DOE "Center of Excellence" for Solid State Thermal Energy Conversion Materials

DOE-EPSCoR Implementation Program
Phase I: 2004 - 2007 -- Phase II: 2007 - 2010

Prof. Terry M. Tritt (PI)

Clemson University

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

South Carolina EPSCoR/IDeA Program

Experimental Program to Stimulate Competitive Research & Institutional Development Awards

Acknowledge Collaborators:

Clemson University Contributors:

Jian He, Joe Kolis, A. Rao, Fivos Drymiotis, H. J. Kang & M. S. Daw: (Faculty)

B. Zhang, N. Gothard, P. Alboni, H. Zhang, Su Zhe, D. Thompson, Tim Holgate Sloan Lindsey, & Jennifer Hubbard (Grad & Undergrad Students)

V. Ponns, X. Gao & Xiaohua Ji: (Research Associates)

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David Mandrus & Brian Sales (Oak Ridge National Lab.)
Veerle Keppens (Univ. of Tenn.)
Nathan Lowhorn, Winnie Wong-Ng & Co-Workers (NIST)

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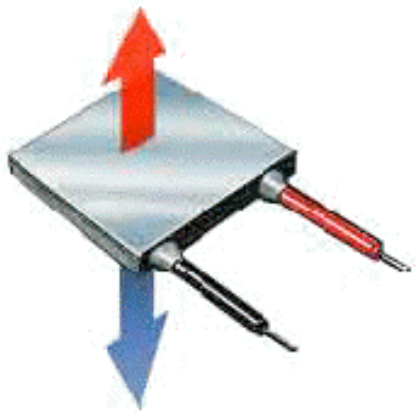
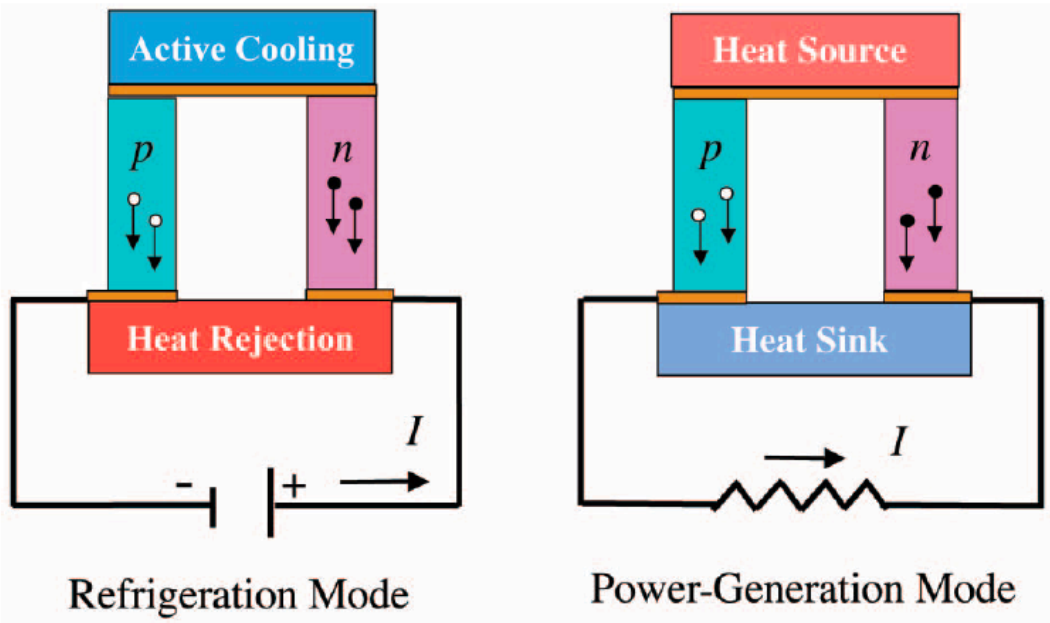
Outline & Introduction:

* Introduction to Thermoelectrics (TE's)
  - Seebeck and Peltier Effects, Definition of ZT!
  - Applications & Uses of TE Devices
  - Motivation for Low Dimensional TE Systems
  - Highlights of TE Nanocomposites

TE Module





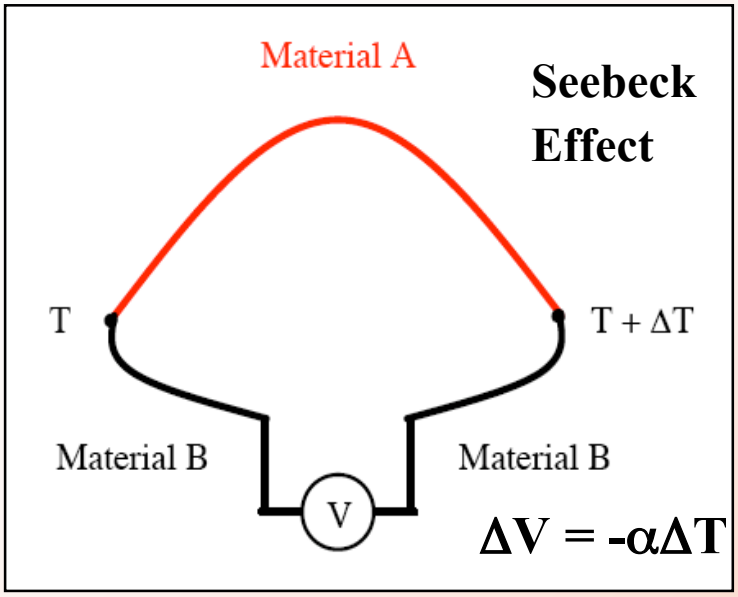
TE Couple (n & p)

