Analysis of the Thermoelectric Properties of SnTe and SnSe

Thesis

By

Michael J Adams

Undergraduate Program in Mechanical Engineering

The Ohio State University

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Thesis Committee:

Joseph Heremans, Advisor

Vish Subramaniam

Abstract

Thermoelectric devices, which convert heat to electricity, could play an important role in supplying a rapidly increasing global energy demand. These devices are especially useful because the process is solid state and reversible. The conversion of heat to electricity relies on the Seebeck effect, which occurs at junctions of dissimilar materials. The efficiency of this process is directly related to the Seebeck coefficients of the materials used. One of the most common materials used in devices is Lead Telluride (PbTe). Since Lead is harmful to the environment, it is desirable to find materials that could replace PbTe while increasing the Seebeck coefficient.

The objectives for this project were to determine the thermoelectric properties of Tin Telluride (SnTe) mixed with varying amounts of dopants, such as Indium, Zinc, and Selenium. Samples were created by melting materials in vacuum sealed ampoules and cutting a section from each ingot. The samples were tested over a range of temperatures for Seebeck coefficient and resistivity. Zinc was found not to have a positive effect on the power factor. Selenium was fully absorbed into the lattice at 20%, but the material became two phase at 30%. Indium resulted in the highest power factor at 2.5%, although there is uncertainty in the measurement.

Acknowledgements

I would like to thank Dr. Heremans for providing the opportunity to work in his lab. Also, special thanks to Yibin Gao, whose support and guidance made this research project possible.

Vita

June 2008.....Jackson High School

2008 to present.....B.S. Mehcnaical Engineeing, The Ohio State University

Fields of Study

Major Field: Mechanical Engineering

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Introduction

As global energy demand increases and current energy resources become costly or unavailable, thermoelectrics may become a major factor in energy sustainability. Direct conversion of heat to electricity has many advantages over other types of energy conversion. The conversion is a solid state process, requiring no moving parts. Therefore, the devices require little maintenance and have a very long lifespan. The reversible process, called the Peltier effect, allows the devices to be used for cooling. Also, thermoelectric devices are very light compared to other energy conversion cycles. This makes the devices very useful for applications where heating or cooling is needed in small spaces or where electrical current is the only available energy source.

Thermoelectric devices can be used at a wide range of scales, making them useful for a large range of applications. Although thermoelectric energy conversion has low efficiency compared to the Carnot cycle, their scalability makes the devices capable of recovering lost energy from an existing system, effectively increasing its overall efficiency. For example, the materials studied in this project could recycle waste heat from a car exhaust system to generate electricity.

Thermoelectric generators (TEGs) are possible because of the Seebeck effect, which occurs at junctions of dissimilar materials. This effect describes a phenomenon by which a heat flux at the junction causes a voltage difference across the materials. The Seebeck coefficient is characterized by[1]

$$S = \frac{\Delta V}{\Delta T}$$

The efficiency of a thermoelectric device is dependent on the non-dimensional figure of merit, zT[1]

$$zT = \frac{S^2 \sigma}{\kappa} T$$

where σ is electrical conductivity, κ is thermal conductivity, and T is temperature. The output of a thermoelectric generator is related to the power factor, $\alpha^2\sigma$. Because the zT of a material depends on temperature, materials are chosen for specific applications to maximize zT.

Modern thermoelectric devices use p-n semiconductor junctions with metal contacts. N-type materials are doped with atoms to provide extra electrons to the sample, while p-type materials are doped with atoms that leave electron vacancies, called holes. The dopants alter the Fermi level of the semiconductor; p-

type materials have a Fermi level near the valence band and n-type materials have a Fermi level near the conduction band.

Suppose a voltage difference is applied to a Peltier (cooling) device, as shown in Figure 1 below. When electrons travel from the metal contact into the p-type semiconductor, they release energy as they drop into the valence band and occupy holes. The electrons then gain energy as they rise out of the holes and enter the metal contact at the exit. Oppositely, electrons travelling from a metal contact into an n-type semiconductor are forced to gain energy to enter the conduction band. The electrons then release energy as the drop from the conduction band and enter the metal contact at the exit. The semiconductors are physically connected such that they are electrically in series and thermally in parallel. Since the current is travelling in opposite directions for the n and p-type materials, both materials are causing heat flow in the same direction.

