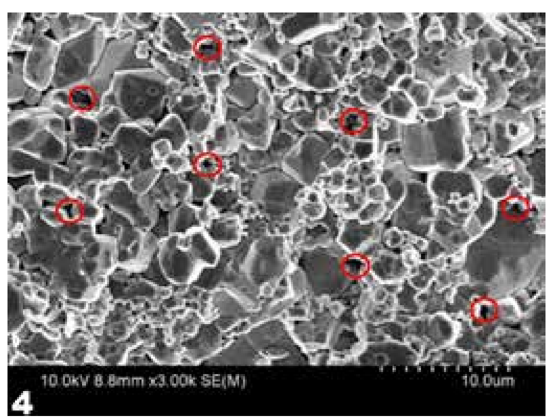


***Figure 1:** SEM image of chalcopyrite thin film on Si substrate. **Figure 2:** ZT calculations from paracostibite phase boundary mapping. **Figure 3:** ZT calculations from paracostibite with excess Te. **Figure 4:** SEM image of y = 0.28 showing micron-sized pores.*