

2007 DEER Conference
Wednesday, Aug. 15th 2007

**Challenges and Opportunities in Thermoelectric
Materials Research for Automotive Applications**

Prof. Terry M. Tritt

email: ttritt@clemson.edu

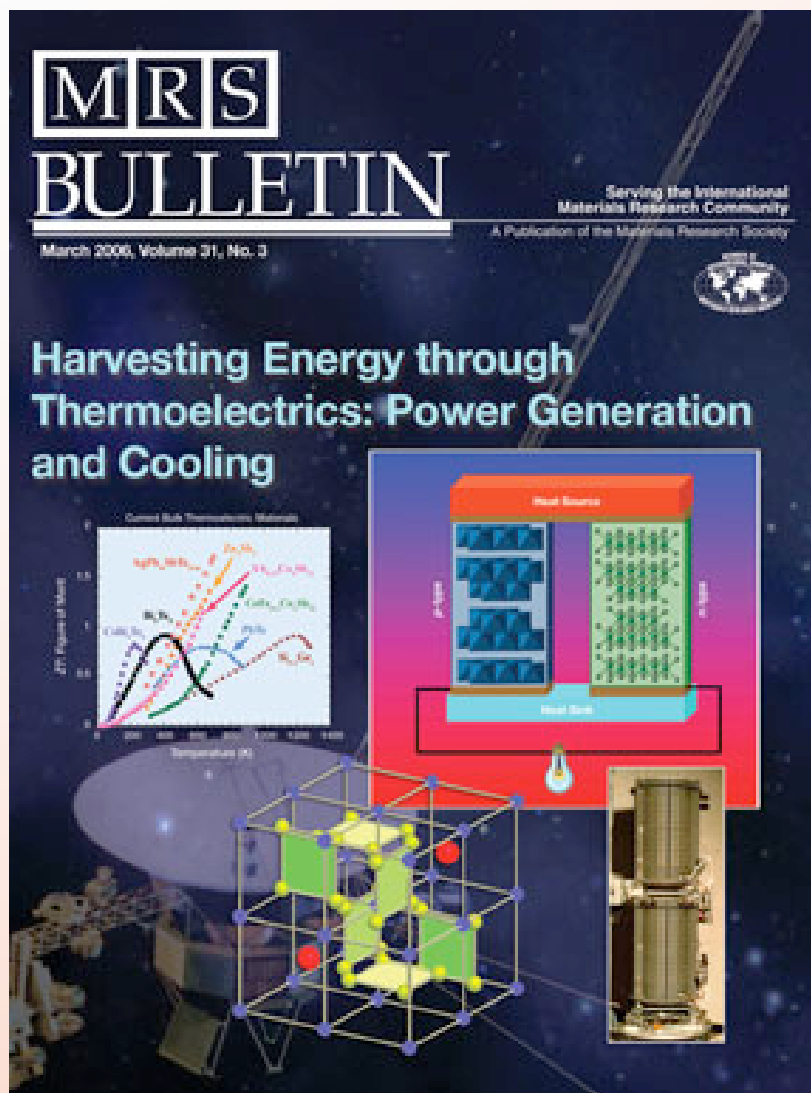
<http://www.clemson.edu/caml/>

Dept. of Physics & Astronomy
Clemson University, Clemson, SC

CAML: Complex and Advanced Materials Laboratory



MRS Bulletin: Thermoelectrics, March 2006
Guest Editors: Terry M. Tritt and M. A. Subramanian



Introduction & Overview

Bulk TE Materials

Oxide TE's

Nano-structured TE Materials

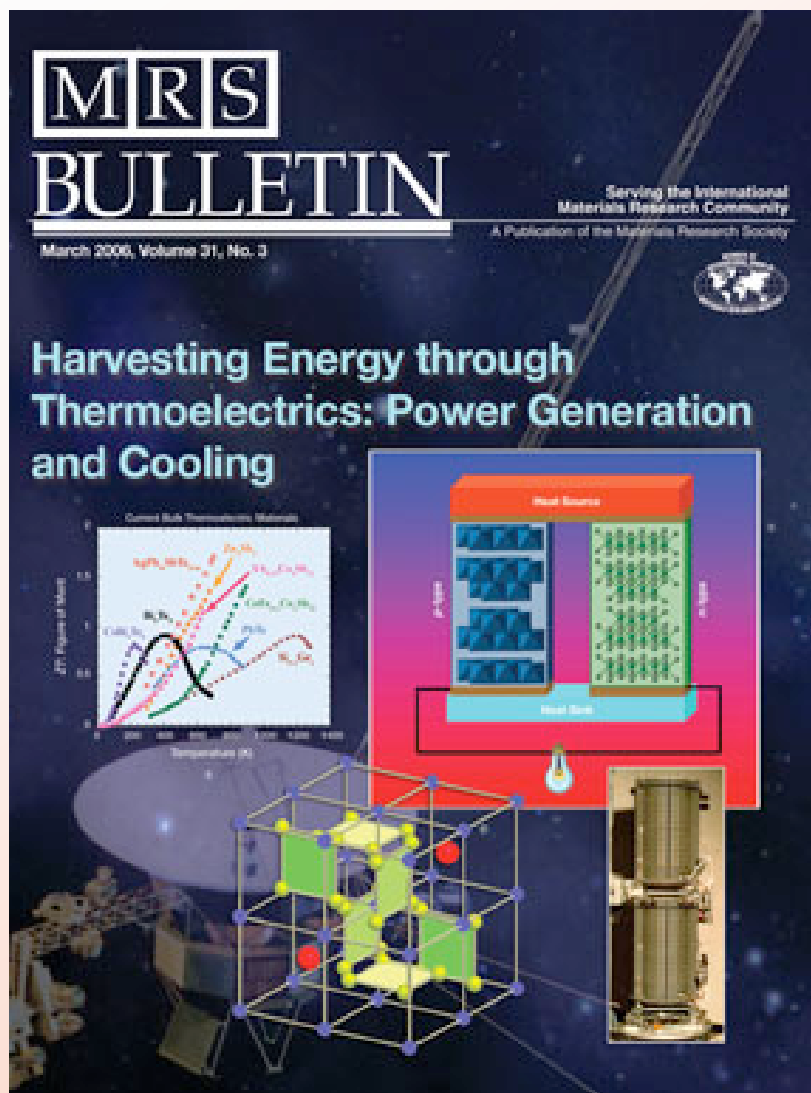
Applications of TE Materials

Thin Film TE's

MRS Bulletin, Volume 31, No 3, March 2006



MRS Bulletin: Thermoelectrics, March 2006
Guest Editors: Terry M. Tritt and M. A. Subramanian



Introduction & Overview

Bulk TE Materials

Oxide TE's

Nano-structured TE Materials

Applications of TE Materials
(Automotive & Deep Space)

Thin Film TE's

MRS Bulletin, Volume 31, No 3, March 2006



Research Drivers

Desperately Need Alternative Energy Sources
over next 20 years

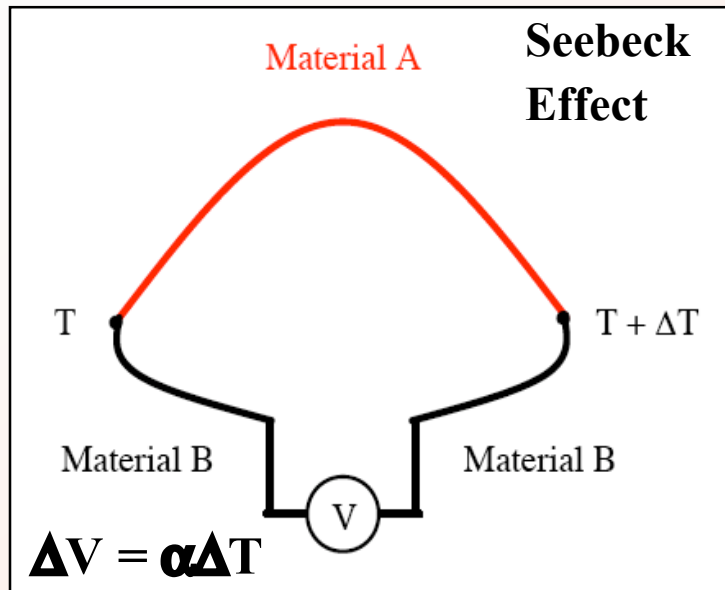
Automotive & Industrial
Waste Heat Recovery (eg. DOE-EERE, etc.)

DOD Needs for
On Board Ship Power Systems & Cooling
Soldier 2020 Power Density Requirements

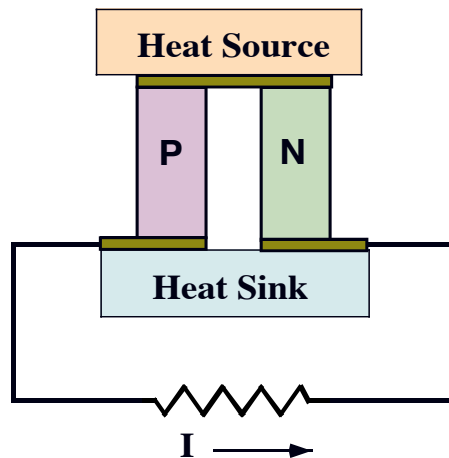
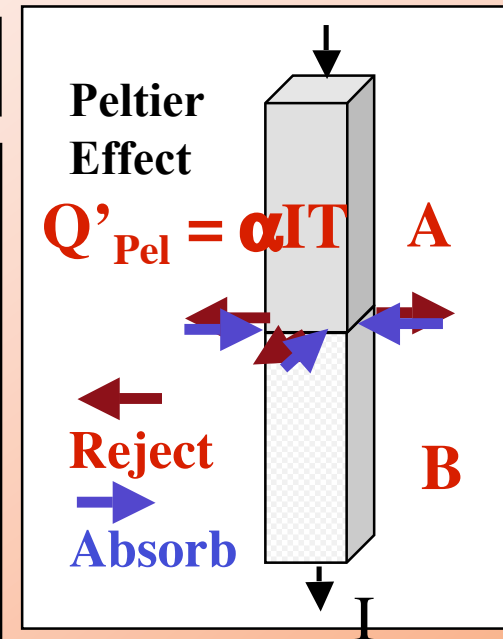
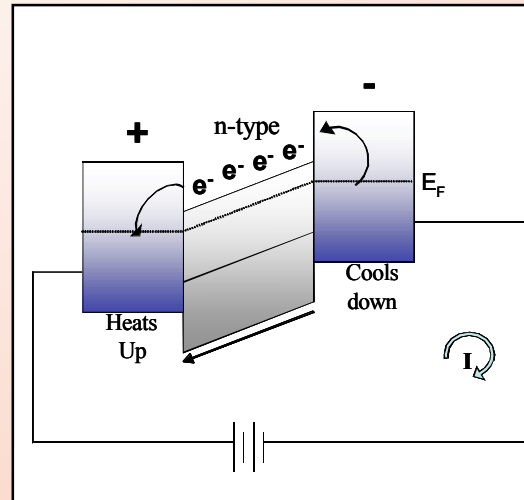
Solar Energy Conversion (DOE-BES)
Solar TE Thermal Storage & Conversion



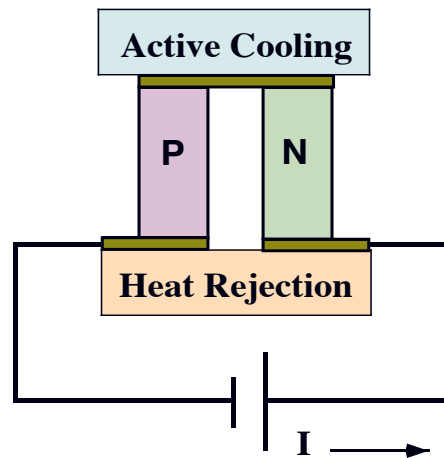
Overview of Thermoelectric Phenomena



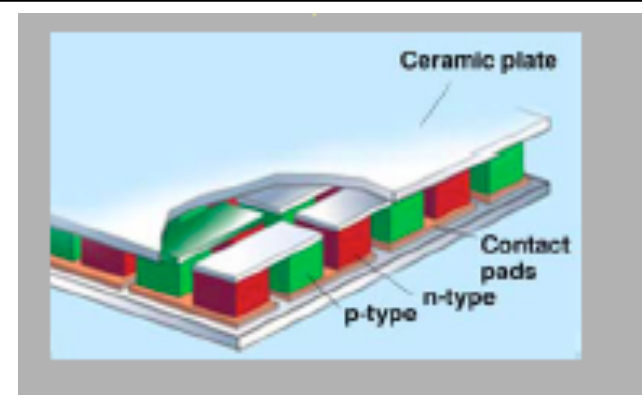
$$Q'_{\text{PEL}} = \alpha IT$$



Power Generation Mode



Cooling Mode



Electrically in Series
Thermally in Parallel



The Thermoelectric Figure of Merit (ZT)

Efficiency ($\eta \approx ZT$)

$$ZT = \frac{\alpha^2 \sigma T}{(\kappa_E + \kappa_L)} = \frac{\alpha^2 T}{\rho} \left(\frac{1}{\kappa_E + \kappa_L} \right)$$

α = Thermopower

σ = Electrical Conductivity

ρ = Electrical Resistivity

κ_E = Electronic Thermal Conductivity

κ_L = Phonon Thermal Conductivity



To Evaluate the **Figure of Merit (ZT)**

Requires the measurement of the properties
over a broad range of temperature.

Low Temperatures ($10\text{K} < T < 320\text{K}$)

High Temperatures ($300\text{K} < T < 1200\text{K}$)

$$ZT = \frac{\alpha^2 \sigma T}{(\kappa_E + \kappa_L)} = \frac{\alpha^2 T}{\rho} \left(\frac{1}{\kappa_E + \kappa_L} \right)$$

α = Thermopower

σ = Electrical Conductivity

ρ = Electrical Resistivity

κ_E = Electronic Thermal Conductivity

κ_L = Phonon Thermal Conductivity



Thermal to Electricity Energy Conversion (TE)

TE Radio Lantern



**TE Module
Converter**

**Thermal
Energy
(Waste Heat)**



**Electrical
Energy**

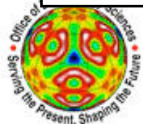
Conceptually Simple Devices

TE Technology

Converts
Waste Heat to
Electrical Energy

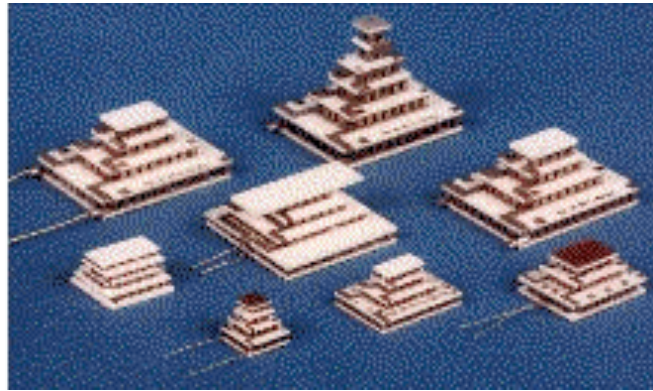
No Moving Parts

Solid State Technology



Several TE Commercial Applications

TE Modules (Marlow Indus.)



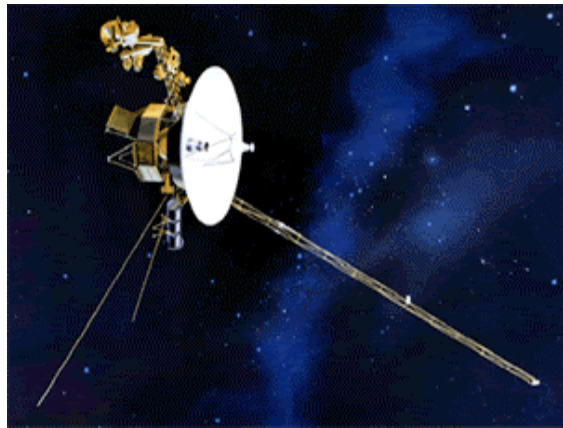
TE coolers/warmers
Coleman -Igloo



Seiko TE Watch



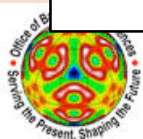
RTG 's -- Deep Space - NASA



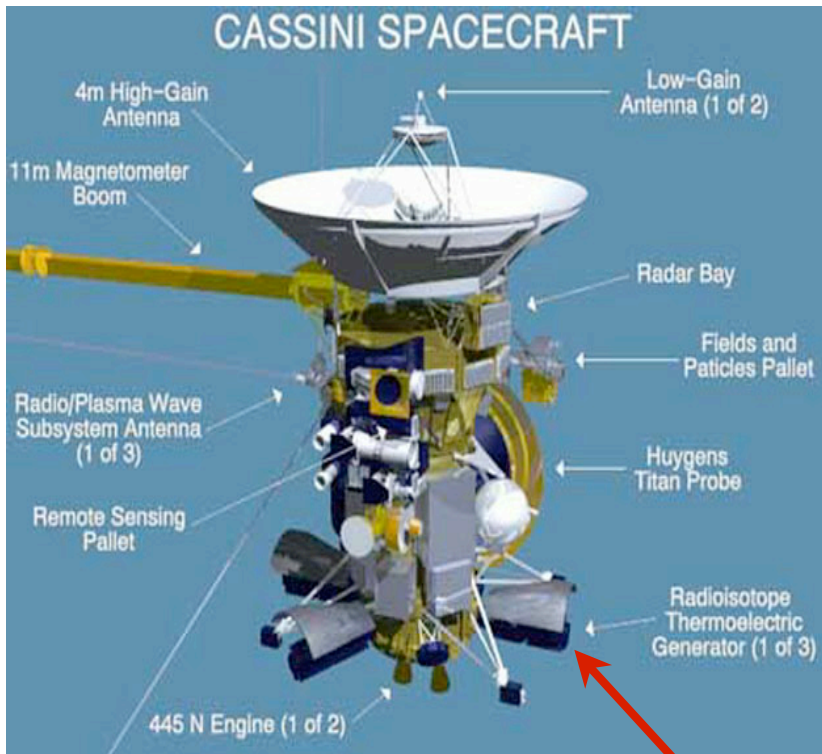
CCS - Climate Controlled Seat
Lexus & Lincoln etc.



