High Performance Zintl Phase TE Materials with Embedded Particles

Ali Shakouri (PI)
Birck Nanotechnology Center, Purdue University, West Lafayette, IN

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

In Collaboration with:
Sabah Bux, Jean Pierre Fleurial (NASA JPL)

3rd Thermoelectrics Applications Workshop, Baltimore, MA, March 20, 2012

GOAL: develop environmentally benign, nanostructured materials that are grown in bulk for enhanced thermoelectric performance (ZT>1.3-1.8) in 500-800K.

Improve Mg_2Si TE properties

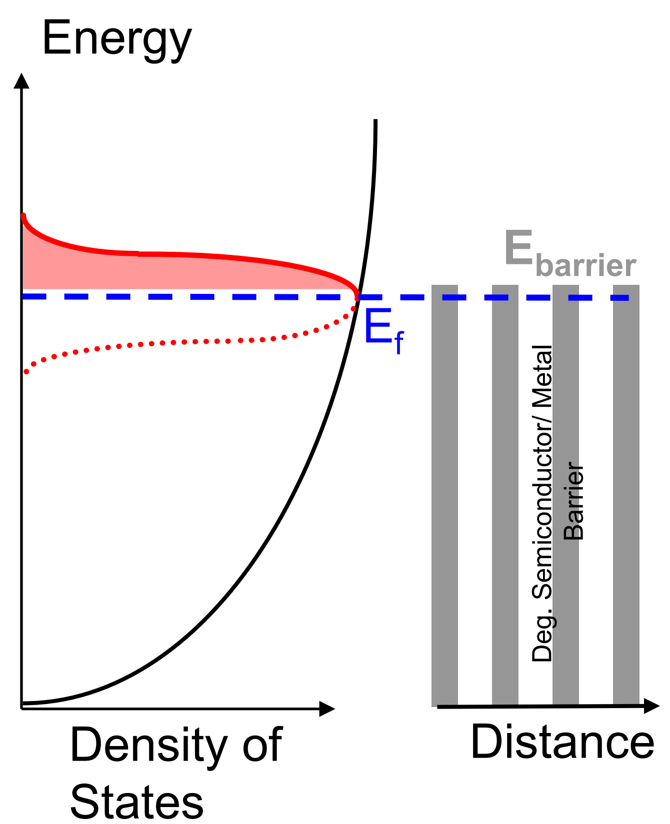
❑ Optimize nanoparticle (NP) size and composition to scattering mid/long wavelength phonons and reduce lattice thermal conductivity

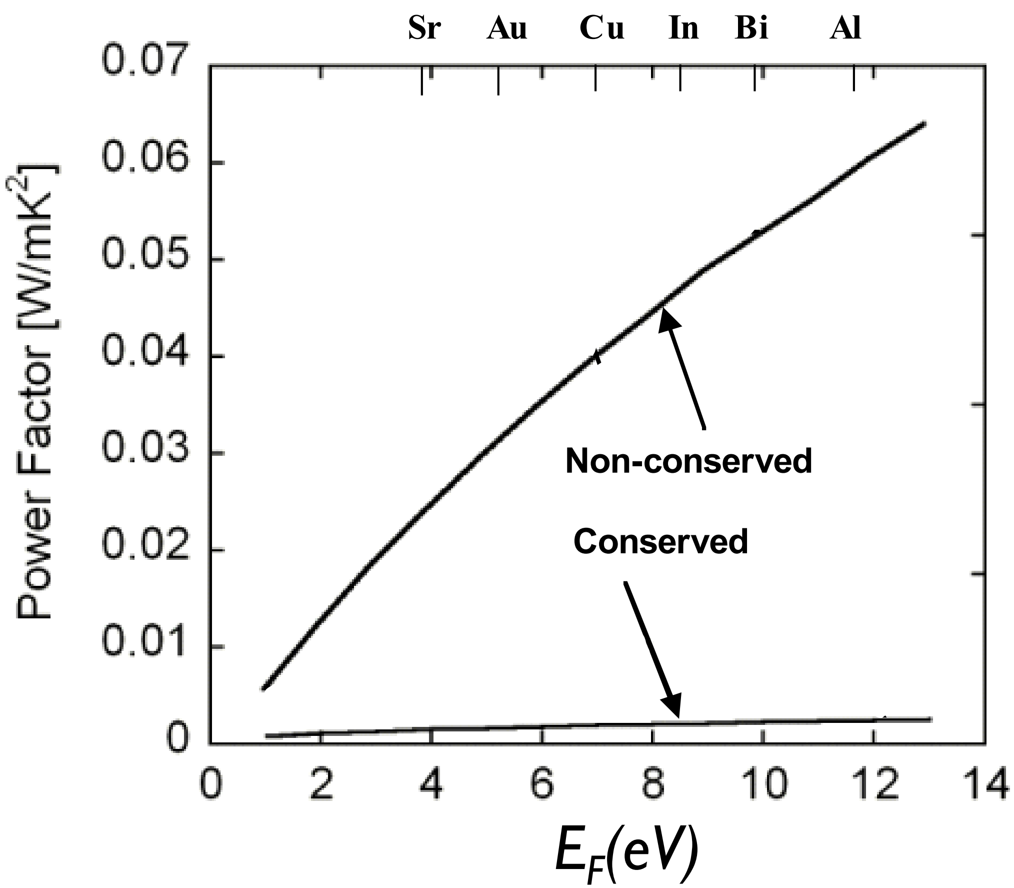
❑ Optimize NP potential profile to benefit from hot electron (hole) filtering and increase the thermoelectric power factor

❑ Use scalable bulk growth techniques

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

Hot electron filtering for enhanced TE power factor

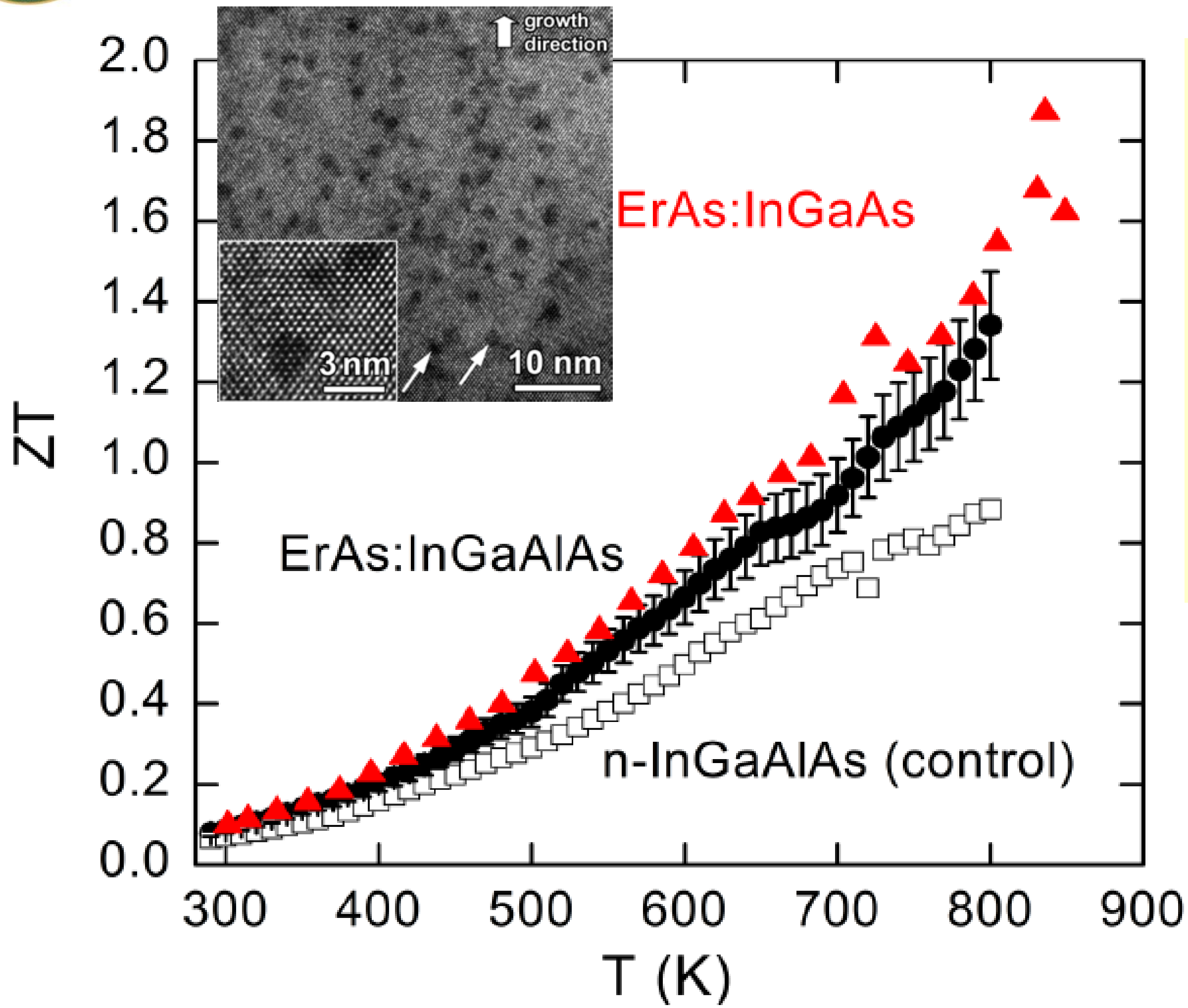


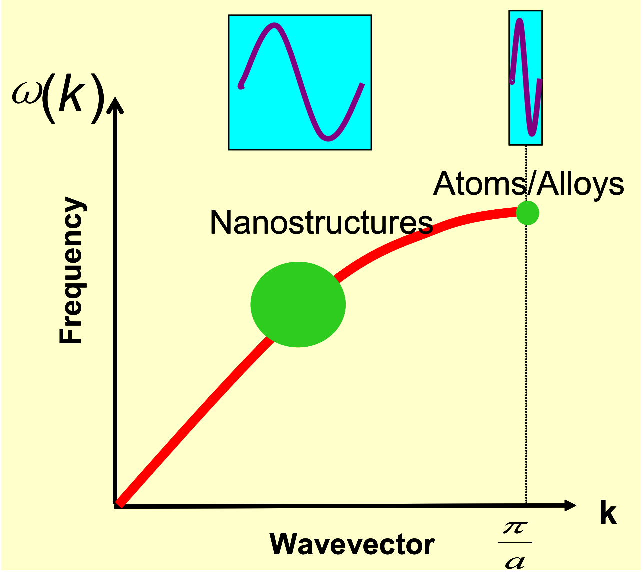


Symmetry of DOS near Fermi energy is the main factor determining Seebeck coefficient.

