Thermoelectrics Theory and Structure

David J. Singh
Oak Ridge National Laboratory

May 11, 2011

PM013

Overview

Timeline

- Started FY08.
- Completion FY12.
- 60% Complete.

Budget

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

* 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).

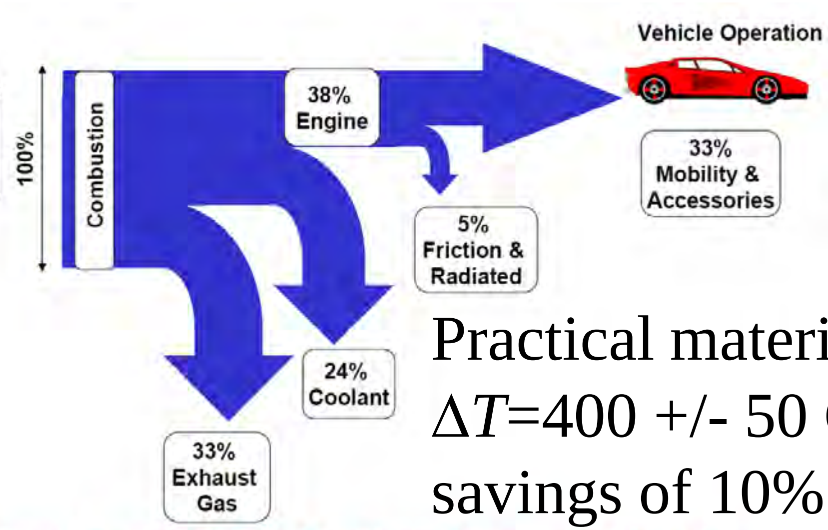
Barriers*

- 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. rare earths.

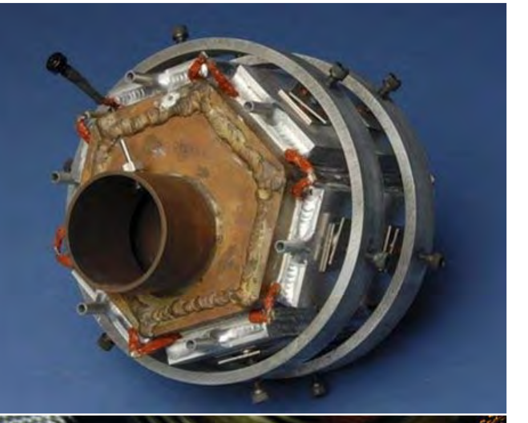
Partners

- Interactions/ collaborations:
  - Corning
  - California Institute of Technology
  - General Motors
  - Naval Research Laboratory
  - Massachusetts Institute of Technology (S^3TEC Center)
- Project lead: ORNL

Relevance

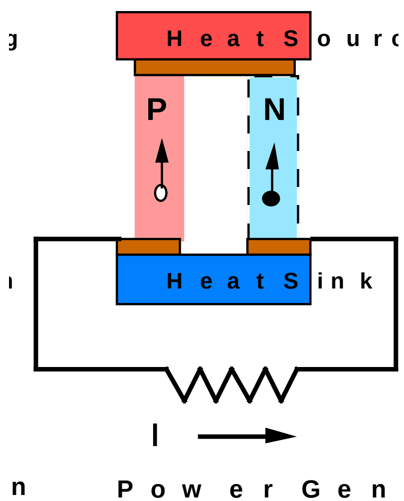


$$ZT = \sigma S^2 T/\kappa$$



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

Synergy with truck electrification.



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.

Relevance

Barriers:

- Need high *ZT* (ideally *ZT*=2 or higher).
- Need low cost ($1/watt or better).
- Need *p*-type and *n*-type.
- Need high availability, manufacturable materials.
- Avoid materials with toxic components.

Te: low abundance, solar cell use.

Rare earths (La, Ce, …, Yb, Lu): Major concerns about availability.

While China's Rare Earth R&D Becomes Ever More Rarified Others Tremble – Science **325**, 1336 (2009).

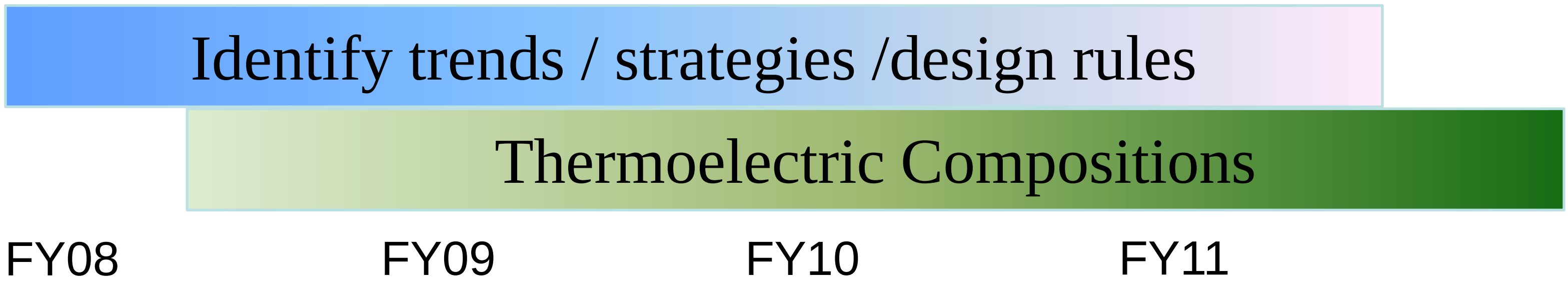
As Hybrid Cars Gobble Rare Metals Shortage Looms – Reuters, August 31 (2009).