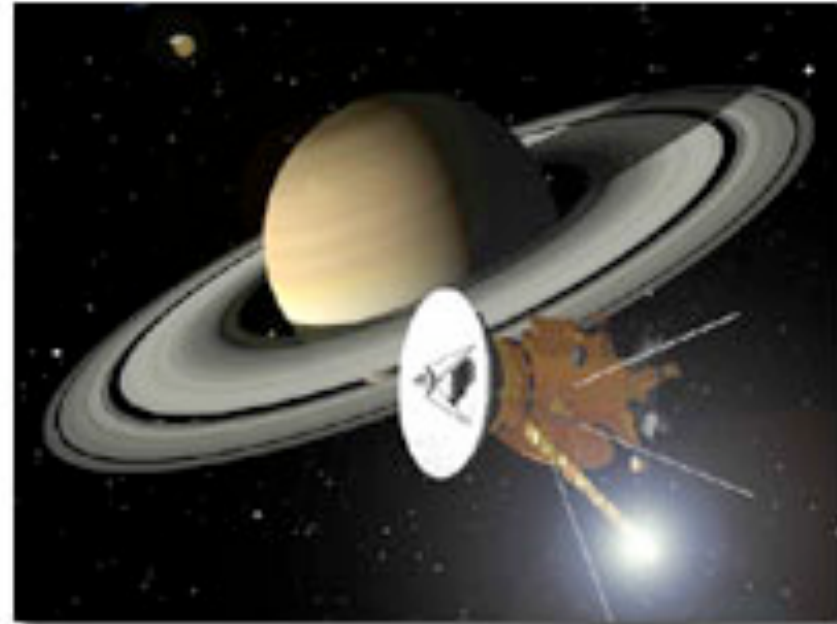
TE Radio Lantern



Radioisotope Thermoelectric Generator (RTG)



Cassini: Saturn's Rings



Also Voyager I & II
(mid 1970's)
Can't use Solar
or Battery Power!

RTG's (1 of 3)
($T_H \approx 800^\circ\text{C}$)
 $\approx 300\text{-}400$ Watts each

Deep Space Probes:

Cassini (≈ 1997)

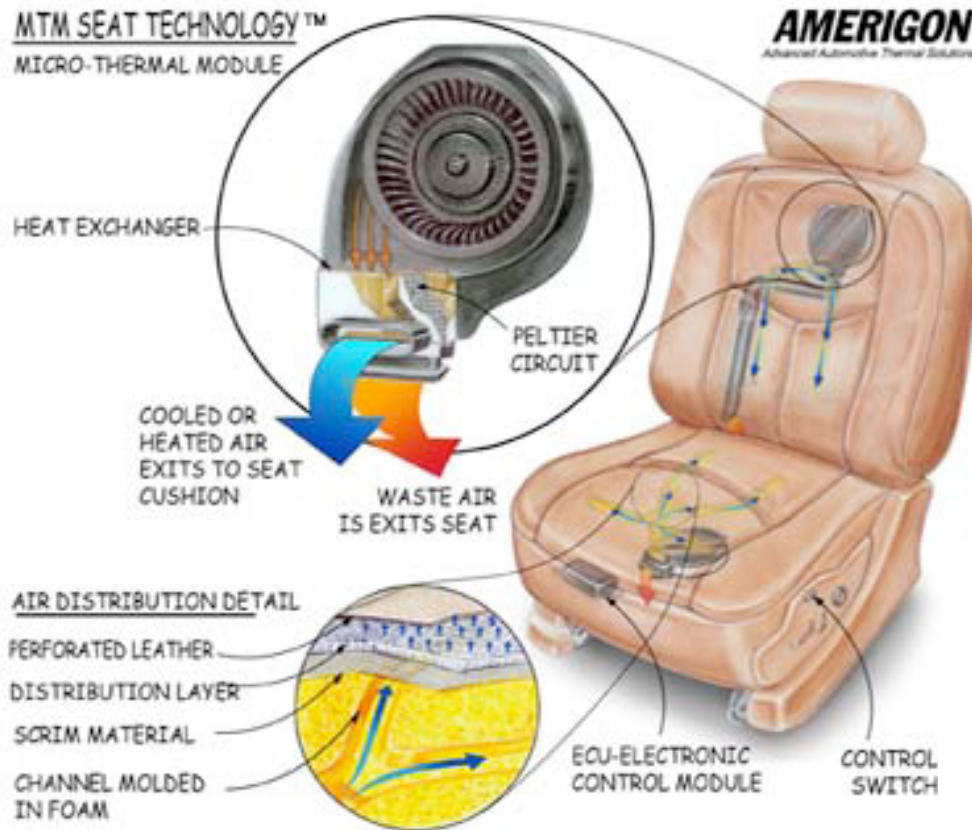
See NASA Website

Pictures of Saturn's Rings

<http://saturn.jpl.nasa.gov/multimedia/>



Automotive: The “Amerigon Climate Controlled Seat”



Climate Controlled Seat:
(cooled or warmed)

Uses new packaging
to improve efficiency.

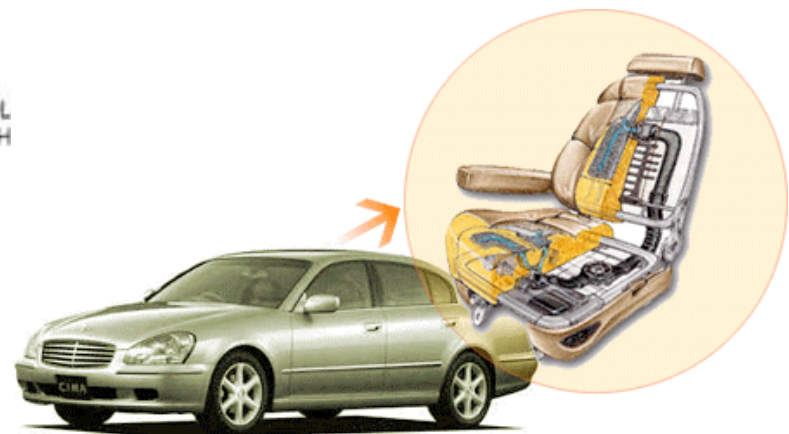
The BSST cycle

In many luxury cars:
(\approx 1 million units
sold in 2005)

Huge New market!

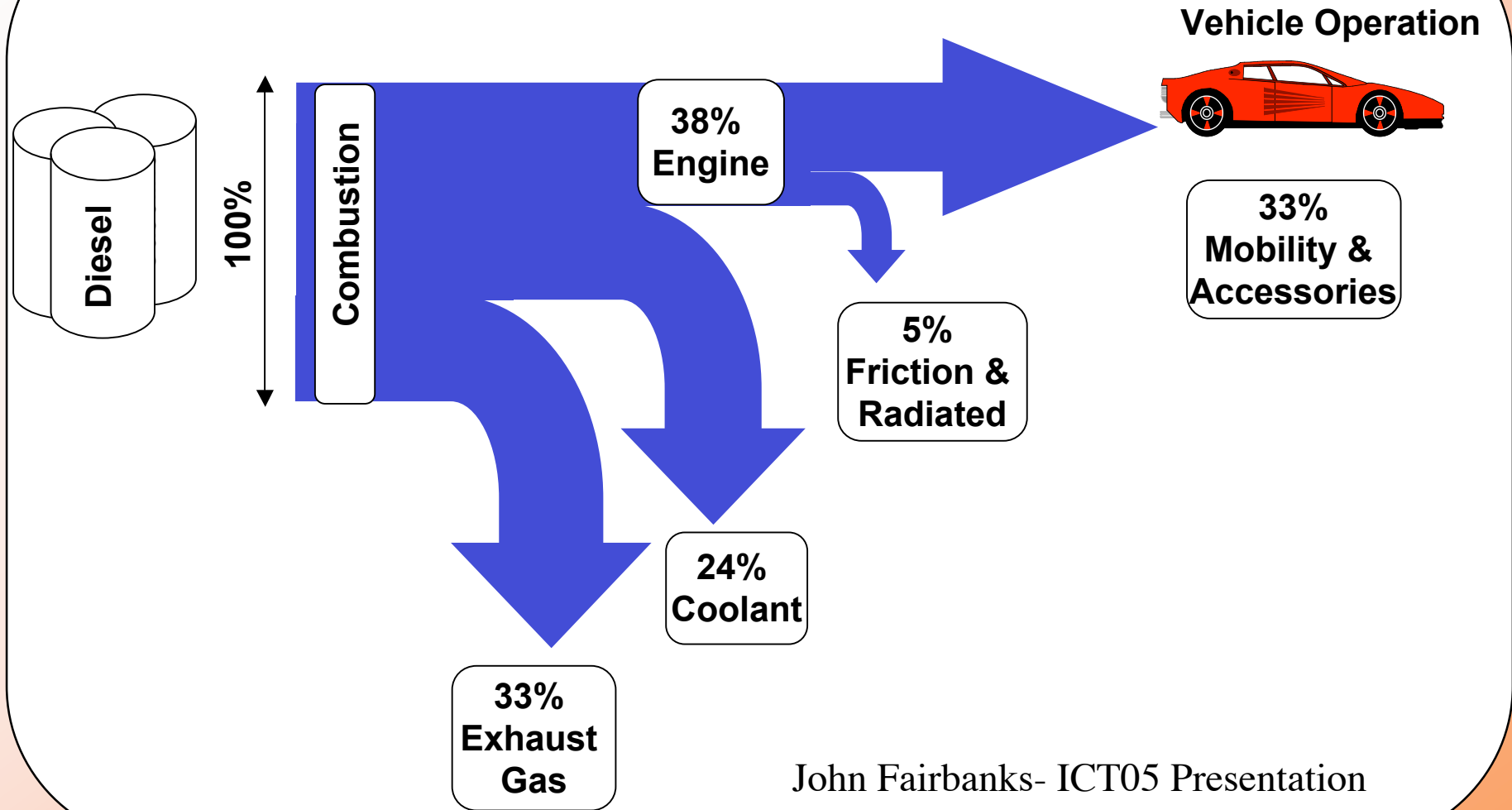
Climate Controlled Seat (CCS)

www.Amerigon.com



Large Waste Heat in Automotive Propulsion System

Diesel Engine (Light Truck or Passenger Vehicle)

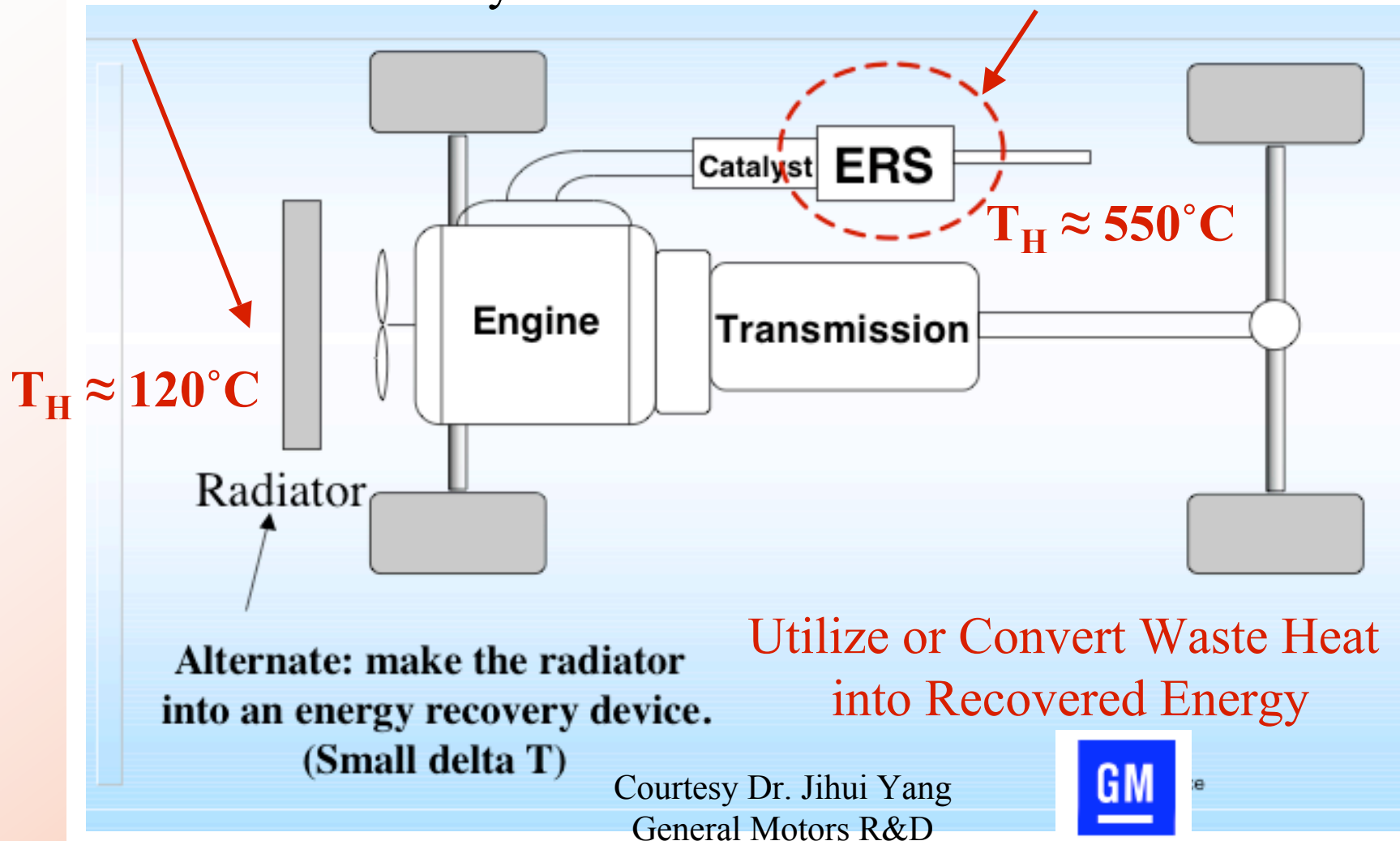


John Fairbanks- ICT05 Presentation

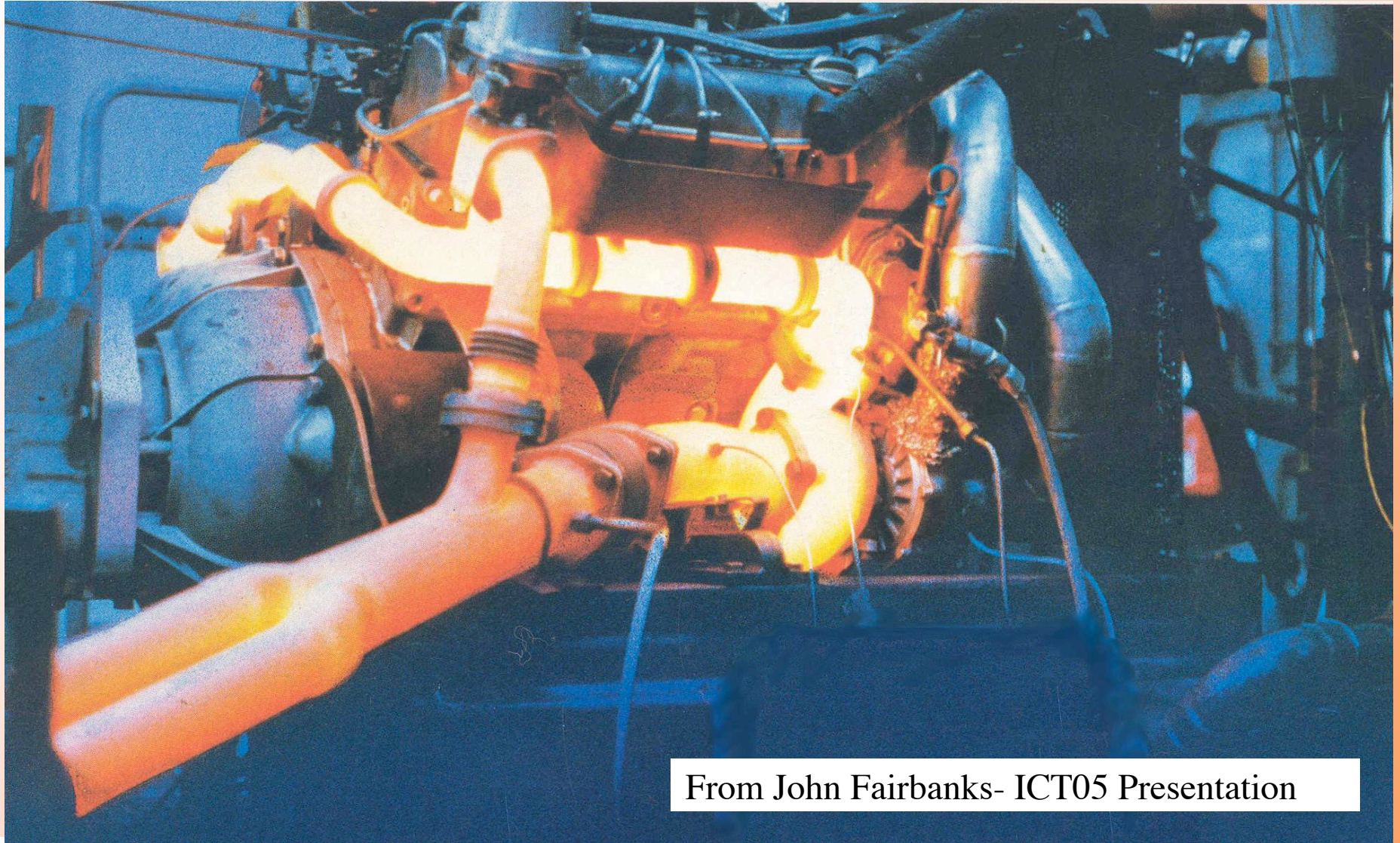
Proposed Energy Recovery System (ESR):