D. Vashaee and A. Shakouri, *Phys. Rev. Lett.* **92**, 106103/1 (2004); ICT 2004

ErAs Semi-metal Nanoparticles embedded in InGa(Al)As Semiconductor Matrix





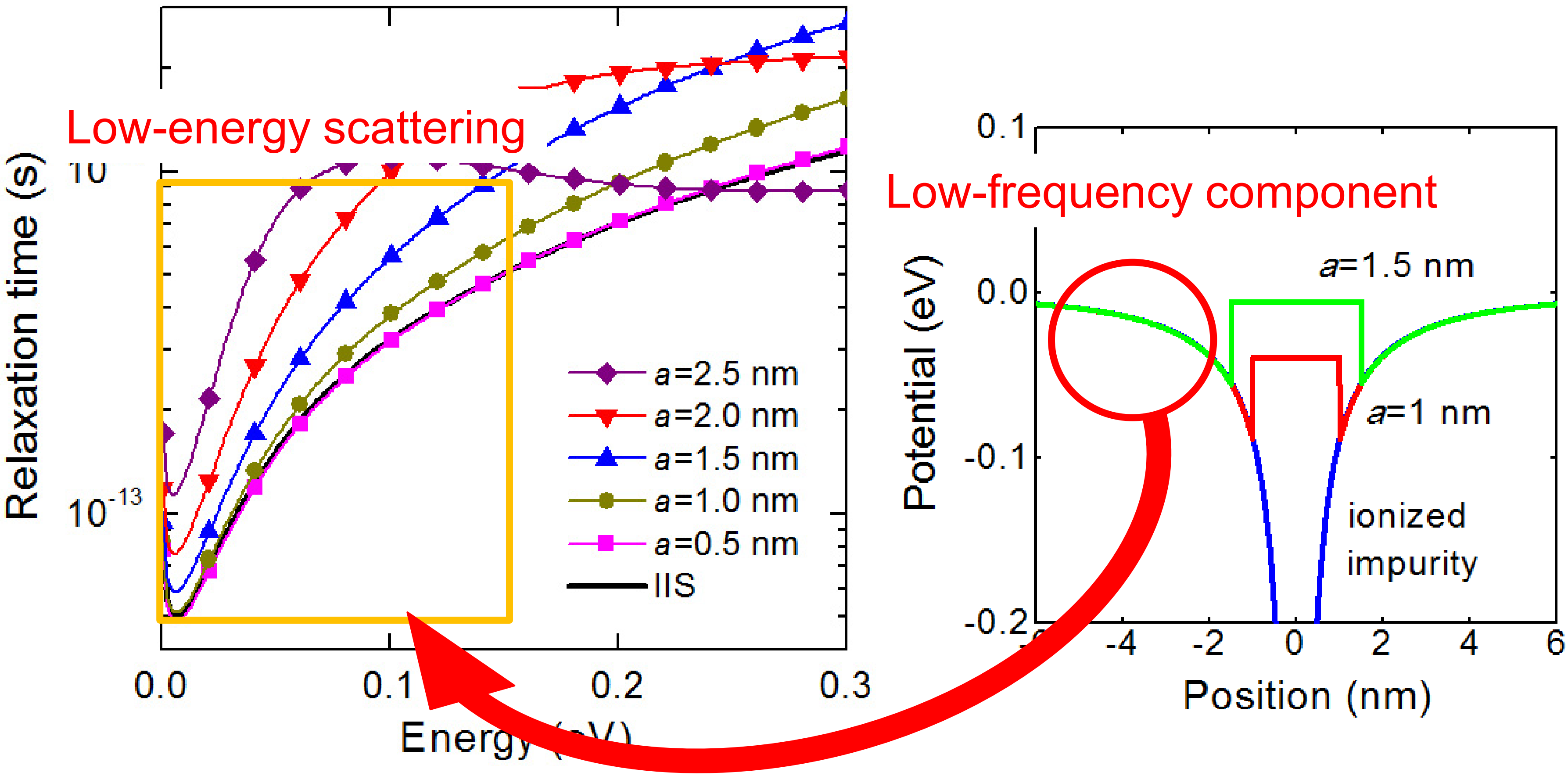
Largest measured ZT~1.7-1.8 at 830K

Zide et al. Journal of Applied Physics (2010); Bahk et al. to be published (2012)

CENTER for ENERGY EFFICIENT MATERIALS

The majority of ZT enhancement is from thermal conductivity reduction. 5% power factor enhancement at 800K.

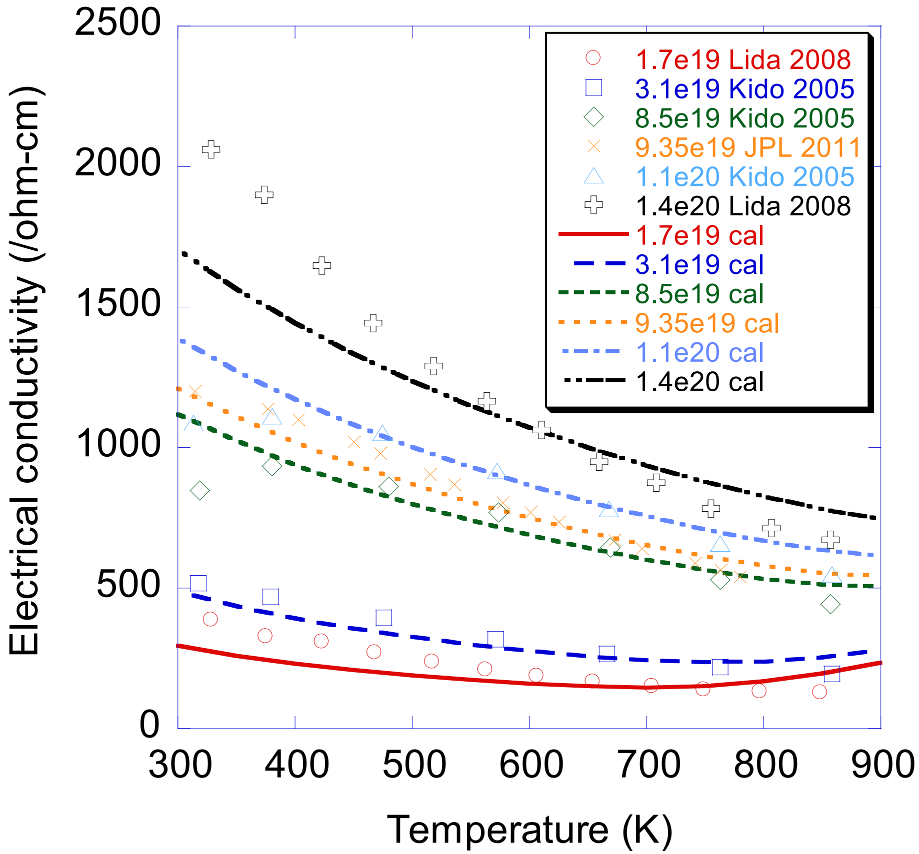
Relaxation time vs. nanoparticle scattering potential profiles

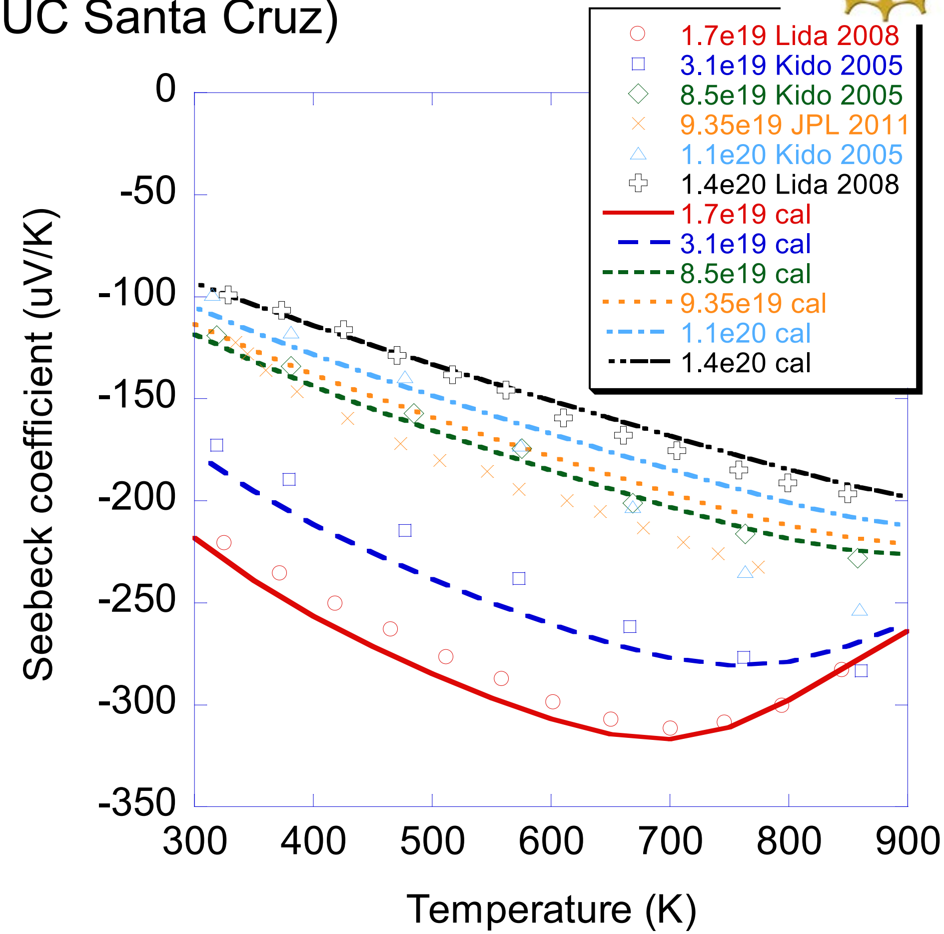


Je-Hyeong Bahk, Parthi Santhanam, Z. Bian et al., Applied Physics Letter 2011

Bulk Mg_2Si, Electron Transport Theory vs. Experiment

Zhixi Bian (UC Santa Cruz)





Using experimental data from: (1) MRS fall meeting, 2007; (2) Physica B 364 (2005) 218-224; (3) JPL unpublished results

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

Boltzmann Transport for bulk $Mg_2Si_{0.4}Sn_{0.6}$

Zhixi Bian (UC Santa Cruz)