Likewise, applying a temperature difference across the device will result in a sum of currents from both materials. This process can be observed as a flow of electrons in the n-type and holes in the p-type travelling in the same direction (or a net flow of electrons in opposite directions). This is the reason p-type materials

have a positive Seebeck coefficient and n-type materials have a negative Seebeck coefficient. The currents can only be added because the coefficients have opposite signs. This demonstrates why alternating p-n junctions are the optimal layout for devices.

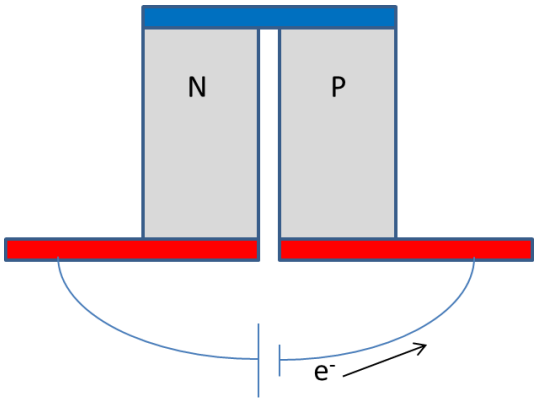

Figure 1: Peltier Cooling Application

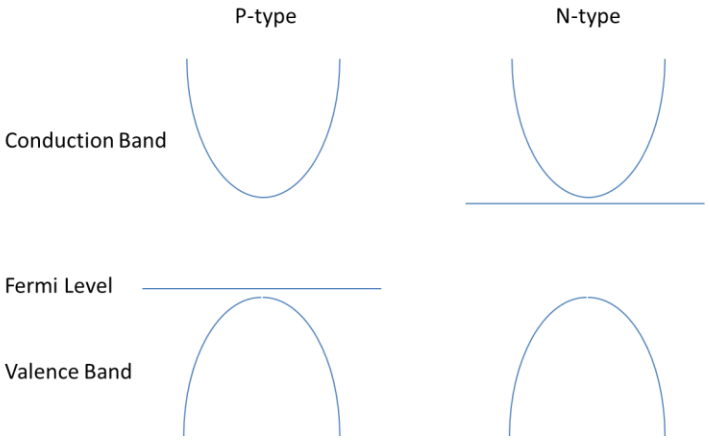

Figure 2: Band Gap with Fermi Level

Objectives

The objective for this project is to analyze non-toxic materials for waste heat recovery in a temperature range of 300K-700K. PbTe is one of the most commonly used materials in thermoelectric generators today. Due to environmental concerns, it is desirable to find suitable materials without Lead. For this project, Tin is chosen as a replacement for Lead. Tin is the element above Lead in the periodic table. SnTe has the same crystal structure (rock salt) as PbTe and there are many similarities in their band structure and transport properties. This project will expand on previous work with SnTe-SnSe[2].

However, one disadvantage of SnTe is the defect chemistry. Unlike PbTe, which can be made either p-type or n-type, SnTe is always Sn-deficit. These Sn defects make SnTe always p-type. The same Sn-defect also makes SnTe have too many carriers, so it is difficult to get to the optimal doping for thermoelectric applications. High carrier concentration limits the Seebeck coefficient, and thus, the power factor. Previous study by Yibin Gao shows that Indium has a resonant level in SnTe. A resonant level can change the density of electronic state near the Fermi level so that the Seebeck coefficient is improved without greatly reducing the electrical conductivity.

Methods of Procedure

Initially, I combined Sn, Te, and Se in varying atomic proportions with varying amounts of doping atoms in vacuum sealed ampoules. I heated the ampoules above the melting point of the metals and allowed them to mix and cool. Samples were taken from the ingots to be characterized by x-ray diffraction.

Some of the samples were analyzed in a cryostat. I cut small sections from the ingots and attached wiring to connect to the cryostat. Some of these wires formed thermocouples, while others supplied current and measured voltage at various points on the sample. The wires were attached by spot welding and/or silver epoxy. I then mounted each sample in the cryostat. The sample was subjected to a varying temperature range, from approximately 77K to 420K, to measure electrical conductivity, Seebeck coefficient, and carrier concentration.

Other samples were analyzed in a Linseis machine (a commercial product for measuring thermoelectric properties of materials). These tests were conducted over a larger temperature range, approximately 300K to 775K. Also, the wiring did not have to be manually constructed for each sample.

Results

First, Zinc was added in the hope that Zn could fill in the tin vacancies. Zn is a metal with the same valence charge, but different in iconicity. 1% and 3% Zn substitution were tested. X-ray diffraction showed that 1% Zn completely entered the SnTe lattice, but the 3% Zn substitution did not. This could be seen by comparing Figures 3 and 4 below. The second, smaller set of spikes indicates that this sample had a second phase.

