Mg_2Si Composites with Embedded Si Nanoparticles for Energy Recovery of Waste Exhaust Heat

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Co-PIs**:** **Z. Bian** (UC Santa Cruz); **S. M. Kauzlarich** (UC Davis)

Industrial partners: **NASA JPL**; **BSST LLC**

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Project ID:ACE070

Overview

Timeline

Start: September 2010

End: August 2013

15% complete

Budget (DOE funding)

2010-11

UCSC $71K; **UC Davis** $71K

2011-12

UCSC $75K; **UC Davis** $75K

Partners

- UCSC (Shakouri, Bian) –lead (transport modeling and thermoelectric characterization)
- UC Davis (Kauzlarich) (material synthesis, structural characterization)
- In collaboration with JPL (Fleurial) and BSST (Bell) (verify thermoelectric measurements, study material uniformity, advice on scale up production)

Barriers

- **Cost** (improve ZT of abundant/non-toxic TE materials)
- **Scale up to practical TE device** (use of bulk synthesis techniques)

Project Objective:

- ❑ To develop environmentally benign, nanostructured materials that are grown in bulk for enhanced thermoelectric performance (ZT>1.3-1.8) in 500-800K range for direct conversion of waste exhaust heat into electricity.

Milestones:

- **Year 1**
  - Synthesis and characterization of n-type Mg_2Si and $Mg_2Si_xSn_{1-x}$ with embedded nanoparticles
  - Boltzmann transport modeling of electron mobility and Seebeck coefficient for Mg_2Si alloys (include nanoparticle scattering)
  - Thermal conductivity modeling including nanoparticle scattering
- **Year 2**
  - Synthesis and characterization of p-Mg_2Si alloys with nanoparticles
  - Boltzmann transport modeling of hole transport including nanoparticles
- Year 3
  - Demonstrate n- and p-type Mg_2Si alloys with ZT>1.8 and >1.0 -1.3 respectively
  - Full thermoelectric property characterization in 300-800K range; verification at **JPL** and at **BSST**

Approach:

- ❑ Optimize Zintl phase Mg_2Si alloys with embedded nanoparticles (NP) for maximum ZT in temperature ranges for conversion of waste exhaust heat.
- ❑ Optimize NP size and composition to scattering mid/long wavelength phonons and reduce lattice thermal conductivity
- ❑ Optimize NP potential profile to benefit from hot electron (hole) filtering and increase the thermoelectric power factor
- ❑ Use scalable bulk growth techniques

Order	Element	Abundance ratio (%)
2^{nd}	Si	25.8
8^{th}	Mg	1.93

Progress: Electron Transport Modeling

Boltzmann Transport

$$\sigma = \int \sigma(E)dE$$

$$S = \frac{1}{eT}\frac{\int \sigma(E)(E-E_F)dE}{\int \sigma(E)dE} \propto \langle E - E_f \rangle$$

Differential Conductivity

$$\sigma(E) = e^2\tau(E)v_x^{\ 2}(E)\rho(E)\left(-\frac{\partial f_0(E)}{\partial E}\right)$$

$$\frac{1}{\tau(E)} = \frac{1}{\tau_{imp}(E)} + \frac{1}{\tau_{phonon}(E)} + \frac{1}{\tau_{nano}(E)}$$

Partial wave method for single particle scattering, exact solution of the Schrödinger equation

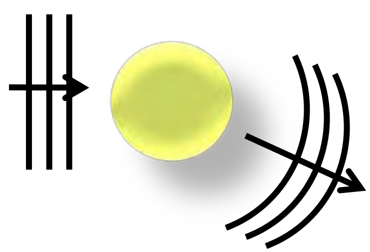


Table 1
Experimental (300 K) and calculated electronic properties of Mg_2Si.

Property	Calc. (from literature)	Calc. (this work)	Exp.
Direct gap $\Gamma_v \rightarrow \Gamma_c$ (eV)	1.55[a] [10], 1.65[b] [9], 2.20[c] [10]	1.75	2.27 [7]
Indirect gap $\Gamma_v \rightarrow X_c$ (eV)	1.3[d] [8], 0.12[a] [10], 0.65[c] [10]	0.21	0.66–0.78 [4–6]
Effective mass $m_\parallel/m_0$	0.69 [8]	0.58	–
Effective mass $m_\perp/m_0$	0.25 [8]	0.19	–

Use band parameters from: Computational Materials Science 50 (2011) 847–851

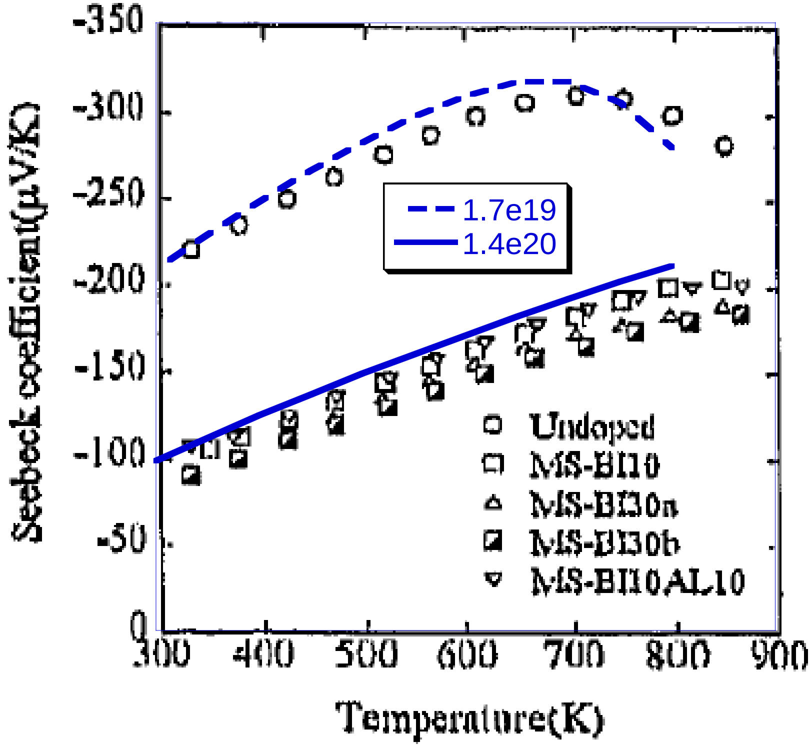
Developed Boltzmann transport model for Mg_2Si taking into account two conduction bands and the impurity and phonon scatterings. Nanoparticle scattering was also added using Partial Wave Method.