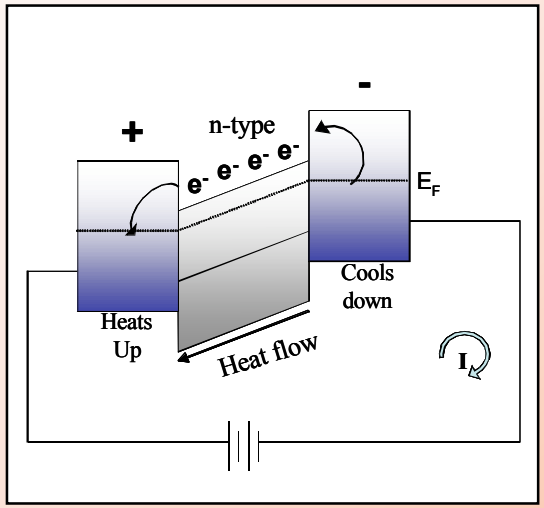
Apply ΔV(I) ➠ ΔT

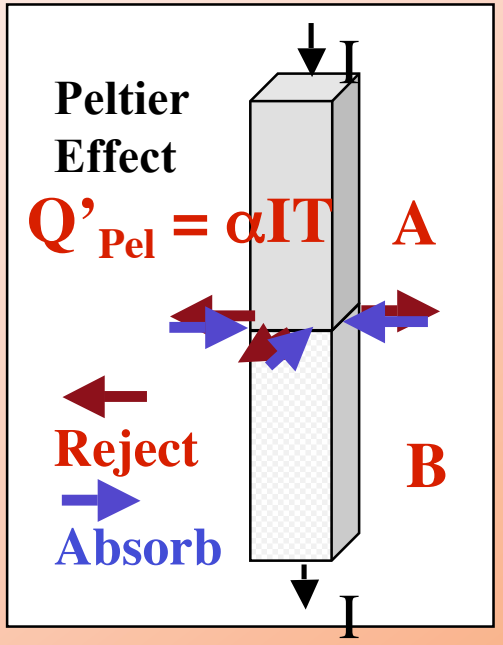
Apply ΔT ➠ I

Heat is carried by Charge carriers!

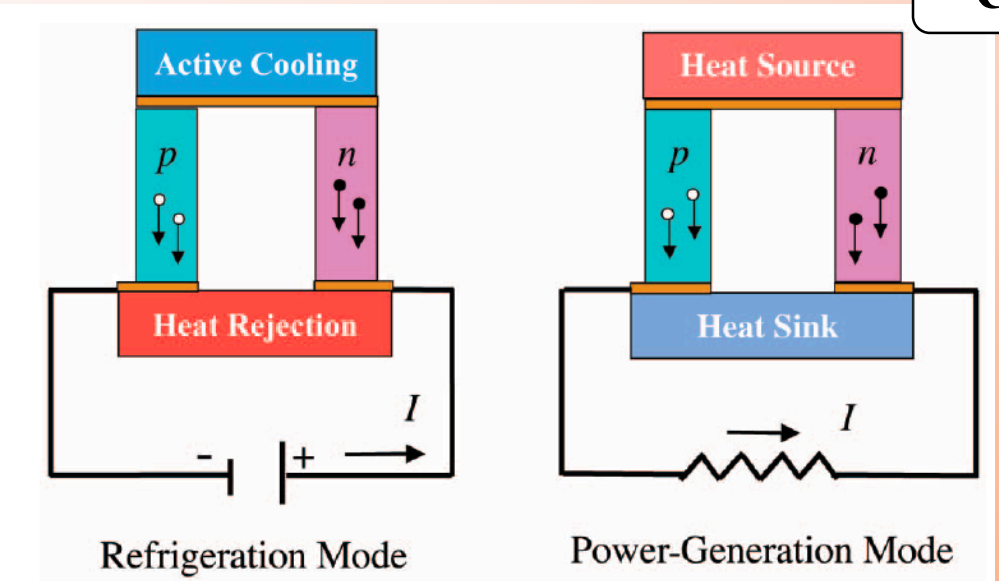
Overview of Thermoelectric Phenomena

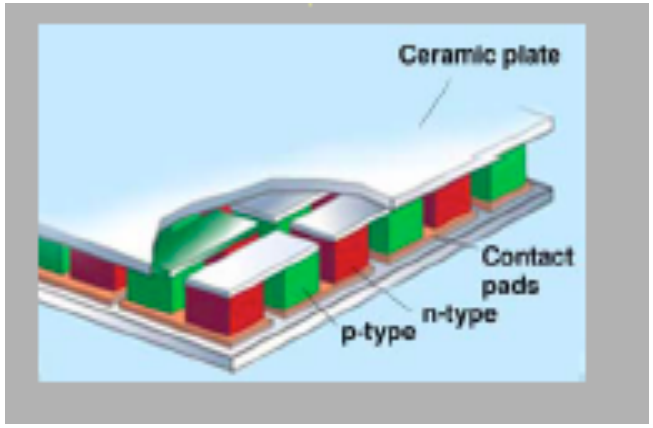






$$Q'_{PEL} = \alpha IT$$





Electrically in Series
Thermally in Parallel

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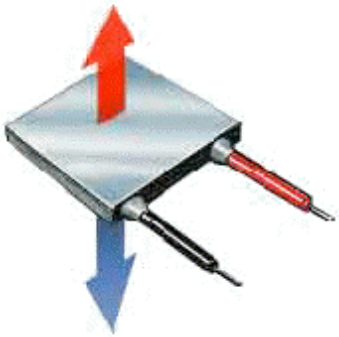
Thermal to Electricity Energy Conversion (TE)



TE Radio Lantern

TE Module Converter

Thermal Energy (Waste Heat)

Electrical Energy

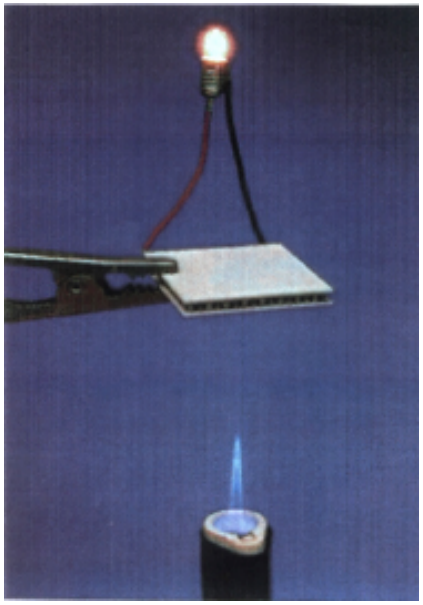
Conceptually Simple Devices

TE Technology

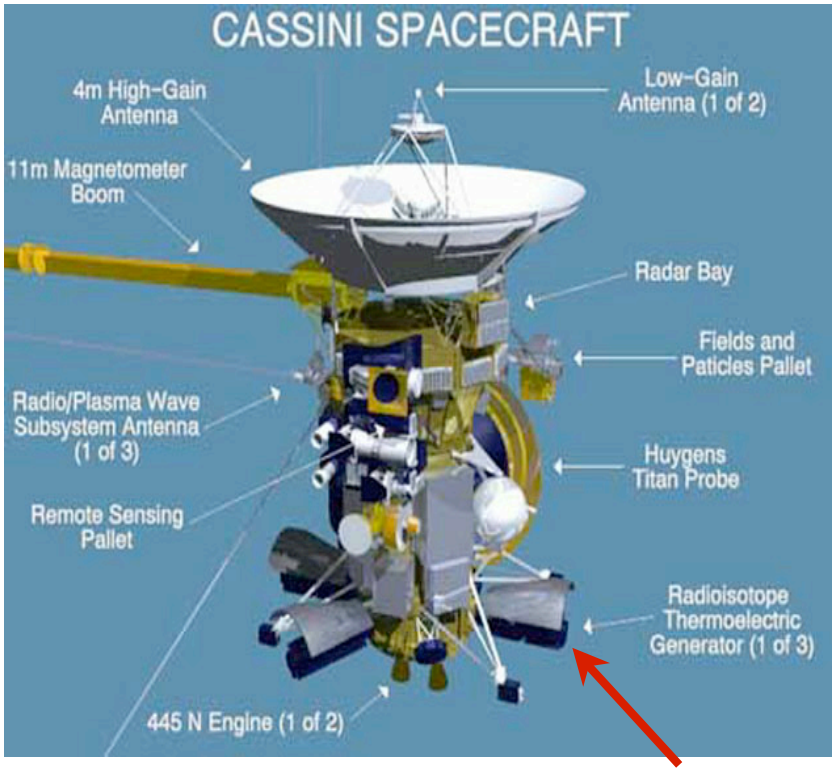
Converts Waste Heat to Electrical Energy