ESR for Radiator System

ESR for Exhaust System



Available Energy in Diesel Engine Exhaust System



From John Fairbanks- ICT05 Presentation



Waste Heat Recovery: TE Power Generation

Heat Rejection
Waste Heat > 50%

$$T_H \approx 500^\circ\text{C}$$

$$T_C \approx 30^\circ\text{C}$$

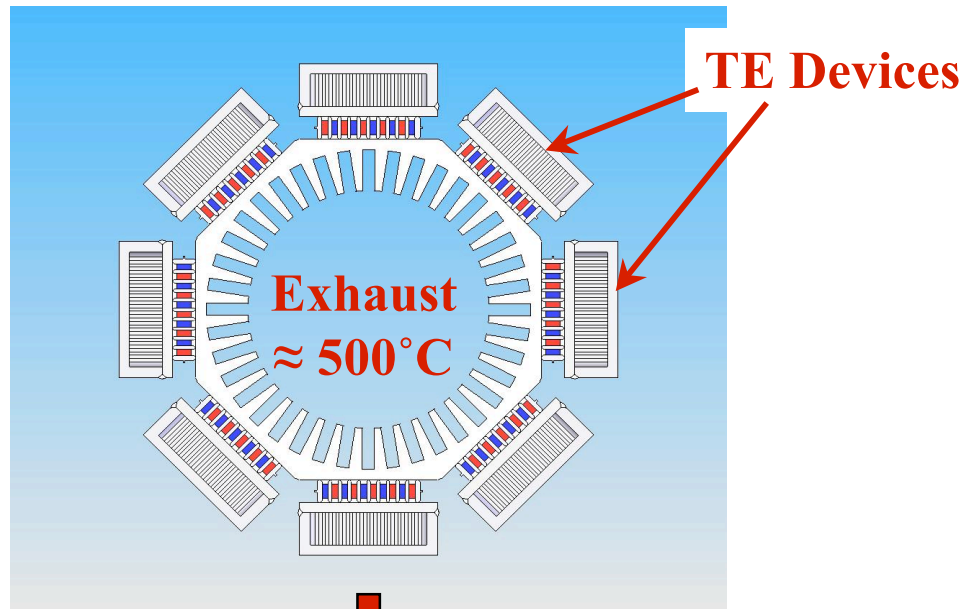


Waste Heat Recovery: TE Power Generation

Heat Rejection
Waste Heat > 50%

$T_H \approx 500^\circ\text{C}$

$T_C \approx 30^\circ\text{C}$



Waste Heat Recovery
Goal > 10%

Waste Heat Recovery: TE Power Generation

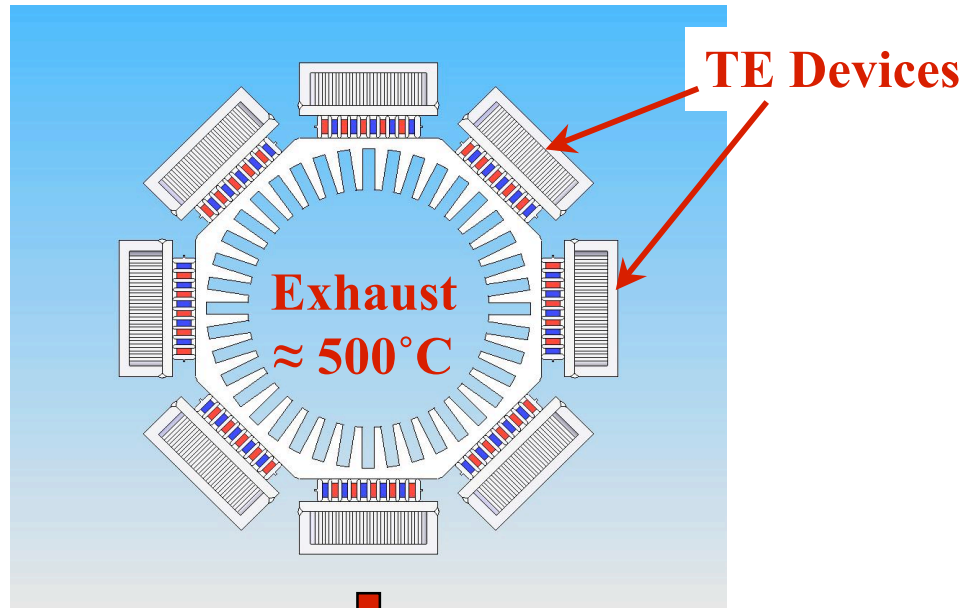
Heat Rejection
Waste Heat > 50%

$T_H \approx 500^\circ\text{C}$

$T_C \approx 30^\circ\text{C}$

Carnot Efficiency

$$\eta_C = \frac{T_H - T_C}{T_H}$$



Waste Heat Recovery
Goal > 10%

Waste Heat Recovery: TE Power Generation

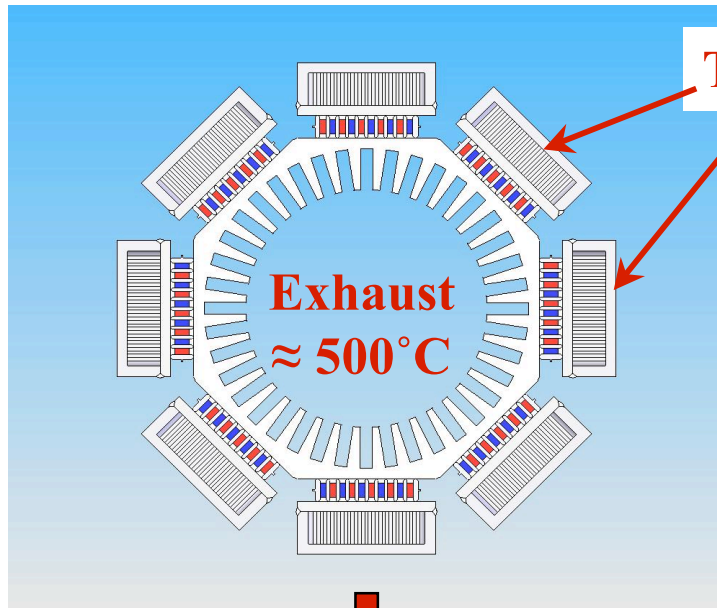
Heat Rejection
Waste Heat > 50%

$$T_H \approx 500^\circ\text{C}$$

$$T_C \approx 30^\circ\text{C}$$

Carnot Efficiency

$$\eta_C = \frac{T_H - T_C}{T_H}$$



TE Devices

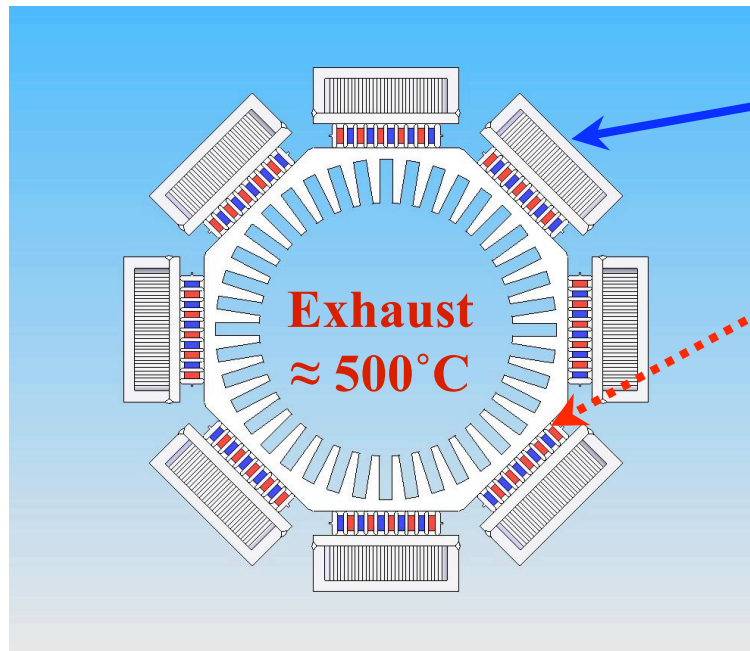
TE Efficiency

$$\eta = \left(\frac{T_H - T_C}{T_H} \right) \left(\frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_C/T_H} \right)$$

$$ZT = \frac{\alpha^2 \sigma T}{(\kappa_E + \kappa_L)}$$

Waste Heat Recovery
Goal > 10%

Automotive Waste Heat Conversion System



Cold Side

Heat Exchangers

Thermal Contact

High Efficiency

Thermoelectric Modules

$ZT \approx 2$

Some Issues

Thermal Stability

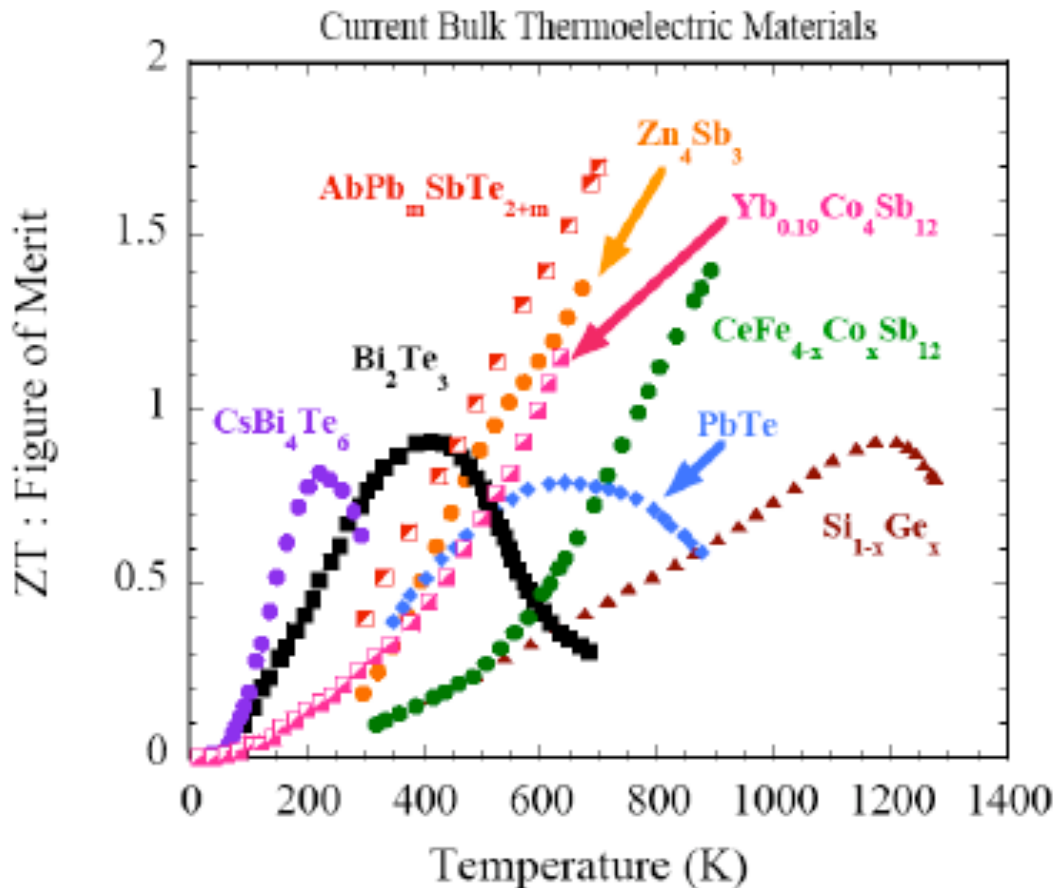
Mechanical Stability

Thermal Cycling

Parasitic Losses

Added Weight & Cost

ZT of Best TE Materials ($ZT \approx 1$):



Terry M. Tritt & Mas Subramanian
MRS Bulletin TE Theme, March 2006

State of the Art
Device TE Materials
($ZT \approx 1$)

$$ZT = \frac{\alpha^2 T}{\rho \kappa}$$

$\text{Bi}_2\text{Te}_3 \rightsquigarrow$ Cooling

$\text{Si}_{1-x}\text{Ge}_x$ & $\text{PbTe} \rightsquigarrow$
Power Generation

Future Material Needs

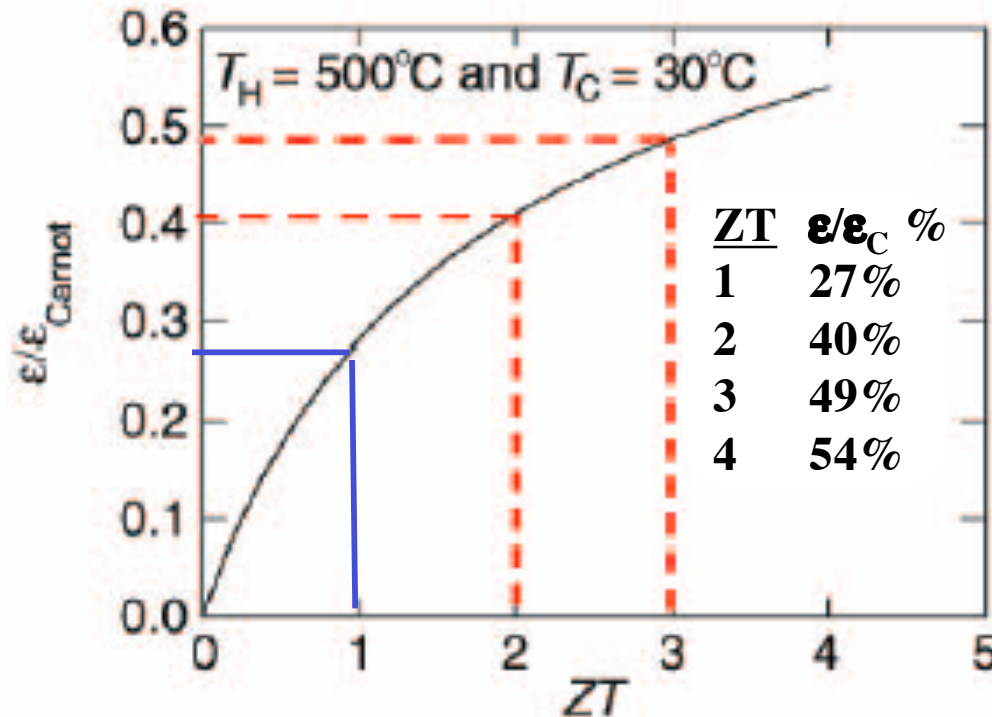
$ZT \approx 2-3!$

$\Rightarrow \eta \approx 20\%$



Why a Goal of $ZT \approx 2-3$?

Yang & Caillat (MRS Bulletin, Vol. **31**, 2006)



$$ZT = \frac{\alpha^2 T}{\rho \kappa}$$

Future Material Needs

$ZT \approx 2-3!$

$\Rightarrow \eta = \epsilon \approx 20\%$

ZT Xtra Eff %

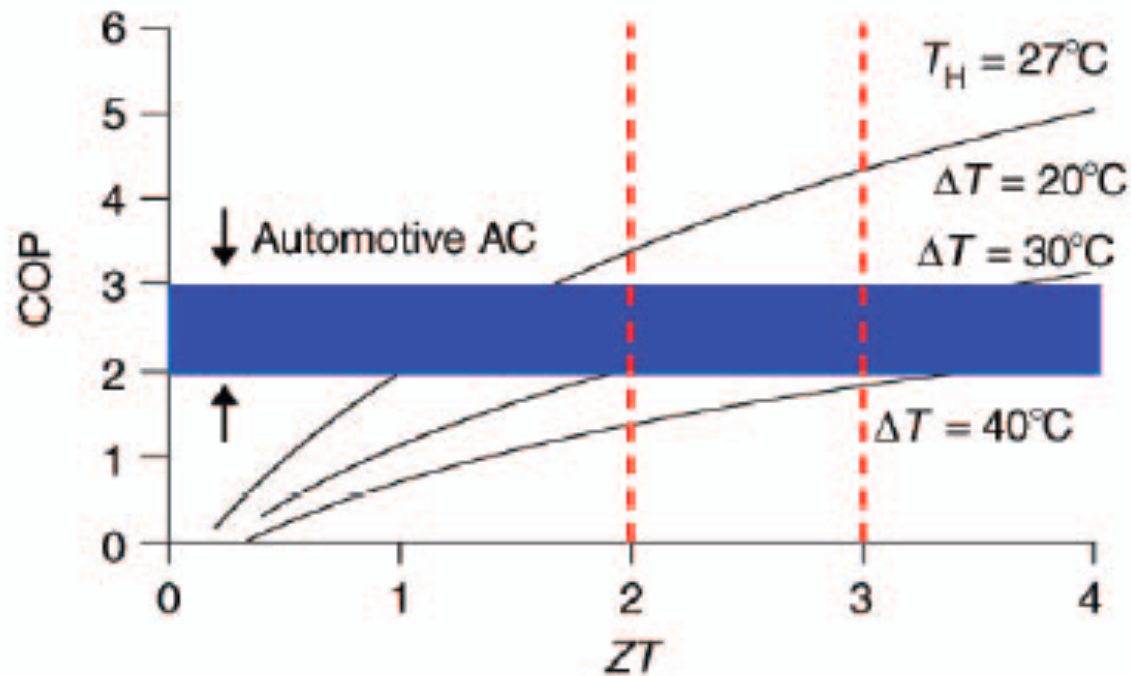
| | |
|----------|------------|
| 1 | - |
| 2 | 48% |
| 3 | 22% |
| 4 | 10% |

As $ZT \gg 1$ then $\epsilon \approx \epsilon_C$ (Carnot efficiency)

Why a Goal of $ZT \approx 2-3$?

For $ZT \approx 2-3$

b TE Cooling Competitive with Conventional COP



Yang & Caillat (MRS Bulletin, Vol. 31, 2006)

Potential Impact of DOE Freedom Car TE Program !!