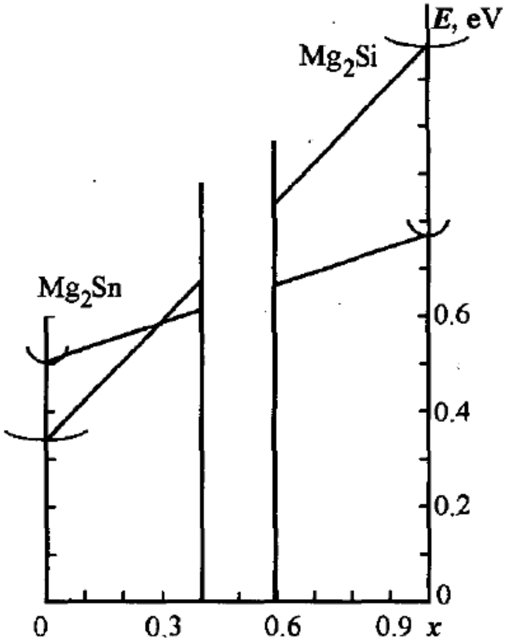
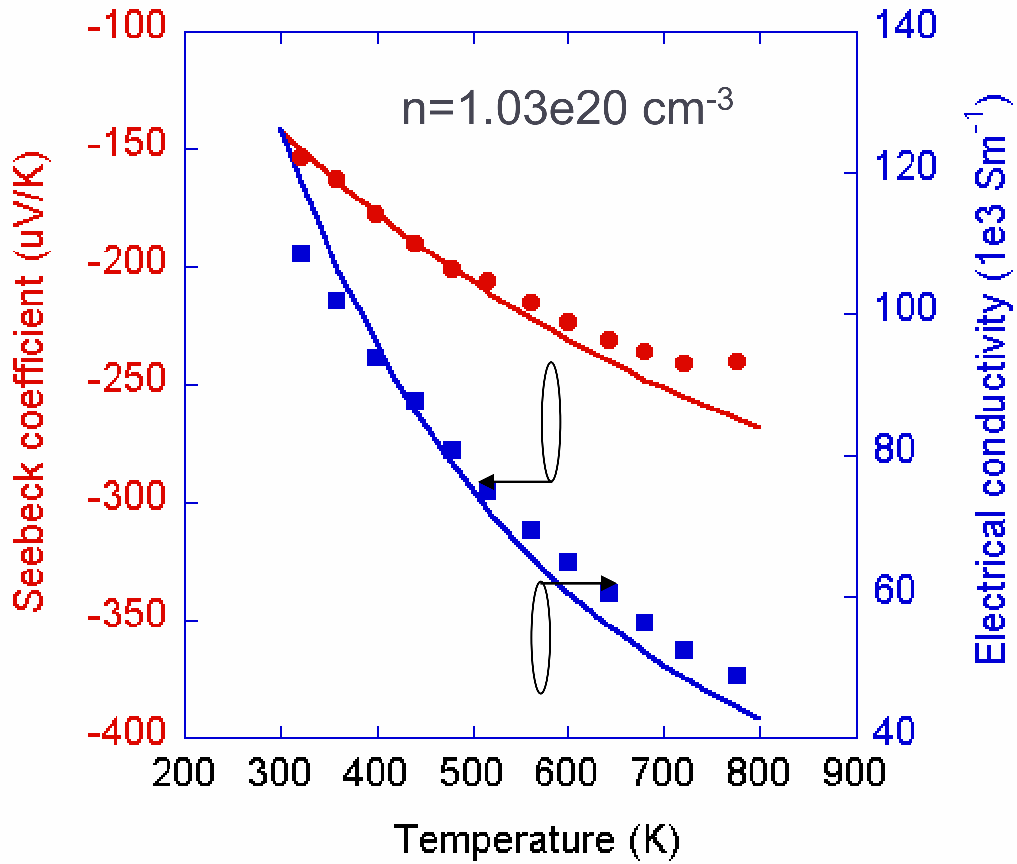


Figure 1: The scheme of energy gap change for the $Mg_2Si_xSn_{1-x}$ solid solutions



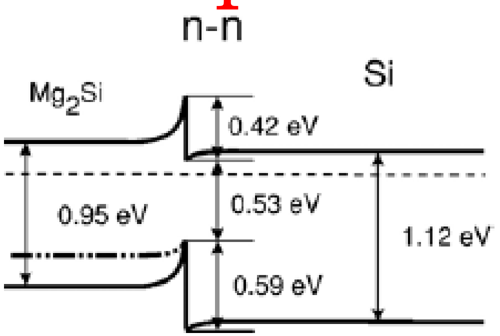
Using 2-conduction bands model from "Features of conduction mechanism in n-type $Mg_2Si_{1-x}Sn_x$," ICT 2003

Experiment data: Applied Physics Letters 93, 102109 (2008)

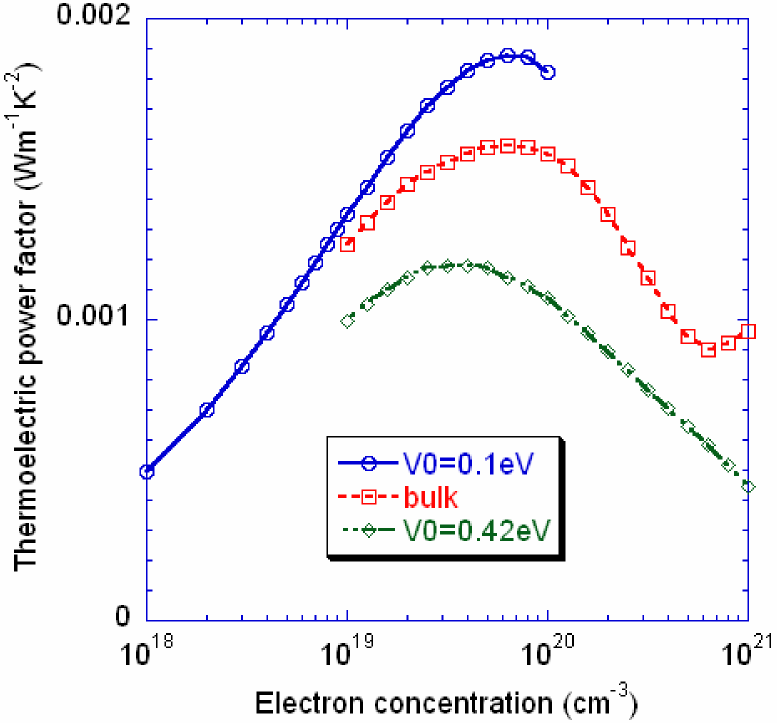
- ❑ Theory can explain temperature-dependence of the Seebeck Coefficient and electrical conductivity for n-doped bulk $Mg_2Si_{0.4}Sn_{0.6}$

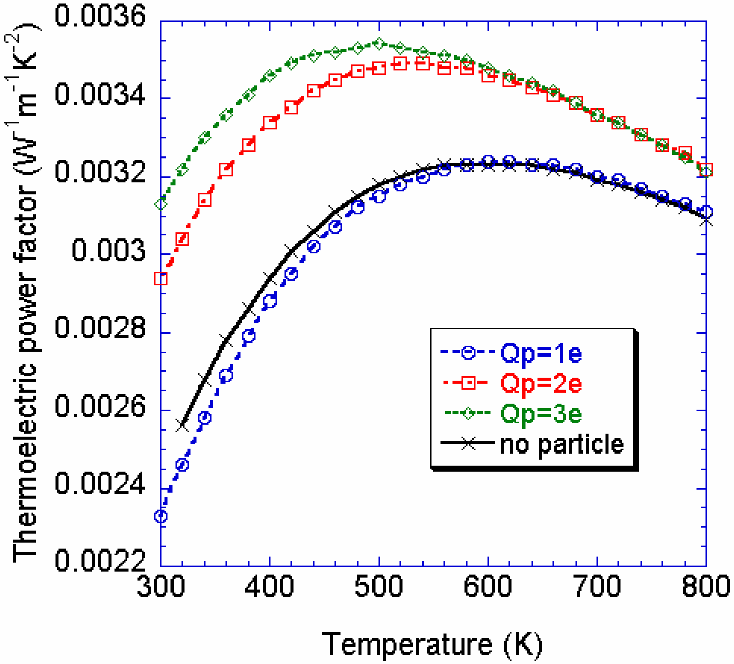
Theory: Si nanoparticle in Mg_2SiSn

Zhixi Bian (UC Santa Cruz)



Band diagram of Mg2Si/Si heterojunction from Thin Solid Films 515 (2007) 3046–3051





- Particle radius 1nm
- 2 electrons per particle

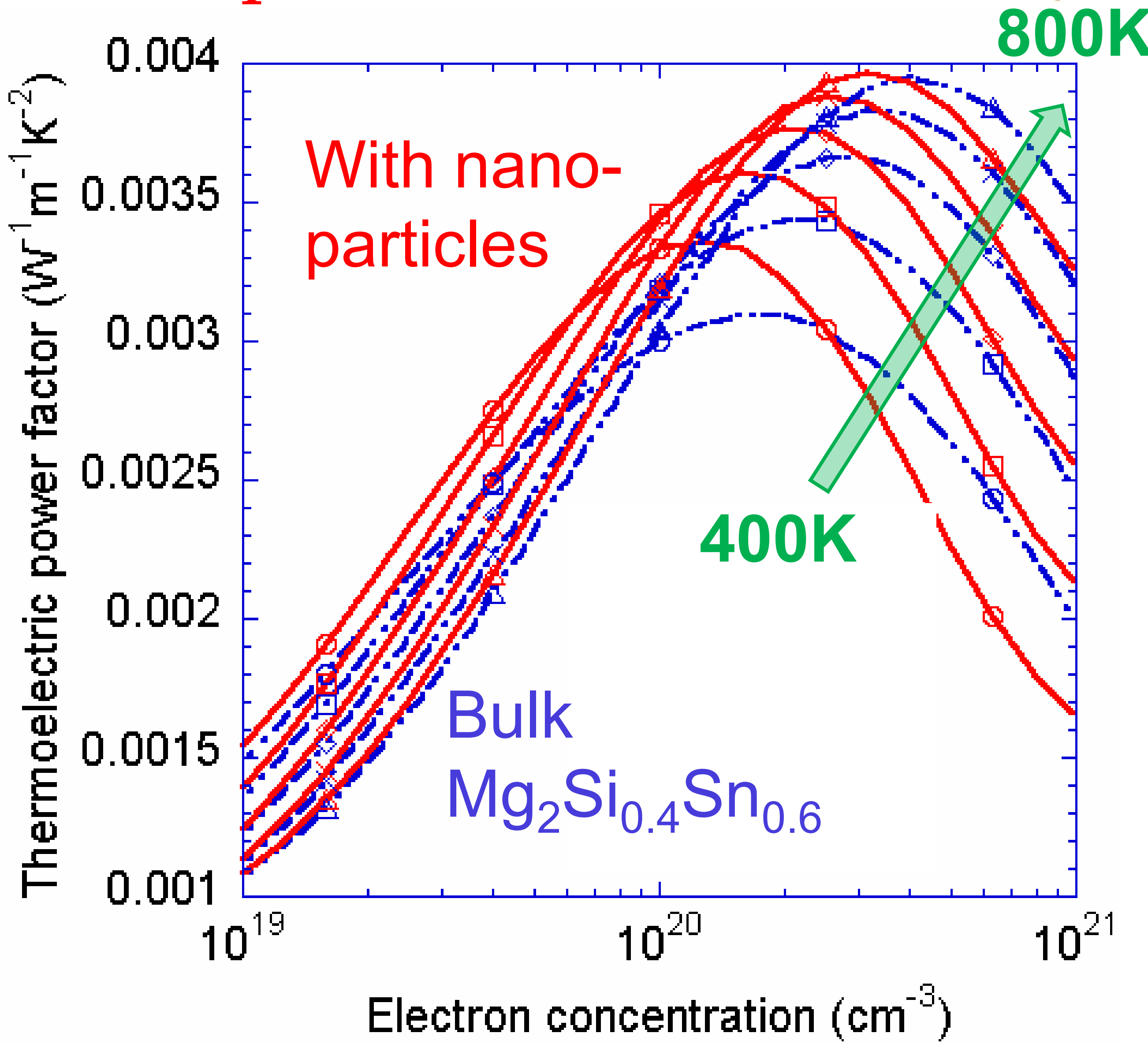
- $Mg_2Si_{0.4}Sn_{0.6}$ / Binary Silicide particles, with particle radius 1nm, Electron concentration 1e20 cm^{-3}
- Electron charge per particle is 1e, 2e, or 3e
- Conduction band offset: 0.1eV