Technical Accomplishments
Electron Transport Modeling

Modeling of bulk Mg_2Si Seebeck

Table I. Grown samples with the results of Hall measurements

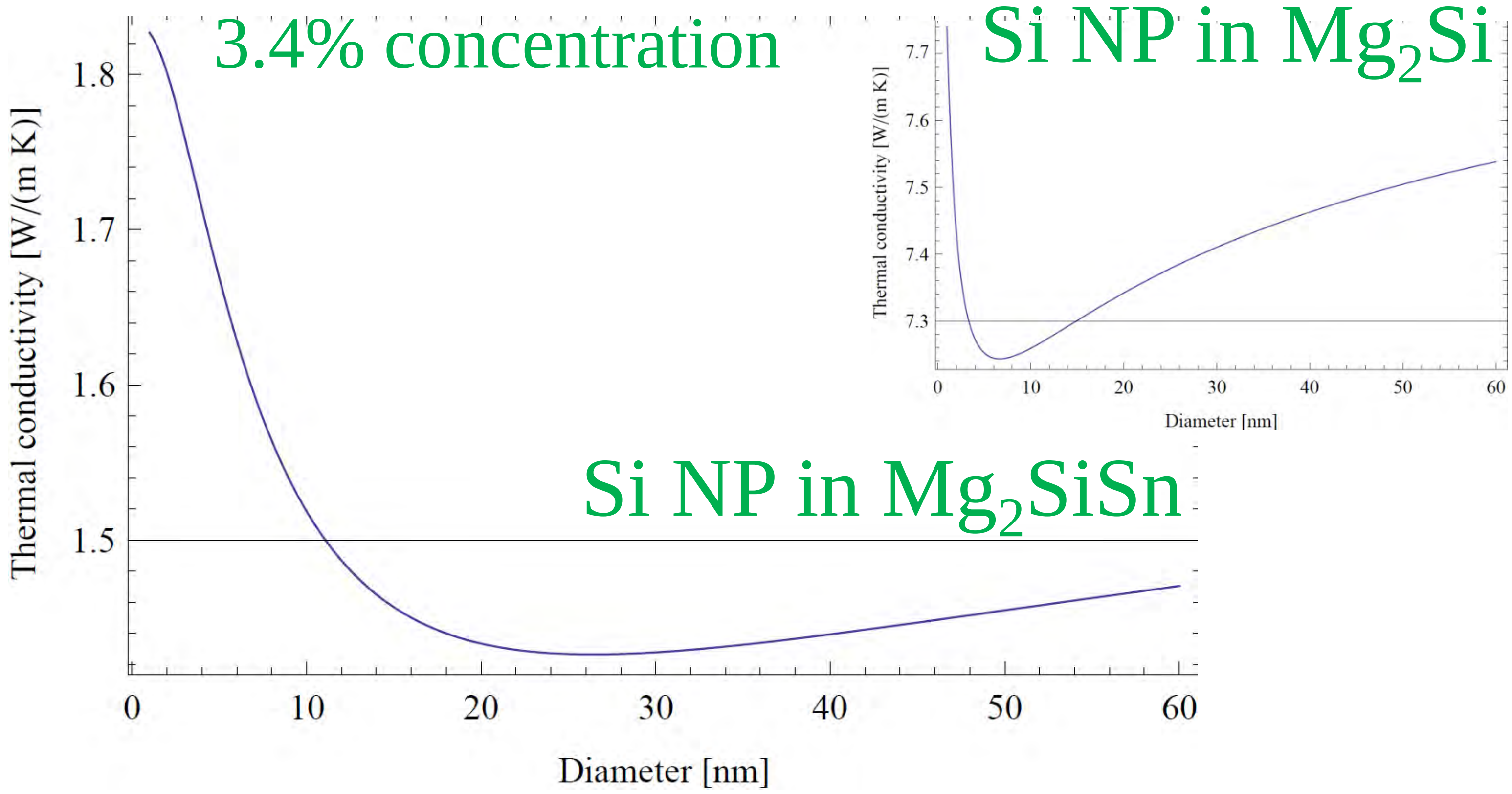
Sample name	Bi doping (atom%)	Al doping (atom%)	Carrier concentration $N_D - N_A$ (cm^{-3})	Hall mobility (cm^2 /Vs)
Undoped	0.0	0.0	1.69×10^{19}	157.9
MS-BI10	1.0	0.0	1.38×10^{20}	95.4
MS-BI10AL10	1.0	1.0	1.41×10^{20}	91.3
MS-BI30a	3.0	0.0	1.31×10^{20}	86.8
MS-BI30b	3.0	0.0	1.39×10^{20}	87.7



Using experimental data from: "Crystal growth of Mg_2Si by the vertical Bridgman method and the doping effect of Bi and Al on thermoelectric characteristics," MRS fall meeting, 2007

