The Study of $ZnSnN_2$ for possible Thermoelectric and Photovoltaic Applications

John Cenker, Dr. Dyck of John Carroll University
Department of Physics, John Carroll University, University Heights, OH 44118

Abstract

In order to replace semiconductors that rely on rare Earth and costly elements, the search for analogous semiconductors formed by plentiful elements began. A recently developed material, ZnSnN2, is the analog to InN. In this project, the Seebeck and Hall effects are measured along with the electrical conductivity. The carrier concentration can then be determined from the Hall coefficient. Using the method of four coefficients and a general theory of these properties, the bounds on effective mass are determined corresponding to the different possible scattering parameters. The results show that samples with carrier concentrations around $6\text{-}9\times10^{19}$ cm^{-3} exhibit properties consistent with the model, but not samples with a higher concentration of 1.02×10^{21} cm^{-3}.

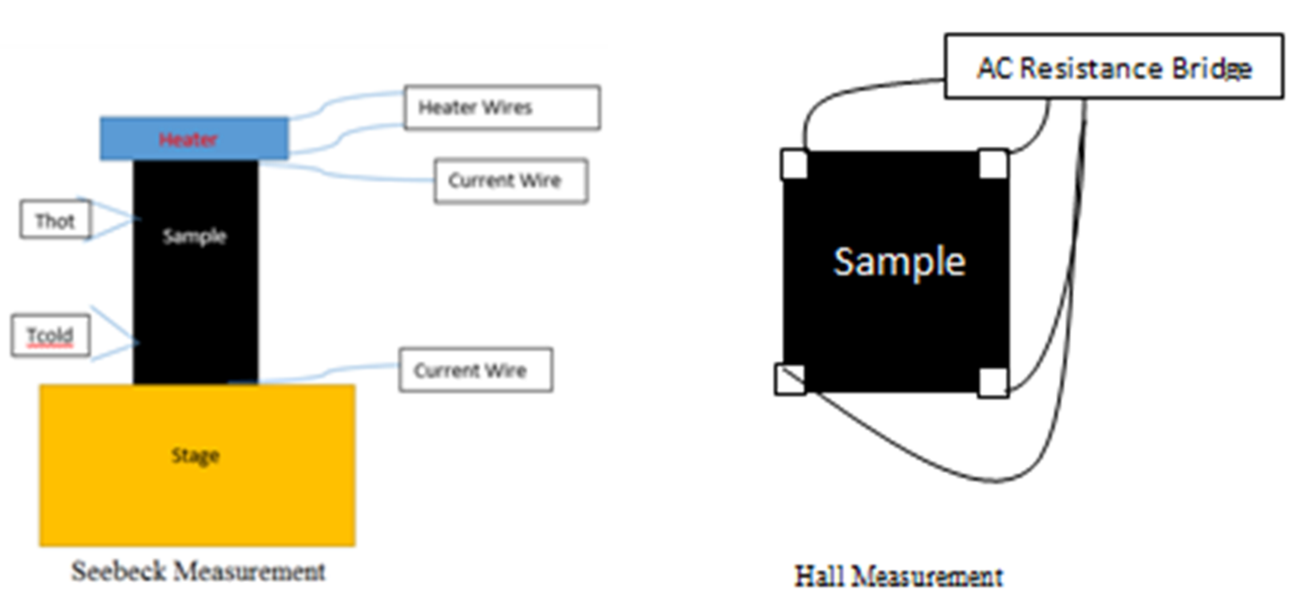
Background

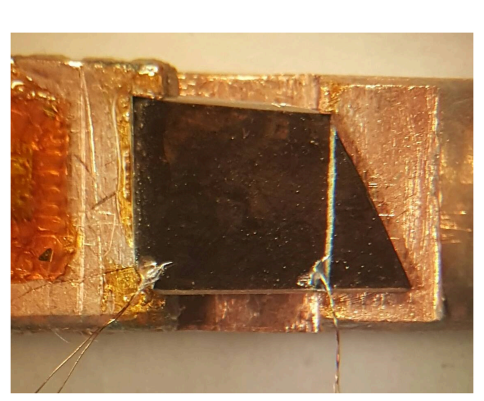
•Semiconductors are important in many electrical applications including almost all modern computers
•A desired semiconductor is InN due to its band gap energies. The increase in demand of indium has led to volatility in it's prices[1]
•Many semiconductors do not have the facilities in place to recycle the costly and rare elements
•$ZnSnN_2$ is the direct analog to InN. This can be easily seen by the position of the elements on the periodic table. Indium is sandwiched by zinc and tin. In essence, the group III element is replaced by II-IV ones. $ZnSnN_2$ is thus the II-Iv-N_2 analog to the III-V InN
•Zinc and tin are orders of magnitude more abundant, and recycling structures are already in place
•Due to it only recently being synthesized, information on $ZnSnN_2$ is lacking. Basic electronic properties such as effective mass have yet to be explored in depth

