Thermoelectrics Theory and Structure

David J. Singh
Oak Ridge National Laboratory

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PM013

Overview

Timeline

- Started FY09.
- Completion FY13.
- 70% Complete.

Budget

- Total project funding.
- 100% DOE.
- FY10: $400K.
- FY11: $400K.
- FY12: $375K (anticipated).

Barriers*

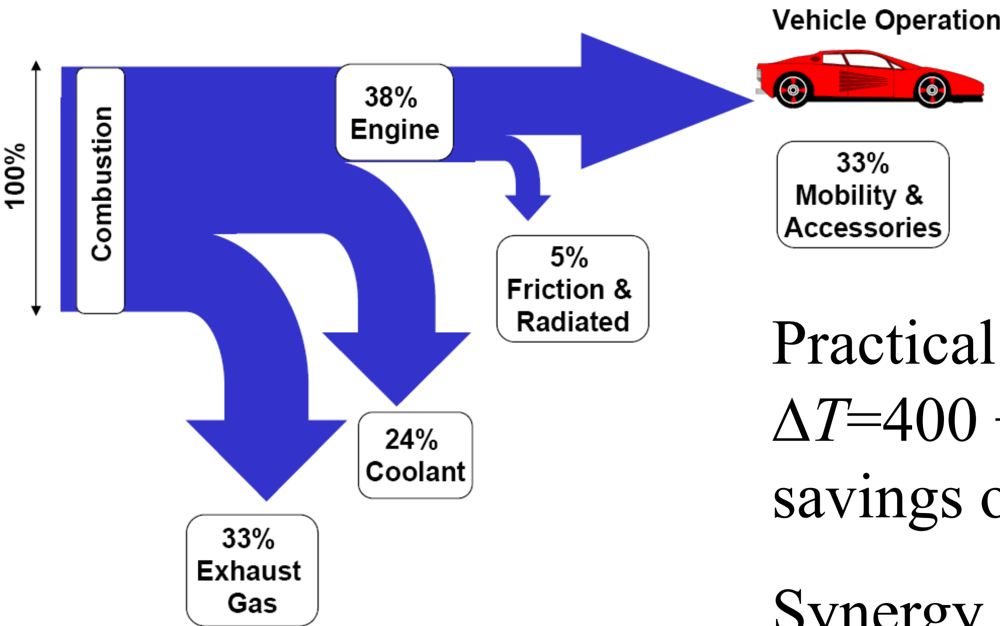
- Need high *ZT* for waste heat recovery (*ZT*>2) for 10% fuel savings.
- Need cost effective materials (target $1/Watt, desirable $0.2).
- Need durable *p*- & *n*-type materials.
- Need materials without rare elements, e.g. Te.

Partners

- Interactions/ collaborations:
  - Massachusetts Institute of Technology (S^3TEC Center)
  - General Motors
  - Ford Motor Co.
  - University of Washington
  - Naval Research Laboratory
  - California Institute of Technology
- Project lead: ORNL

* DOE Vehicle Technologies Multi-Year Program Plan 2011-2015, Solid State Energy Conversion 2.3-4 and 2.3-5; Propulsion Materials Technology 2.5-3, Task 2 (Materials for Exhaust Systems and Energy Recovery) and Task 4 (Materials-by-Design).

Relevance



$$ZT = \sigma S^2 T/\kappa$$

Practical materials with $ZT > 2$ for ΔT=400 +/- 50 C can yield fuel savings of 10%. [1,2]

Synergy with truck electrification.

Exhaust and EGR loop gas have potential for substantial energy recovery.

Efforts at General Motors, Ford, Toyota/Denso, BMW, Volkswagen, Bosch, Amerigon/BSST, Siemens, Cummins …

[1] DOE Vehicle Technologies Program Plan 2011-2015
[2] "Science Based Approach to Development of Thermoelectric Materials for Transportation Applications: A Research Roadmap", DOE FCVT (2007).

2.3.2 Solid State Energy Conversion

Goals

The goal of the Solid State Energy Conversion activity is to develop advanced thermoelectric technologies for recovering engine waste heat and converting it to useful energy that will help improve overall engine thermal efficiency to 55 percent for Class 7 and 8 trucks, and 45 percent for passenger vehicles while reducing emissions to near-zero levels. More specifically,

- By 2015, achieve at least a 17 percent on-highway efficiency of directly converting engine waste heat to electricity which will increase passenger and commercial vehicle fuel economy by 10 percent.
- By 2015, reduce by at least 30 percent, the fuel use to maintain occupant comfort through the use of thermoelectric heaters/air conditioner (TE HVAC) systems.