TE transport in $Mg_2Si_{0.4}Sn_{0.6}$ with embedded nanoparticles

Zhixi Bian (UC Santa Cruz)

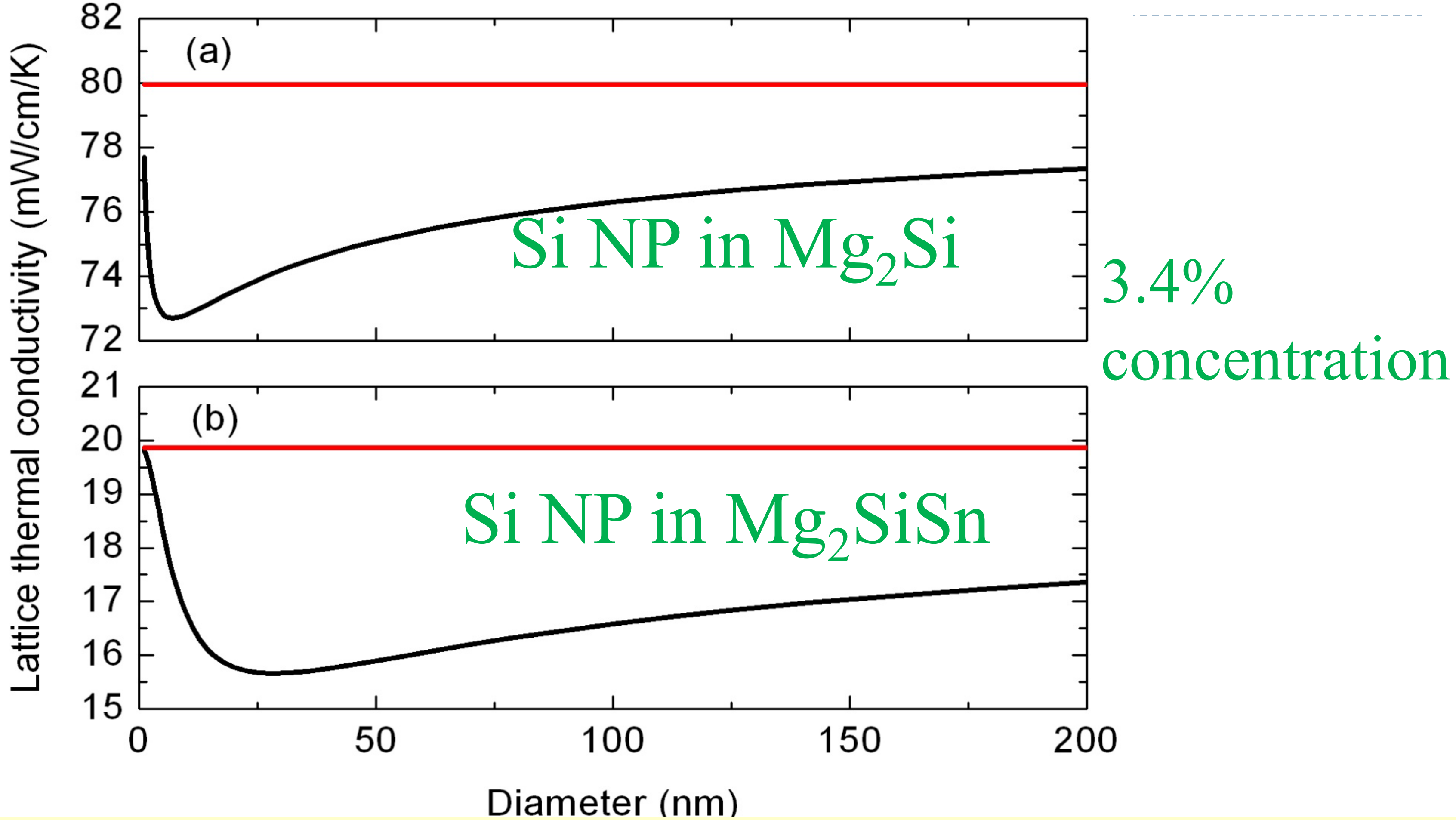
- ❑ Particle radius 1nm, conduction band offset 0.1eV, electron charge per particle 2e

- ❑ At higher temperatures, the power factor enhancement by using nanoparticles is reduced



Phonon Transport Modeling

Natalio Mingo (UC Santa Cruz, CEA)

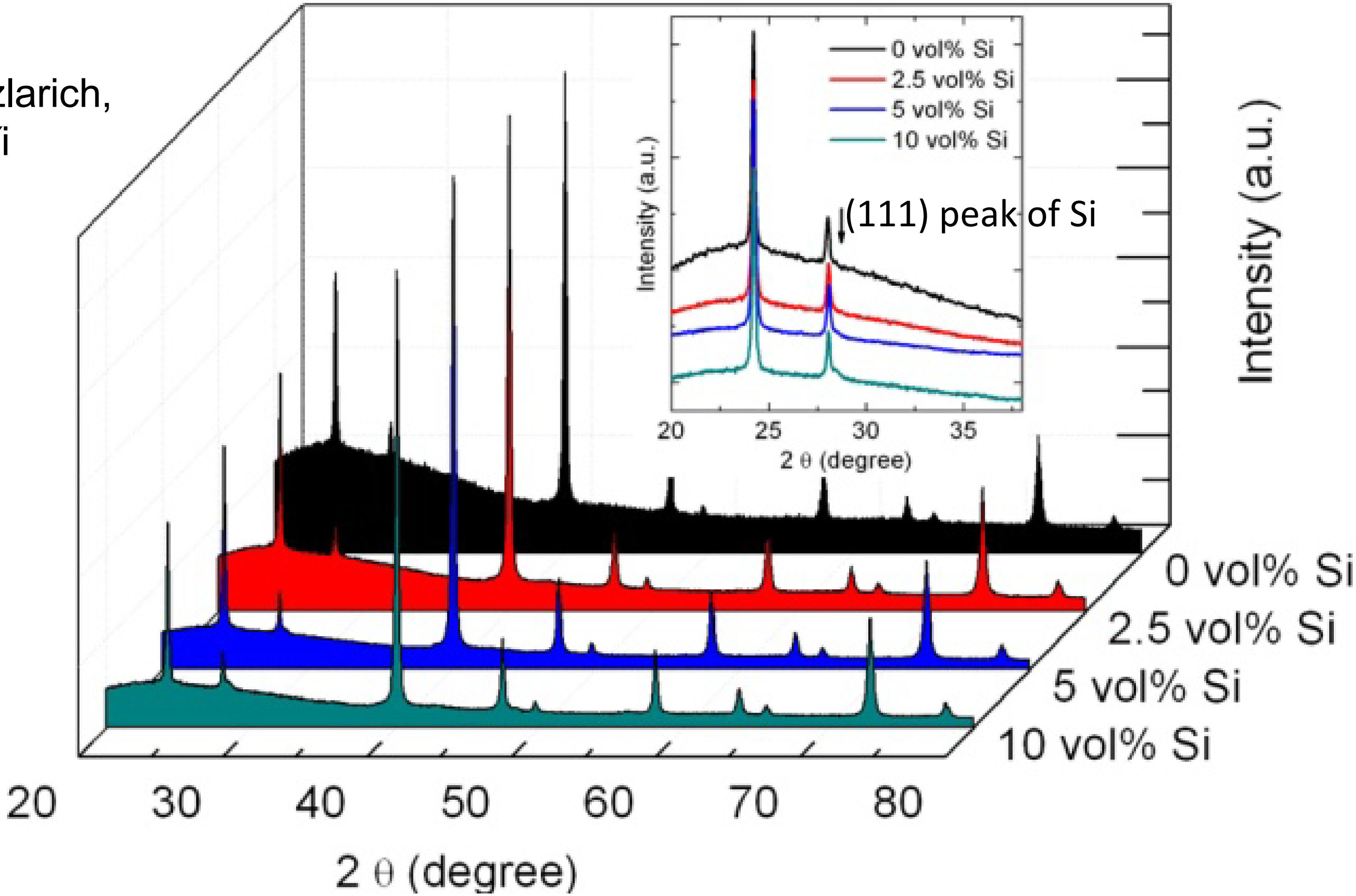


- ❑ Modeled the effect of Silicon nanoparticles on the thermal conductivity of Mg_2Si and Mg_2SiSn
- ❑ Optimum nanoparticle size for lowest thermal conductivity identified