❑ Theory can explain both doping and temperature-dependence of the Seebeck Coefficient for n-doped bulk Mg_2Si

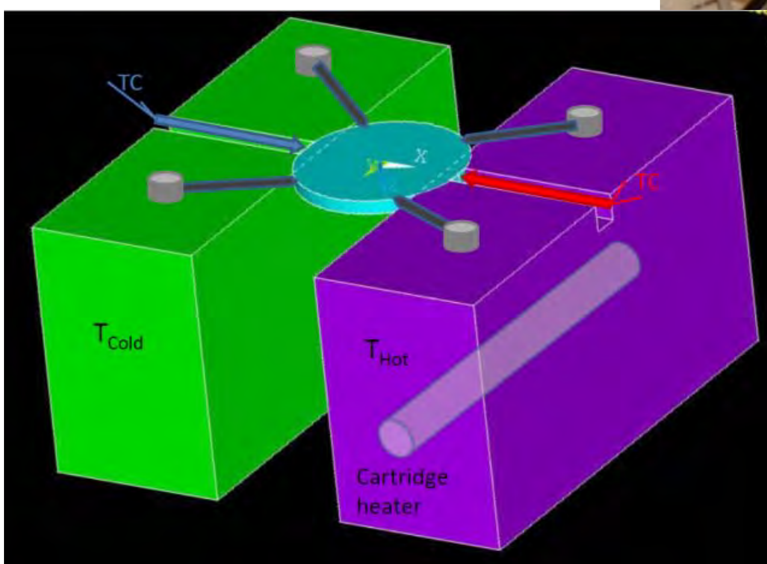
Technical Accomplishments
Phonon Transport Modeling

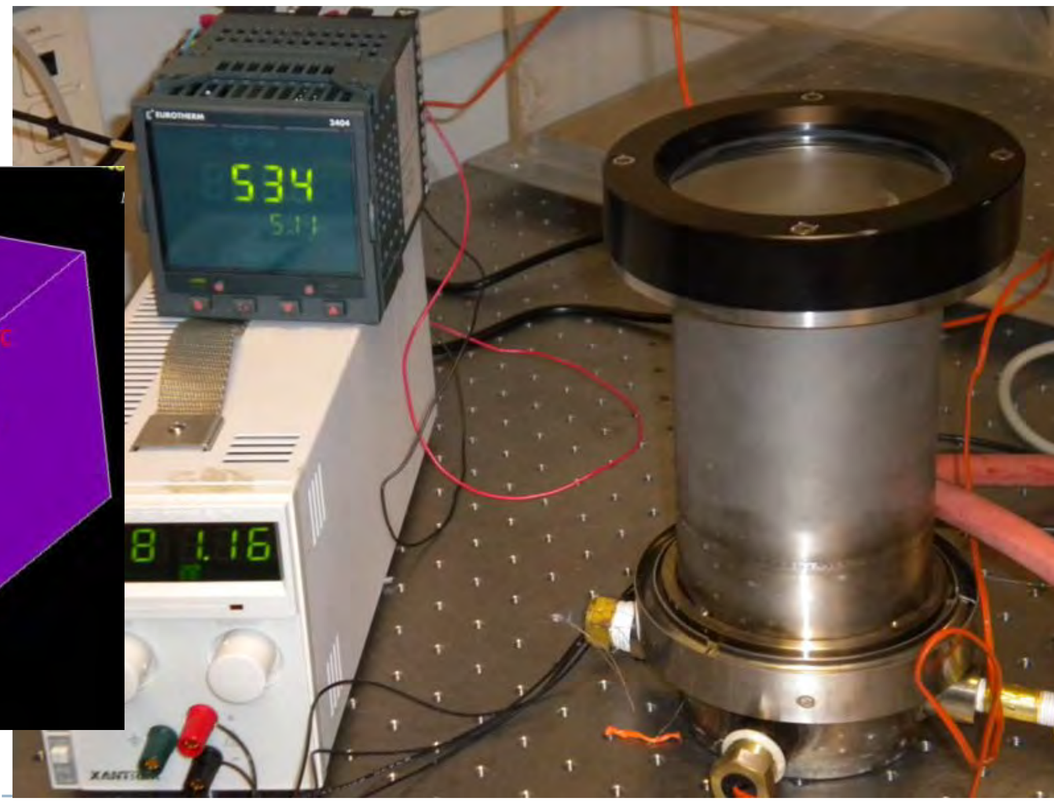


- ❑ Modeled the effect of Silicon nanoparticles on the thermal conductivity of Mg_2Si and Mg_2SiSn
- ❑ Optimum nanoparticle size for lowest thermal conductivity identified

Progress:
High Temperature Characterization Apparatus

Designed a set up for simultaneous Van der Pauw and Differential Seebeck measurement (in order to characterize the new materials rapidly).