This activity also supports the overall engine efficiency goals of the FreedomCAR and Fuel Partnership, and 21st CTP. The technical targets for Solid State Energy Conversion are shown in Table 2.3-4.

Significant effort, and accomplishments, on thermoelectric materials for vehicle climate control (see Accomplishments)

Relevance

Barriers:

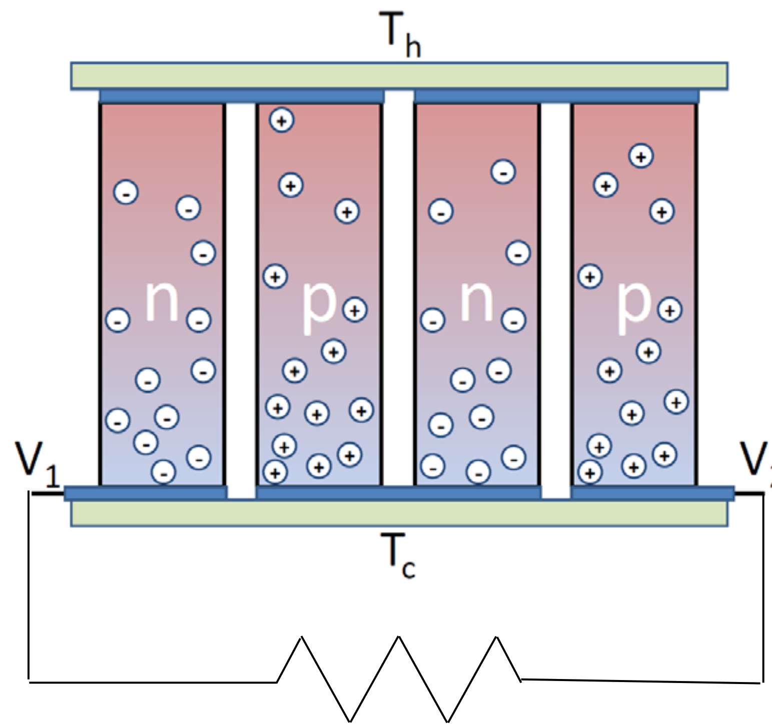
•Need high *ZT* (ideally *ZT*=2 or higher for waste heat recovery, ZT >1 for climate control).

•Need low cost ($1/watt or better).

•Need *p*-type and *n*-type.

•Need high availability, manufacturable materials – concern with Te: low abundance, solar cell use

•Avoid materials with toxic components – Pb practical but undesirable

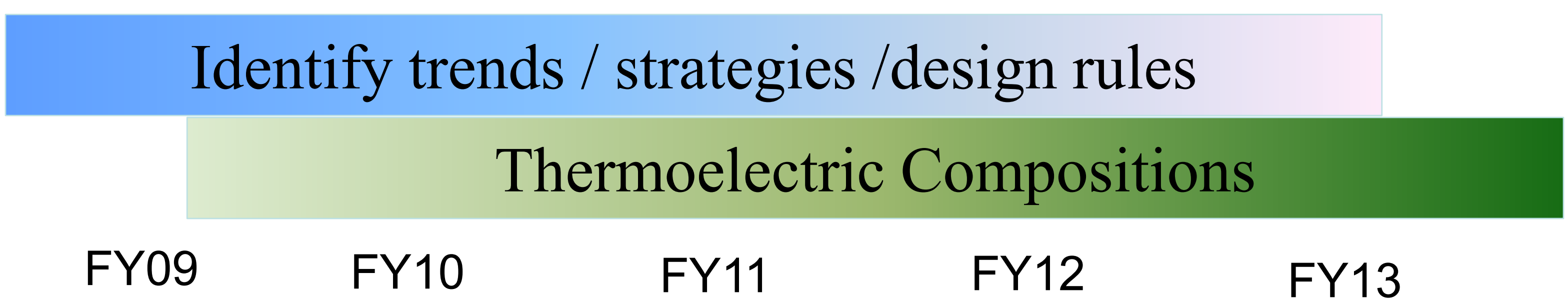


Thermoelectric generator

To save energy a technology must not only work – it must be used.

Thermoelectrics Theory and Structure

- Find promising thermoelectric compositions for waste heat recovery in vehicles (waste heat → electrical power).
- Focus on inexpensive materials that can be used.
- Use science based approach especially materials design strategies based on first principles.
- Potential additional benefit: Improved materials for climate control systems → Impact on Electric Vehicles.