Enhancement of TE performance of Mg_2Si with embedded Si nanoparticles

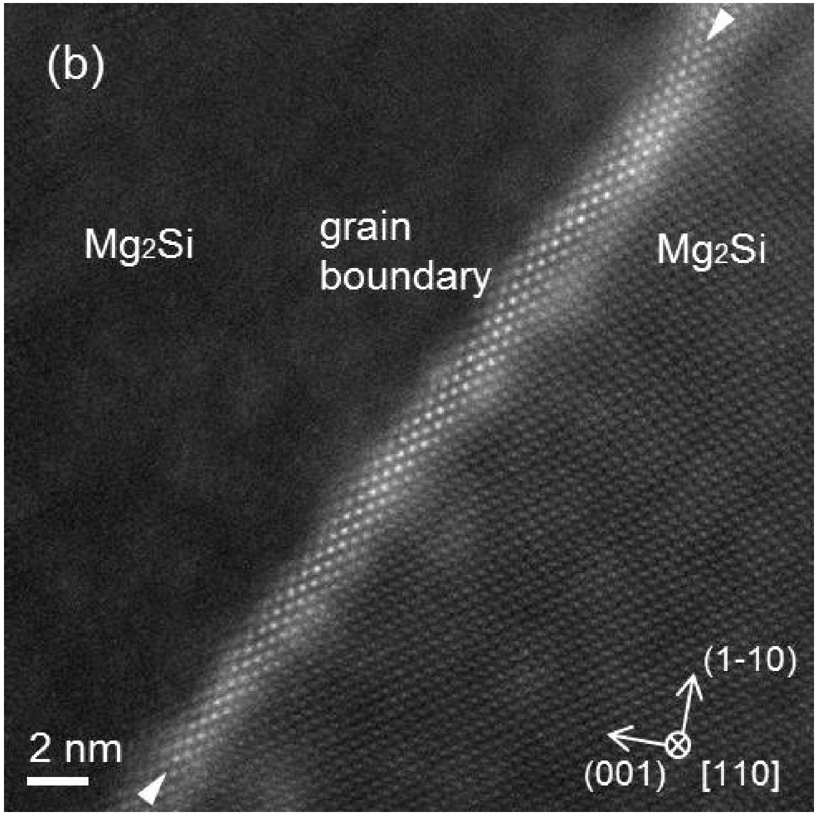
❑ Low temperature synthesis: Oxides free products; Grain size control; Easy nano inclusions

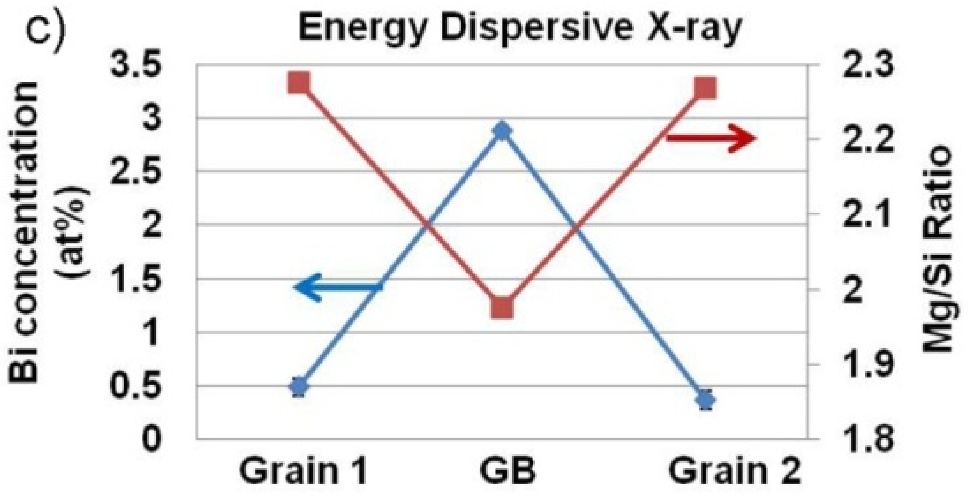
Susan Kauzlarich,
Tanghong Yi



Optimize the charge carrier concentration with proper amount of Bi dopant

Bi inclusions sit at grain boundaries (GB), and preferentially substitutes Mg at GB

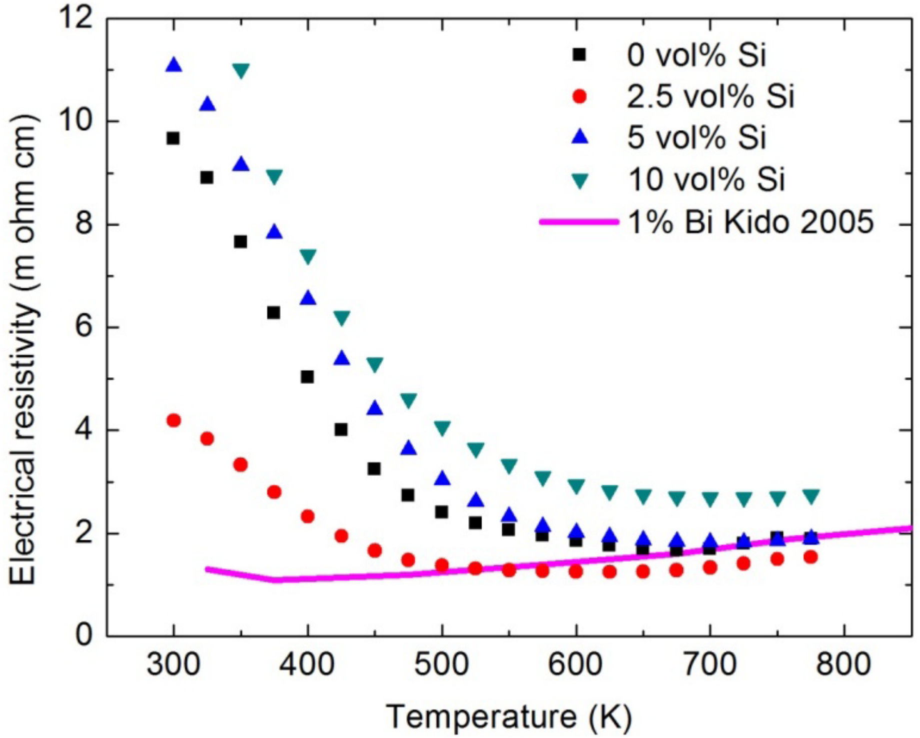


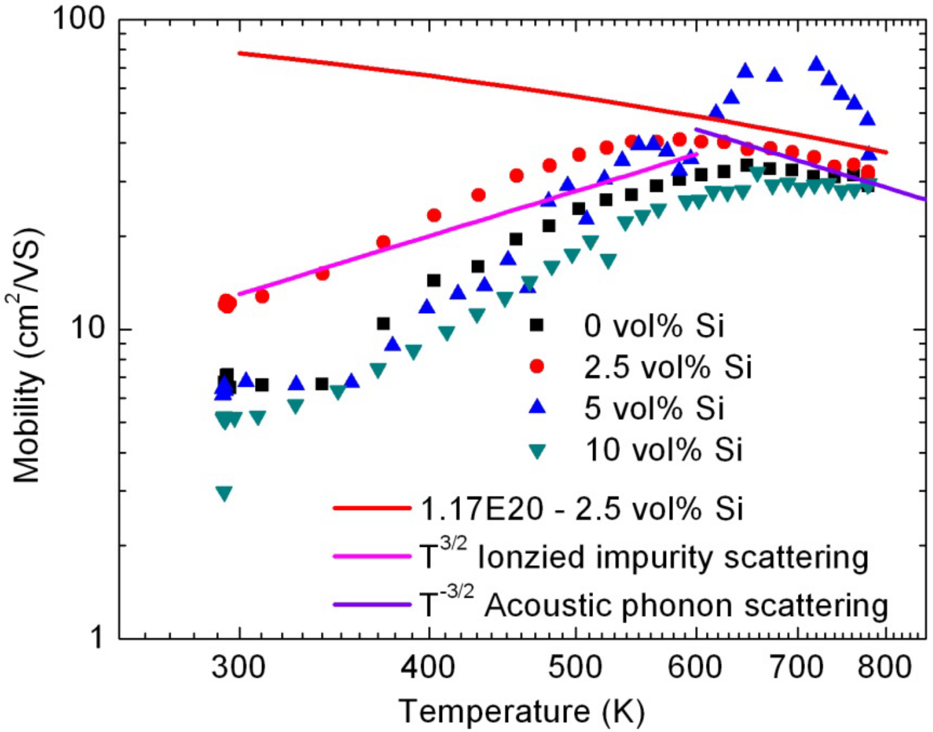


- Susan Kauzlarich, Tanghong Yi, Hao Yang, and Nigel Browning (PNNL)

Resistivity and Hall Mobility

Mg_2Si/xSi (x = 0, 2.5, 5, 10 vol.%)