China's Control of Rare Earth Metals Threatens Jobs, Tech – Business Week, March 17 (2010).

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

9/30/2010: ***Identify a phase with predicted high temperature thermoelectric performance exceeding that of standard PbTe, but without Te or rare earth elements. Describe this material and the scientific basis for the predictions in a technical report.***

We studied numerous materials related to PbTe using detailed modeling and computation. Found that, with carefully controlled doping, PbSe can be made better than standard PbTe, even though it was commonly held that PbSe is much inferior. Predicted ZT=1.5 at 800 K and near 2.0 at 1000 K if fully optimized.

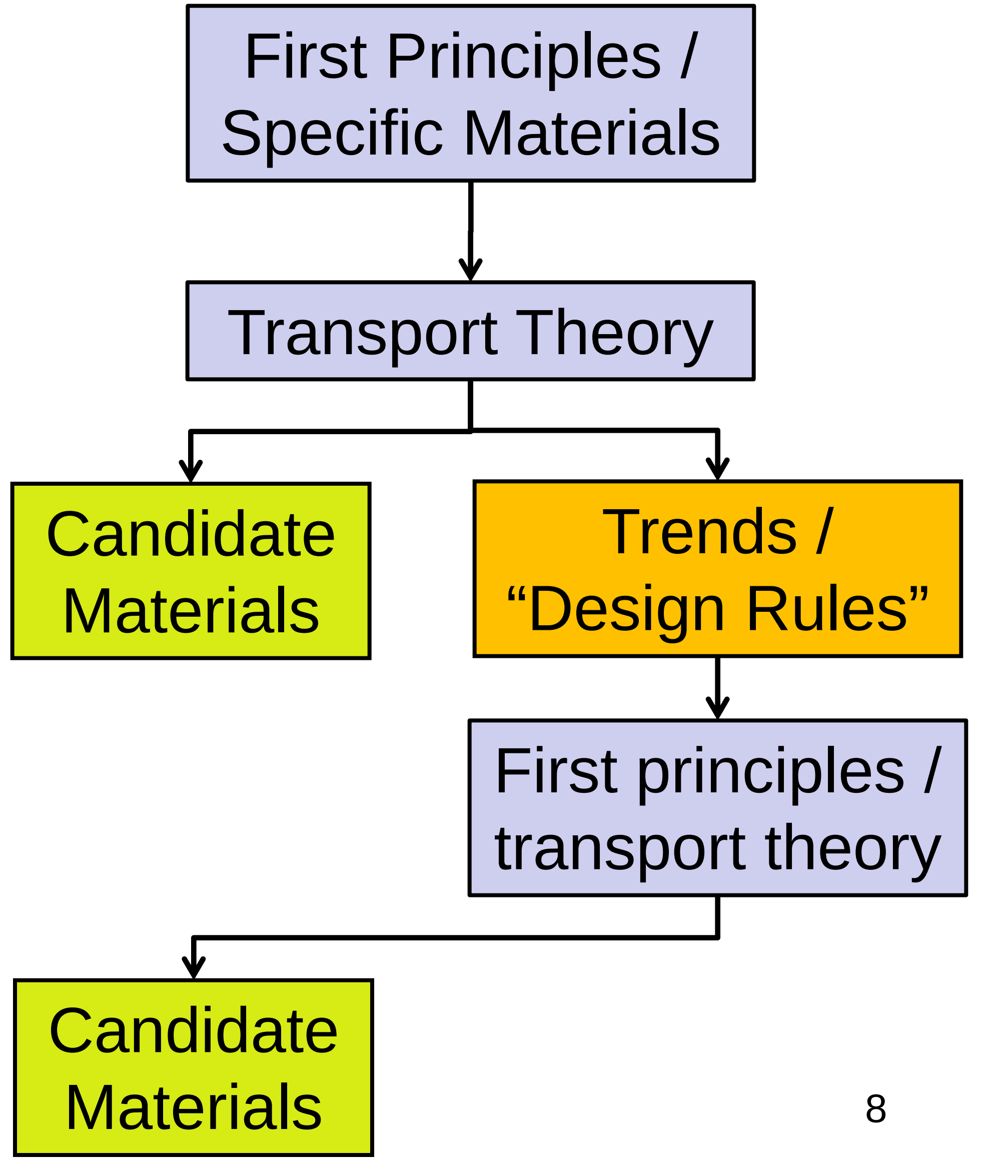
Technical Report: D. Parker and D.J. Singh, Physical Review B **82**, 035204 (2010).

Communicated results to G.J. Snyder, California Institute of Technology: Samples were made and tested to ~850 K. Experimental ZT exceeds 1.2 at 800 K on partially optimized samples made to date.

“for commercialization PbSe offers an inexpensive alternative to PbTe as Se is more abundant and less expensive” - H. Wang, Y. Pei, A. LaLonde and G.J. Snyder, Advanced Materials (2011).