Milestones

9/30/2011: ***Identify a potentially practical and low cost material that has a high thermopower in the temperature range from 300 to 600 Celsius and other properties indicating an optimized figure of merit exceeding that of currently used materials for waste heat recovery, and document this in a technical report describing the scientific basis for this identification***.

We examined (through our in-house Boltzmann transport code along with first principles calculations) the potential thermoelectric performance of a number of materials. In this we are able to calculate essential quantities such as the doping and temperature-dependent Seebeck coefficient and the electrical conductivity anisotropy.

From these materials we down-selected Mo_3Sb_7, a cubic material that has already shown a ZT of 0.93 at high temperature at a highly unoptimized doping level. Found that this material may show ZTs as high as 1.8 at 1000 K if doping is optimized to a level, and in a manner, specified in the technical report.

Technical Report: D. Parker, M.H. Du and D.J. Singh, Physical Review B **83**, 245111 (2011).

Milestones

12/31/2011: ***Identify a potentially practical and low cost material that has a high thermopower in the temperature range from -25 to 50 Celsius and other properties indicating an optimized figure of merit exceeding that of currently used materials for climate control, and document this in a technical report describing the scientific basis for this identification***.

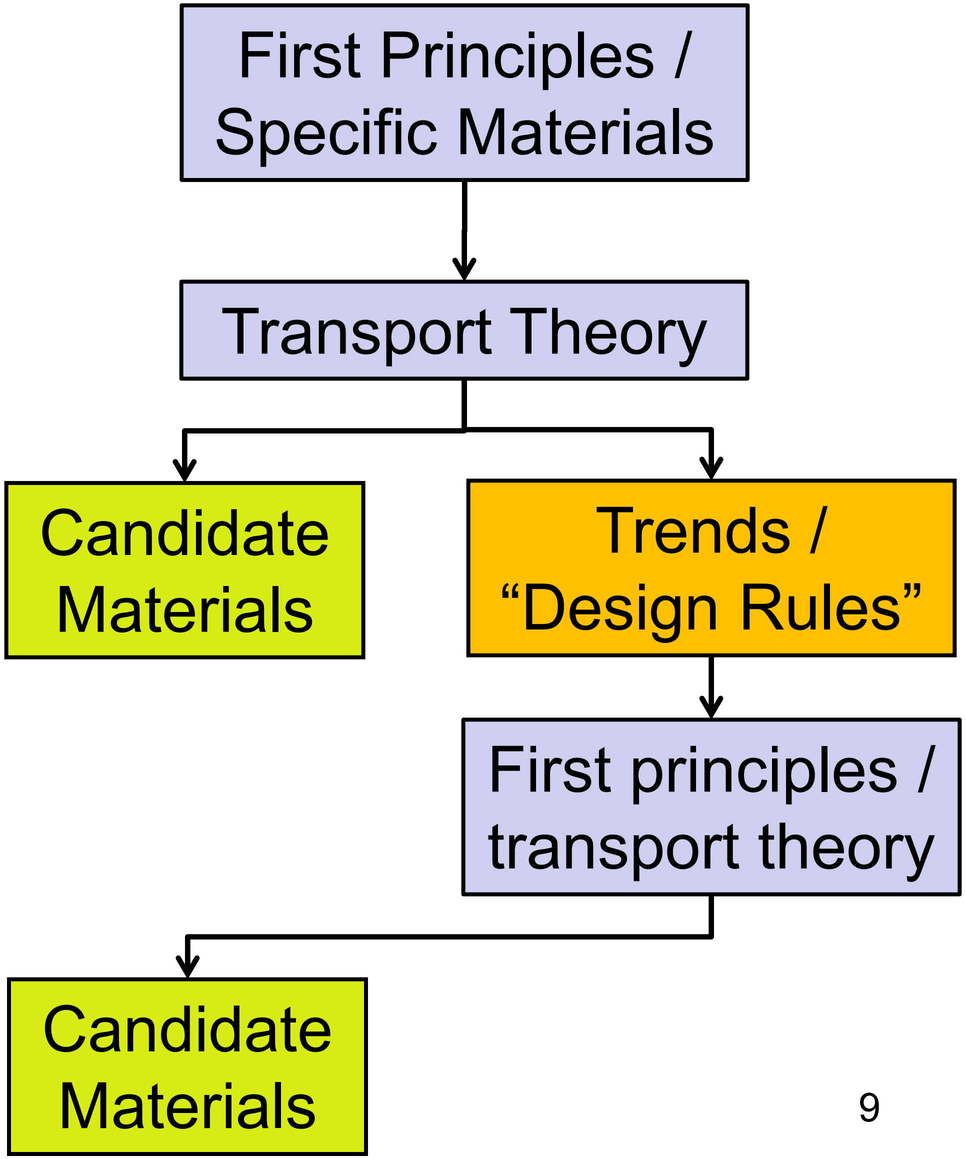
After studying a number of materials, we identified two such materials: bulk nanostructured Bi_2Se_3, and $CuBiS_2$ – both comprised of low cost elements. Found that if suitably optimized, hole-doped Bi_2Se_3 could show ZT values over 1 at room temperature and thus may be a viable replacement for Bi_2Te_3. Similarly found from our theoretical calculations that $CuBiS_2$ should exhibit large Seebeck coefficients and may show good performance if properly doped and optimized.