No Moving Parts

Solid State Technology



Radioisotope Thermoelectric Generator (RTG)



Cassini: Saturn's Rings

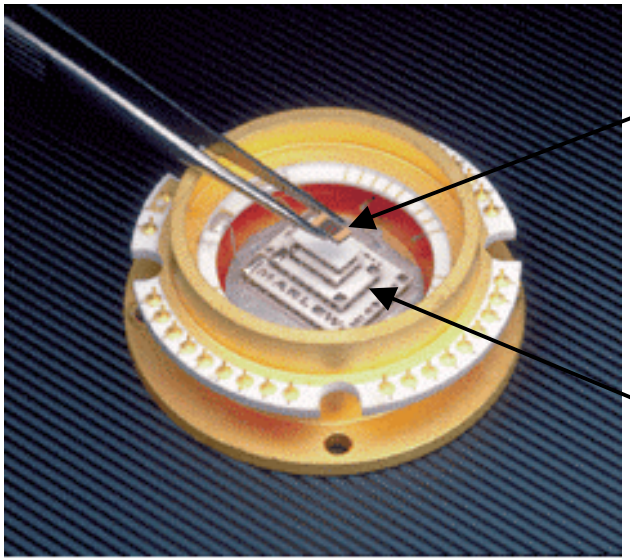
RTG's (1 of 3)
≈ 300-400 Watts each

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

Deep Space Probes:
Cassini (≈ 1997)
See NASA Website
Pictures of Saturn's Rings
http://saturn.jpl.nasa.gov/multimedia/

Opto-electronic TE Applications

Thermoelectrically cooled IR detectors beat the heat
Andrew W. Allen (Laser Focus World March 1997)

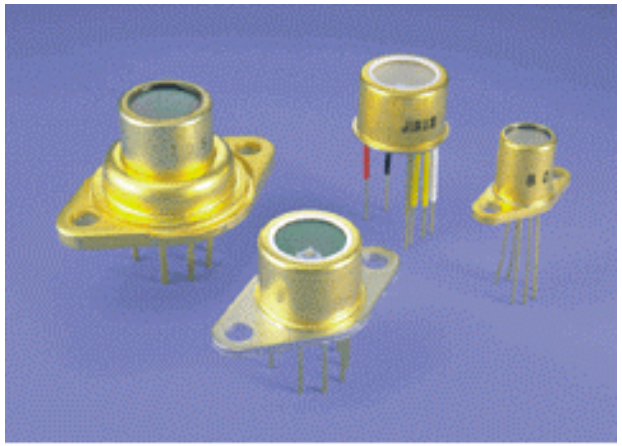


IR Detector Chip

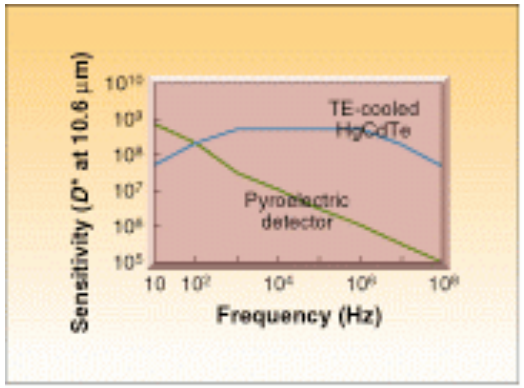
Enhanced Performance & Sensitivity for Thermal Imaging -- Small-Self Contained Packaging Unit

TE Module

Higher Sensitivity

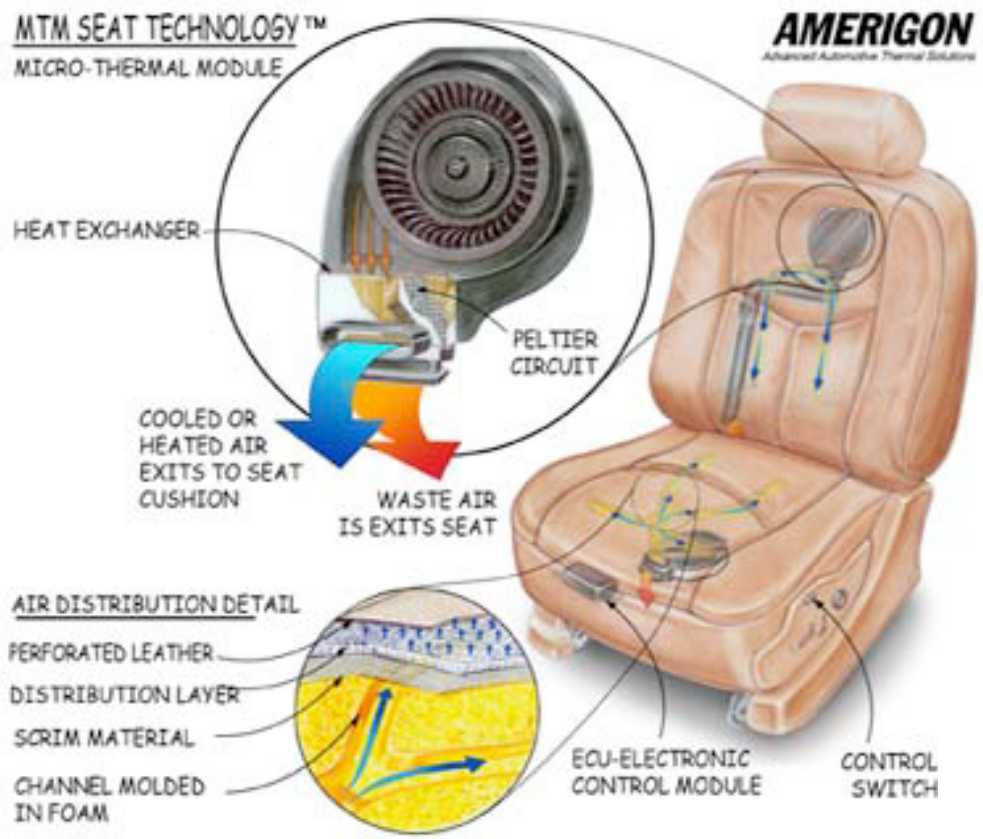


Packaged Solid State Detection and Cooling



3-DH-2 97 Fig. 3

Automotive: The "Amerigon Climate Controlled Seat"