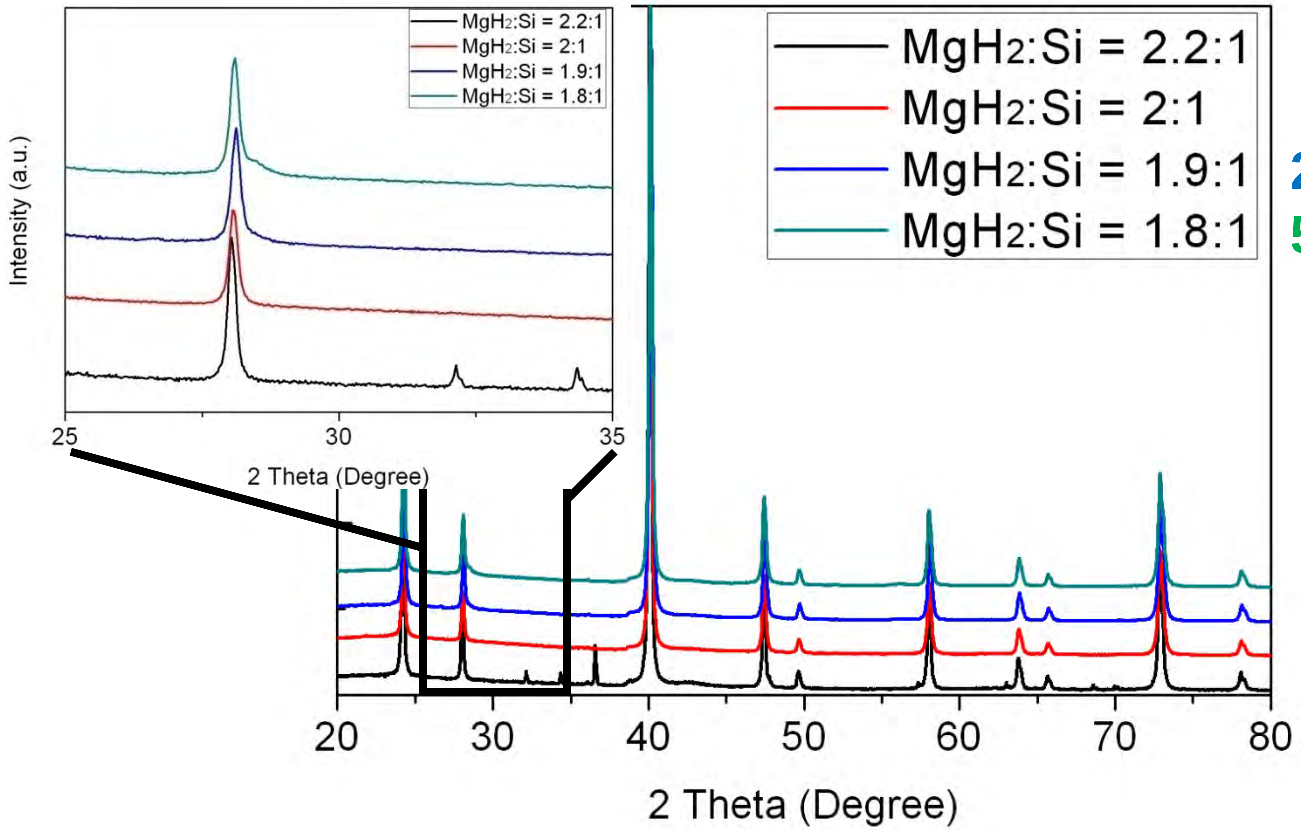




Progress: Preliminary Material Synthesis

$2MgH_2 + (1+x)\text{nano } Si(Bi) \rightarrow Mg_2Si/xSi(Bi)$ (x = 0%, 1.25%, 2.5%, 5%)

Powder X-ray Diffraction



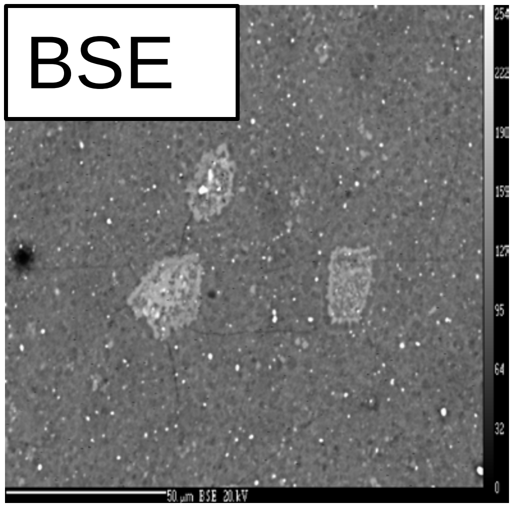
2.5 mol% Si

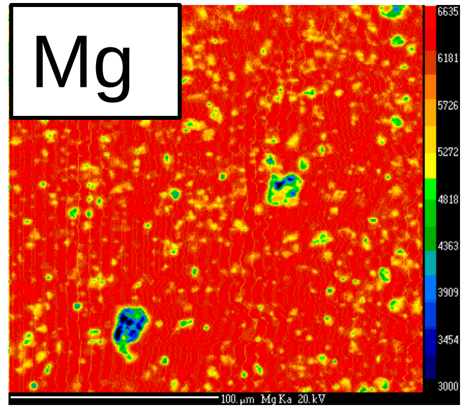
5 mol% Si

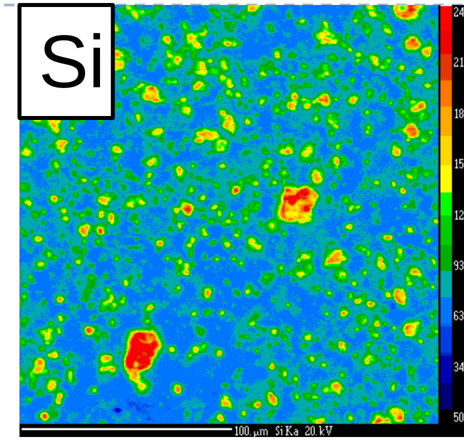
Control the amount of nano-Si inclusions through stoichiometry. The very small shoulder on the right of the peak at ~27 degrees is due to Si and we can fit the spectrum to determine the weight percentage and thereby the atomic percentage.