**DOE's Freedom Car Program in TE's:
Incorporate TE Conversion Devices on Exhaust of Heavy Trucks:
Convert Waste Heat into Electrical Energy**

Rough Program Goals:

**10% Increase in Fuel Efficiency
(No added emissions)**

\approx 1 KW TE System (min 350 Watts)

\approx \$ per Watt (Cost effective)



Transport
Truck/Trailer

A



Diesel Engine (Potential Fuel Savings w/ 10% gain)

| | ISB Dodge Pickup | ISX Class 8 Truck |
|---|-------------------------|--------------------------|
| Emissions Useful Life | 185,000 miles | 435,000 miles |
| Typical Fuel Consumption | 16 mpg | 5 mpg |
| Fuel Consumed During the Useful Life | 11,500 Gallons | 87,000 Gallons |
| Fuel Consumed with Improved Efficiency | 10,500 Gallons | 79,100 Gallons |
| Fuel Saved | 1000 Gallons | 7900 Gallons |
| Money Saved (\$2.00 gallon) | \$2000 | \$15,800 |

John Fairbanks- ICT05 Presentation

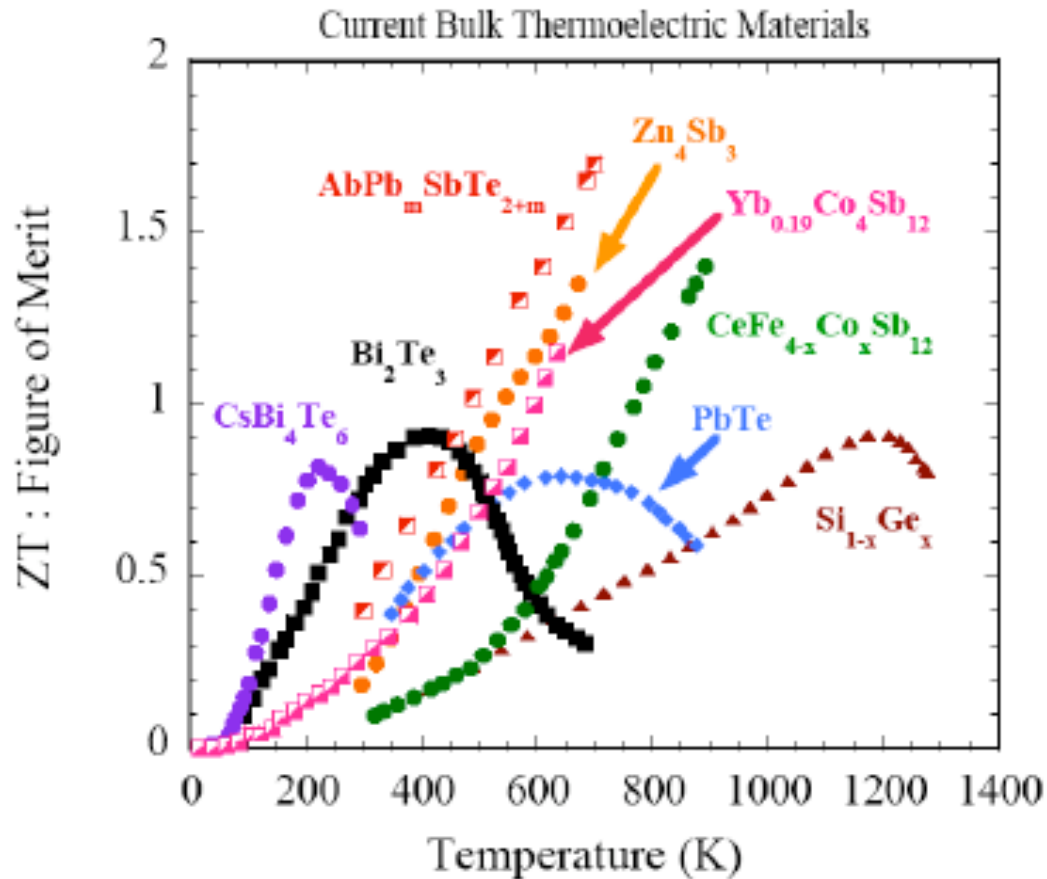


We have discussed the applications & needs

→ Focus on the Materials Research.



Figure of Merit for Bulk TE Materials



Terry M. Tritt & Mas Subramanian
MRS Bulletin, Vol. 31, March 2006

$$ZT = \frac{\alpha^2 \sigma T}{(\kappa_E + \kappa_L)}$$

Future Material Needs

$ZT \approx 2-3!$

$\Rightarrow \eta \approx 20\%$

**Broad Range of
Temperatures!**

TE Measurements!



PGEC Research Strategy: High ZT!

What Knobs to Turn? \Rightarrow Design Material Properties!

Bulk Nanocomposites
Interface - Phonons
Quantum - Seebeck

Lower $\kappa_L \Rightarrow$ Scatter Phonons
“Rattlers” in the Cage Structure
Mass Fluctuation
Defect & Grain Boundary Scattering
Heavy Atoms, Complex Structure

$$ZT = \frac{\alpha^2 \sigma T}{(\kappa_E + \kappa_L)}$$

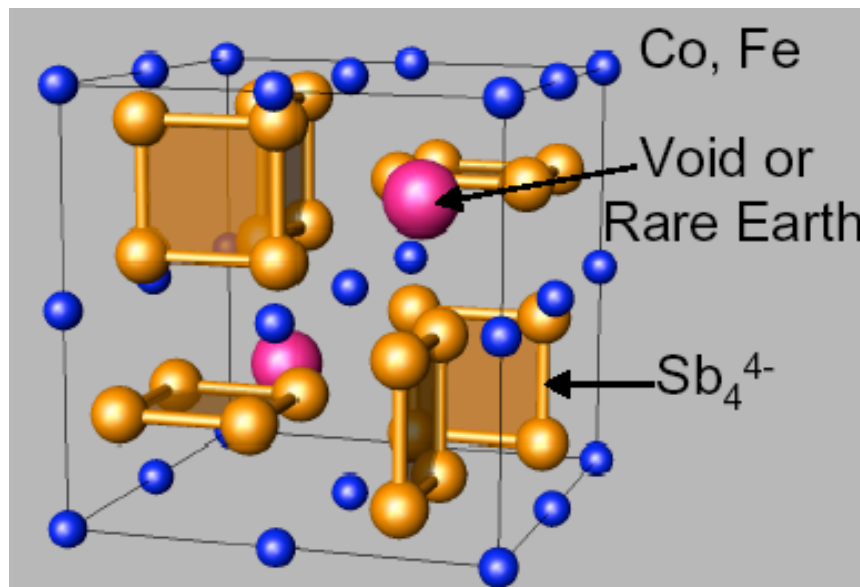
High ZT??

High Seebeck (α)
Tune Bandgap ($\alpha \approx E_{\text{GAP}}$)
Limit Minority Carriers
Large dn/dE at $E = E_F$
Low Dimensional Systems
Large Effective Mass (m^*)

High Electrical Conductivity (σ)
Doping ($n \approx 10^{19}$ carriers)
High Mobility Carriers
Narrow Gap Semiconductors
Minimize Electron Scattering



Skutterudites eg. $\text{Re}_2\text{Co}_4\text{Sb}_{12}$



Cage Structures \Rightarrow
Rattling Modes

Lower κ_L !

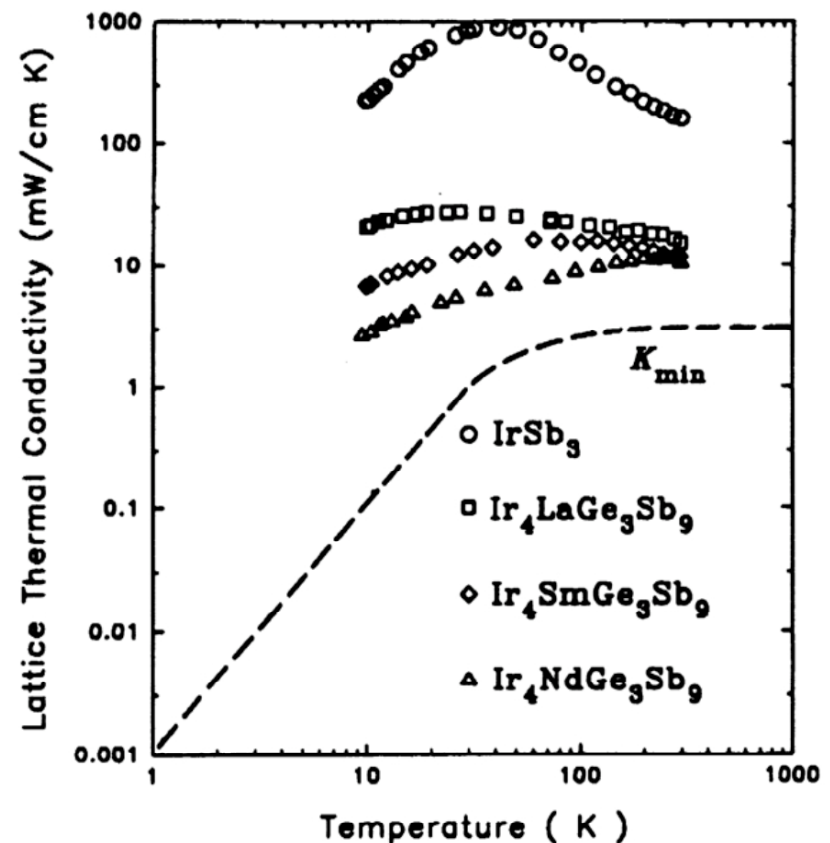


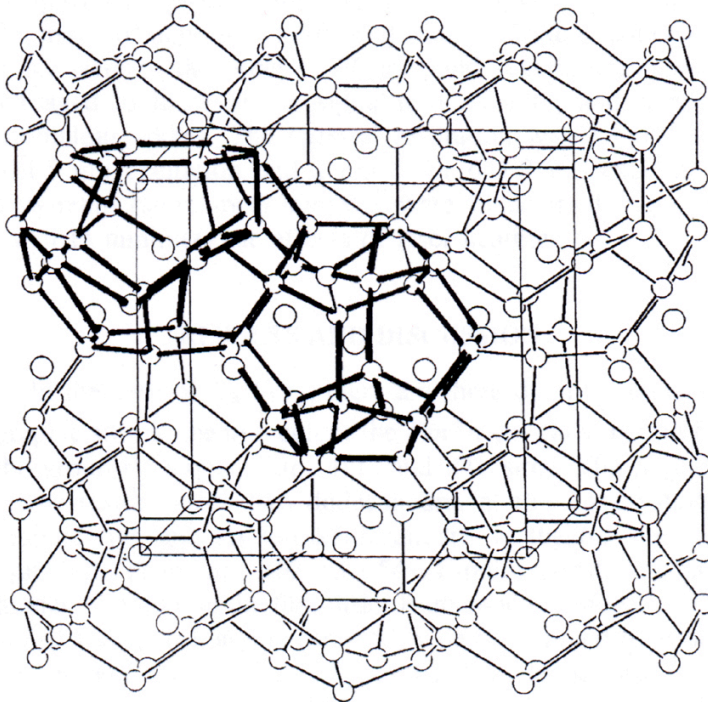
FIG. 2. Lattice thermal conductivity vs temperature for the La-, Nd-, and Sm-filled-skutterudite samples as well as the unfilled-skutterudite sample. The calculated minimum thermal conductivity κ_{\min} for IrSb_3 is also included in the figure. In effect, the lattice thermal conductivity cannot be made smaller than κ_{\min} .

G. S. Nolas, G. A. Slack, D. T. Morelli, T. M. Tritt, and A. C. Ehrlich, J. Appl. Phys. **79**, 4002 (1996).



Cage Structure Clathrates

eg: $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$
or $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$



Nolas & Slack, Am. Scientist, **89**, 136, 2001

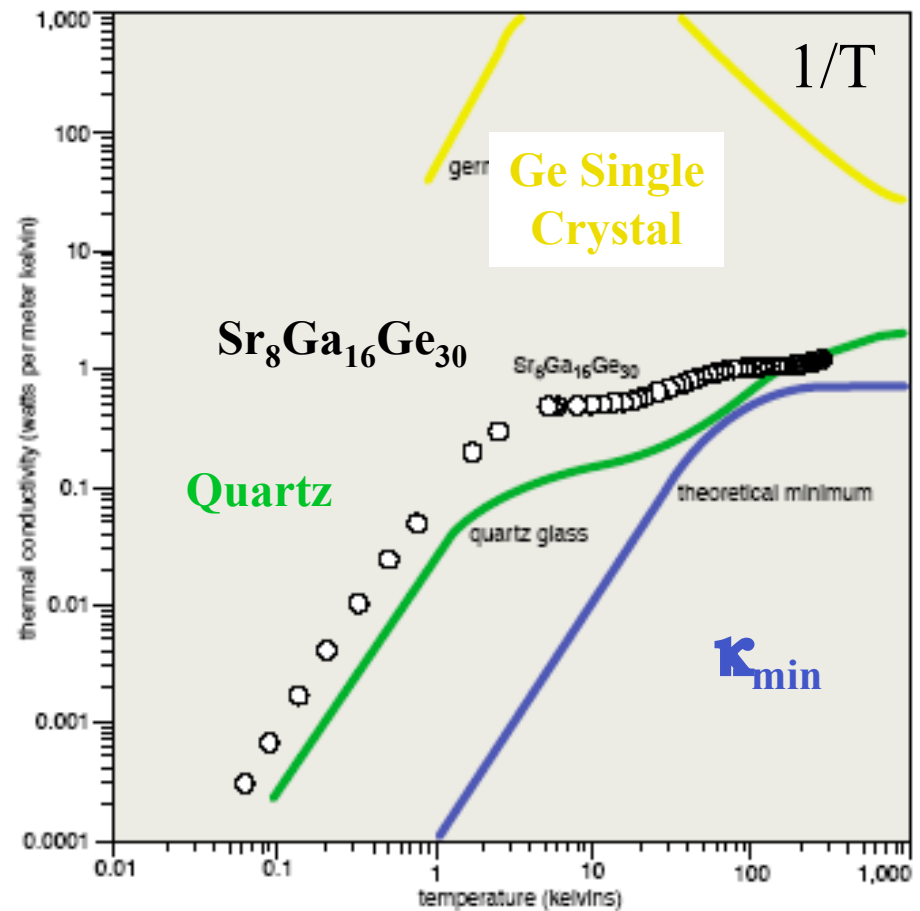
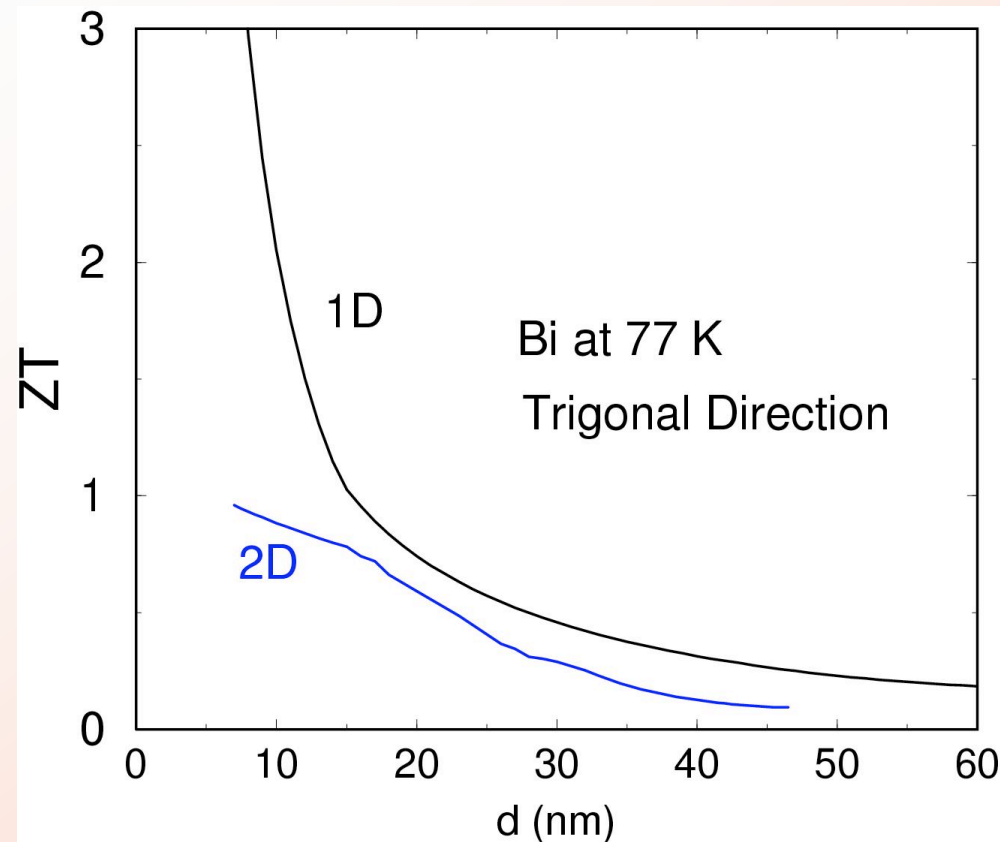
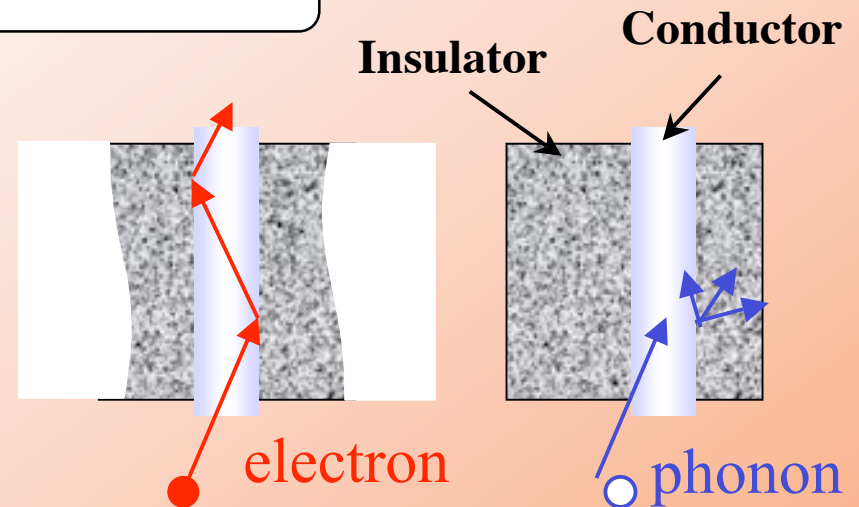


Figure 7. Thermal conductivity of a candidate clathrate material, $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ (open circles), is considerably lower than that of a pure germanium crystal (yellow). Above a temperature of about 200 kelvins (~73 degrees Celsius) the value dips even below the thermal conductivity of quartz glass (green) and approaches the theoretical minimum (blue). Such low thermal conductivity is a requirement for a high-efficiency thermoelectrics, which would waste energy if thermal conduction allowed heat to flow from the hot to the cold side of a device.