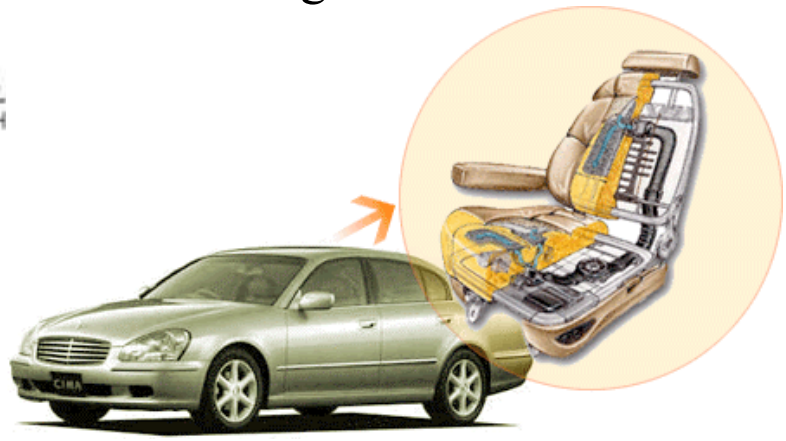


Climate Controlled Seat:
(cooled or warmed)

Uses new packaging
to improve efficiency.
The "BSST cycle"

In many luxury cars:
(≈ 1 million units in 2005)
(8 million total so far)

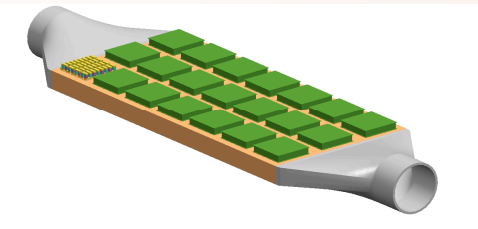
Huge New market!



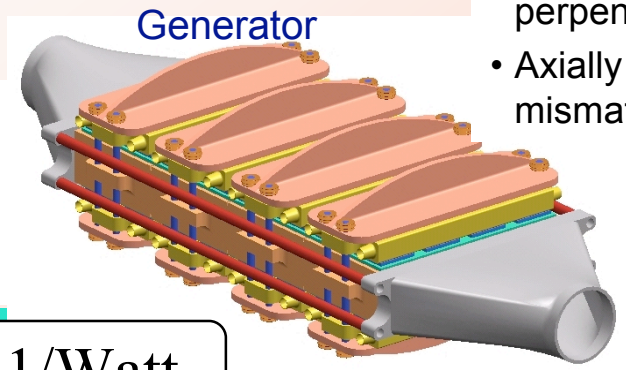
Climate Controlled Seat (CCS)
www.Amerigon.com

Exhaust Generator Design

Interior View
(module mounting)



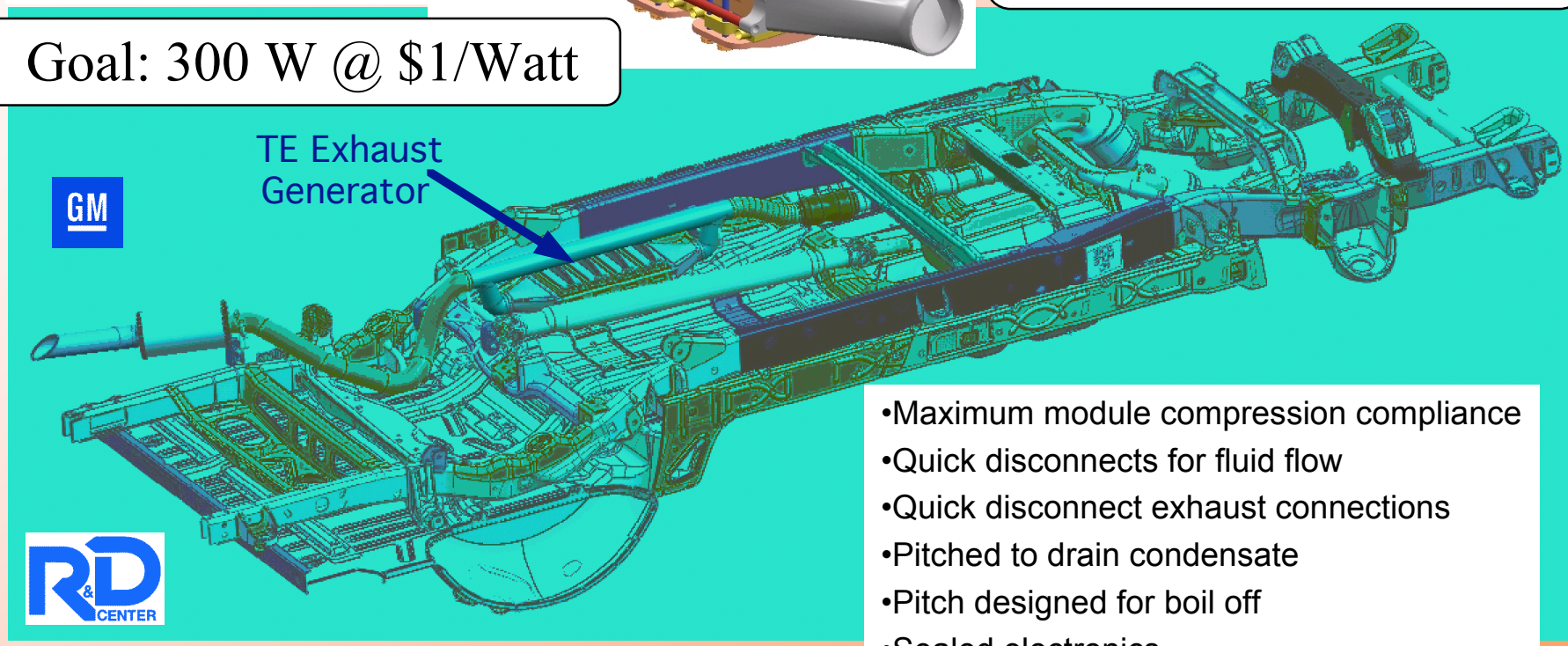
TE Exhaust
Generator



- Located where current muffler is placed; new muffler will be located behind the axle perpendicular to vehicle axis
- Axially compliant for thermal expansion mismatch