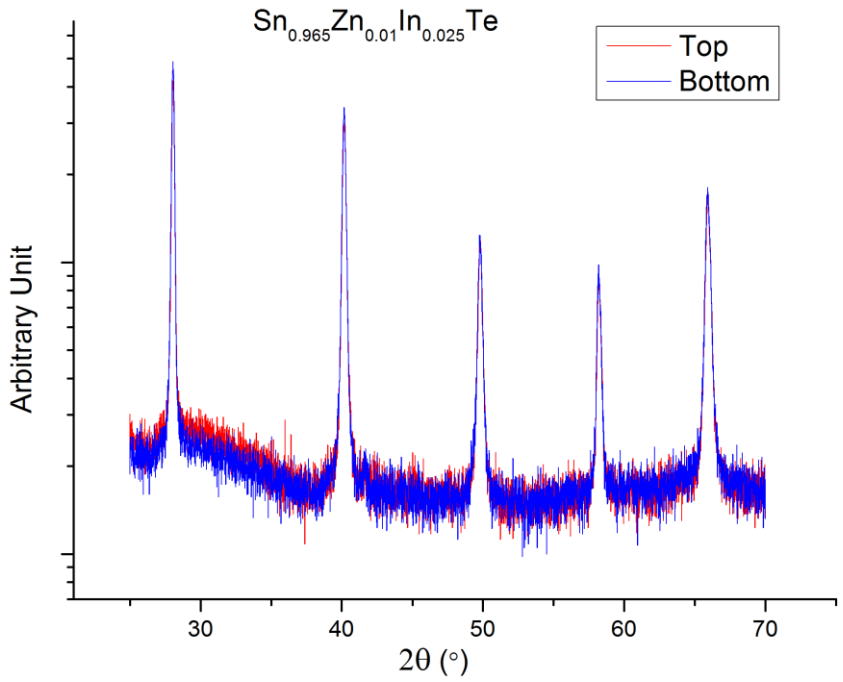

Figure 3: X-Ray Diffraction with 1% Zn

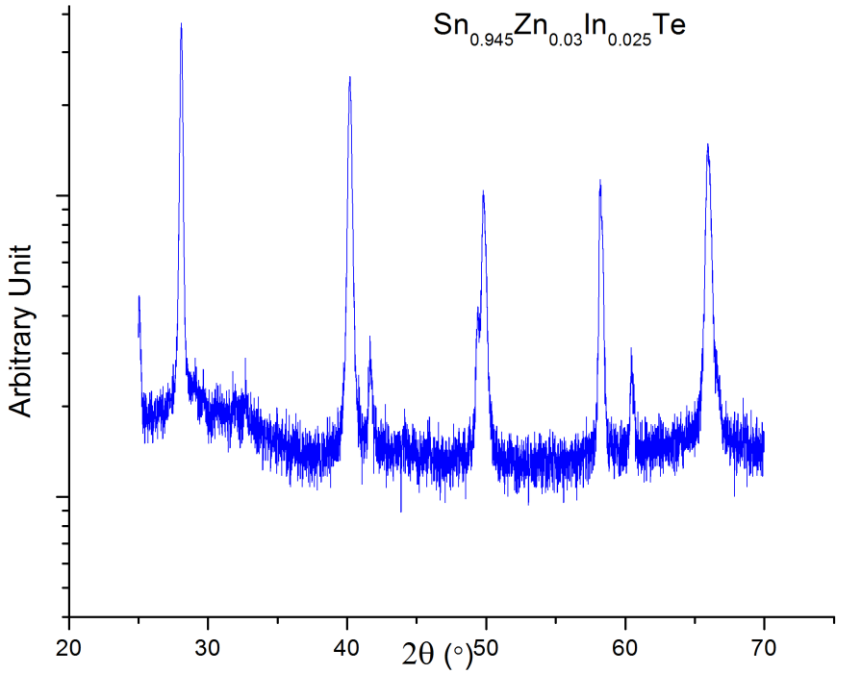

Figure 4: X-Ray Diffraction with 3% Zn

Selenium was added as a substitute for Tellurium, which is relatively expensive. By substituting as much as possible without reducing the power factor, the material can become less costly. Optimization of power factor with different Selenium and Indium concentrations verified that 20% Se substitution for Te can form a solid solution in SnTe-SnSe. As shown in Figure 5, 20% Se completely entered the lattice. 30% Se was attempted, but resulted in a second phase and too high resistivity for thermoelectric applications, as seen in Figures 6 and 7.