Technical Reports:

- D. Parker and D.J. Singh, Physical Review X **1**, 021005 (2011).
- D. Parker and D.J. Singh, Physical Review B **83**, 233206 (2011).

Approach/Strategy

- First principles calculations.
- Transport theory ➔ electrical transport quantities (T and n-dependent Seebeck coefficient, conductivity anisotropy)
  - ORNL developed BoltzTraP code.
  - Materials-by-Design type approaches to accelerate materials discovery.
- Focus on materials that promise potential low cost.
- Focus on 3D materials.
- Complementary to ORNL project on mechanical properties related to packaging / devices.



Approach – Predictive

Compute doping and temperature dependent thermopower of selected material (no adjustable parameters) from DFT band structure, viz.

$$S(\mu, T) \;=\; \frac{-1}{eT\sigma(T)} \int dE\, \sigma(E)\, (E-\mu)\, sech^2(\beta(E-\mu)/2)$$ with

$$\sigma(E) = N(E) v^2(E) \tau(E)$$

$$\sigma(T) = \int dE \sigma(E) sech^2(\beta(E-\mu)/2)$$

If S is promising ($|S| > 200\mu V/K$ at operating temperature and typical doping ranges of 10^{19}-10^{21} cm^{-3}), combine with information on carrier mobility μ_m, lattice thermal conductivity $\kappa_{lattice}$ to estimate potential *ZT*.

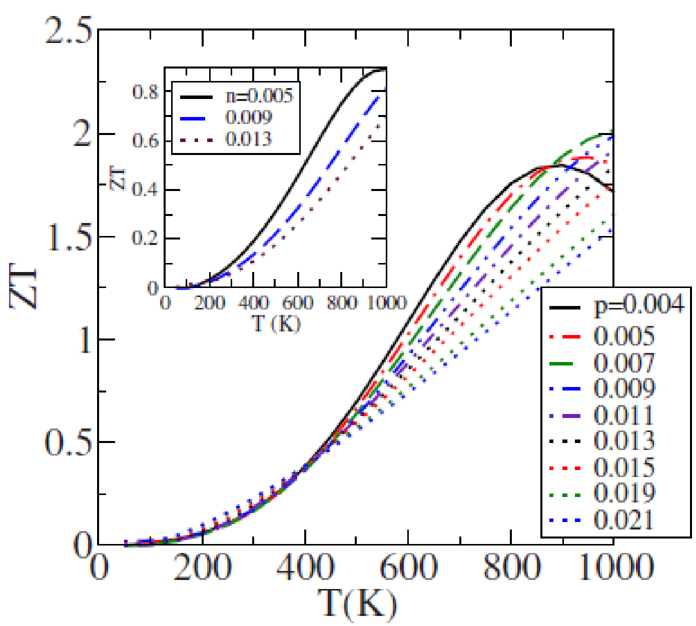
Must make assumption regarding temperature dependence of $\mu_{m,}$ $\kappa_{lattice}$ (usually α 1/T), and doping dependence of μ_m (if data available).