Courtesy of Dr. J. Yang
General Motors R & D

Goal: 300 W @ $1/Watt



- Maximum module compression compliance
- Quick disconnects for fluid flow
- Quick disconnect exhaust connections
- Pitched to drain condensate
- Pitch designed for boil off
- Sealed electronics

The Thermoelectric Figure of Merit (ZT)

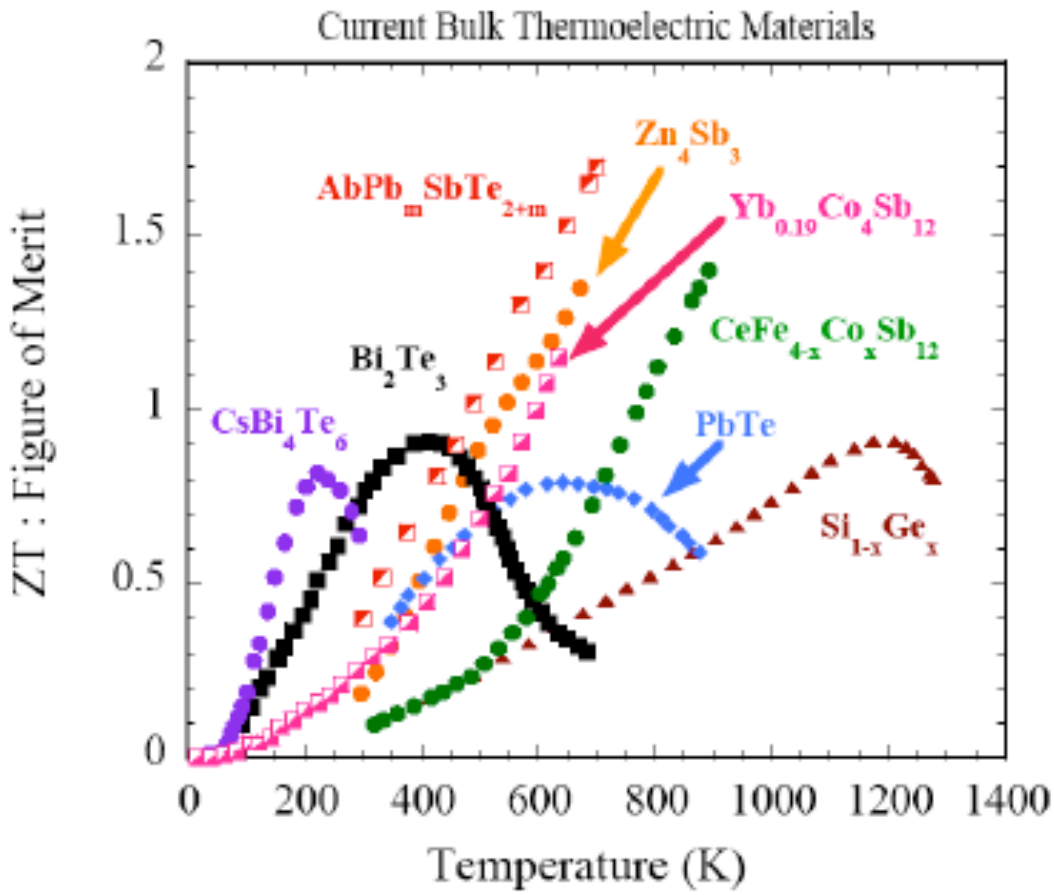
Efficiency ($\eta \approx ZT$)

Materials Parameters: Characterization Over a Broad Range of Temperature (to 1000˚C) !!

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

α = Thermopower
σ = Electrical Conductivity
ρ = Electrical Resistivity
κ_E = Electronic Thermal Conductivity
κ_L = Phonon Thermal Conductivity

ZT of Best TE Materials (ZT ≈ 1):



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

State of the Art
Device TE Materials
(ZT ≈ 1)

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

Bi_2Te_3 ➠ Cooling

$Si_{1-X}Ge_X$ & PbTe ➠
Power Generation

Future Material Needs
ZT ≈ 2-3!
➠ **η ≈ 15 - 20%**

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MRS Bulletin: Thermoelectrics, March 2006

Guest Editors: Terry M. Tritt and M. A. Subramanian

Introduction & Overview
(T. M. Tritt & M. Subramanian)

Bulk TE Materials
(G. S. Nolas, S. J. Poon & M. Kanatzidis)

Oxide TE's
(K. Kuomoto, I. Terasaki & R. Funahashi)

Nanostructured TE Materials
(A. M. Rao, X. Ji &T. M. Tritt)

Applications of TE Materials
(J. Yang & T. Caillat)

Thin Film TE's
(H. Bottner, G. Chen & R. Venkatasubramania)

MRS Bulletin, Volume 31, No 3, March 2006

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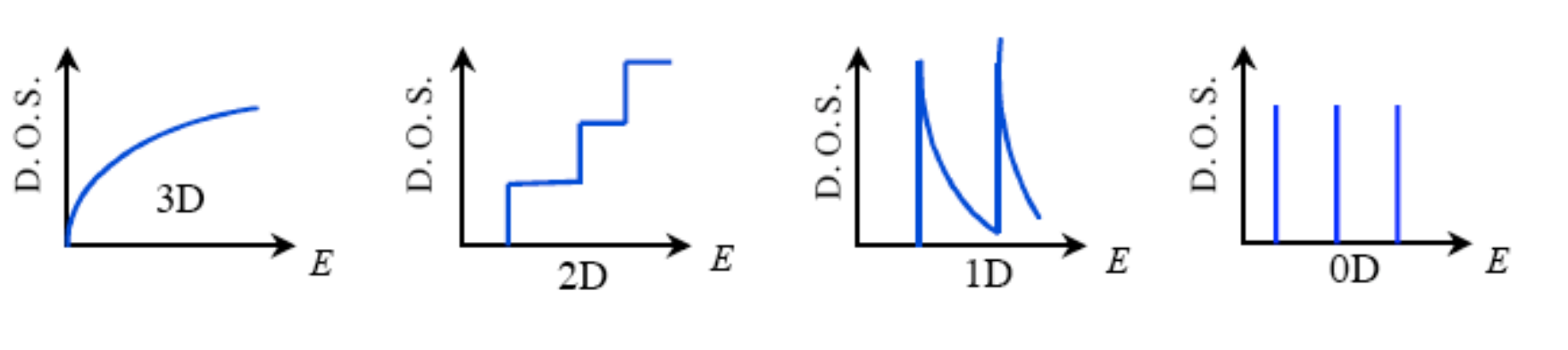
Role of Lower Dimensions in Thermoelectrics:

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.