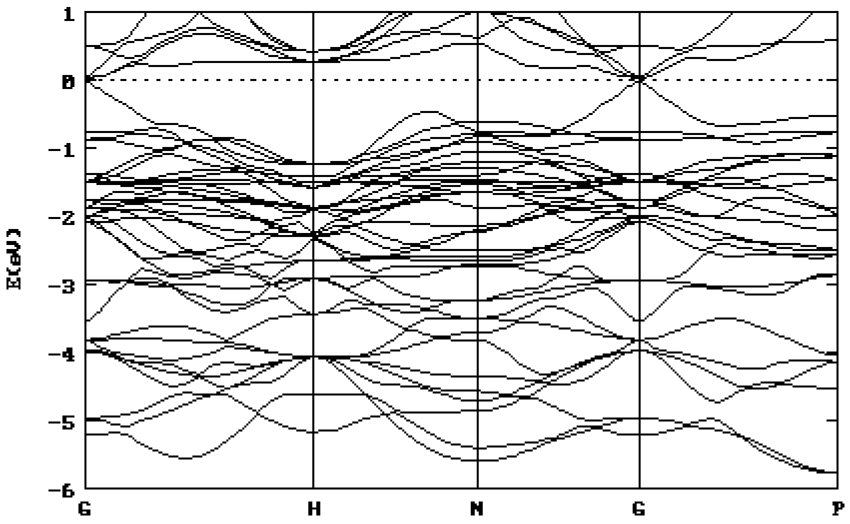
Approach/Strategy

- First principles calculations.
- Transport theory → electrical transport quantities.
  - 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

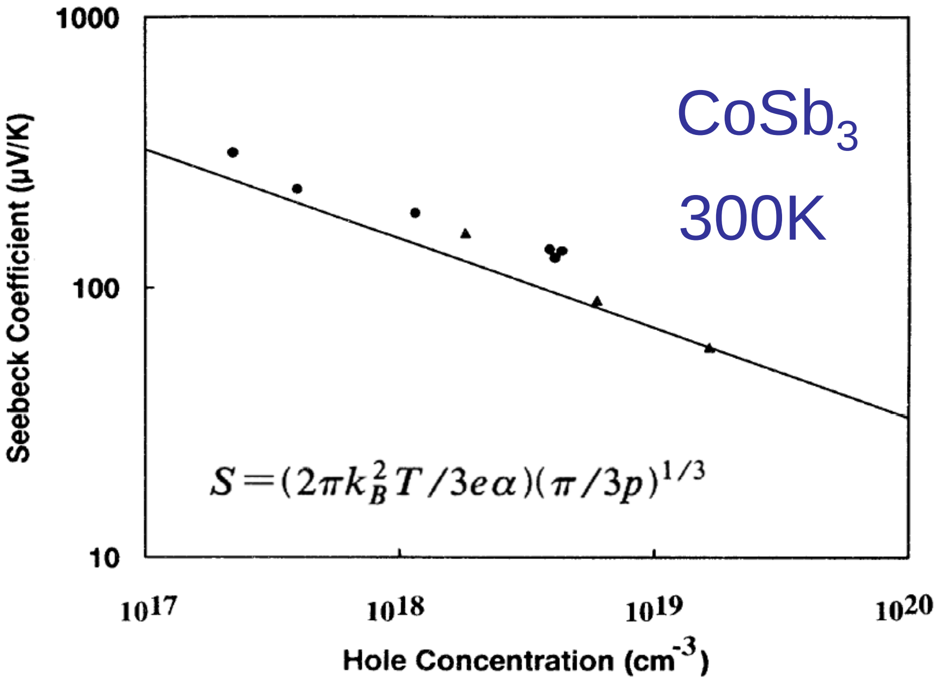
$CoSb_3$ – basis of skutterudite thermoelectrics:



We found very small gap and linear dispersion - not expected. Boltzmann prediction:

- parabolic: $S/T \propto n^{-2/3}$
- linear: $S/T \propto n^{-1/3}$

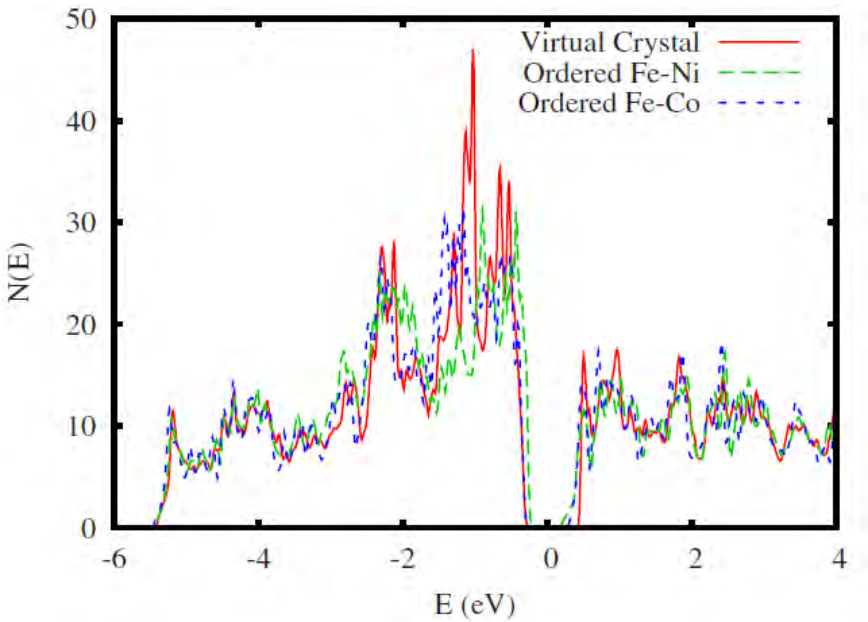
General Motors Data: D.T. Morelli *et al.*