Motivation for Low Dimensional TE Materials:



Hicks & Dresselhaus, PRB 1993
Dresselhaus, Plenary Talk - ICT 05



Quantum Enhancement
Increase Seebeck

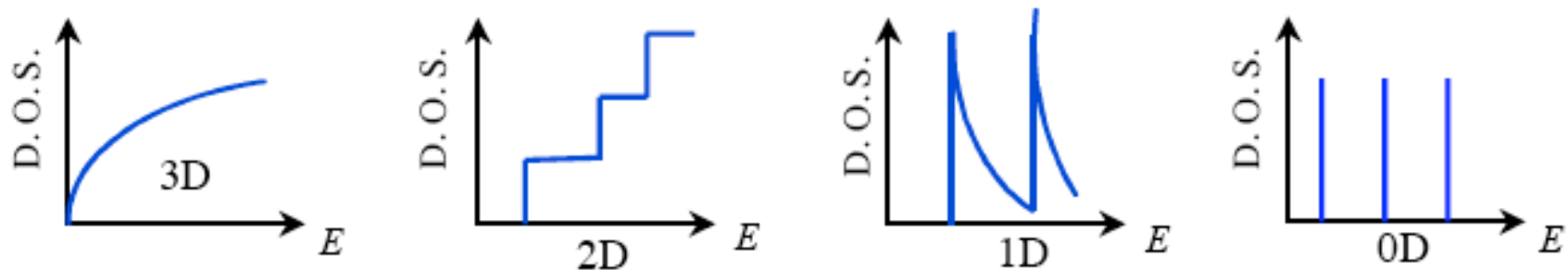
Interface Scattering
Large Kapitza Resistance
Reduce κ_L



Role of Lower Dimensions in Thermoelectrics:

Density of States (DOS) for Low D

Hicks & Dresselhaus, PRB, 47, 12727 (1993)



$$ZT = \frac{\alpha^2 \sigma T}{(\kappa_E + \kappa_L)}$$

Large variation of DOS yields
large Seebeck Coef.

$$\alpha \propto \left. \frac{\partial \text{DOS}}{\partial E} \right|_{E_F}$$

Low D yields large $dn(E)/dE$

$$ZT \approx \alpha^2 \sigma \approx \alpha^2 n$$

$$ZT_{2D} \geq ZT_{3D}$$

$$\alpha = \frac{\pi^2 k_B^2 T}{3e} \left[\frac{\partial \ln \sigma}{\partial E} \right]_{E_F}$$

M. Dresselhaus et al,
APL **63** 3230 (1993)



Recent Results: $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ Superlattices

$ZT > 2.4 @ 300\text{K}$

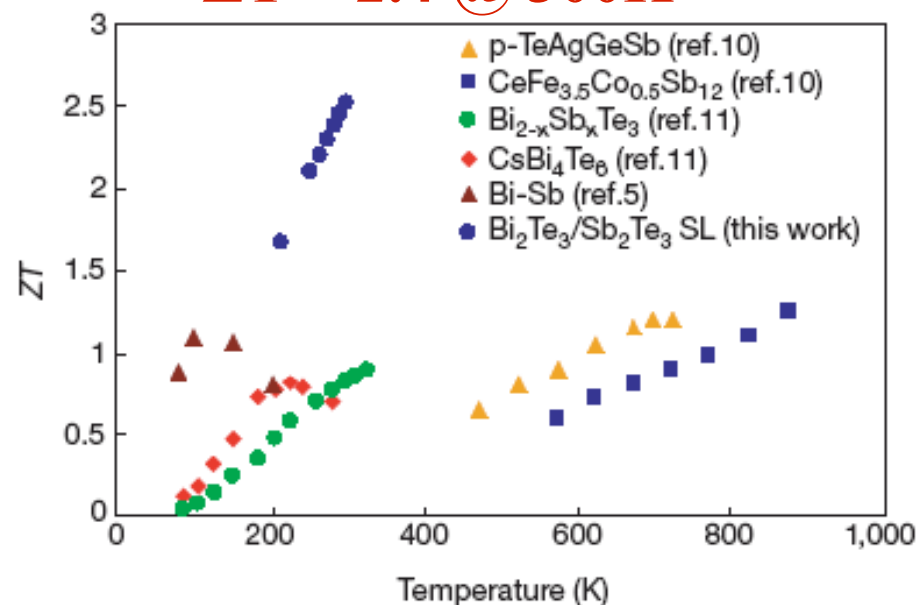
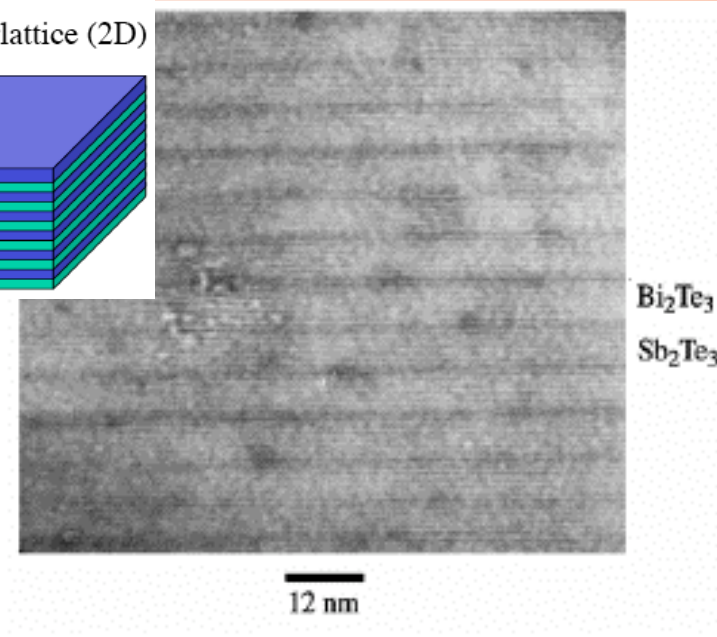
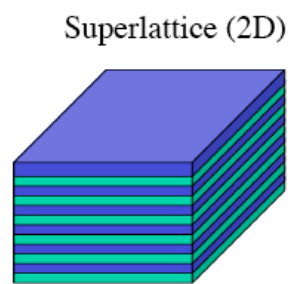


Figure 3 Temperature dependence of ZT of $10\text{\AA}/50\text{\AA}$ p-type $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice compared to those of several recently reported materials.



Applied Physics Letters, 75, 1104 (1999).

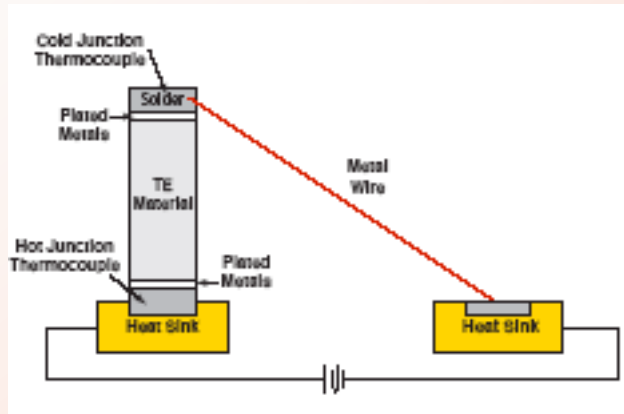
$\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ Superlattice
R. Venkatasubramanian, et. al.,
Nature, **413**, 597, 2001

| $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ | Superlattice | Bulk |
|---|--------------|------|
| Power Factor($\mu\text{W}/\text{cmK}^2$) | 40 | 50.9 |
| Thermal Conductivity(W/mK) | 0.5 | 1.26 |



Recent Results: PbTe Quantum Dots

PbTe Quantum Dot Superlattice
T. Harman et.al, Science, **297**, 2229 (2002)



Device $ZT_D \approx 1.4$ @ 300K
Materials $ZT > 2$ @ 300K

Table 1. 300 K thermoelectric properties of Bi-doped (n-type) QDSL $\text{PbSe}_{0.98}\text{Te}_{0.02}/\text{PbTe}$ samples grown by MBE and an n-type BiSbSeTe alloy sample.

| Sample | $S(\mu\text{V/K})$ | ZT | Carrier conc. (cm^{-3}) | Carrier mobility ($\text{cm}^2/\text{V}\cdot\text{s}$) |
|--------------|--------------------|-------|------------------------------------|--|
| n-QDSL A | -219 | 1.6* | 1.2×10^{19} | 370 |
| n-QDSL B | -208 | 1.3* | 1.1×10^{19} | 300 |
| n-BiSbSeTe A | -228 | 0.9** | 4.6×10^{19} | 110 |

*Values based on thermal conductivity values of 5.8 mW/cm-K calculated from the QDSL device test data. **Value based on a measured thermal conductivity value of 13.6 mW/cm-K.

Fig. 1. Schematic cross section of the quantum-dot superlattice structure investigated.

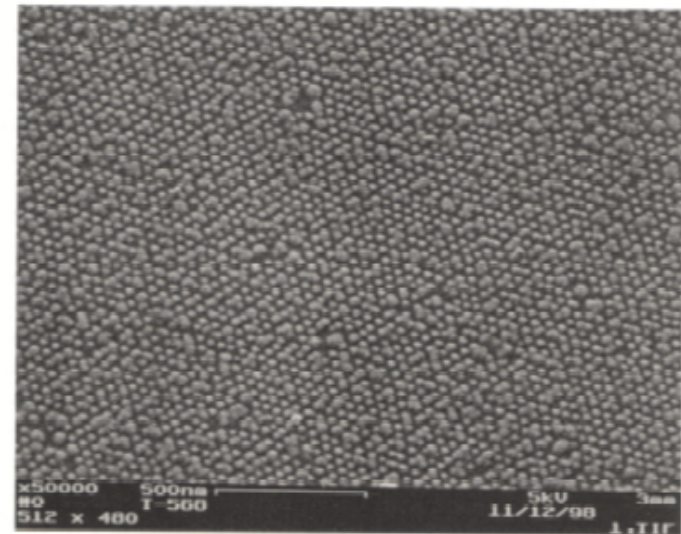
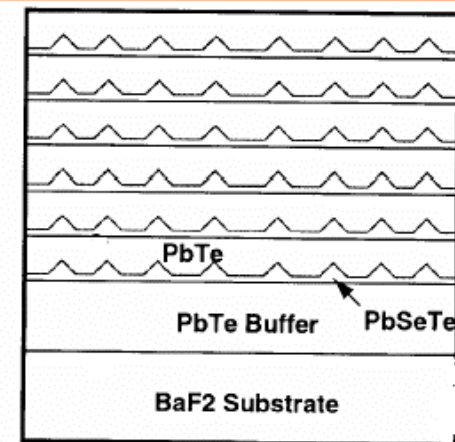
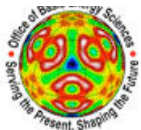


Fig. 2. Field-emission SEM image of quantum-dot superlattice structure.



$\text{PbSe}_x\text{Te}_{1-x}$ quantum dots in PbTe layers



Relative Importance of α^2/ρ and κ

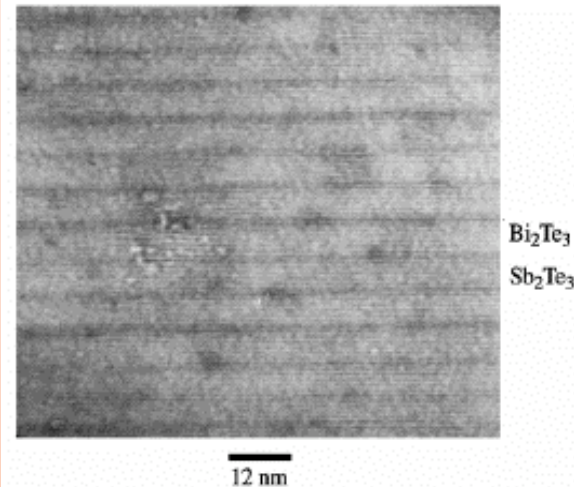
| $\text{Bi}_2\text{Te}_3 / \text{Sb}_2\text{Te}_3$ | Nano | Bulk |
|--|------|------|
| $\alpha^2/\rho (\mu\text{W}/\text{cm}\cdot\text{K}^2)$ | 40 | 51 |
| $\kappa (\text{W}\cdot\text{m}^{-1}\text{K}^{-1})$ | 0.6 | 1.45 |
| ZT (T = 300K) | 2.4 | 1.0 |

Venkatasubramanian et.al., Nature 413, 597, 2001

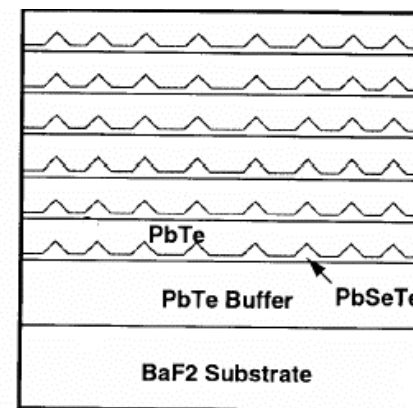
| PbTe/PbSeTe | Nano | Bulk |
|--|------|------|
| $\alpha^2/\rho (\mu\text{W}/\text{cm}\cdot\text{K}^2)$ | 32 | 28 |
| $\kappa (\text{W}\cdot\text{m}^{-1}\text{K}^{-1})$ | 0.6 | 2.5 |
| ZT (T = 300K) | 1.6 | 0.3 |

T. Harman et.al, Science, 297, 2229 (2002)

$\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ Superlattice



PbTe/PbSeTe Quantum Dots



$\text{PbSe}_x\text{Te}_{1-x}$ quantum dots in PbTe layers

Relative Importance of α^2/ρ and κ

Thermal Conductivity Reduction

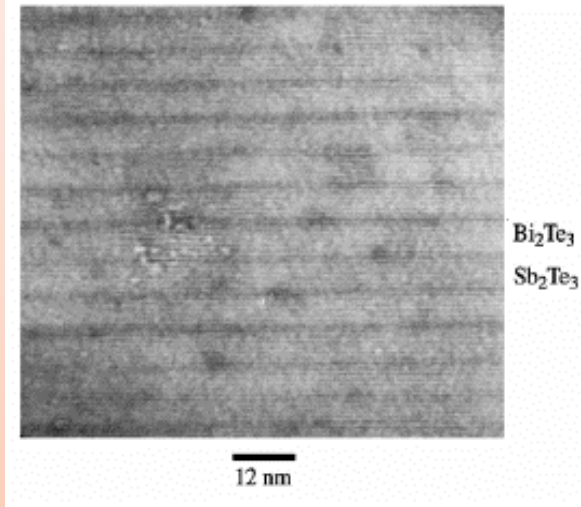
| $\text{Bi}_2\text{Te}_3 / \text{Sb}_2\text{Te}_3$ | Nano | Bulk |
|--|------|------|
| α^2/ρ ($\mu\text{W}/\text{cm}\cdot\text{K}^2$) | 40 | 51 |
| κ ($\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$) | 0.6 | 1.45 |
| ZT (T = 300K) | 2.4 | 1.0 |

Venkatasubramanian et.al., Nature 413, 597, 2001

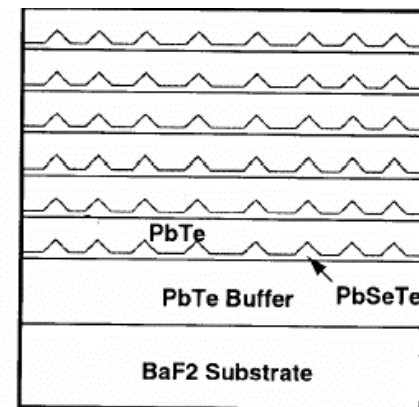
| PbTe/PbSeTe | Nano | Bulk |
|--|------|------|
| α^2/ρ ($\mu\text{W}/\text{cm}\cdot\text{K}^2$) | 32 | 28 |
| κ ($\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$) | 0.6 | 2.5 |
| ZT (T = 300K) | 1.6 | 0.3 |

T. Harman et.al, Science, 297, 2229 (2002)

$\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ Superlattice



PbTe/PbSeTe Quantum Dots



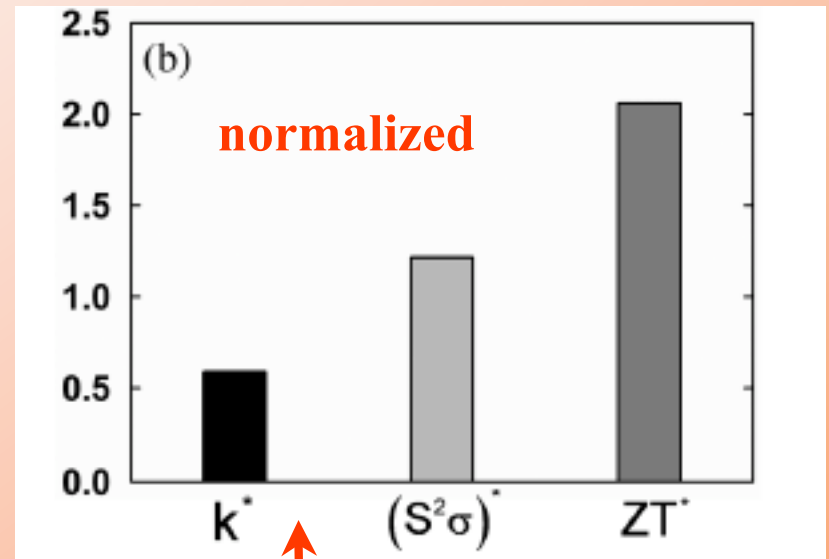
$\text{PbSe}_x\text{Te}_{1-x}$ quantum dots in PbTe layers

Embedding Nanoparticles in Crystalline Semiconductors

ErAs nanoparticles in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ matrix
Epitaxial growth
Goal to “Beat the Alloy Limit”
Uncorrelated Phonon Scattering

W. Kim et.al., PRL, 96-045901 (2006)
Santa Cruz & Berkeley Groups

- Reduction in κ_L (“nano- phonon effect”)
Depends on ML thickness (ErAs nano)*
- Power Factor about same
but ErAs can act as a dopant
- ZT significantly enhanced
- Theoretical analysis showed that
 - ErAs nanoparticles scatter
mid to long λ phonons*
 - While atomic scale defects scatter
short λ phonons.