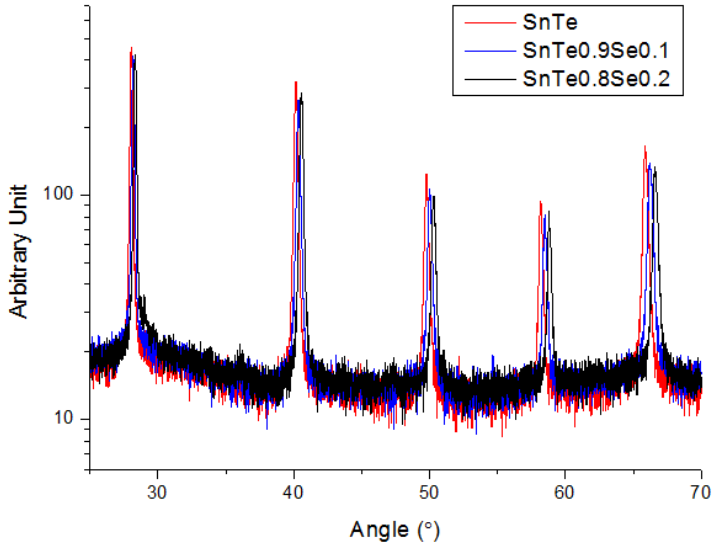

Figure 5: X-Ray Diffraction with up to 20% Se

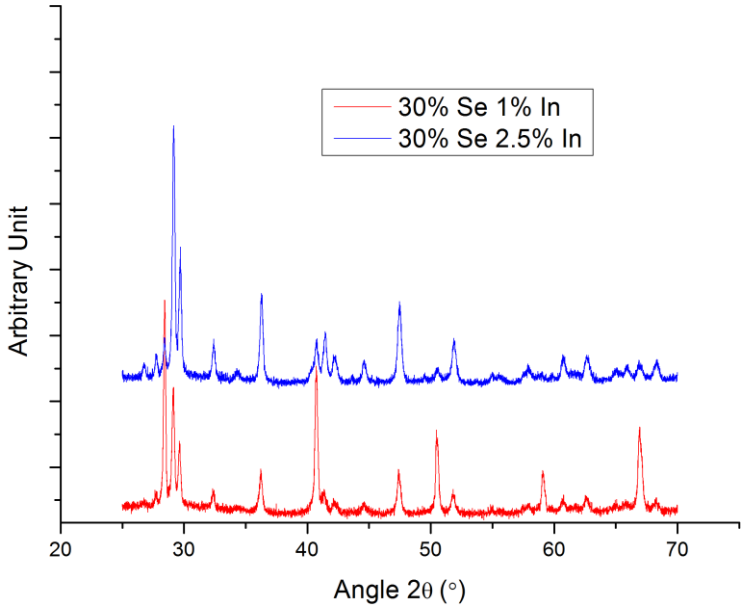

Figure 6: X-Ray Diffraction with 30% Se

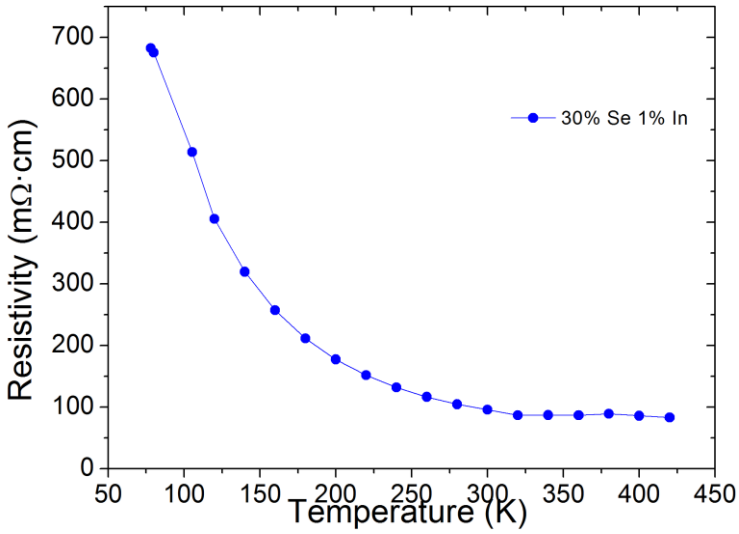

Figure 7: Resistivity with 30% Se

When the optimal amount of Selenium was determined, 1%, 2.5% and 4% Indium were added. These samples were measured in the Linseis. The Seebeck coefficient, resistivity and power factor for these samples are shown in Figures 8, 9, and 10 below.