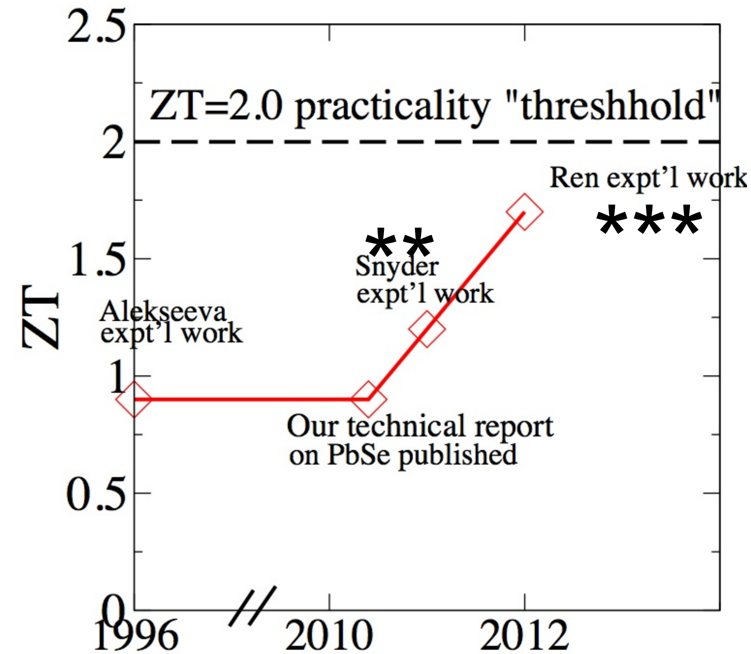
Combine this information with Wiedemann-Franz relation ($\kappa_{electron}=L_0\sigma T$) and use expression for *ZT*: $ZT = \sigma S^2 T/\kappa$

Based on ORNL co-developed transport code “BoltzTraP”.

Approach – Predictive

PbSe: potential high performance thermoelectric, overlooked until our prediction* of p-type ZT as high as 2 at 1000 K, 1.7 at 800 K





1.7 ZT confirmed, 2.0 nearly confirmed

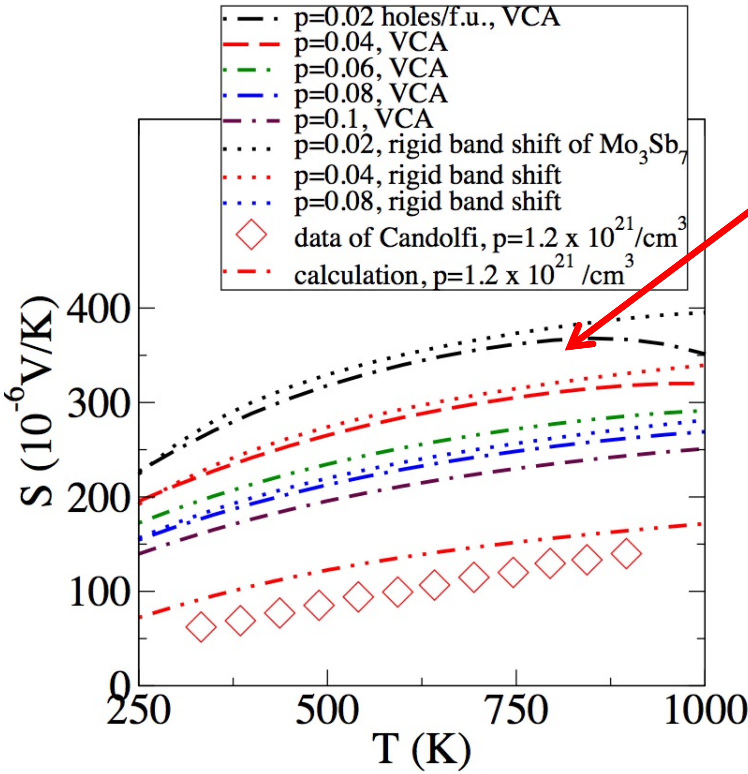
N-type ZT of 1.3 found by Ren+ (our calculations find this also)

*D. Parker and D.J. Singh, Phys. Rev B **82**, 035204 (2010)

Y. Pei et al, Adv. Mat. **23, 1367 (2011); ***Q. Zhang et al, unpublished (2012); +Q. Zhang et al, Energy and Env. Sci **5**, 5246 (2012)

Current Year Accomplishments – Mo_3Sb_7

- Detailed transport calculations (thermopower)
- Calculations of the phonon dispersions (thermal conductivity)
- Preparation and publication of a detailed technical report*.