Sample Preparation

•Three samples were provided by Dr. Steve Durbin at Western Michigan University[2]
•The samples displayed X-ray diffraction peaks consistent with the expected peaks of $ZnSnN_2$ and likely have wurtzitic structure
•Grown with molecular beam epitaxy to a thickness of ~100 nm on insulating YsZ (111) substrate
•The different growth parameters for the samples include different grow temperatures, times, and zinc and tin fluxes. These variations produce different purities, carrier concentrations, and different structural phases

Experimental



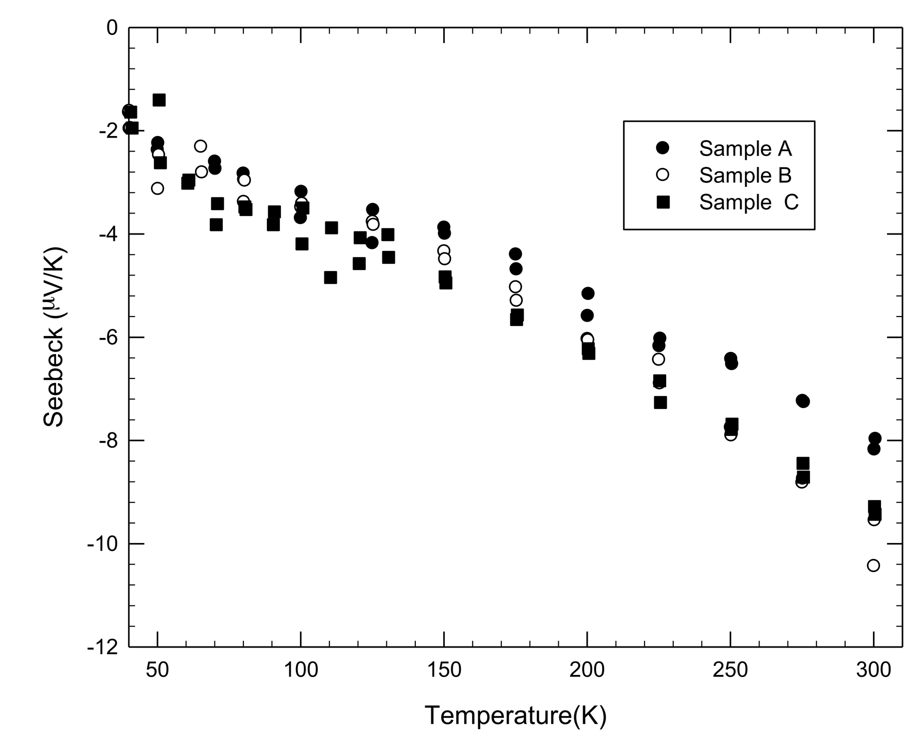


➢ A photograph of sample C with thermocouples attached. The heater is seen on the left side

•Copper wires connected to the sample with indium contacts were used for Hall measurements
•For Seebeck measurements, a copper-constantan thermocouple was used
•The edges were sanded in order to prevent shorting to the backside
•Keithley 2182 nanovoltmeters used for thermocouple measurements
•Lakeshore 370 AC Resistance Bridge and Lakeshore electromagnet operated from -.7 to +.7 Tesla were used for Hall measurements
•Hall and Seebeck measurements were taken at a variety of temperatures ranging from 7-300K using a closed cycle helium cooling system at a vacuum of 10^{-6} torr