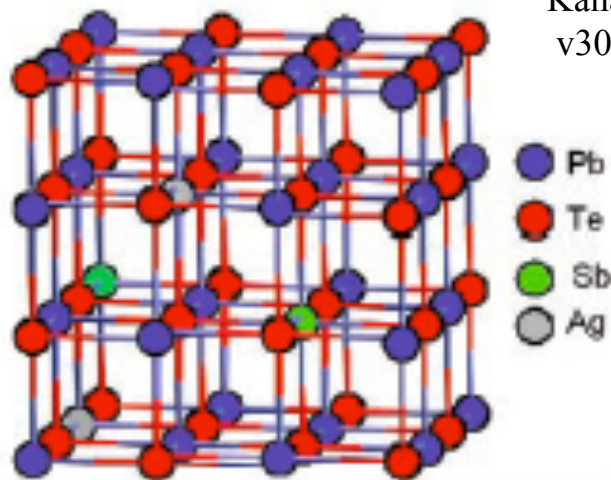


κ_L reduced a factor of 2
below the alloy limit!
ZT enhanced a factor of 2 !



Complex Chalcogenides - $\text{AgPb}_{18}\text{SbTe}_{20}$

$\text{AgPb}_{18}\text{SbTe}_{20}$ (LAST)

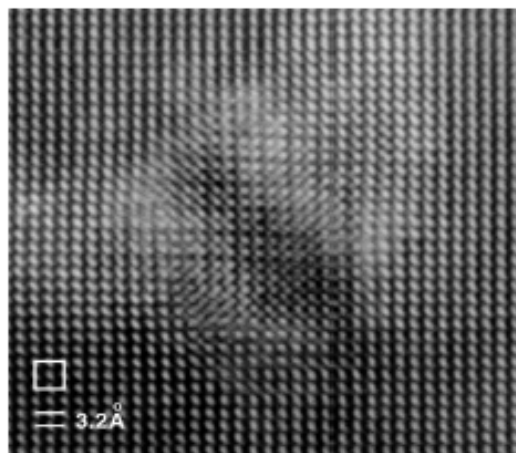


Kanatzidis Group, Science, v303, p818 2004

**Mich. St.
Results:**

**Results Show
»»» $ZT > 2$**

**Cubic material
Nanoscale
microstructure !!**



AgSb-rich Nanodot in $\text{AgPb}_{18}\text{SbTe}_{20}$

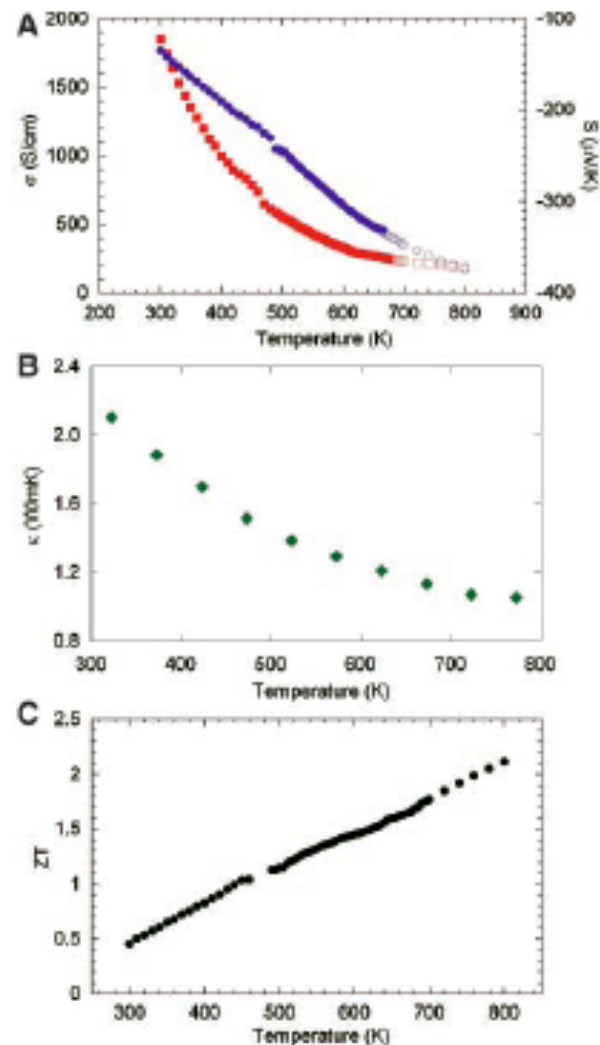


Fig. 3. Variable-temperature charge transport and thermal transport data for $\text{AgPb}_{18}\text{SbTe}_{20}$.

Bulk Materials Need “**Tuning Knobs**” for Improvement!

The Low Dim. approaches give us potential new directions in TE's, however, there are some disadvantages of these materials.

1. The superlattices and quantum dots are expensive.
2. The superlattices and quantum dots are too small to be used in routine industry applications.
3. For the $\text{AgPb}_m\text{SbTe}_{2m}$, it is hard to control the nano-sized dots (inhomogeneity) in the materials.

So the need is to grow a bulk material with controlled nano-scale inclusions?

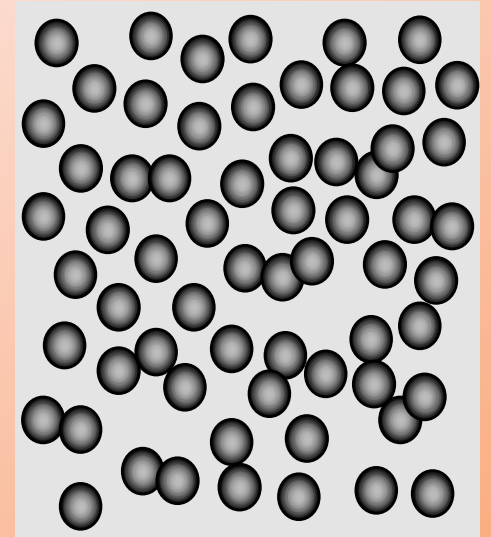


Combine the “**Nano and Bulk**” - TE Composite Material

Potential route to enhance ZT
Incorporate nanoparticles into bulk matrix phase
Or directly press nanoparticles into pellets,
Yield “**Bulk Nano-Composites**”

Goals:

Phonon scattering at interface could significantly
Reduce the lattice thermal conductivity.
Or Quantum Enhancement Effects due to Low
Dim. **Enhance Seebeck Coefficient**



Bulk TE Material
w /Nanoparticles!

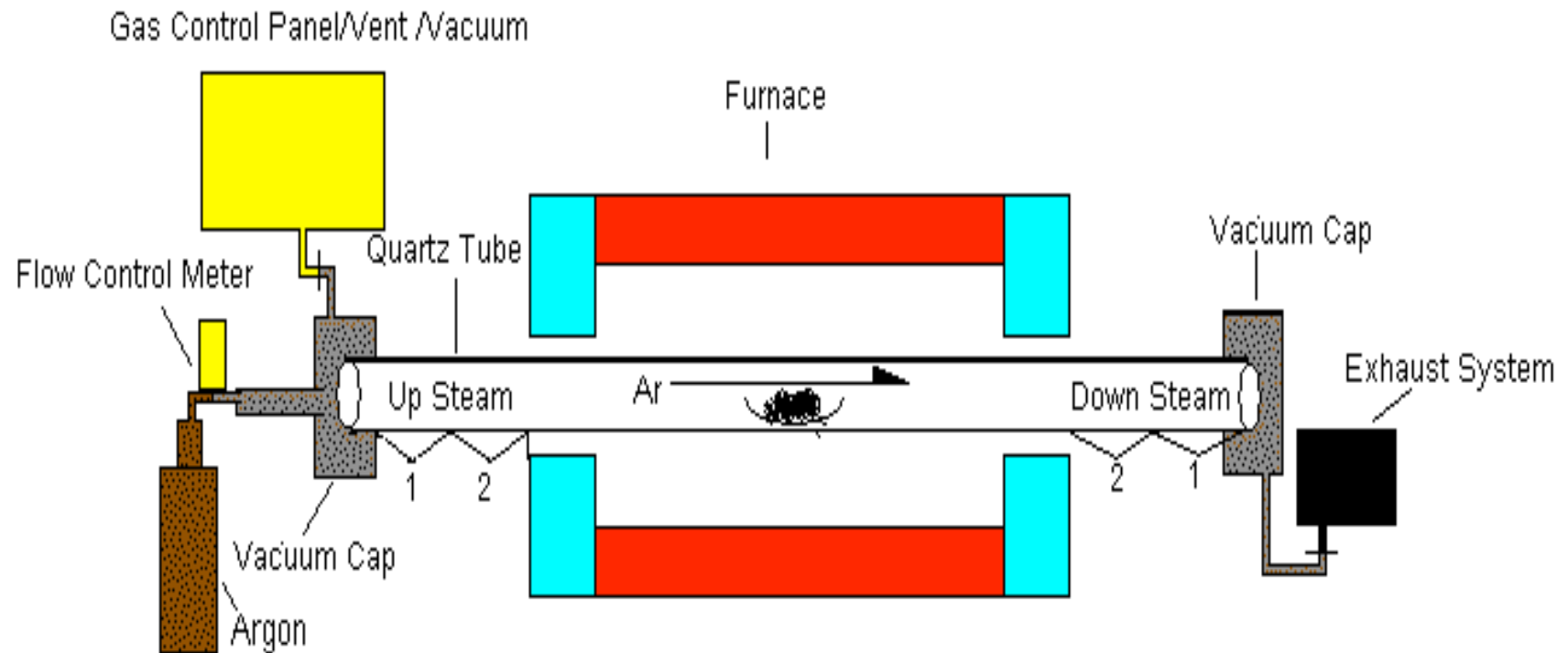
*How to grow large amount of size-controllable
TE nanoparticles?*



Chemical Vapor Deposition: Synthesis of Nanoscale TE Materials

Diagram of CVD:

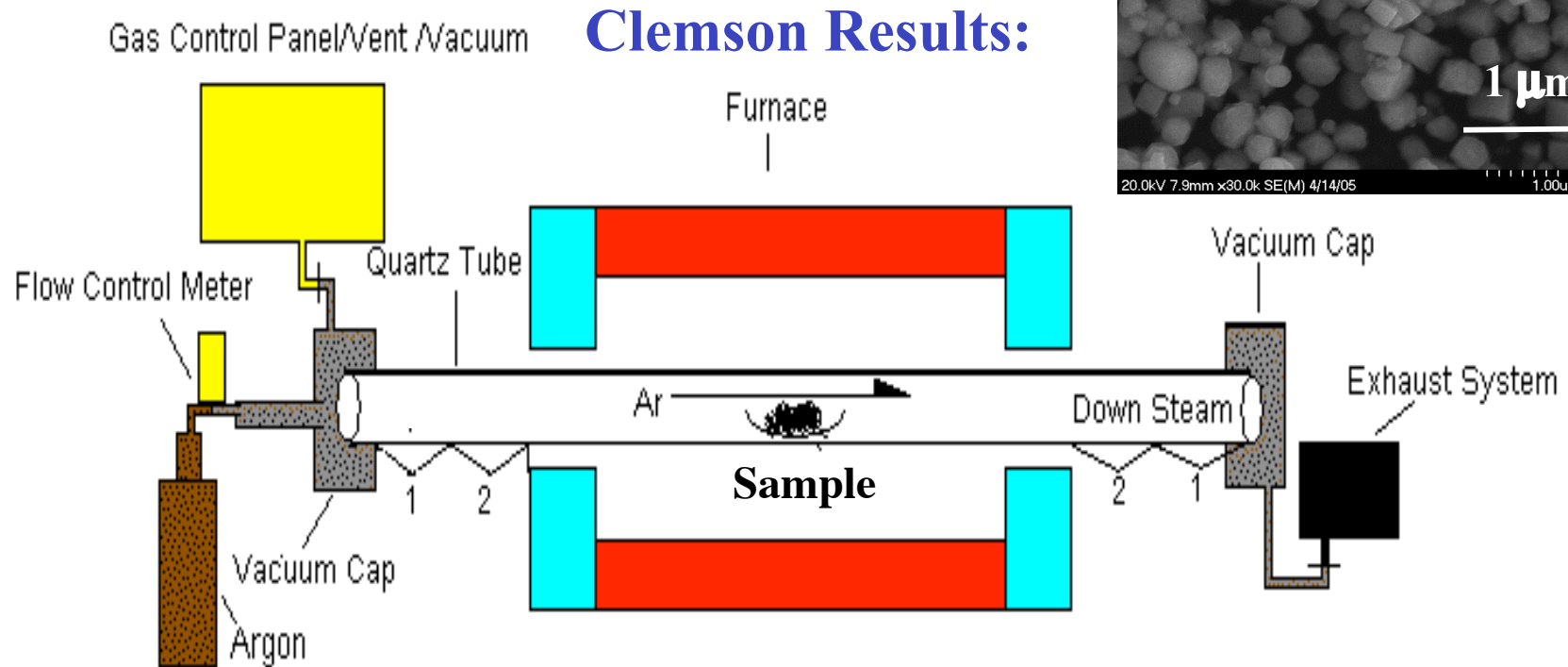
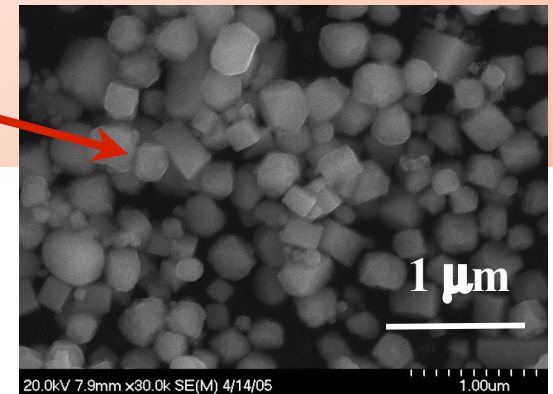
Requires 1200 °C Furnace, Ar Gas, Au Seed Particles and Flow Meters

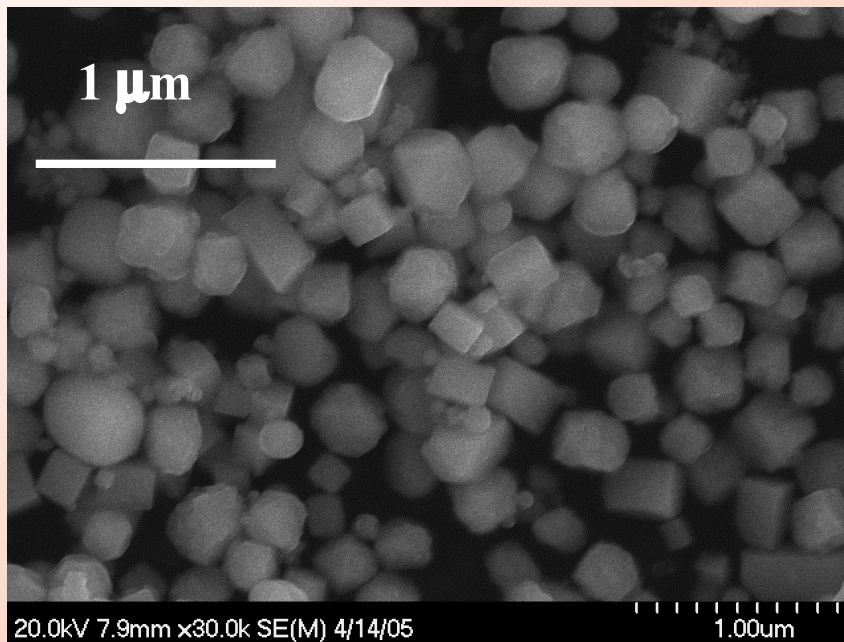
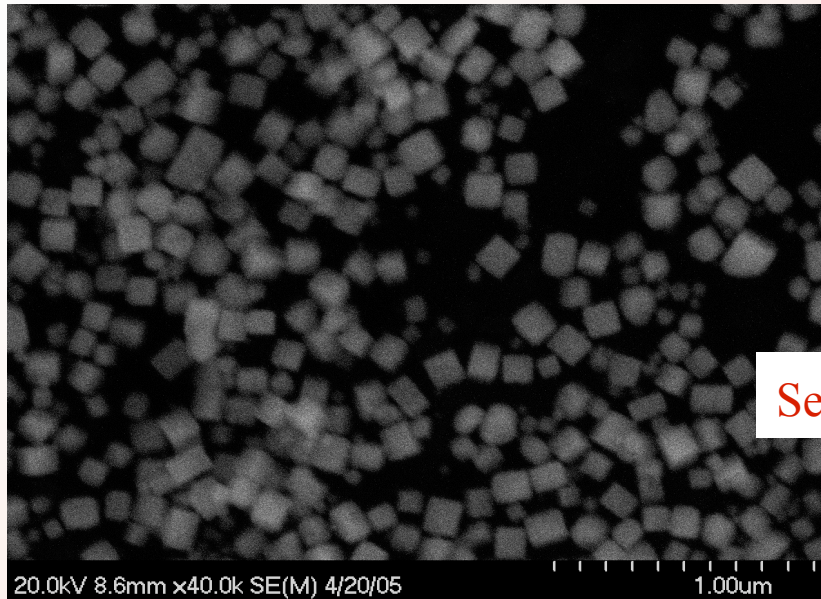


Chemical Vapor Deposition: Synthesis of Nanoscale TE Materials

Diagram of CVD: For Growth of Nano-particles of TE Materials!