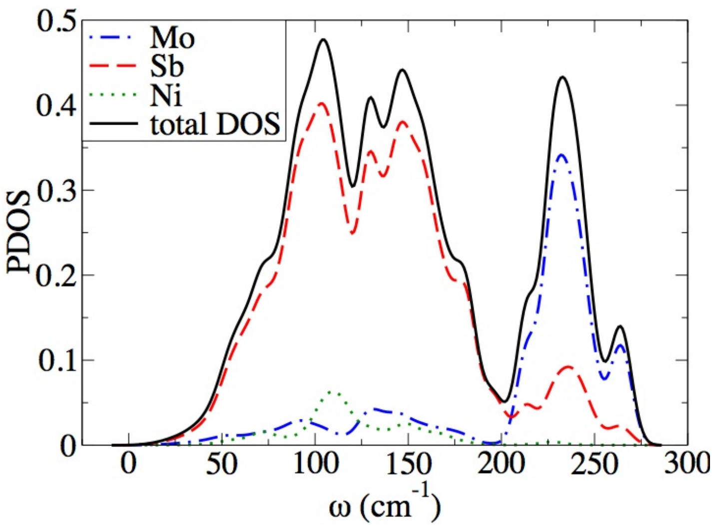


Note thermopowers above 250 μV/K in wide temperature range above 600 K – well suited for exhaust waste heat recovery with variable temperatures

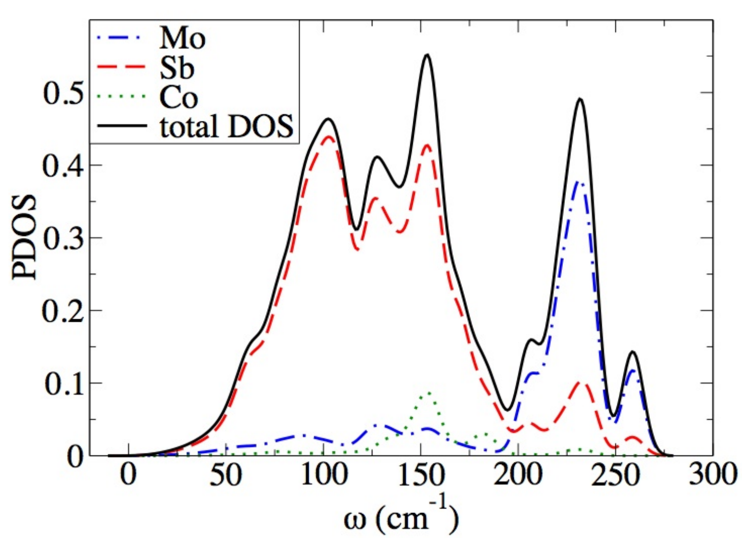
*D. Parker, M.H Du and D.J. Singh, Phys. Rev. B **83**, 245111 (2011)

Current Year Accomplishments – Mo_3Sb_7

Calculated phonon DOS tells likely impact of alloying on lattice thermal conductivity – key for materials optimization



Ni doping on Mo site



Co doping on Mo site

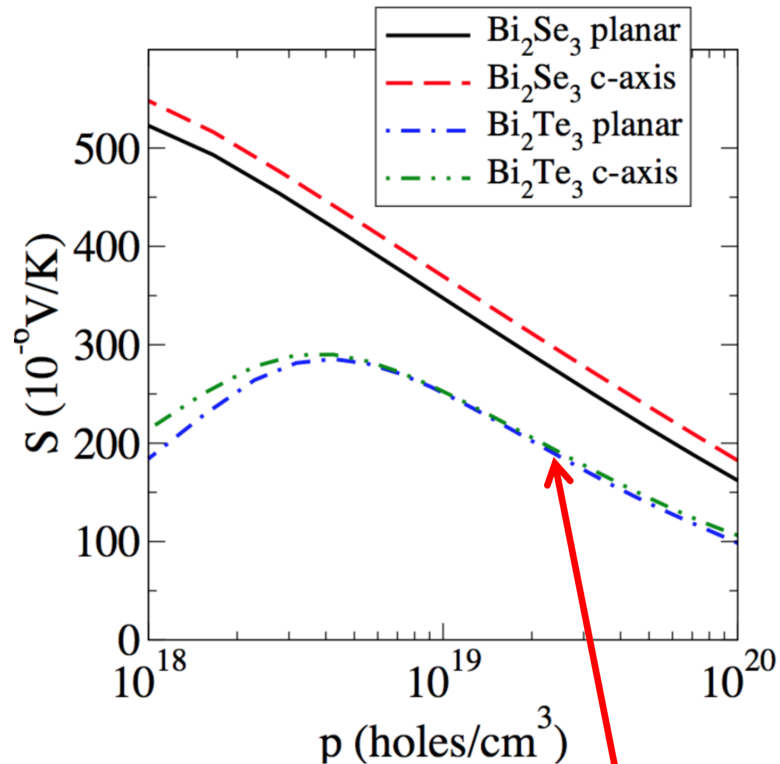
Variation of DOS with dopant (only 1 atom changed in 20 atom supercell) suggests doping beneficial in reducing lattice thermal conductivity

Current Year Accomplishment: p-type Bi_2Se_3 as ambient temperature heating/cooling material

Bi_2Te_3 standard material for room temperature heating/cooling (viz. EV/HEV without engine heat or fan belt to drive A/C compressor).