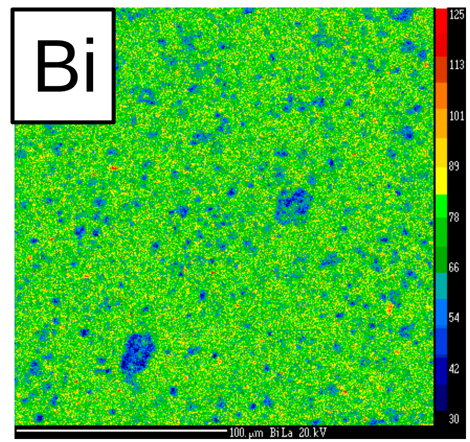
Progress: Microprobe analysis of Mg_2Si with Si Nanoparticles

5% Si, 1% Bi







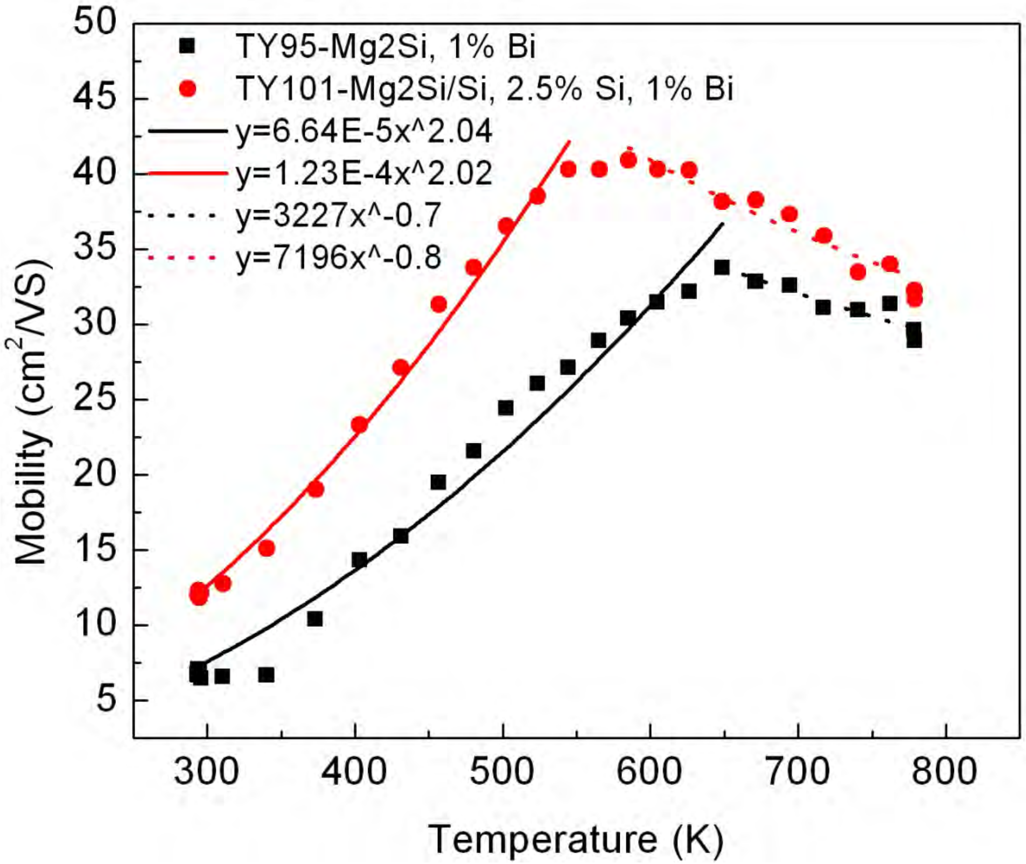


Majority phase $Mg_{2.10(2)}Si_{0.99(3)}Bi_{0.01(002)}$

Si rich areas are the Bi deficient areas. Therefore, most of the Bi diffused into Mg_2Si matrix. Si rich areas are at micro level, which indicates that Si particles agglomerated.