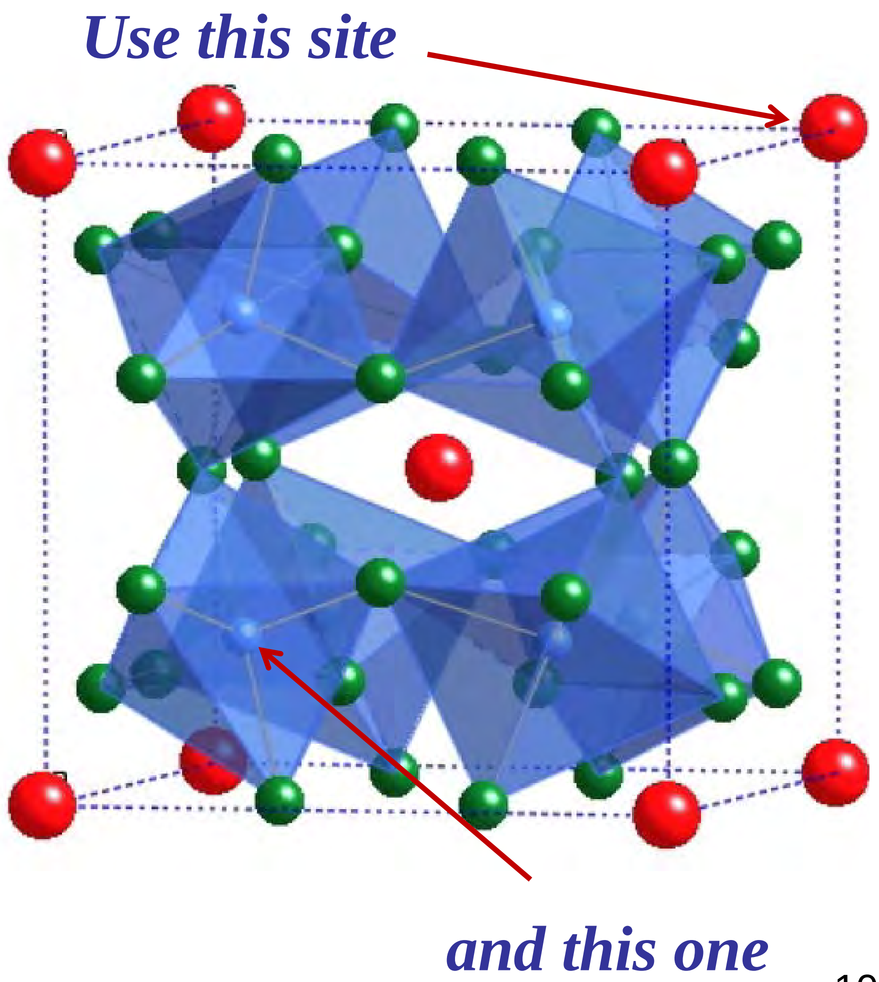
Prediction confirmed

Accomplishments - Skutterudites

High performance thermoelectrics investigated by General Motors and others for waste heat recovery. – excellent *ZT* especially for *n*-type. Compositions are e.g. multi-filled $(Ba,Yb)Co_4Sb_{12}$. Data shows bi-polar conduction at low *n*, high *T*.