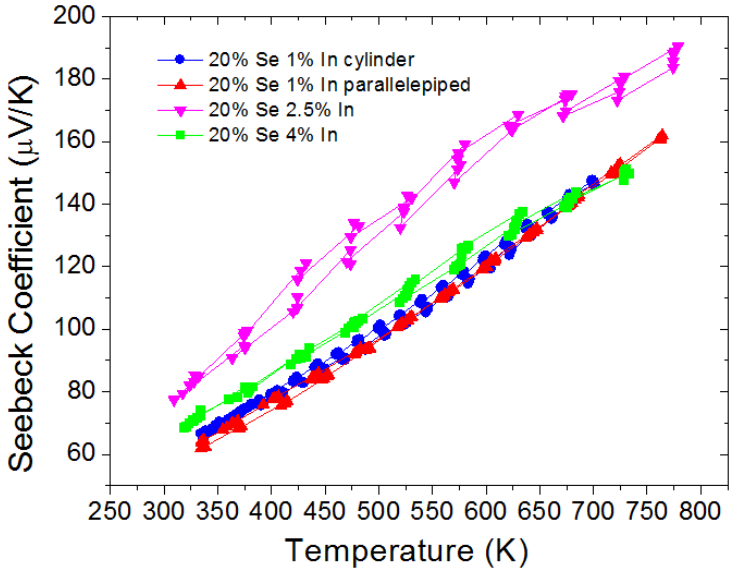

Figure 8: Seebeck Coefficient for Indium Doped Samples

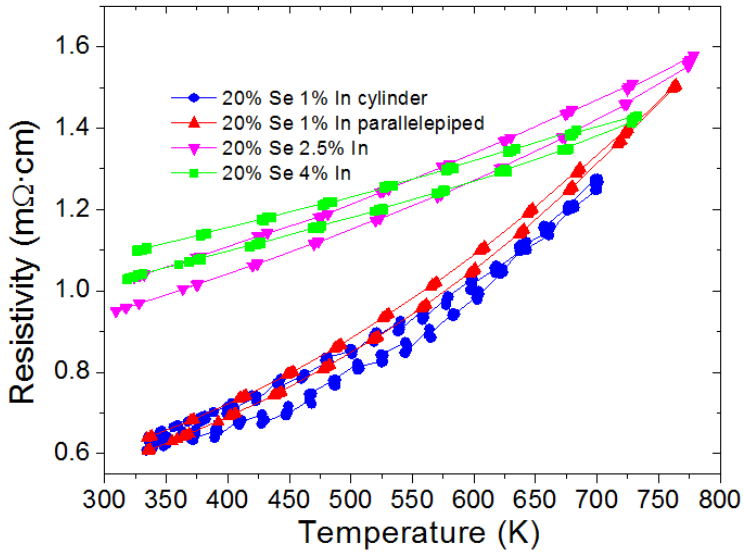

Figure 9: Resistivity for Indium Doped Samples

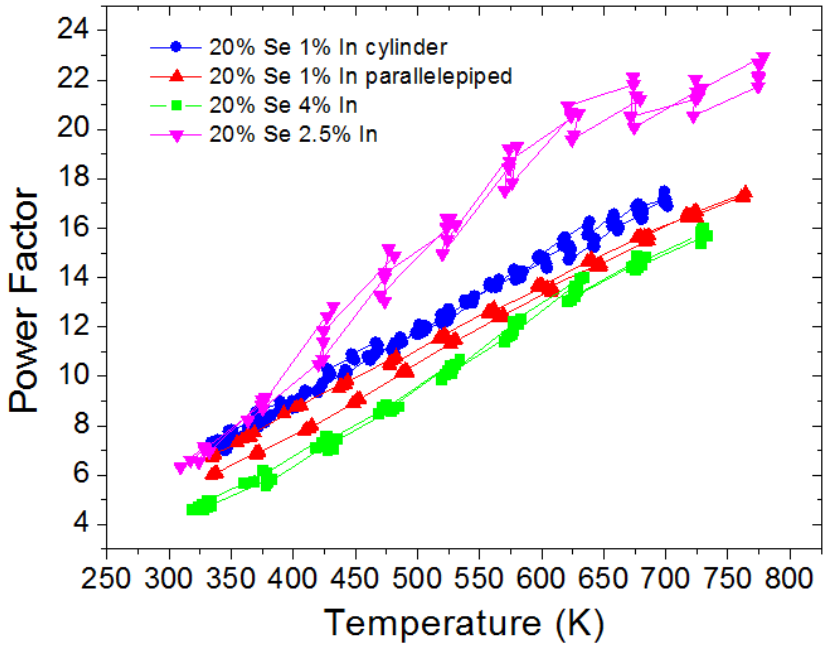

Figure 10: Power Factor for Indium Doped Samples

Note that 2.5% and 4% Indium were parallelepiped shaped samples. The result show that 2.5% Indium had the highest Seebeck coefficient of the samples, indicating there is an optimum Seebeck coefficient in between 1% and 4%. Also, resistivity increased as Indium was added to the sample. The total effect in power factor is that 1% and 2.5% Indium are close, and better than 4% Indium. There is a suggestion that for 20% Se, 2.5% Indium has higher power factor than 1%. However, there is further complication in uncertainty of the Linseis instrument at high temperature. As shown in Figure 11, there was significant error in Linseis measurements as the temperature difference was varied. We are currently

investigating how to more accurately measure the Seebeck coefficient at high temperature.

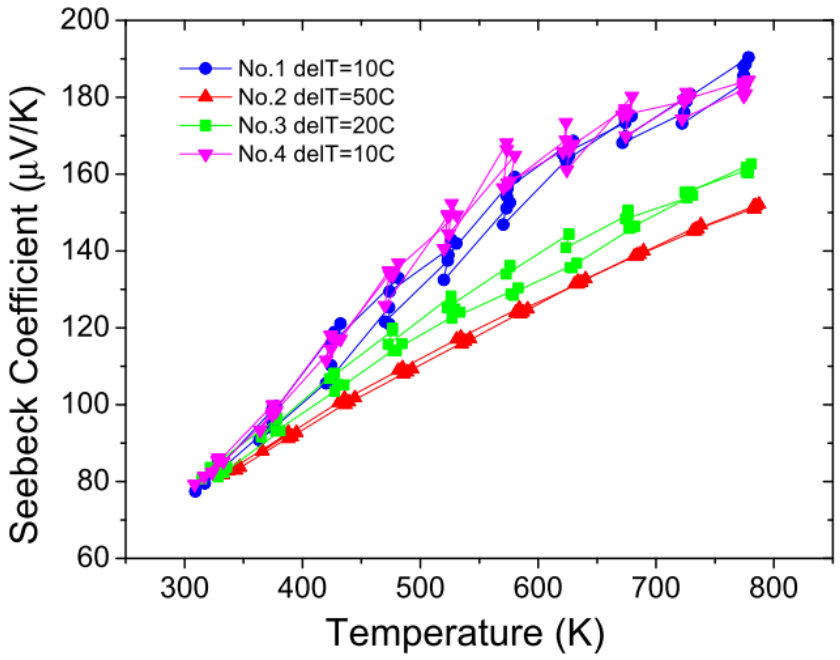

Figure 11: Linseis Uncertainty

Conclusion

Zinc was added to SnTe to fill Sn vacancies, which increase carrier concentration and decrease power factor. Zinc fully entered the SnTe lattice at 1%, but created a second phase at 3%. However, Zinc was unsuccessful in increasing the power factor.

Selenium was substituted for Te to reduce the cost of the material without greatly reducing the power factor. 20% Se fully entered the lattice, but 30% created a second phase and greatly increased resistivity. This indicates that there is an optimal maximum amount of Selenium that will fully enter the SnTe lattice between 20% and 30%.

Indium was added in varying amounts to the 20% Se samples. 2.5% resulted in the greatest power factor. The data indicates that there is an optimal level between 1% and 4% In. However, uncertainty in the high temperature measurements is currently being investigated.

Bibliography

1. Rowe DM, Bhandari CM. Modern thermodynamics. Reston (VA): Reston Publishing Co. Inc.; 1983.

2. Stevens, KR. Two thermoelectric materials: thermoelectric properties of SnTe-SnSe and synthesis of skutterudite Na1+xFe4P12 [senior thesis]. [Internet]. [Kenosha (WI)]: Carthage College; 2010 [cited 2011 Sept 3]. Available from: http://dspace.carthage.edu/xmlui/handle/123456789/72