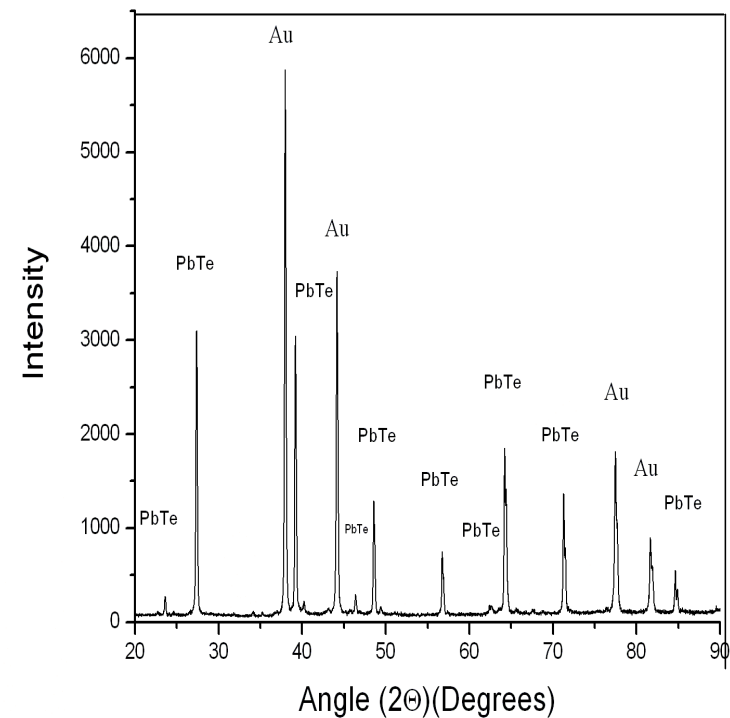
PbTe Cubic Nano Particle (≈ 200 nm)
Size Selective & Mono Dispersed



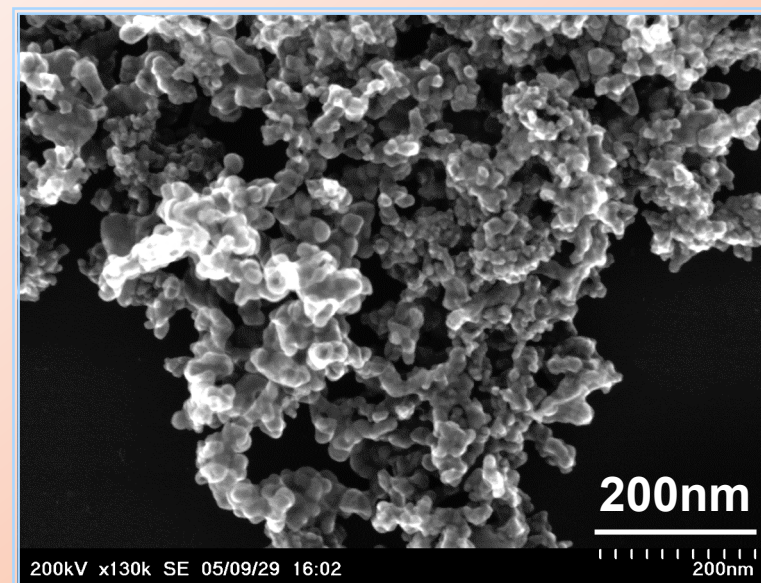
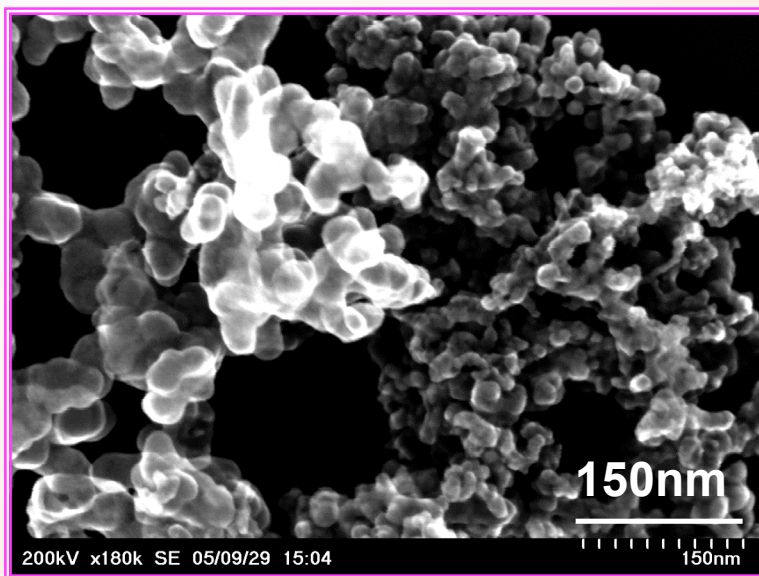


PbTe Nanocrystals
 ≈ 200 nm cubic structures
 Sharp X-Ray Diffraction peaks

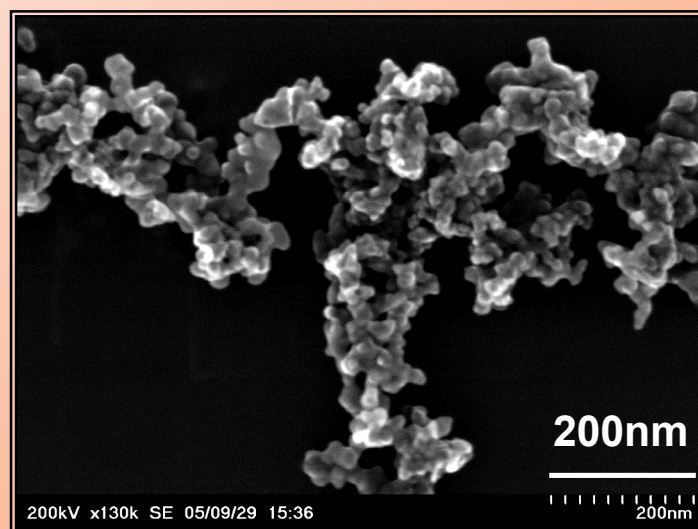
See B. Zhang , Appl. Phys. Lett., **88**, 043119 2006



Hydrothermal Synthesis of Nanomaterials: Bi_2Te_3 & CoSb_3



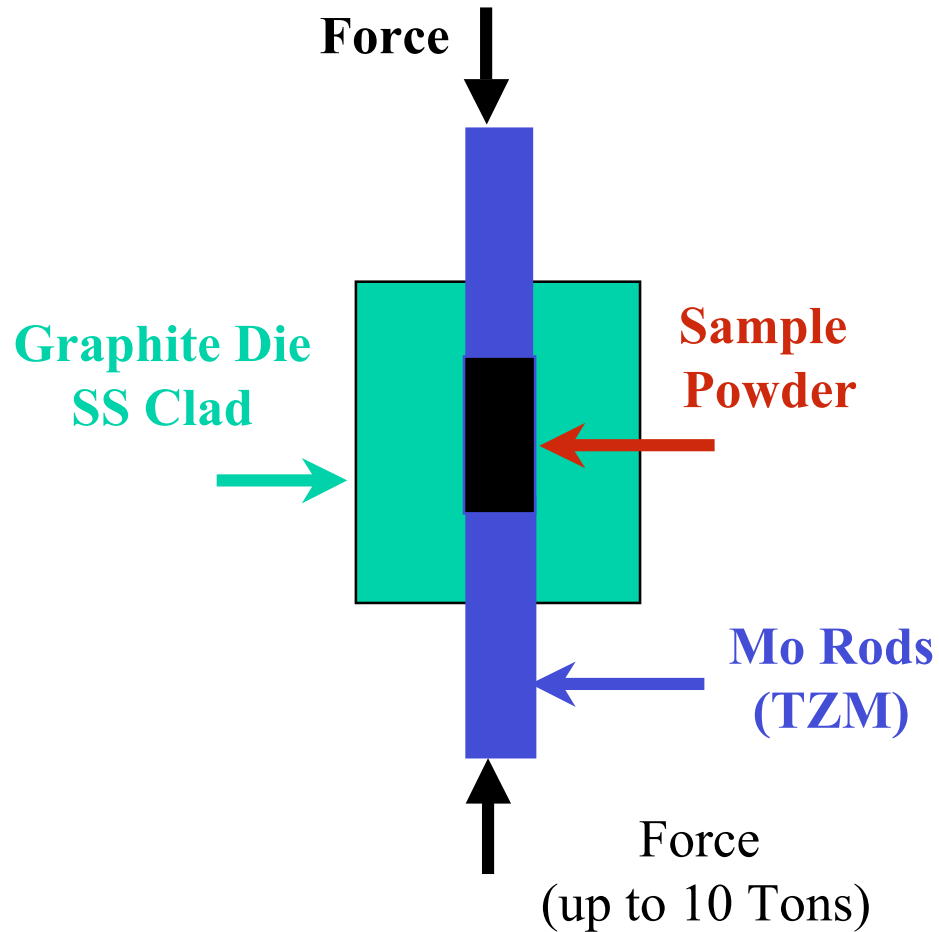
Skutterudite (CoSb_3)
Nano Structures
20-40 nm



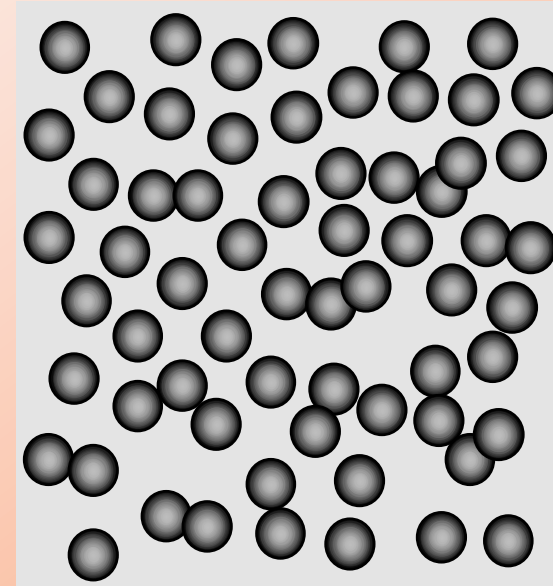
**We made the Nano-materials!
So How to Make the Nano-Composite?
Needs to be Densified!**



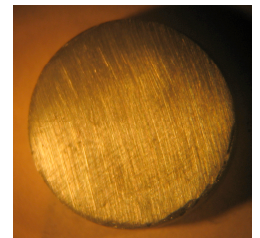
Hot Isostatic Press 10 Ton, 2000°C



Composite Bulk & Nano



1/2" diameter
≈ 3/8" Long Sample



Success: Able to grow nanostructures!

Thermal conductivity is reduced!

Issue: When mixing PbTe or CoSb₃ nanoparticles

Homogeneous mixing and control of the bulk powders
& the nanostructures?

Typically High Resistivity.



Success: Able to grow nanostructures!

Thermal conductivity is reduced!

Issue: When mixing PbTe or CoSb₃ nanoparticles

Homogeneous mixing and control of the bulk powders
& the nanostructures?

Typically High Resistivity.

Developed a **Nano-Coating Process**

Start with ball milled seed particles (several microns)

Coat Hydrothermally (tens of nm) -- Then Hot press:

Stability of the nanostructure within the composite?



Hydrothermal Nano-Coating Process for CoSb_3

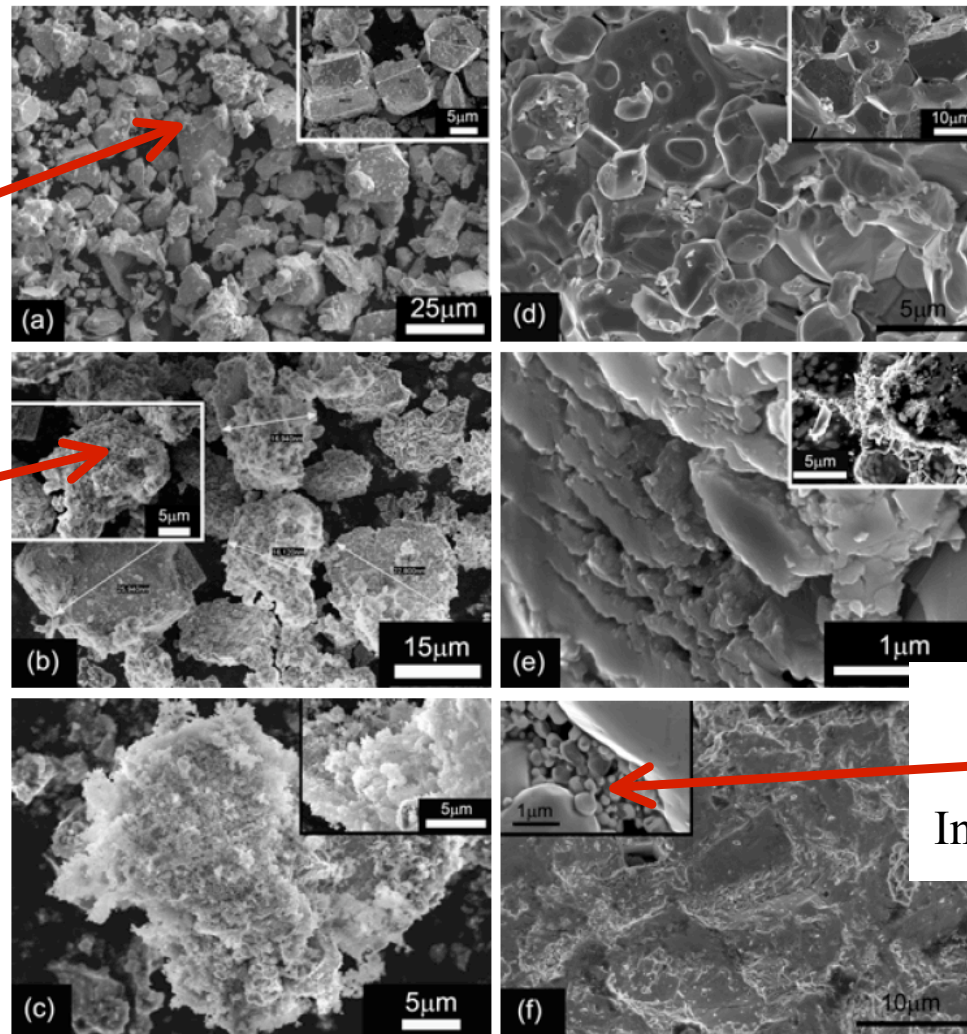
Before Hot Press

After Hot Press

CoSb_3 Seed Particles
Several μm 's

CoSb_3 Hydrothermal
Coating

CoSb_3 Hydrothermal
Coating



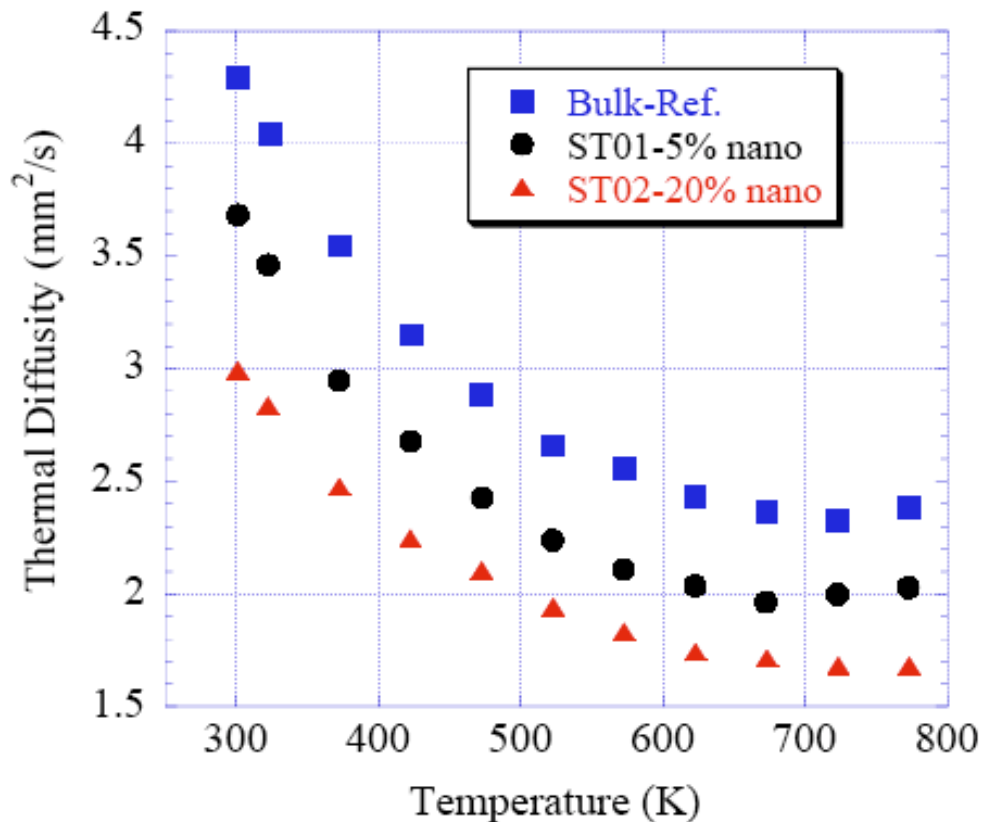
CoSb_3 Nano-
Coating
In Grain Boundaries



Hydrothermal Nano-Coating Process for CoSb_3

Effect on Thermal Properties

High Temperature Thermal Diffusivity



NETZSCH LFA 457
Thermal Diffusivity (d)

$$\kappa = d\rho_D C_V$$

Three Samples

All three from same starting powders

- 1.) Bulk Ball Milled Powder
- 2.) Bulk with 5 wt% nano
- 3.) Bulk with 20 wt% nano