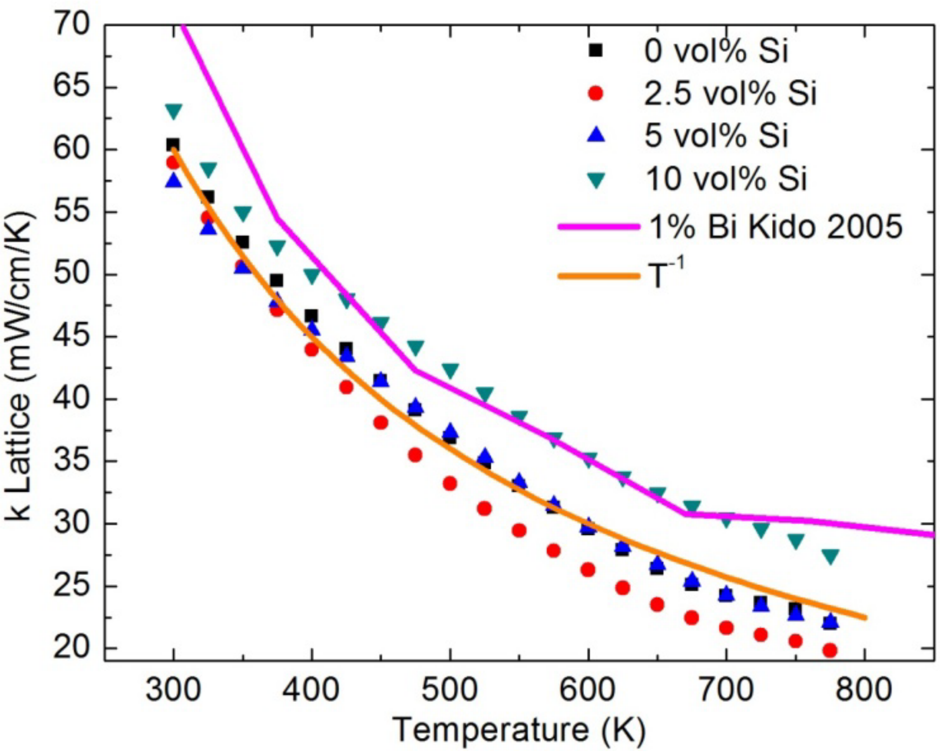


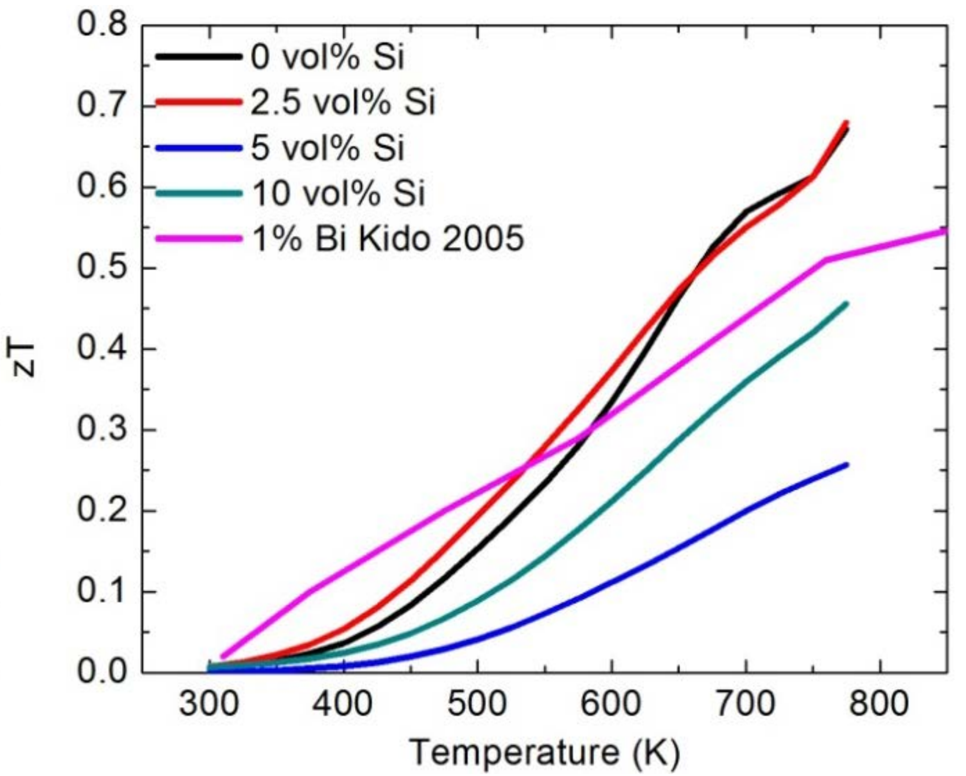


- Susan Kauzlarich, Tanghong Yi, Sabah Bux (JPL)

- Lattice thermal conductivity can be successfully lowered by nanoparticles (NP).

- ZT ~ 0.7 for $Mg_2Si/2.5vol\%Si_{1\%Bi}$ at 775 K





- Susan Kauzlarich, Tanghong Yi, Sabah Bux (JPL)

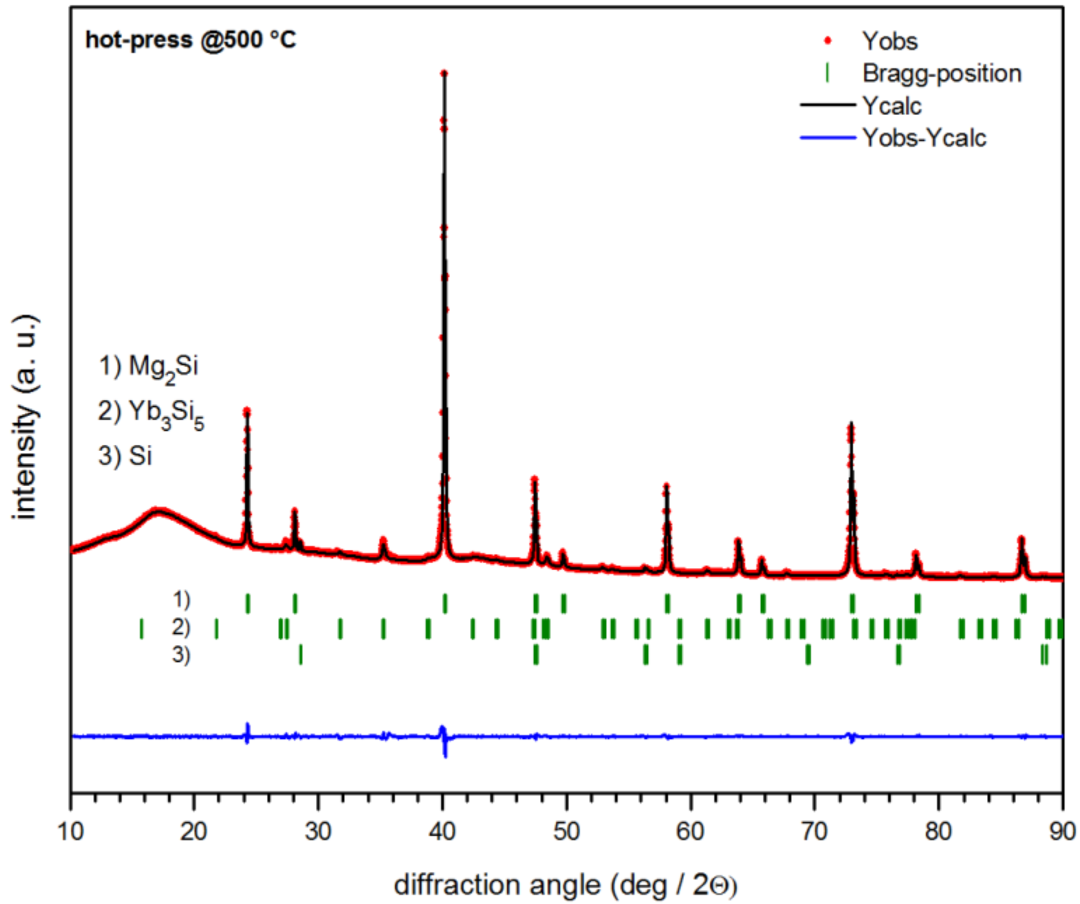
Yb-doping of Mg_2Si

Susan Kauzlarich, Oliver Janka

Motivation

Yb could be doped on the Mg site in Mg_2Si to reduce thermal conductivity.

Yb^{2+} should substitute the isovalent Mg^{2+}



Synthesis

MgH_2 and YbH_2 reacts with Bi-doped Si using hot-pressing or SPS techniques.

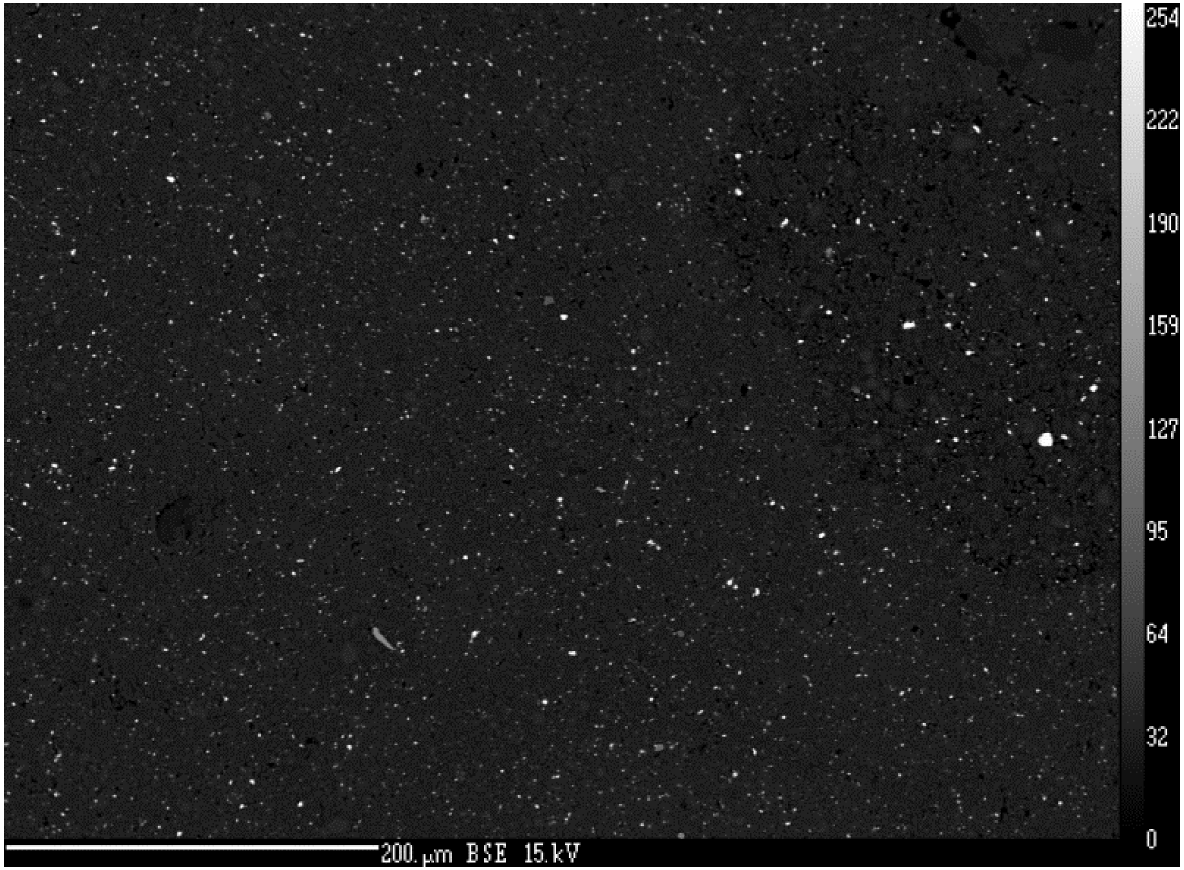
Susan Kauzlarich, Oliver Janka

Yb-doping of Mg_2Si

Powder XRD: Yb_xSi_y-phase is formed during the hot-pressing or SPS-ing of the reactants.

Electron microprobe analysis: BSE image where the bright spots indicate the Yb_xSi_y locations.