But Te costly (~ $100/lb.), scarce (~100 ton/year world production) – unlikely candidate for widespread use in EV/HEVs

Desirable to have alternative. Found* that p-type Bi_2Se_3 may be good alternative if appropriately doped and “bulk nanostructured”



300 K calculated thermopower of Bi_2Te_3/Bi_2Se_3 – note much higher Bi_2Se_3 values at optimal heavy doping

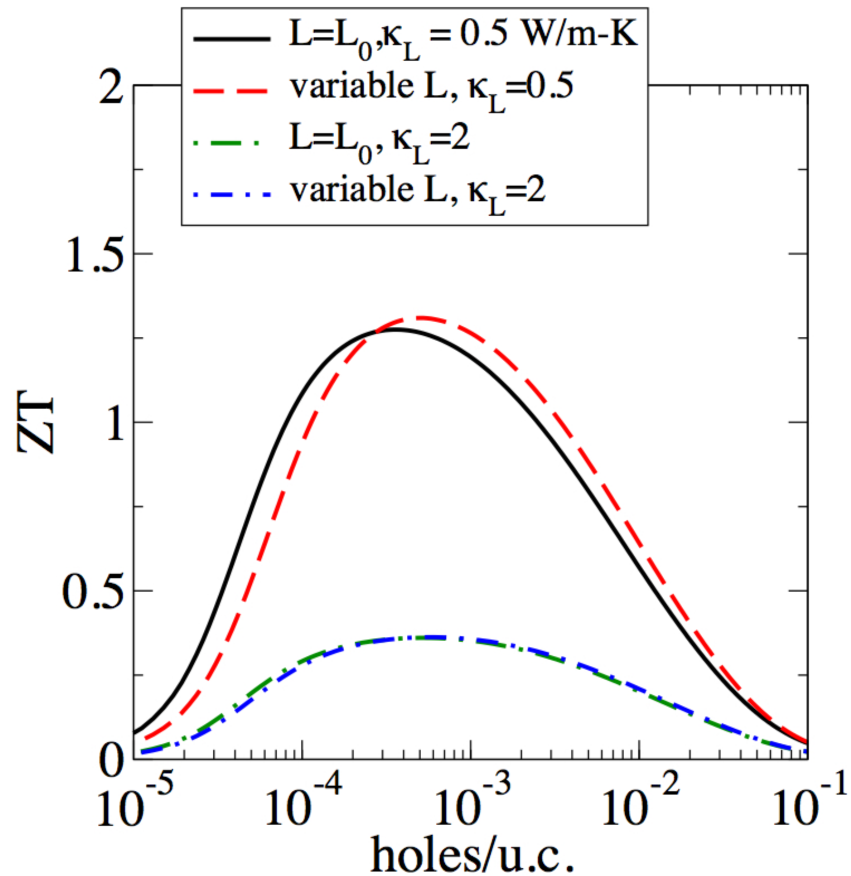
*D. Parker and D.J. Singh, Phys. Rev. X **1**, 021005 (2011).

Current Year Accomplishment: Bi_2Se_3

ZT values at 300 K as high as 1.3 predicted, depending on what degree of lattice thermal conductivity reduction by "bulk" nanostructuring. If 1.3 ZT confirmed would likely meet DOE COP goals for climate control.