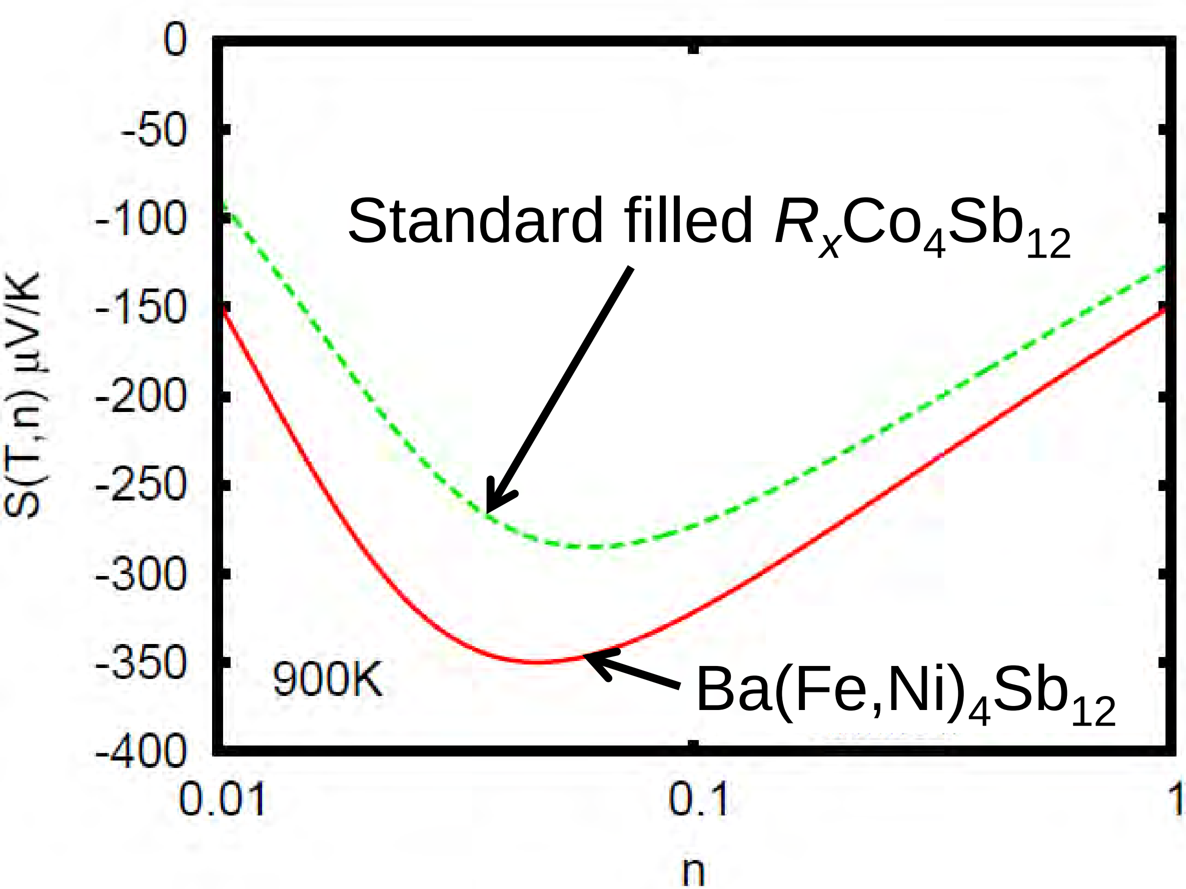


Last year showed preliminary results: it may be possible to eliminate rare earths and substitute Co by Fe-Ni alloys ➔ reduce cost while preserving performance.



Current Year Accomplishments

- Detailed transport calculations (thermopower) for new skutterudites.
- Calculations of the phonon dispersions (thermal conductivity).
- Comparison of different fillers.
- Preparation and publication of a detailed technical report.



We get flexibility in choosing lower cost elements by co-doping on the transition metal site, and at the same time improve performance!

Separate control of carrier concentration and filling.

Significance: Material Cost

Bi_2Te_3:

- Bi: very cheap
- **Te: ~$100/lb limited supply, price fluctuations**

PbTe, LAST:

- **Pb: very cheap, environment?**
- **Te: ~$100/lb limited supply, price fluctuations**

Filled skutterudite, $R\mathrm{Co_4Sb_{12}}$:

- ***R*: La, Ce (<$10/lb), others expensive, supply?**
- **In: ~$300/lb**
- **Rh: ~$37,000/lb**
- Co: ~$20/lb
- Sb: ~$3/lb
- Fe: very cheap (<$0.3/lb)

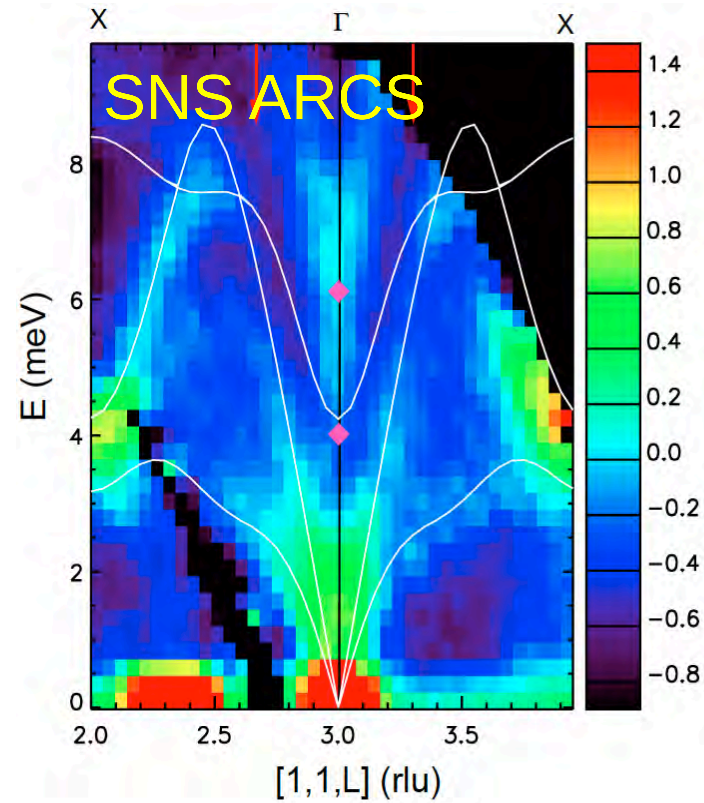
(Ca,Sr,Ba)$\mathbf{Fe_{4-x}Ni_xSb_{12}}$:

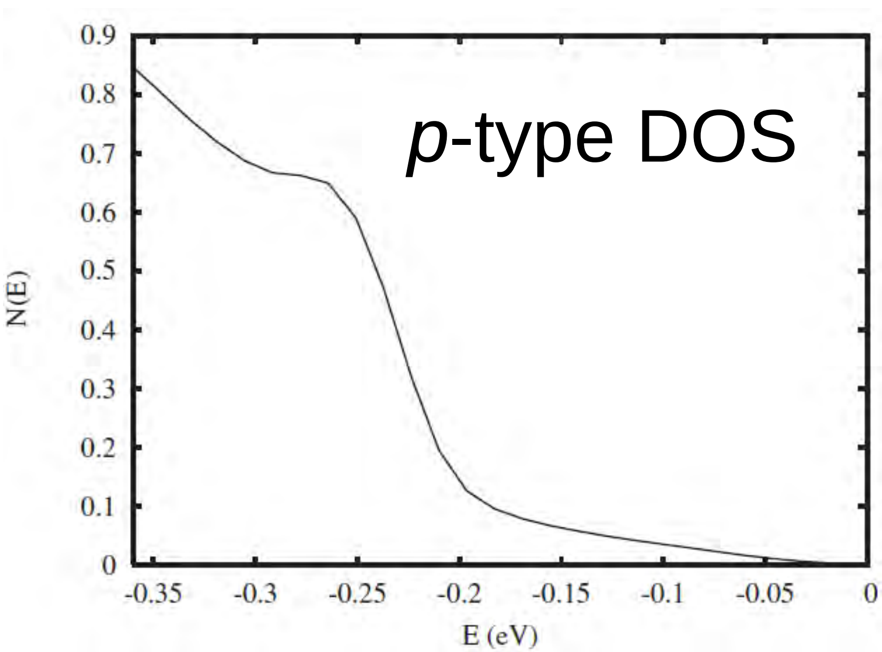
- Ca, Sr and Ba compounds are very cheap and safe.
- Eliminated rare earth elements.
- Replaced Co (~$20/lb) by half the quantity of Ni (~$12/lb).
- Results indicate excellent performance.