The islands seem to be well distributed over the whole imaged area but vary in size



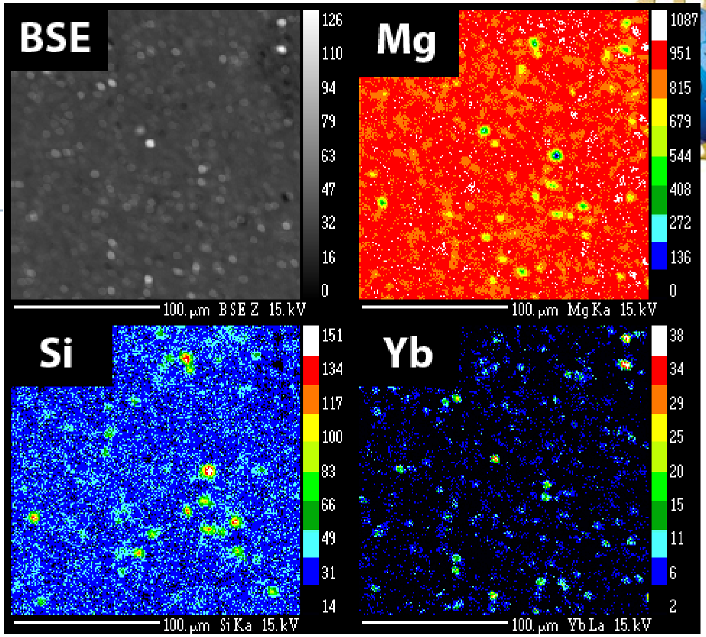
Susan Kauzlarich, Oliver Janka

Yb-doping (continued)

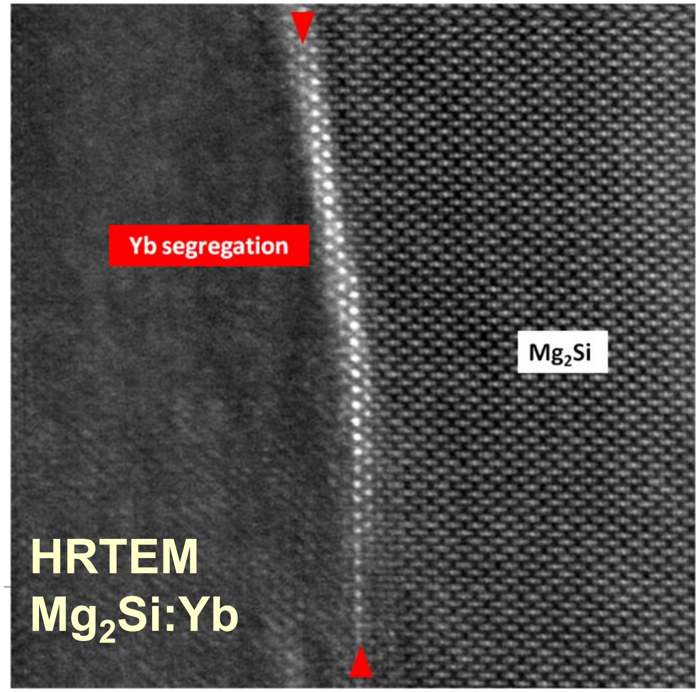
The Yb map shows that besides the Yb-silicide islands, Yb has also been doped on the Mg sites in the Mg_2Si matrix.

HRTEM investigations verify Yb doping on the Mg sites (1.0% Yb doped with no Bi doping). The bright spots show Yb sitting at the grain boundary.

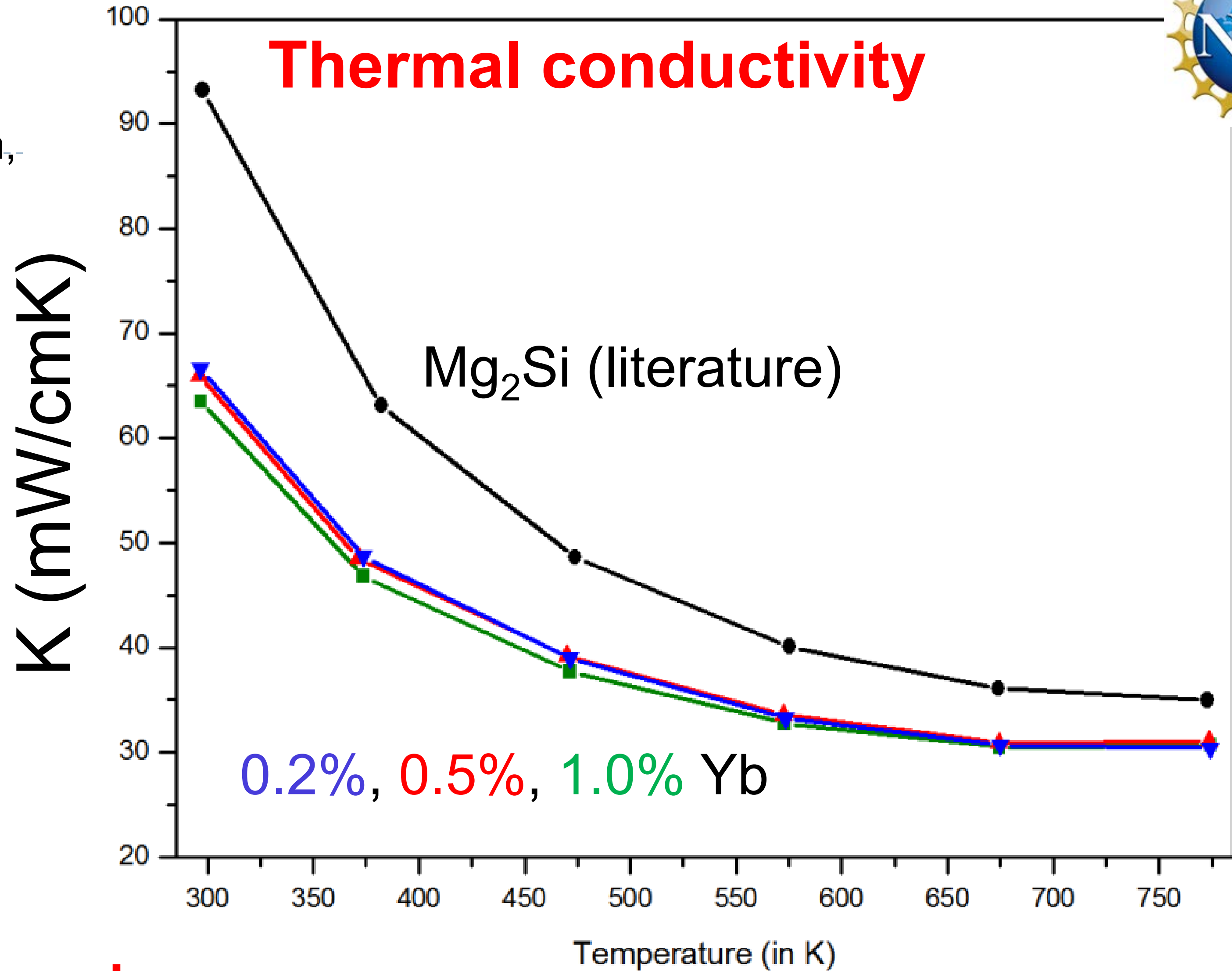
The bright Yb spots sit at the Mg site.



Elemental mapping



Susan Kauzlarich,
Oliver Janka,
Sabah Bux (JPL)



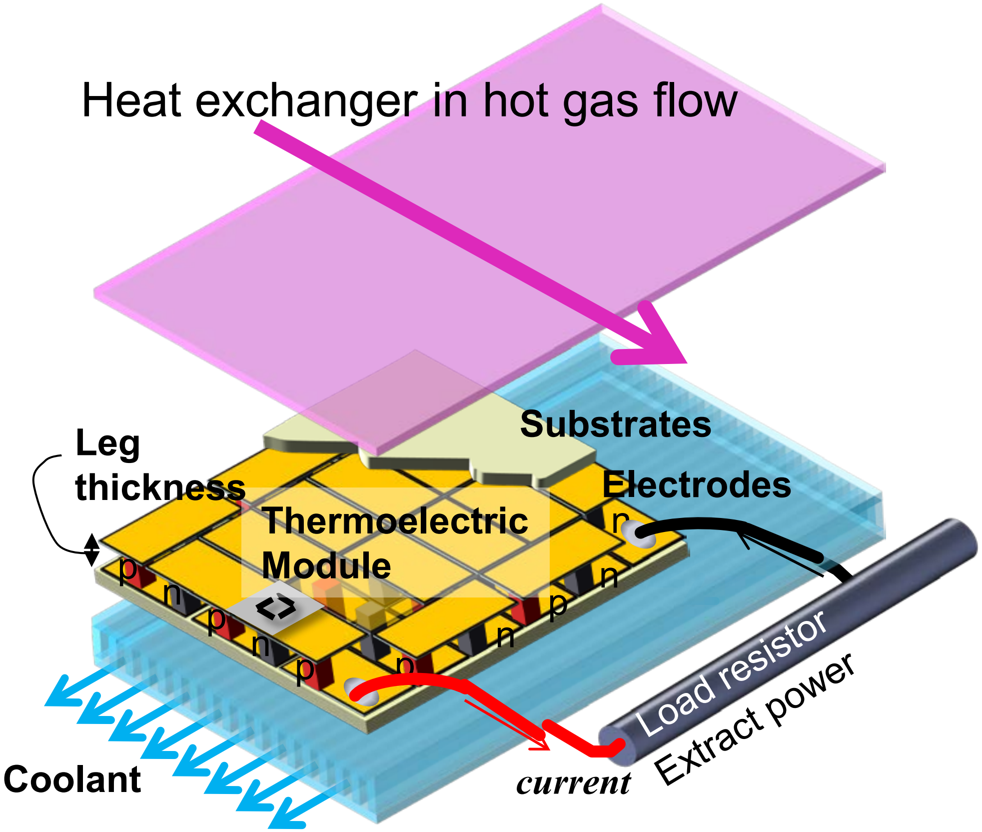
Future work

Optimize carrier concentration via Bi-doping.