"Bulk" means mechanical techniques like hot-pressing, melt-spinning – already effective for Bi_2Te_3*

ORNL group (A. Safa-Sefat) conducting experiments to test predictions



300 K predicted ZT

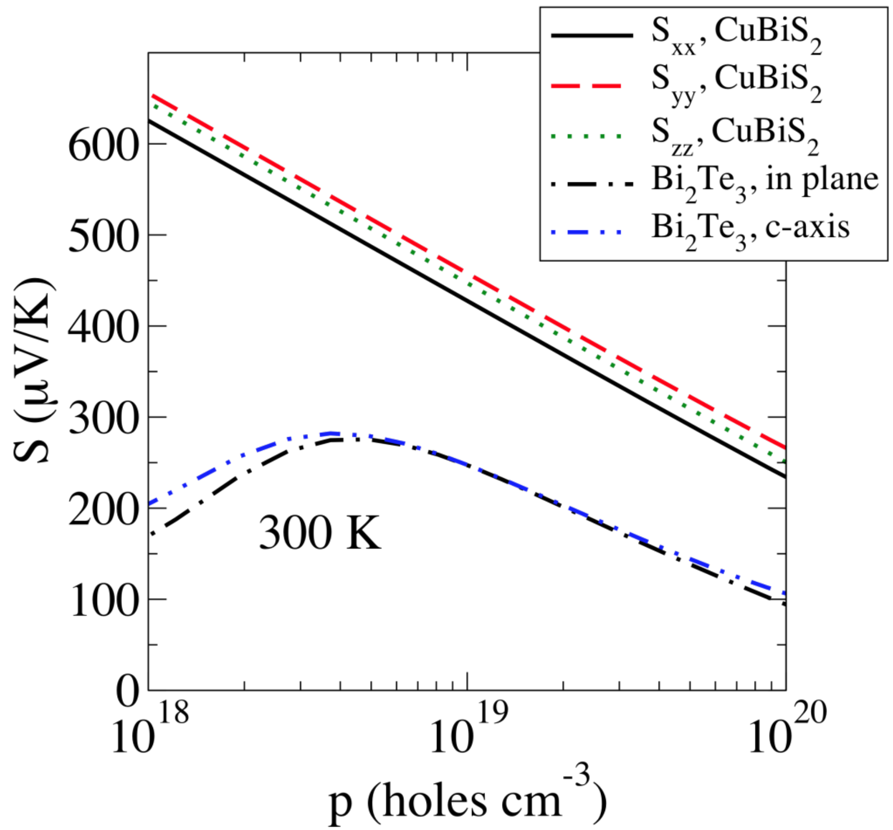
*B. Poudel et al, Science **320**, 634 (2008); W. Xie et al, Appl. Phys. Lett. **94**, 102111 (2009).

Current Year Accomplishment: p-type $CuBiS_2$ as "alternative pathway" heating/cooling material

For vehicle cooling/heating, desirable to have "alternative pathway" from abundant, inexpensive materials

$CuBiS_2$ meets these criteria; has heavy band leading to thermopower nearly double that of Bi_2Te_3 – published technical report* on this material

Several experimental groups (Michigan State (Morelli), Princeton (Cava), Boston College (Ren) have attempted synthesis



300 K calculated thermopower of $Bi_2Te_3/CuBiS_2$

D. Parker and D.J. Singh, Phys. Rev. B 83, 233206 (2011).

Collaborations

- Massachusetts Institute of Technology
  - S^3TEC center - thermoelectric power generation technology.
  - MIT very synthesis oriented → good avenue for transitioning results.
  - Discussions/communications – especially low cost skutterudites, vehicular heating/cooling applications
- General Motors
  - Discussions/communications – especially low cost skutterudites, vehicular heating/cooling applications
- Ford
  - Discussions/communications – vehicular heating/cooling applications
- University of Washington
  - Collaboration on publication studying transport in p-type skutterudites
- Naval Research Laboratory
  - Discussions/communications – thermal conductivity
- California Institute of Technology
  - Discussions/communications – waste heat recovery materials

Proposed Future Work – FY13

- Search for potential thermoelectric materials free of Te (scarcity) and Pb (toxicity)

- Study (via Boltzmann transport and lattice dynamics calculations) low cost families of potential thermoelectric materials – focus on materials with isotropic or near isotropic properties, heavy mass bands, soft phonons and other properties indicative of thermoelectric performance.

Summary

- Project addresses key barriers to the implementation of thermoelectric waste heat recovery: (1) materials performance, (2) need for *p*-type and *n*-type material, (3) need for low cost materials → *overcoming these barriers can yield 10% fuel savings.*
- Project also impacts climate control – similar barriers as above but need room temperature performance
- Identified trends, and established design rules for thermoelectric materials – results published in peer reviewed technical journals.
- Published technical report on Mo_3Sb_7, low cost isotropic material good for exhaust waste heat recovery
- Published technical reports on Bi_2Se_3, $CuBiS_2$, low cost thermoelectric materials with high thermopower in -25 – 50 C temperature range, suitable for vehicle cooling/heating applications