Progress

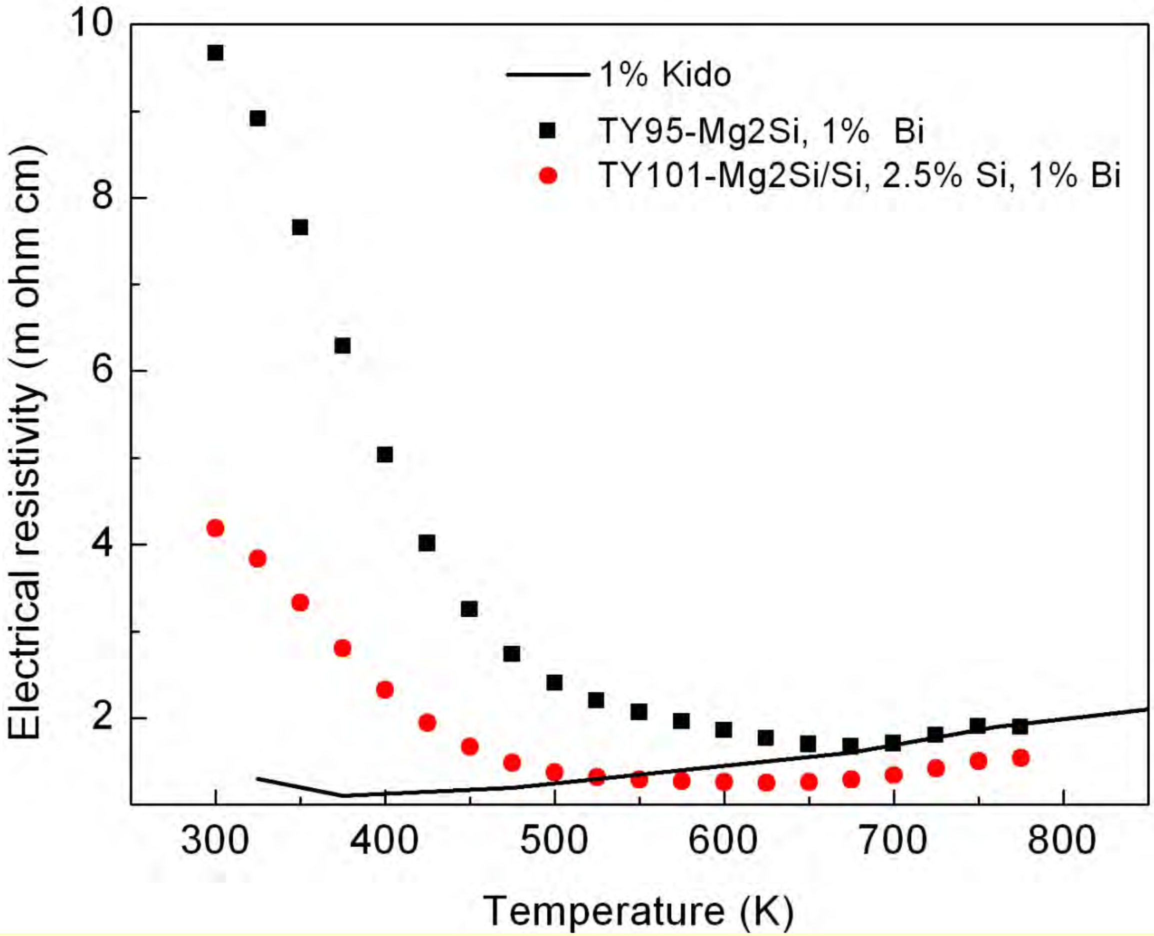
Transport Properties: Mobility



We see impurity scattering at low temperatures. We are planning additional characterizations to see if we can understand this. It is possible that grain boundaries contributing to this effect.

Progress

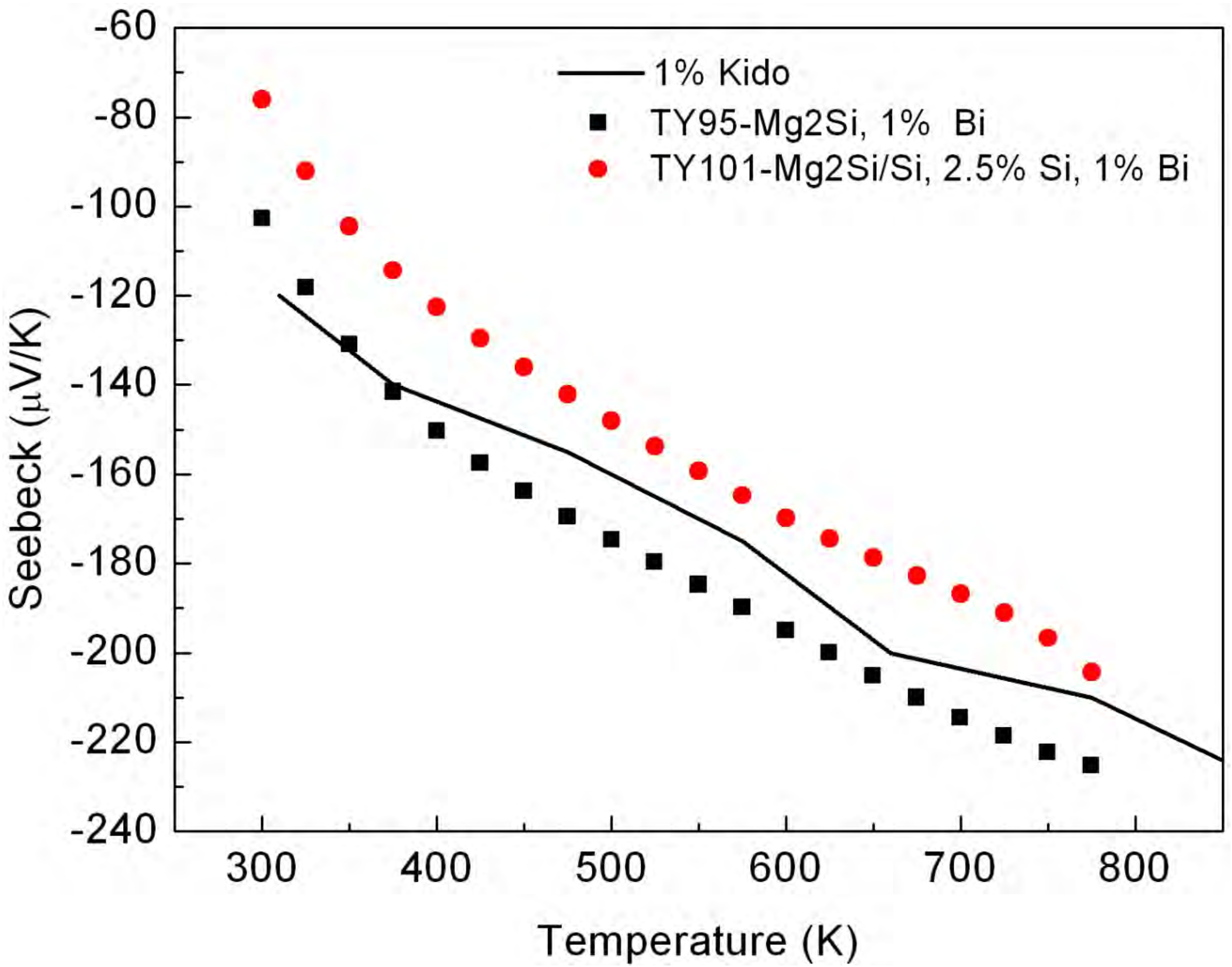
Transport Properties: Electrical Resistivity



This shows the expected resistivity for doped Mg_2Si, behaving like a normal heavily doped semiconductor. The two samples made by our method show impurity scattering at low temperatures.