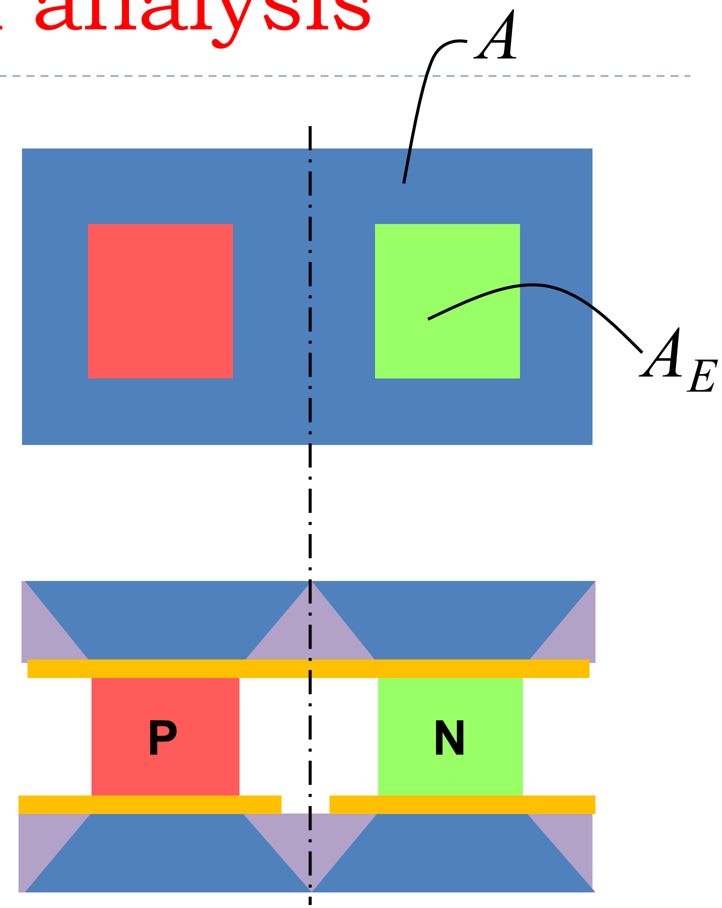
Optimize Yb-doping to maximize the reduction of the thermal conductivity.

Measure thermoelectric properties of optimized samples.

Model of TE module + heat exchanger for cost/efficiency trade off analysis



Cold side
Heat exchanger

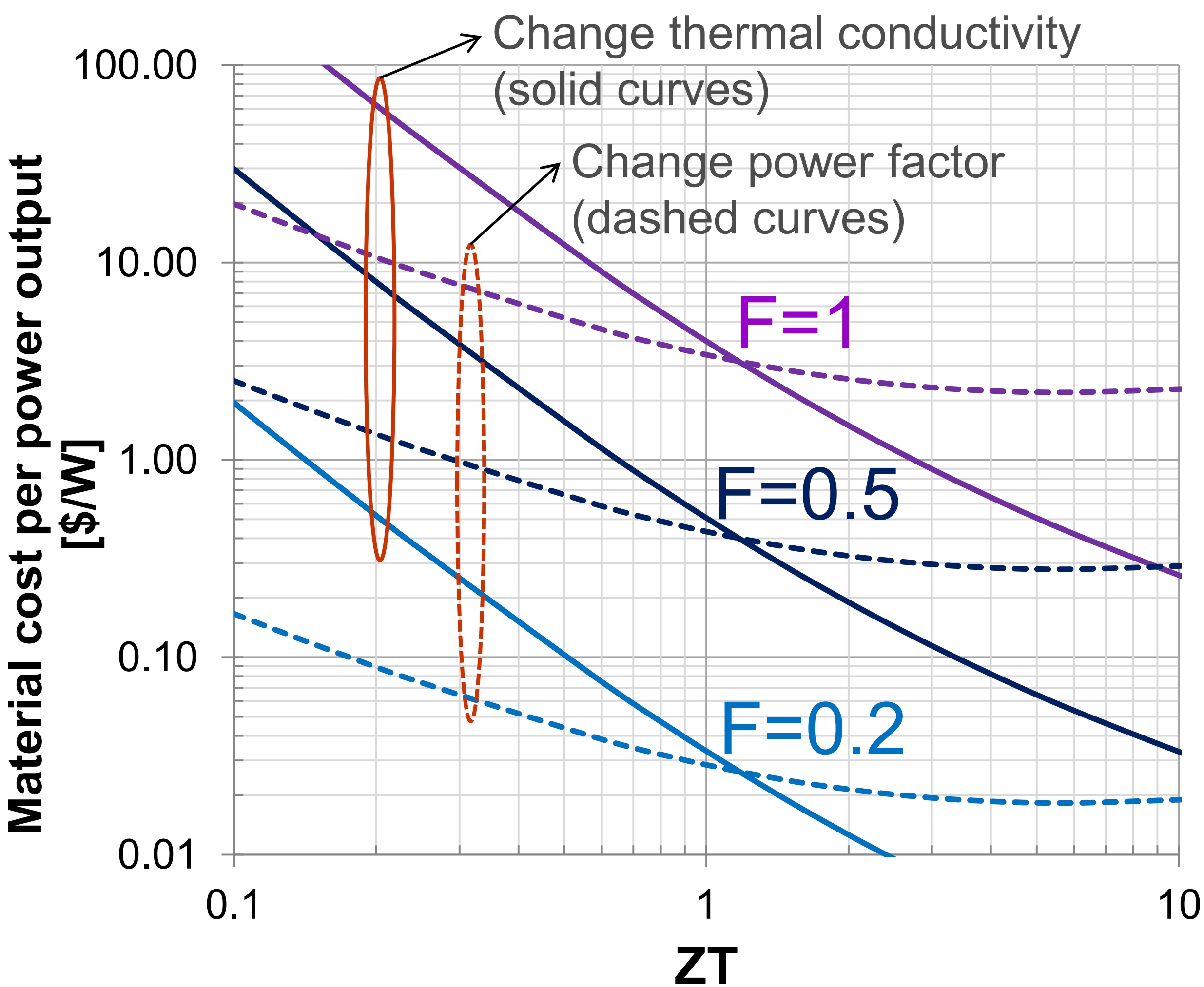


Fractional area coverage

$F = A_E/A$

K. Yazawa and A. Shakouri, Env. Science and Technology (July 2011)

TE Module Material cost per Watt



ZT=1, β=1.5 W/mK, β_{sub}=23 W/mK, t_{sub}=0.2mm,

Ts=900K, Ta=330K, Pump efficiency 30%

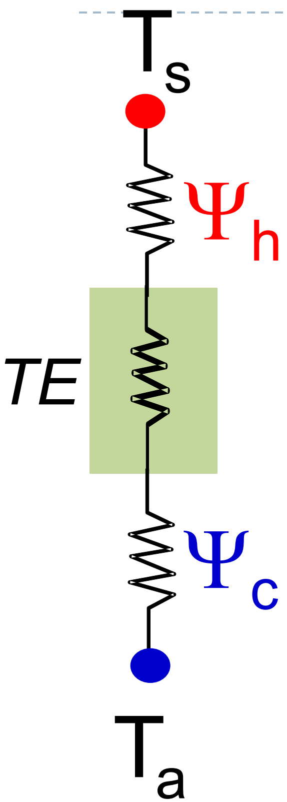
TE: $500/kg,
Alumina substrate: $ 5/kg,
Copper heat sink: $ 20/kg

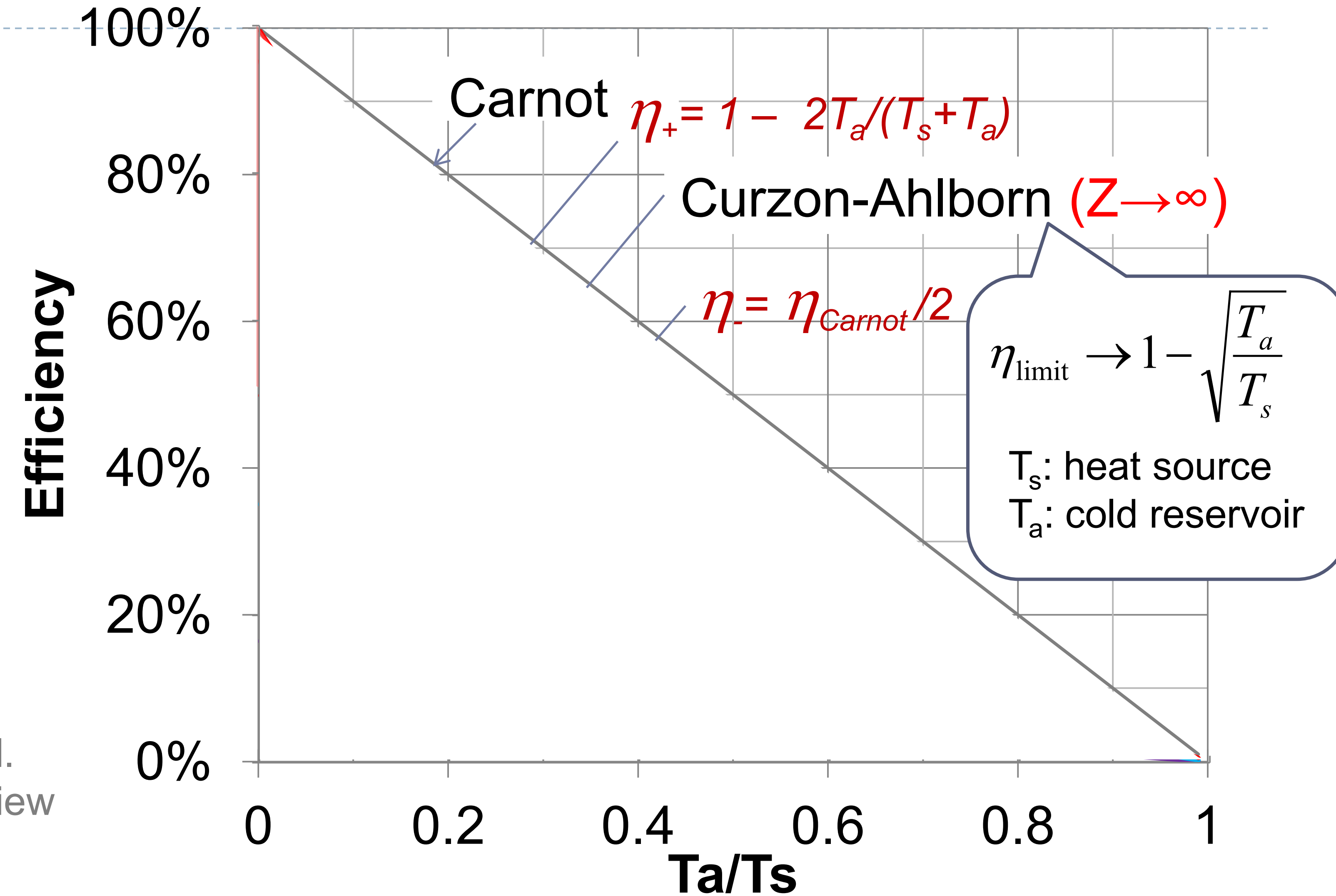
U_h=4.6x10^{2}W/m^{2}K
U_c=1.5x10^{3}W/m^{2}K (U_c/U_h=0.3)

Yazawa & Shakouri; Journal of Material Research 2012 (to be published)

TE Efficiency at maximum output power

(role of asymmetric thermal contacts with reservoirs)





Esposito et al.
Physical Review
Letters 2011

CENTER for ENERGY EFFICIENT MATERIALS

K. Yazawa, A. Shakouri, J. Appl. Phys. 111, 024509 (2012)