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

Low D yields large dn(E)/dE

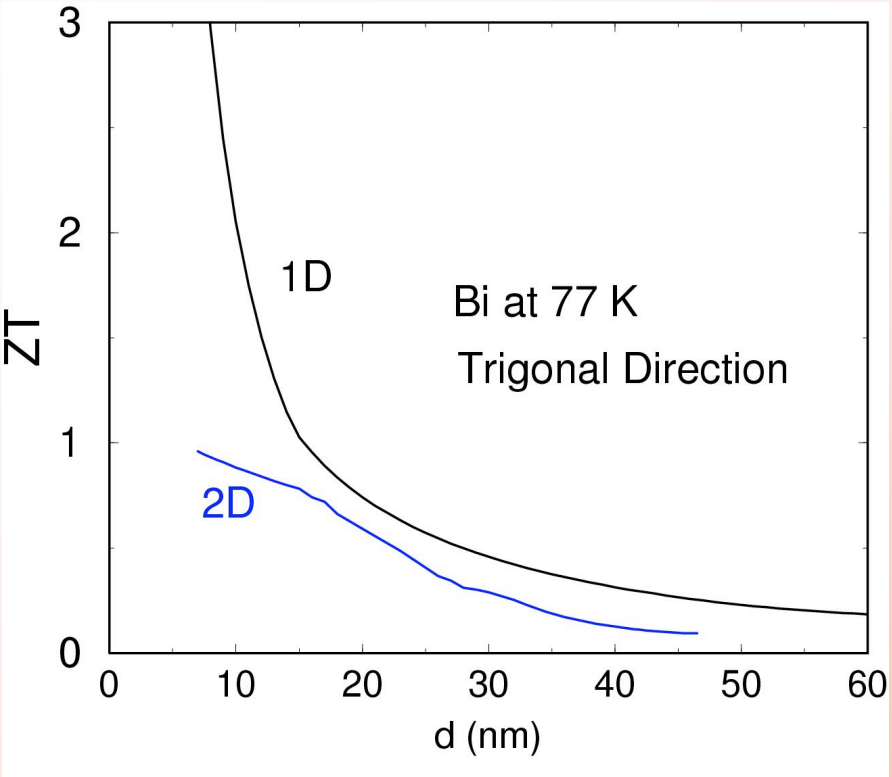
$$ZT \approx \alpha^2 \sigma \approx \alpha^2 n$$

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

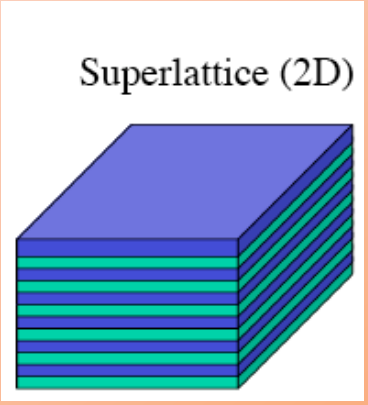
$$\alpha = \frac{\pi^2 k_B^2 T}{3e}\left[\frac{\partial \ln \sigma}{\partial E}\right]_{E_F}$$

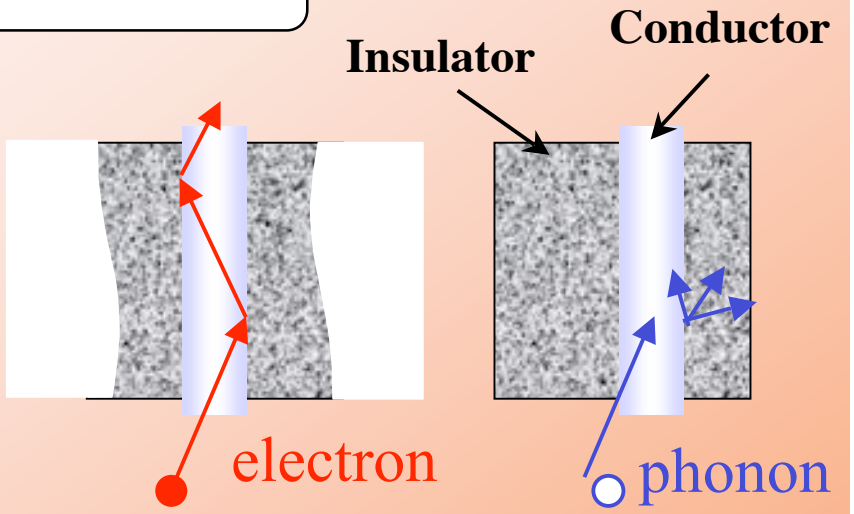
M. Dresselhaus et al, *APL* **63** 3230 (1993)

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

High ZT Observed in Low Dim Systems !!

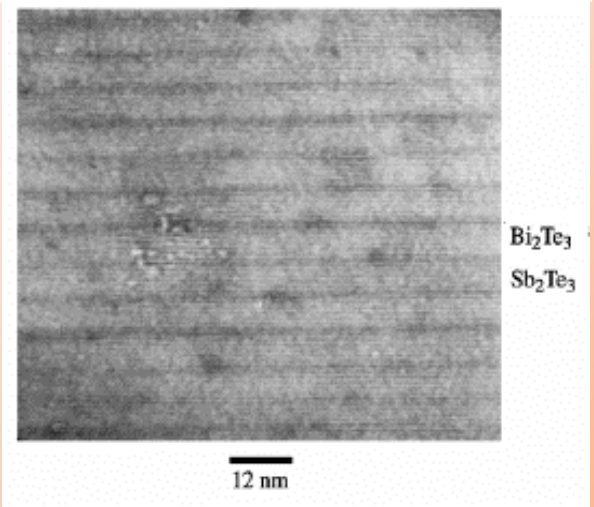
Bi_2Te_3 / Sb_2Te_3	Nano	Bulk
α^2/ρ (μW/cm-K^2)	40	51
κ (W-m^{-1}K^{-1})	0.6	1.45
ZT (T =300K)	2.4	1.0

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

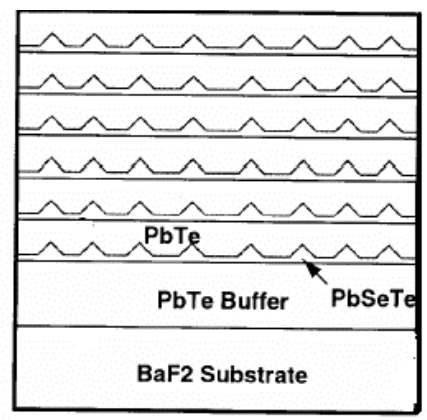
PbTe/PbSeTe	Nano	Bulk
α^2/ρ (μW/cm-K^2)	32	28
κ (W-m^{-1}K^{-1})	0.6	2.5
ZT (T =300K)	1.6	0.3