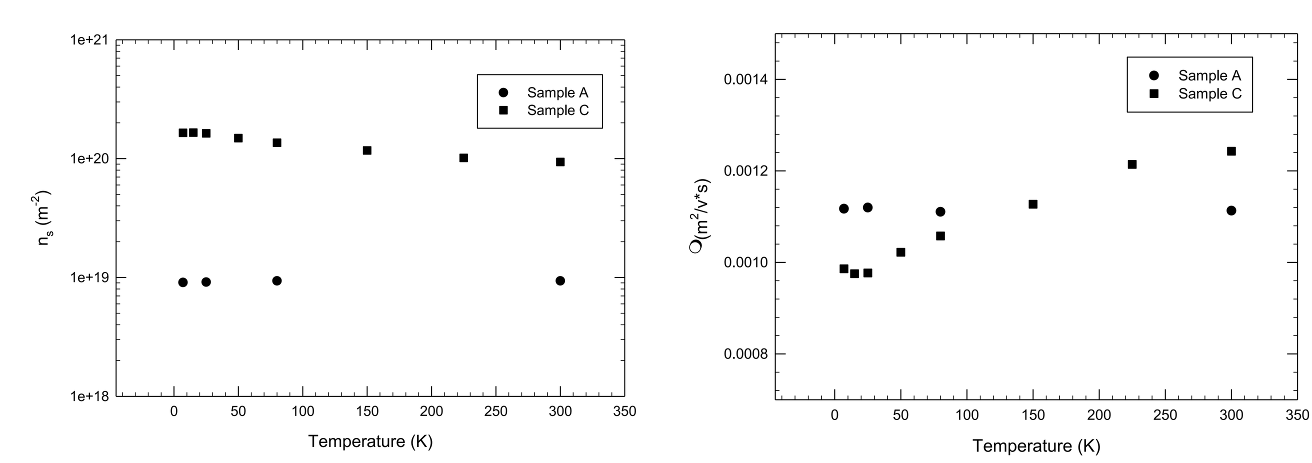
Transport Properties

Seebeck Effect



•These measurements were not corrected for the possible Seebeck effects due to the wires connected to the sample
•A sign change was observed at low temperatures
•Taken with automated LabVIEW program

Sheet Density and Mobility



•Sheet density (which equals carrier concentration divided by thickness), and mobility remain relatively constant with temperature
•However, there is much more of a temperature evolution for the sample with the higher carrier concentration

Model Comparison

•The material is modeled as having a parabolic band gap and a charge carrier scattering time dependent on E^r where E is the energy and r is the scattering

$$n(\eta,T)=4\pi(2 m_{eff} m_e k_B T)^{3/2} * F(1/2,\eta)/h^3$$

Carrier Concentration
m_{eff} = effective mass
m_e = electron mass
T = Temperature

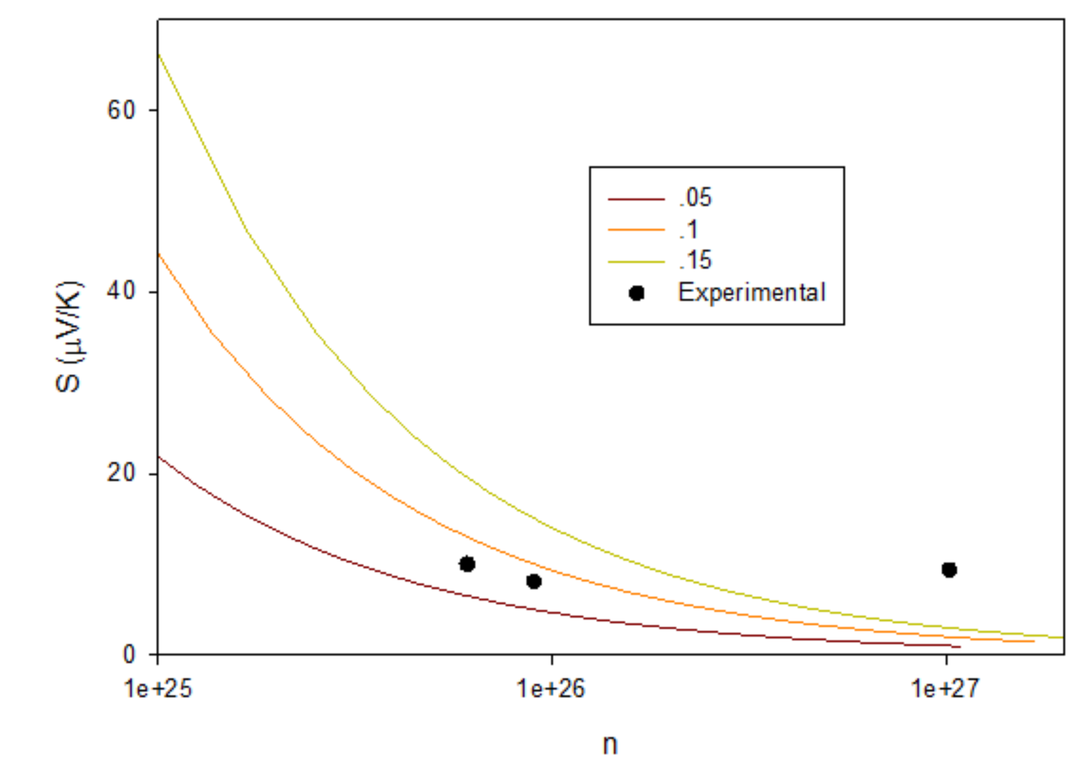
$$S(r,\eta)=10^6 * \frac{k_B}{e}\left[\frac{\left(r+\frac{5}{2}\right)F\left(r+\frac{3}{2},\eta\right)}{\left(r+\frac{3}{2}\right)F\left(r+\frac{1}{2},\eta\right)}-\eta\right]$$