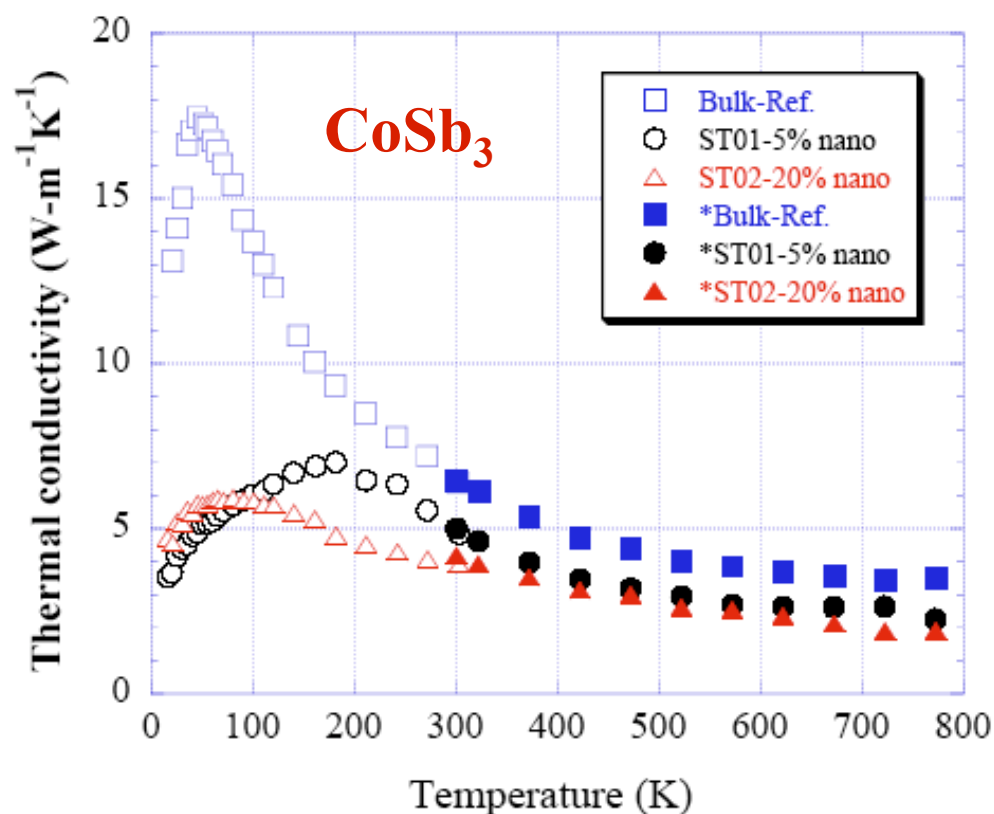


Hydrothermal Nano-Coating Process for CoSb_3

Effect on Thermal Properties

High & Low Temperature Thermal Conductivity

See X. Ji. *et.al* , Rap. Res.. Lett.,
in press 2007



Major Points:

- 1.) Very good match high & low temp
- 2.) Thermal conductivity reduces with addition of nano-coating
- 3.) More amorphous-like behavior evident at low T
- 4.) Future Work: Filled Skutterudites



CoSb₃ Work Summary

**Used rather low purity starting materials
Even bulk CoSb₃ --- high resistivity**

**Wanted to see effect of thermal conductivity
Proof of Concept**

**Nano-coating lowered resistivity by 20%
Probably due to self doping**

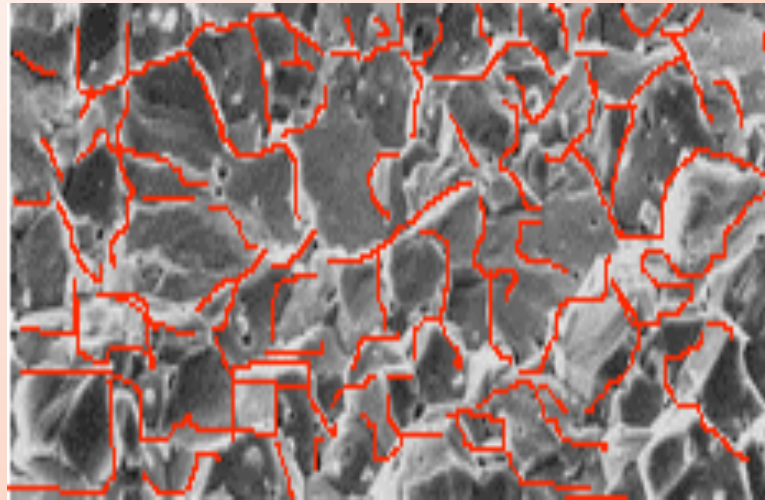
**Move to PbTe Coating Project
More control over the starting seed particles**



Nanocomposites made by Surface Modification of PbTe Micron Particles.



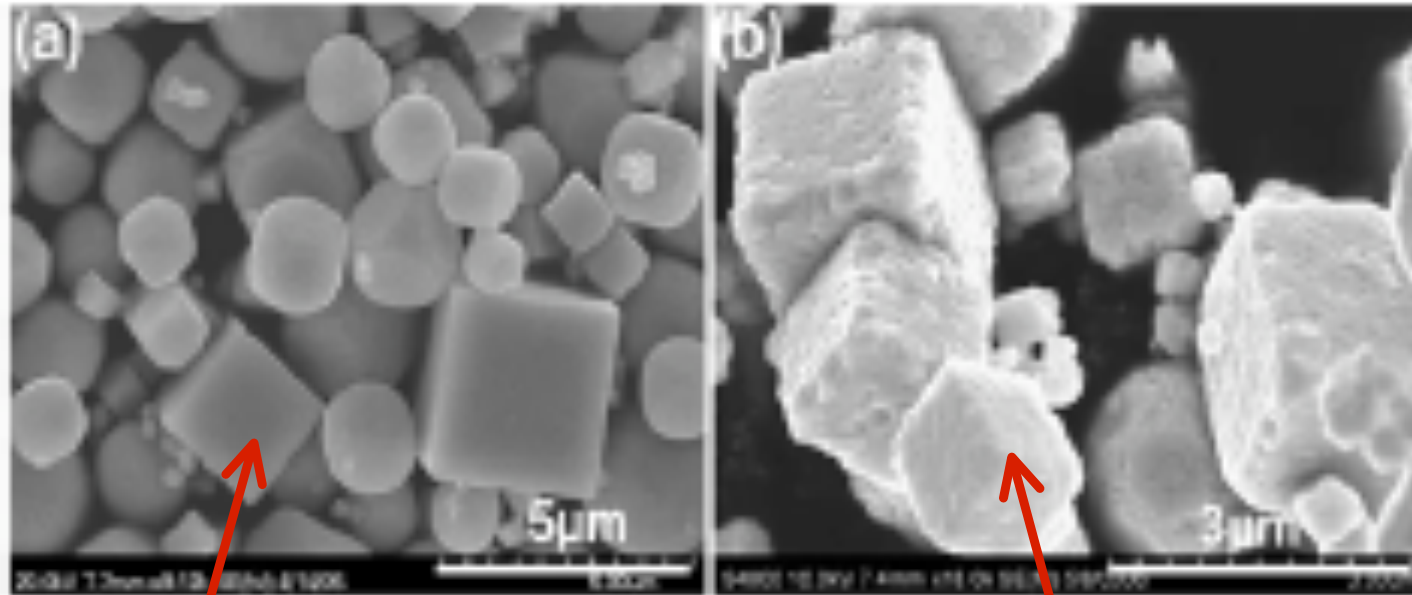
Nanolayer of PbSe



Approximately 500
layers/mm along one direction

1. Homogenous distribution of Nanostructures
2. Naturally prevent Nanostructures and Grain Growth.

Hydrothermal Nano-Coating Process on PbTe



PbTe: As grown via CVD

PbTe: after hydrothermal
Treatment with PbSnSe --
Notice thin coating

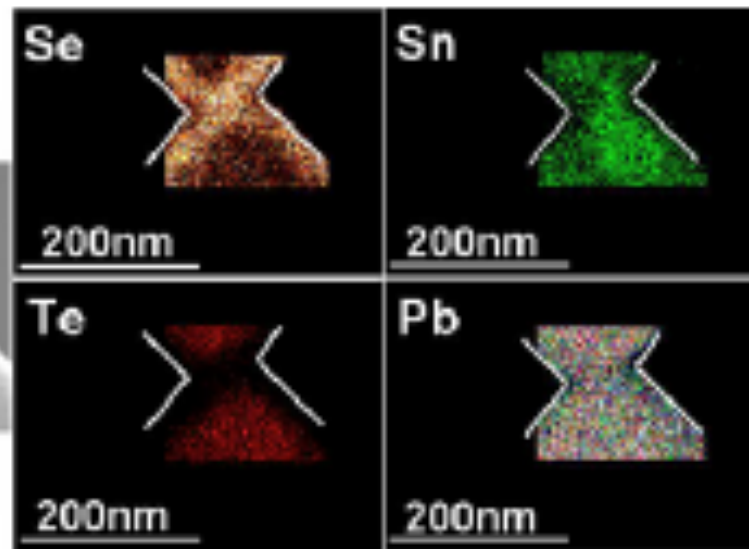
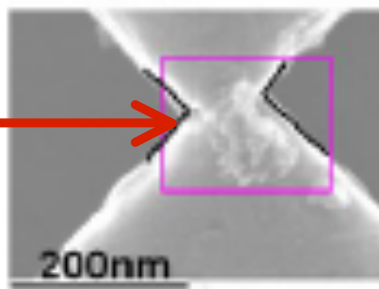
Hydrothermal Nano-Coating Process on PbSnTe

Start with PbSnTe Seed particle (several μm)
Hydrothermal Nano-Coating (PbSnSe)

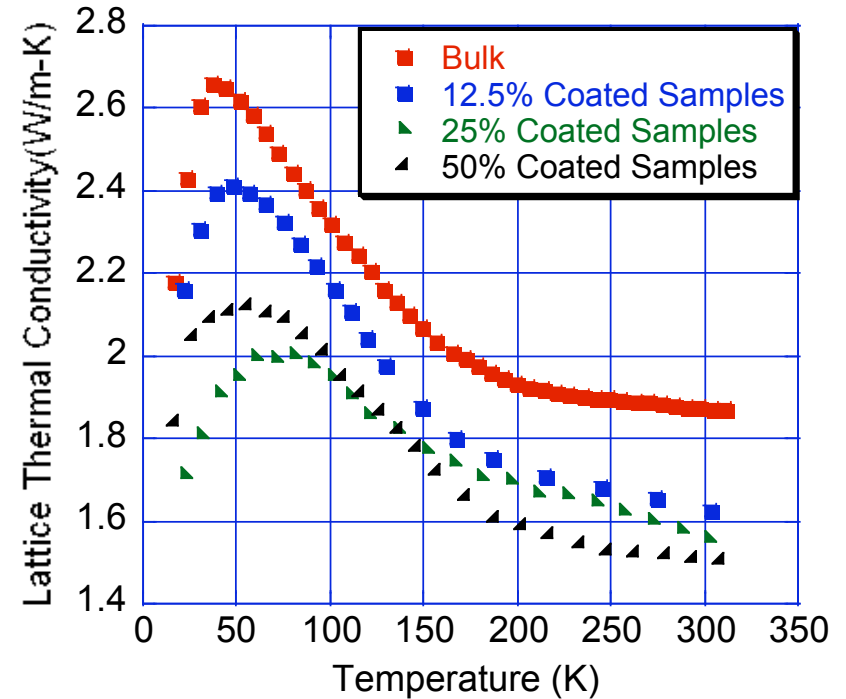
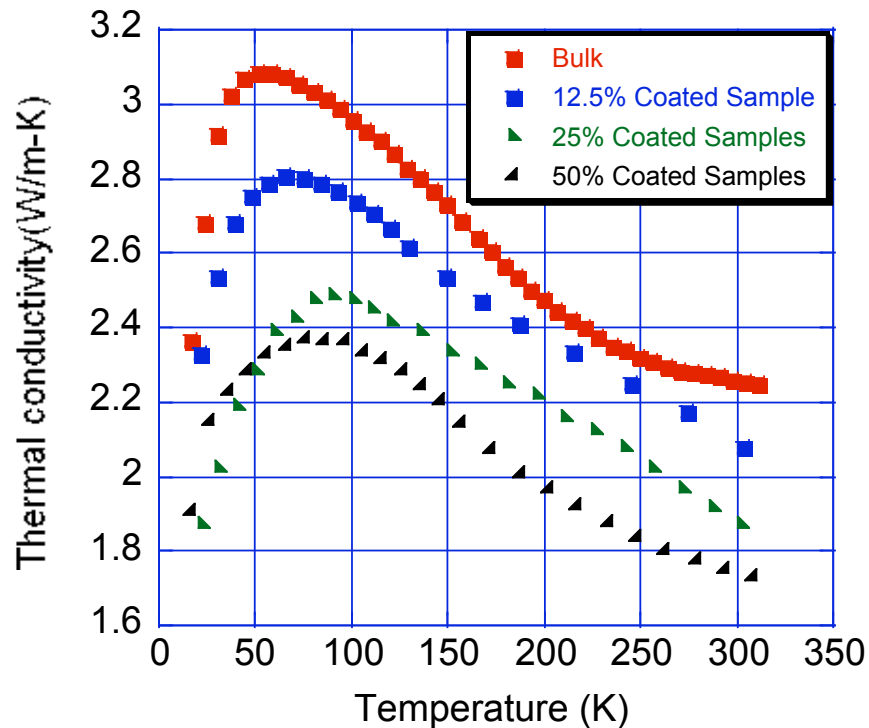
B. Zhang, *et.al.*, Appl. Phys. Lett.,
88, 022101(2006)

Elemental “Smart Map”

Focus
On this
area

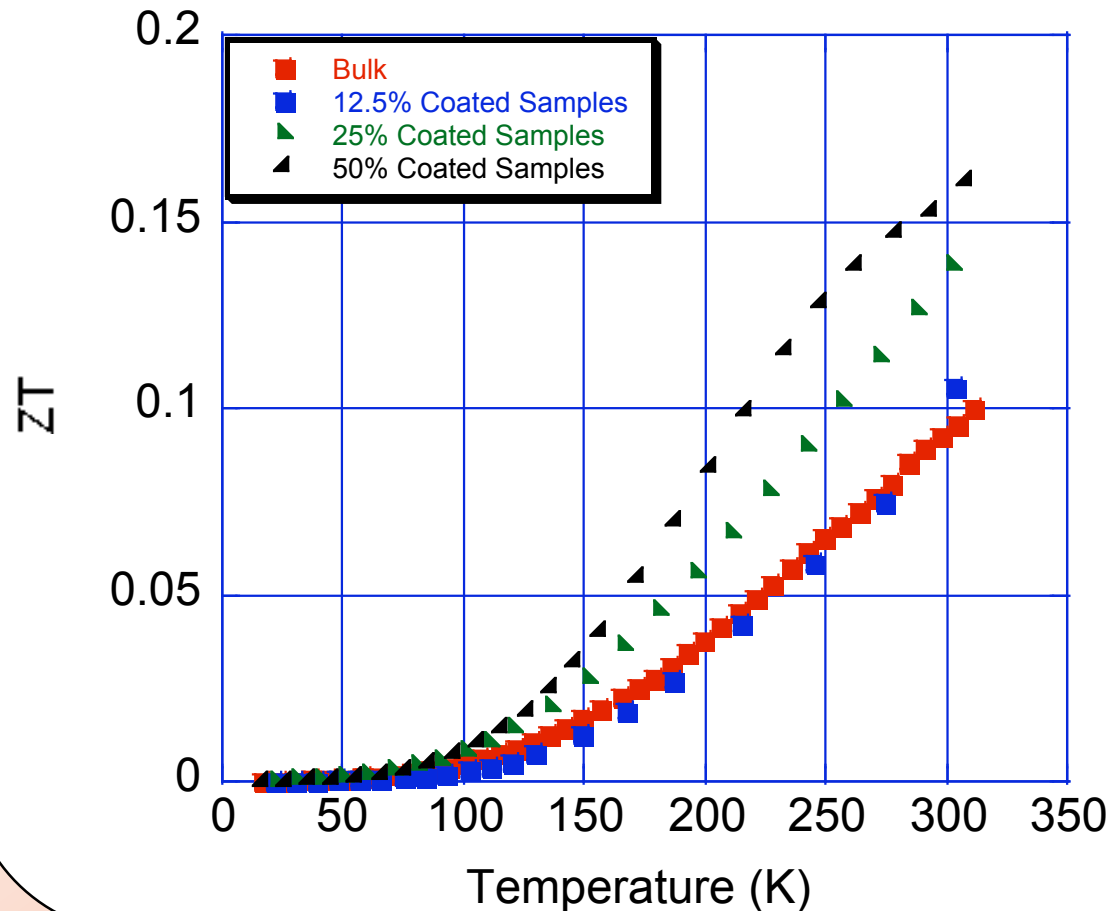


Hydrothermal Coated PbSnTe: Thermal Conductivity



κ_L systematically lowered in coated samples

Hydrothermal Coated PbSnTe: Figure of Merit



**ZT is enhanced in the coated samples
By about 50%**

**Note: Bulk means
uncoated seed
particles.**

Concluding Remarks

- Increased Demands for Alternative Energy Systems
- Significant Progress in TE's in Last 10 Years
- Thermoelectrics: (Shift to Waste Heat Recovery)
Efficiency & Stability is a Materials Issue.
- Thermoelectric Materials Research:
“Designer Materials” Approach
Complex Structures & Transport
Challenges in Theory, Synthesis & Characterization
- Many Opportunities in Nanocomposites or
Nanoscaled Bulk TE Materials (Several Active Groups)
- More Theoretical Modeling & Insight Needed
- Materials Research is the KEY to Significant Advances.



Thermoelectric Power Generation for Automotives

- Current TE Materials are Viable ($\eta \approx 7\text{-}8\%$ efficiency)
- Need a High ΔT ($\approx 500^\circ\text{C}$)
- ≈ 300 watt systems are being produced
- Likely Market (Heavy Duty Trucks - Tractors etc.)
- Desired 1 KW System

- Will Need Better Thermal Management Design
(eg. BSST - see later talks)
- Need Higher Efficiency Bulk TE Materials
($ZT \approx 2\text{-}3$, $\eta \approx 15\text{-}20\%$ and $\$/\text{Watt}$ in right range)
- “Nano-Engineered” Bulk TE Materials
Likely Candidates.



Acknowledgements:

Dept. of Energy: DOE EPSCoR Implementation Grant
(DOE #: DE: FG02-04ER-46139)

Office of Naval Research (ONR DEPSCoR)
(ONR Grant #N00014-0310787)

SC EPSCoR & Clemson University

Thank You !!



*Basic Energy
Sciences
DOE EPSCoR*



*South Carolina
EPSCoR / IDeA
Program*



*Office of Naval
Research*



MRS Fall Meeting
Boston, MA
Thermoelectric Power Generation
Symposium U

November 25th - 30th, 2007
Over 100 Oral & Poster Presentations

Tim Hogan, Michigan St.
Jihui Yang, GM R&D
Terry M. Tritt, Clemson University
Ryoji Funahashi, AIST, Japan





Tritt Research Group: Summer 2006



EPSCoR
DEPARTMENT of ENERGY



CLEMSON
UNIVERSITY





EPSCoR
DEPARTMENT of ENERGY



CLEMSON
UNIVERSITY