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

Bi_2Te_3/Sb_2Te_3 Superlattice



PbTe/PbSeTe Quantum Dots



$PbSe_xTe_{1-x}$ quantum dots in PbTe layers

Relative Importance of α^2/ρ and κ

Thermal Conductivity Reduction

Bi_2Te_3 / Sb_2Te_3	Nano	Bulk
α^2/ρ (μW/cm-K^2)	40	51
κ (W-m^{-1}K^{-1})	**0.6**	**1.45**
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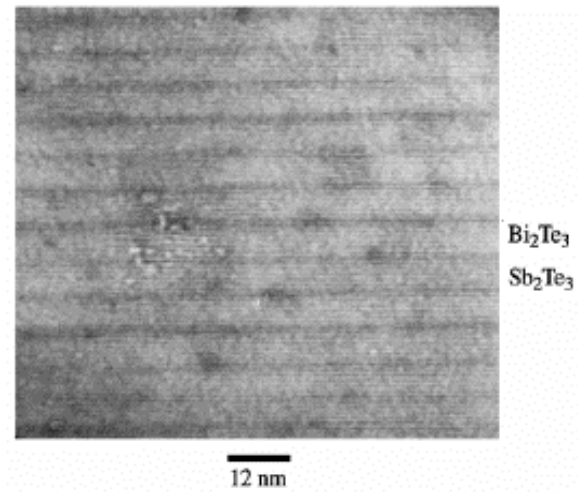
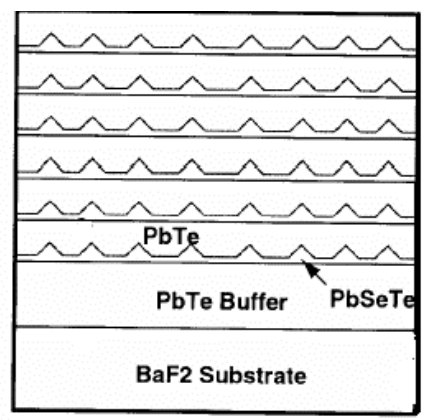


PbTe/PbSeTe Quantum Dots



$PbSe_xTe_{1-x}$ quantum dots in PbTe layers

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Issue:
MBE Growth of SL and QDots expensive!

Merge Attributes of Low Dimensional TE Systems
Interface Scattering for Phonons
Quantum effects: Seebeck

Bulk TE Materials (PGEC)
Higher Efficiency
Lower Cost of Production
Control & Reproducibility
of TE Properties

Highlights of TE Research @ Clemson!

TE Nanomaterials Growth,
TE Nanocomposites &
Grain Boundary Engineering

Not Included in this talk is our work on:
Zintl Phase Materials, Double Filled Skutterudites,
Half Heusler Alloys, Complex Antimonides,
Oxide TE Materials, LAST materials
& Other Bulk TE Materials

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Sketch map of solution-chemical method

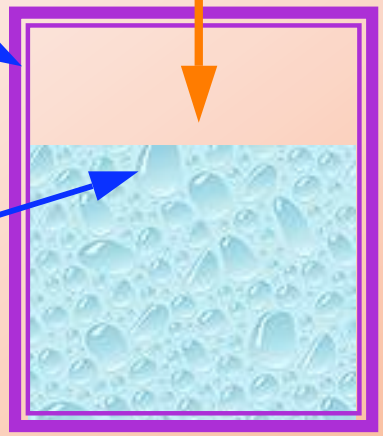
Co (Bi, lead)-salts
Sb salts / Te powder
or Te-salts