Seebeck Coefficient
r = scattering coefficient

$$F(n,\eta)=\int_0^{\eta_{upper}}\frac{x^n}{1+\exp(x-\eta)}dx$$

Fermi Integral
η = Fermi Energy

•Different values of r correspond to different modes of scattering: r = 3/2 corresponds to ionized impurities, r=0 to neutral impurities, and r = -0.5 to acoustic phonon scattering.
•Using the integral form of these coefficients, a plot of Seebeck coefficient as a function of carrier concentration is generated which allows comparison between experimental data and the model



•Here S is plotted vs n for different effective masses of .05, .1, and .15
•The sample with the high carrier concentration does not fit the model, while the other samples have general agreement
•Under the model, Sample C would have a much higher effective mass
•Possibly indicate more than a single band at the highest values of n

Summary

•Transport measurements were performed on three samples of $ZnSnN_2$
•All three samples exhibited similar Seebeck coefficients despite one having significantly higher carrier concentration
•The sample with the higher carrier concentration does not fit the model, possibly indicating multiple bands

	n (cm^{-3})	ρ (Ω*cm)	μ (cm^2/V*s)	Seebeck (μV/K)	r=-1/2	r=3/2	r=0
A	9.01×10^{19}	5.98×10^{-3}	11.6	8.08	0.081	0.03	0.05
B	$6.1E\times10^{19}$	6.65×10^{-3}	15.4	10	0.085	0.03	0.06
C	1.02×10^{21}	4.83×10^{-3}	12.7	9.36	0.45	0.15	0.3

•This table shows all of the measured properties and the calculated effective mass for the different scattering modes
•Clearly, Sample C does not agree with the results of Sample A and B

Future Work

•More analysis into why Sample C does not fit the model is needed
•Measuring more samples, particularly those with lower carrier concentrations would help fill in the graph of S vs n
•There are two different structures of this sample: wurtzite, and a more pure, structured orthorhombic structure[3]
•These samples are suspected to be wurtzite, and thus they have more impurities. Studying the other type of $ZnSnN_2$ may show more promise as a replacement to InN

References

1) N. Feldberg, B. Keen, J.D. Aldous, D.O. Scanlon, P.A. Stampe, R.J. Kennedy, R.J. Reeves, T.D. Veal, and S.M. Durbin: ZnSnN2: a new earth-abundant element semiconductor for solar cells. *Proc. of the 38th IEEE Photovoltaic Specialists Conference*, Austin, TX, p. 2524 (2012). 6 L. Lahourcad
2) N. Feldberg, J.D. Aldous, W.M. Linhart, L.J. Phillips, K. Durose, P.A. Stampe, R.J. Kennedy, D.O. Scanlon, G. Vardar, R.L. Field, Iii, T.Y. Jen, R.S. Goldman, T.D. Veal, and S.M. Durbin, Appl. Phys. Lett. **103**, 042109 (2013)
3) A. N. Fioretti, A. Stokes, M. R. Young, B. Gorman, E. S. Toberer, A. C. Tamboli, A. Zakutayev, Adv. Electron. Mater. 2017, 3, 1600544.

Acknowledgements

•SURF Program and the Colleran-Weaver Fund
•Dr. Steve Durbin