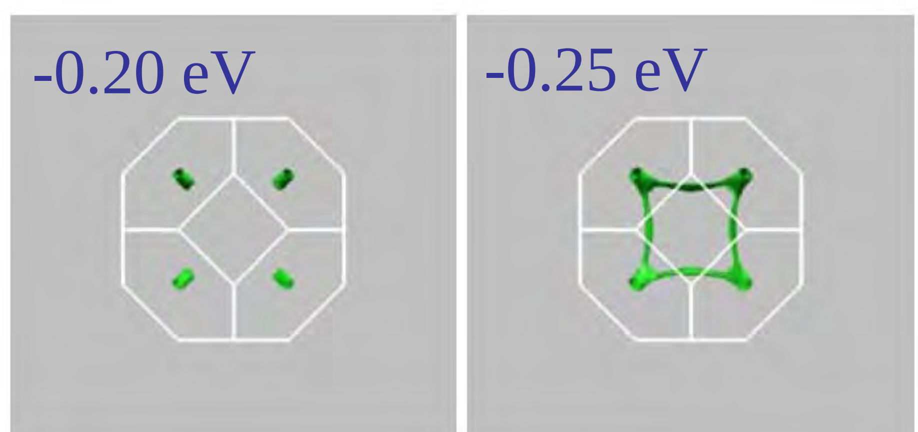
Goal is high performance material at acceptable (low) cost.

Current Year Accomplishment: PbTe

- PbTe is an accepted useful thermoelectric for waste heat recovery, but standard PbTe does not meet performance requirements.
- Heremanns and co-workers reported much higher *ZT* in Tl doped PbTe – problem: Tl is highly toxic.
- Extensive electronic structure, phonon and transport (thermopower) calculations. Collaborated with SNS via (MIT/S^3TEC EFRC) for phonon measurements.

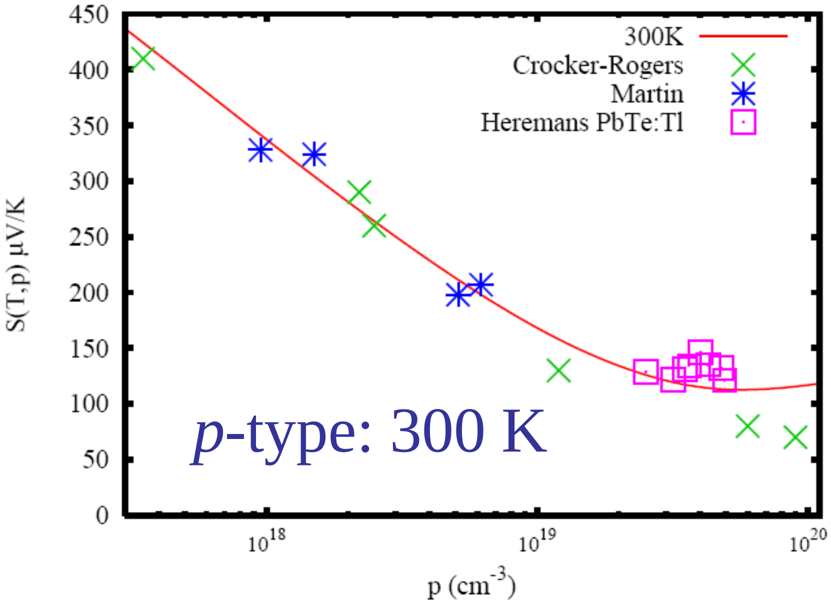


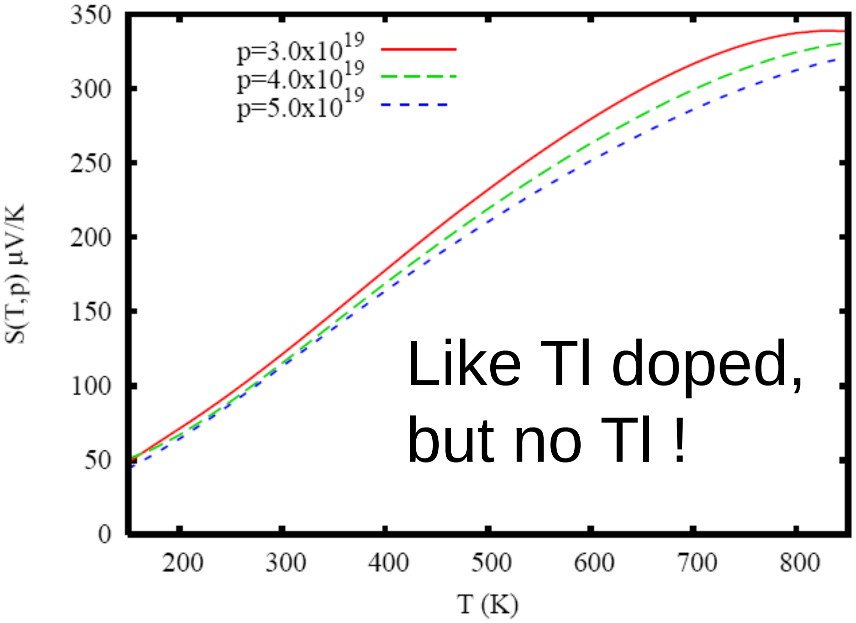




Current Year Accomplishment: PbTe

- Transport (Thermopower) calculation:

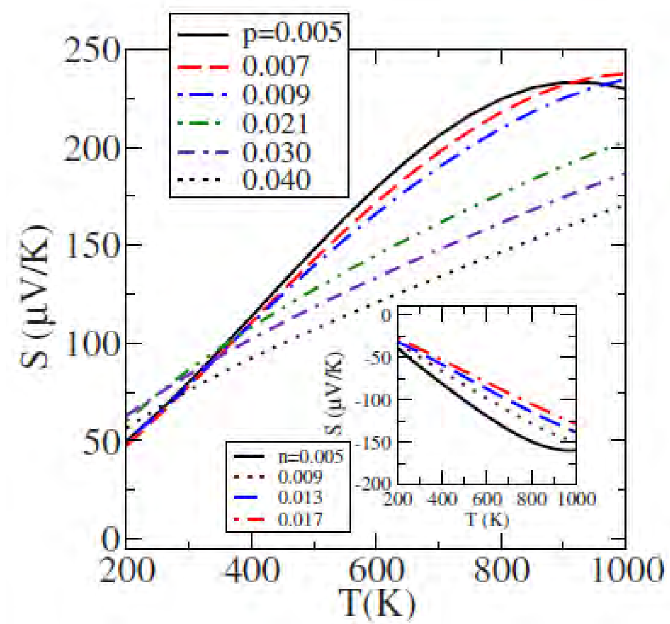


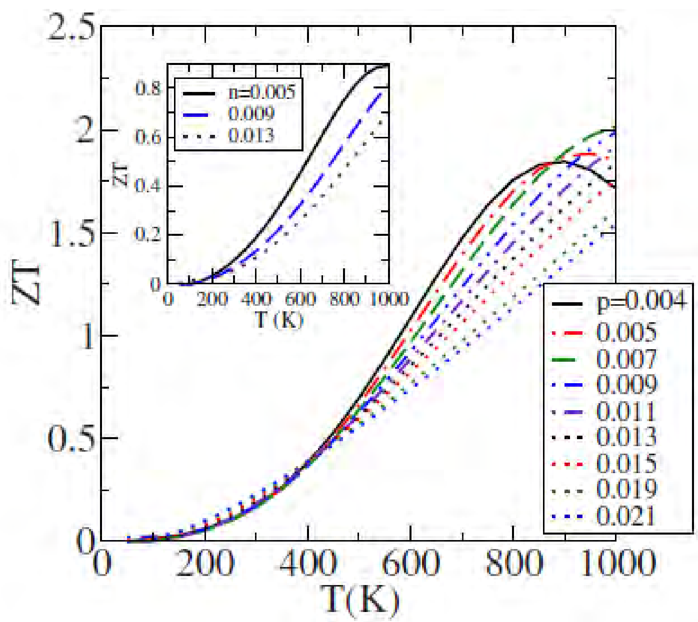


- Obtain very similar behavior to Tl doped samples, via proper control of doping but no toxic Tl: Communicated result and published technical report.
- Result was confirmed by measurements done by two groups and now published: Northwestern University (M. Kanatzidis) using Na/K co-doping; California Institute of Technology (G.J. Snyder) using Na doping.
- Amerigon/ZT Plus reports producing high performance Tl free PbTe for automotive application (2011 DOE thermoelectrics applications workshop).

Current Year Accomplishment: PbSe

- Computational survey of PbTe related chalcogenides.
- Found that *p*-type PbSe is a very high performance material, as good as PbTe even though it has long been thought that PbSe is inferior – issue is according to our calculations PbSe needs very high doping levels that were not explored before.
- Communicated results to G.J. Snyder (Caltech) who made samples and tested to ~850 K. Experimental ZT exceeds 1.2 at 800 K on partially optimized samples.