Progress

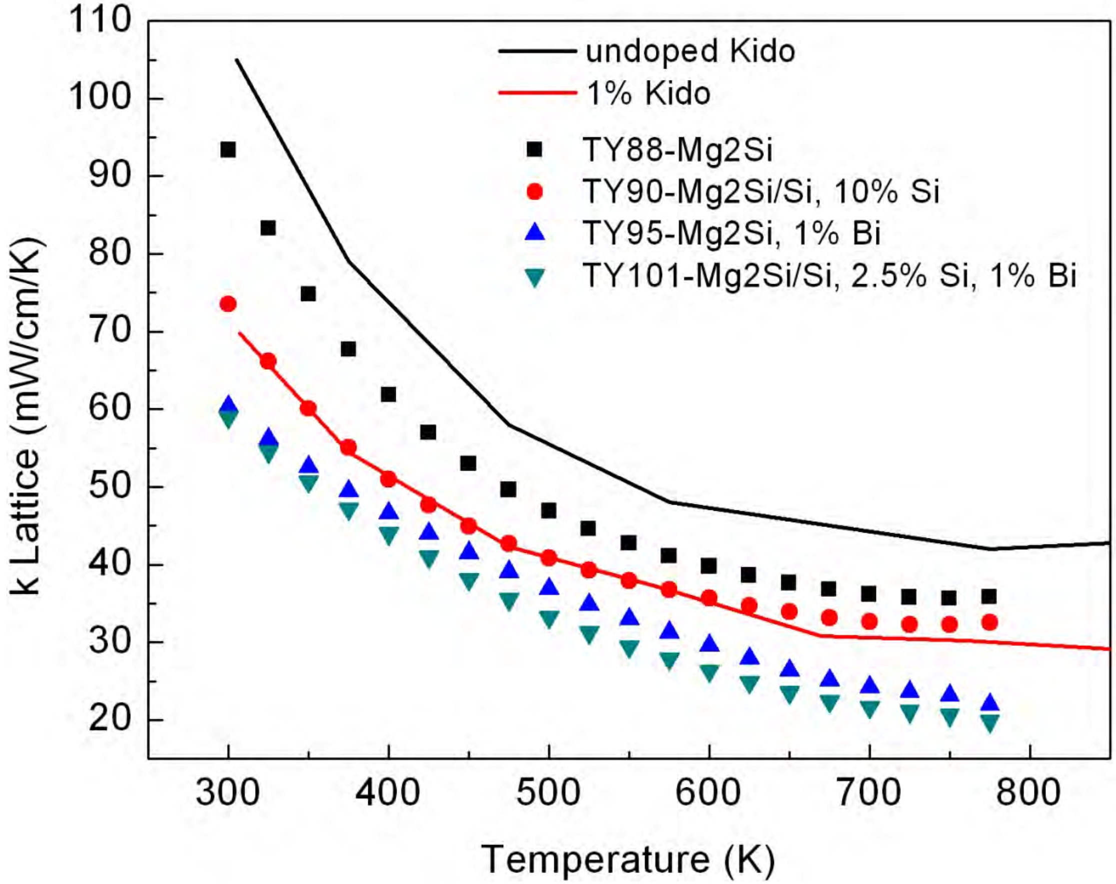
Transport Properties: Seebeck



Seebeck is as expected for a degenerate semiconductor

Progress:

Transport Properties: Thermal Conductivity

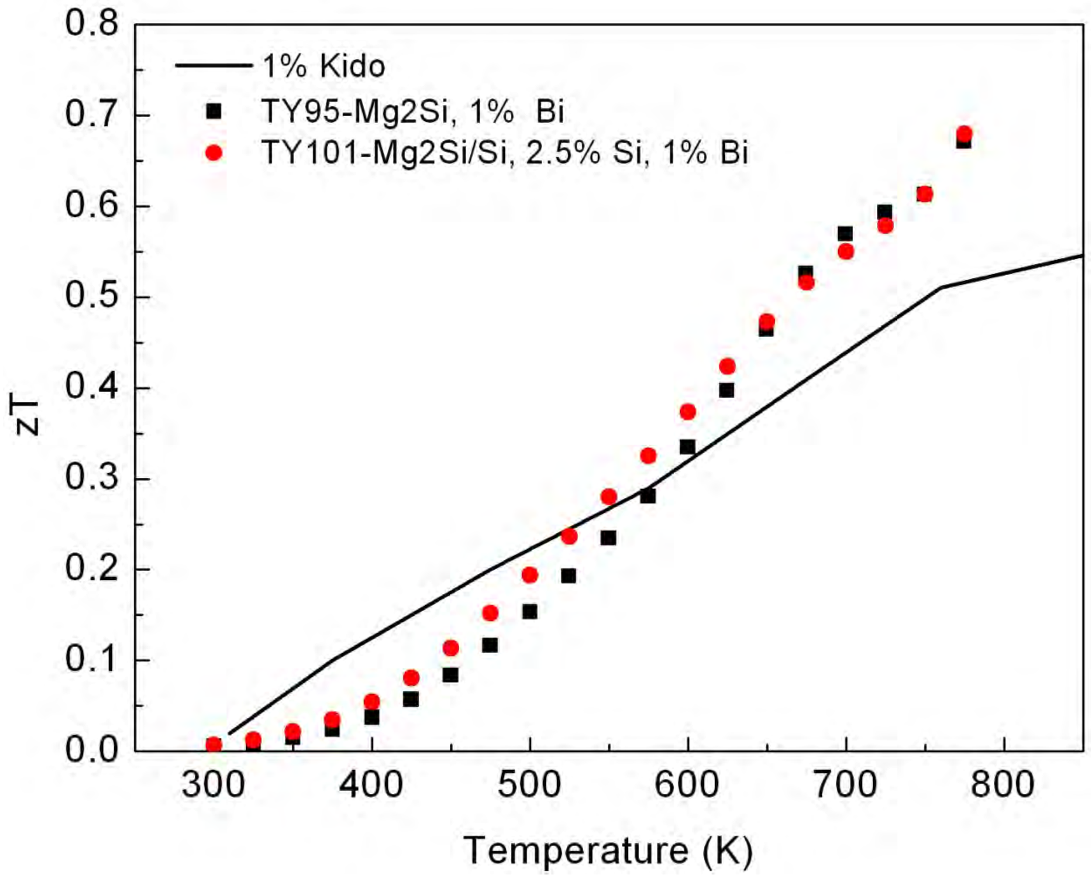


❑ Extracted lattice thermal conductivity: Measure thermal conductivity using laser flash method and subtracting the electronic contribution

❑ The results are comparable (and slightly lower) than that of Kido et al.

Technical Accomplishments

Transport Properties: Figure of Merit (ZT)



The figure of merit ZT of 1% Bi doped Mg_2Si with 5% of Si nanocomposite is 0.68 at 775 K, which is approximately 30% improvement compared to 1% Bi doped Mg_2Si (ZT ~0.52) reported by Tani, Kido, *Physica B* **2005,** *364* (1-4), 218-224.

Collaborations

- **Tela Favaloro, Zhixi Bian, Natalio Mingo and Ali Shakouri**

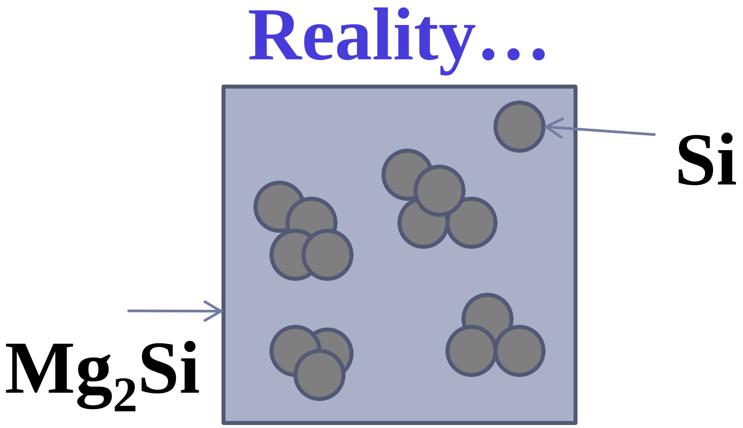
  Electrical Engineering Department, University of California, Santa Cruz, California 95064
- **Tanghong Yi, Oliver Janka and Susan Kauzlarich**

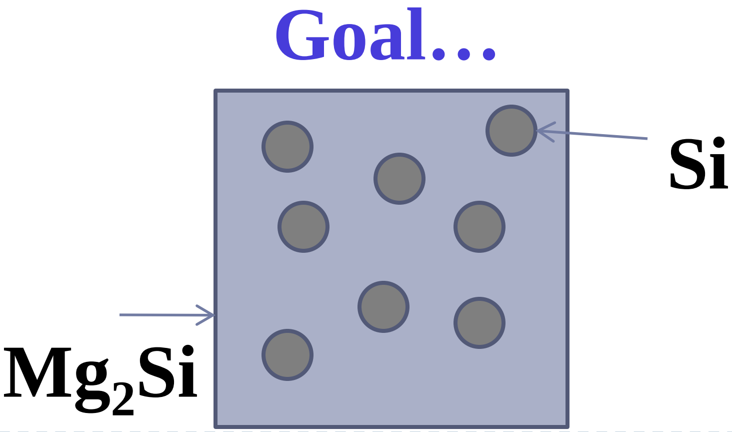
  Department of Chemistry, University of California, Davis, California 95616
- **Sabah Bux, and Jean-Pierre Fleurial**

  Jet Propulsion Laboratory, Pasadena, California 91109

Proposed Future Work

- ❑ Detailed comparison of theory/experiment; understand the origin of mobility degradation at low temperatures
- ❑ Optimize the growth condition (make the silicon nanoparticles isolated and homogeneously distributed with the assistance of solution synthesis)
- ❑ Identify high performance p-doping (Year 2)
- ❑ Improve ZT by optimizing nanoparticle size and potential distribution profile





Summary

- Optimization of Mg_2Si Composites for thermoelectric waste heat recovery in vehicle exhaust has been investigated
- Technical Accomplishments
  - Preliminary electron transport modeling based on Boltzmann including two conduction bands and impurity/phonon scattering (Seebeck of bulk Mg2Si)
  - Preliminary thermal conductivity modeling (optimum Si nanoparticle size for minimum lattice thermal conductivity)
  - A series of Mg2Si samples with embedded Si nanoparticles have been synthesized and extensively characterized in a wide temperature range.
  - Current ZT~0.7 at 800K shows 30% improvement compared to bulk Mg_2Si.
  - Microprobe shows that Si rich areas are at micro level (agglomeration), and Bi is preferentially distributed in Mg2Si.
  - We are investigating the cause of additional impurity scattering at low temperatures.