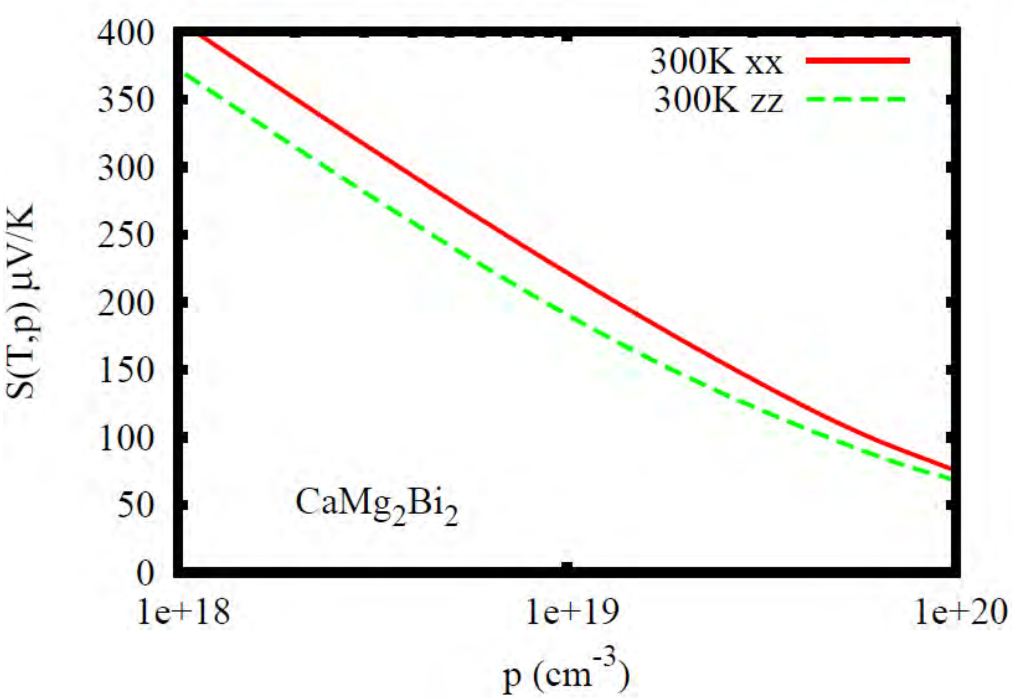


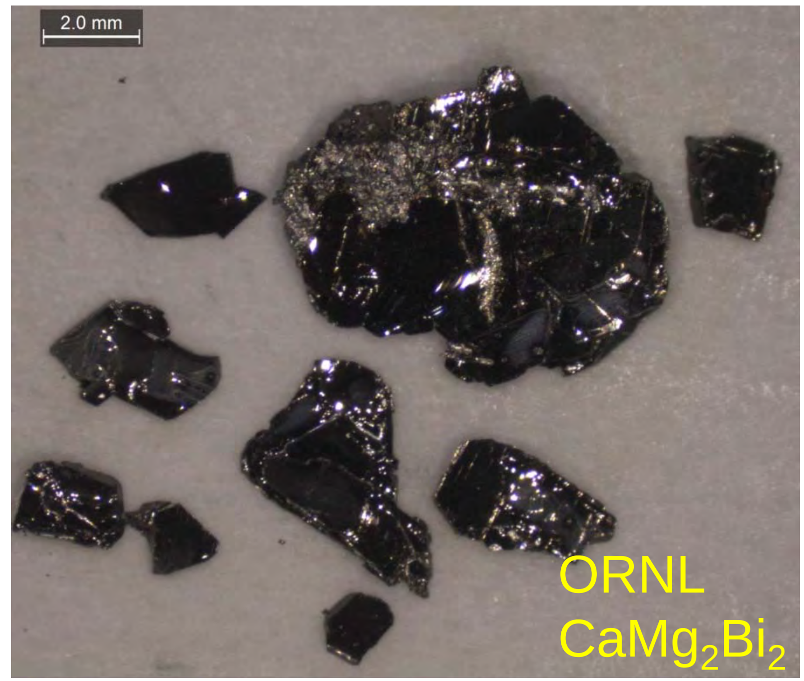
"for commercialization PbSe offers an inexpensive alternative to PbTe as Se is more abundant and less expensive" - H. Wang, Y. Pei, A. LaLonde and G.J. Snyder, Advanced Materials (2011).

Current Year Accomplishments

Found a very promising family of low cost materials with exceptional properties that may be excellent room temperature thermoelectrics (climate control). Communicated preliminary results to an experimental group doing synthesis.

$\mathit{Ae}\mathrm{Mg}_2\mathit{Pn}_2$





Need more detailed properties – especially related to heat conduction (phonons).

Collaborations

- California Institute of Technology
  - Elucidation of heavy / band light band approach: ORNL and experiment at Caltech.
  - Caltech doing synthesis work for Pb chalcogenides. Caltech confirmed key predictions: (1) High thermoelectric performance in PbSe and (2) that the toxic element Tl can be replaced by Na to obtain the high ZT in resonantly enhanced PbTe.
- Naval Research Laboratory
  - Thermal conductivity of skutterudites based on first principles calculations at ORNL and molecular dynamics at NRL.
- Massachusetts Institute of Technology
  - S^3TEC center - thermoelectric power generation technology.
  - MIT very synthesis oriented → good avenue for transitioning results.
- General Motors
  - Discussions/communications – especially low cost skutterudites.
  - Did calculations on PbTe dynamics in response to a request from GM.
- Corning
  - Interactions on oxide thermoelectrics.
  - Support for Corning modeling effort using ORNL/Aarhus developed BoltzTraP code.

Proposed Future Work – FY12

- Seek ways of improving the performance of *p*-type skutterudites, which is invariably inferior to high quality *n*-type – low cost high performance *p*-type and *n*-type skutterudite has the potential to displace PbTe.
- Do detailed calculations for Zintl compounds, including $AeMg_2Pn_2$ where we have promising preliminary results.
- Survey other low cost families of potential thermoelectric materials to identify candidates for development – 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.
- Identified trends, and established design rules for thermoelectric materials – results published in peer reviewed technical journals.
- Found a low cost skutterudite thermoelectric with excellent potential.
- Identified way of making high performance PbTe without Tl (Tl cannot be used in vehicle manufacturing because of toxicity).
- Found that *p*-type PbSe can be as good as or better than *p*-type PbTe.
- Identified new promising low cost Zintl materials.
- Predictions were independently confirmed by experiment.