+

reductant
(Na/K)OH,
($NaBH_4$)
and/or alkali

Autoclave

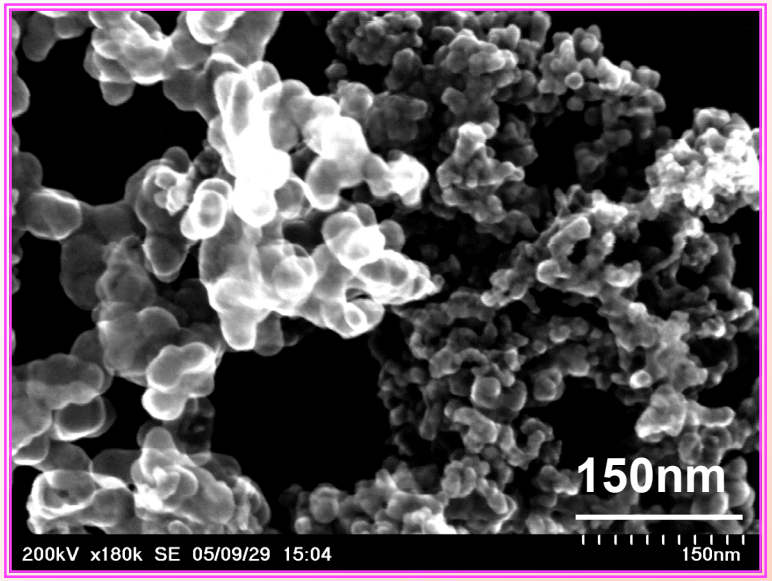
Teflon-lined Autoclave Or a beaker

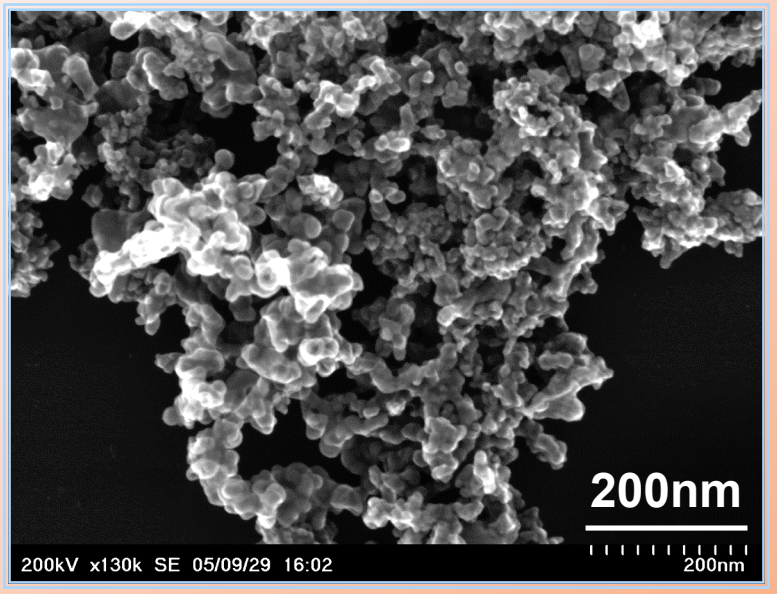


Organic solvents or water

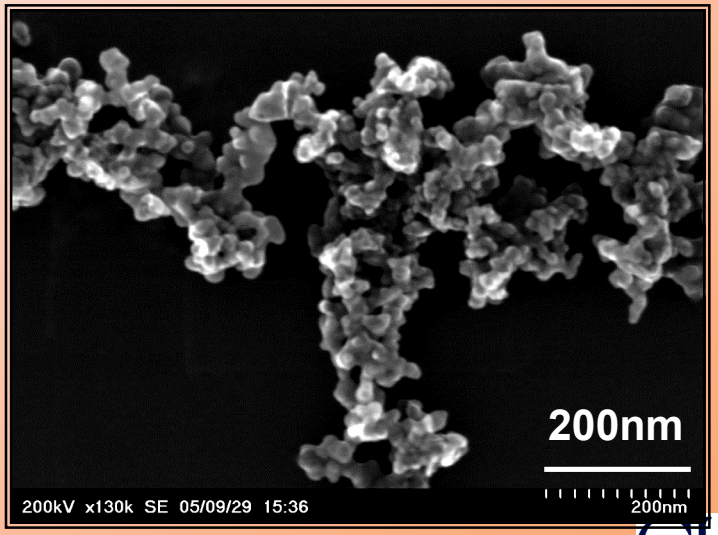
- **Sealed (in closed system) or opened**
- **heated to higher/lower than 100°C**
- **10 ~ 50 hr reaction**
- **cooled down naturally**
- **powders washed & dried**

Hydrothermal Synthesis of Nanomaterials: Bi_2Te_3 & $CoSb_3$





Skutterudite **($CoSb_3$)**
Nano Structures
20-40 nm



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Hot Pressing Capabilities

Thermal Technology
Hot Isostaic Press
≈ 7 feet tall

Capabilities
2000˚C & 10 tons

Highly Densified Samples

High Quality
Polycrystalline Materials

> 95% Theoretical
Density

Funded by DOE EPSCoR

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EPSCoR DEPARTMENT of ENERGY
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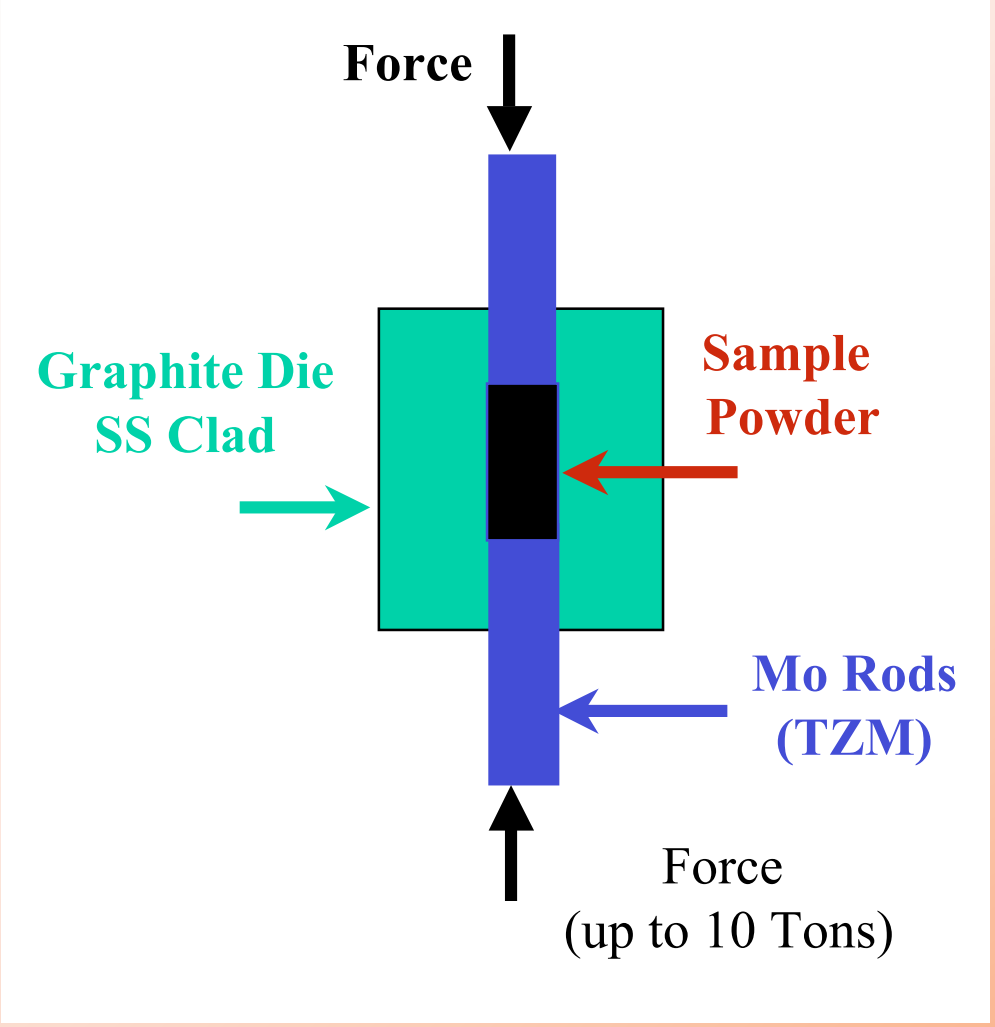
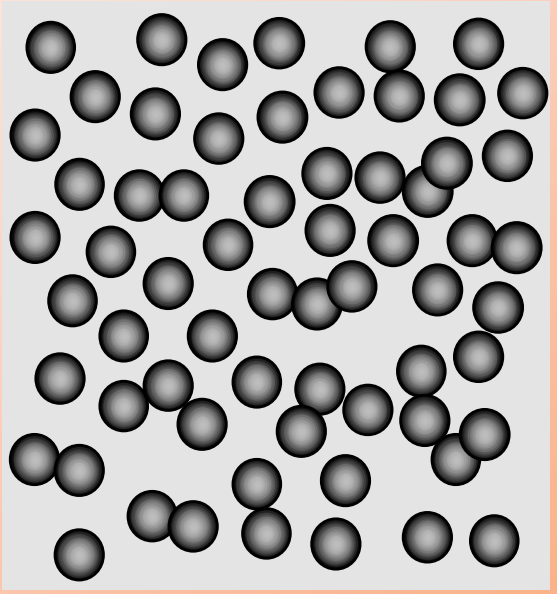
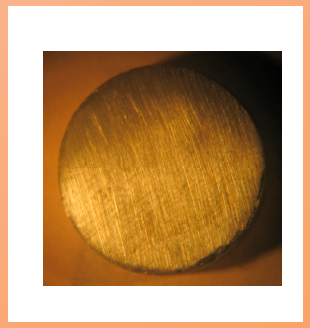
Hot Isostatic Press
10 Ton, 2000˚C



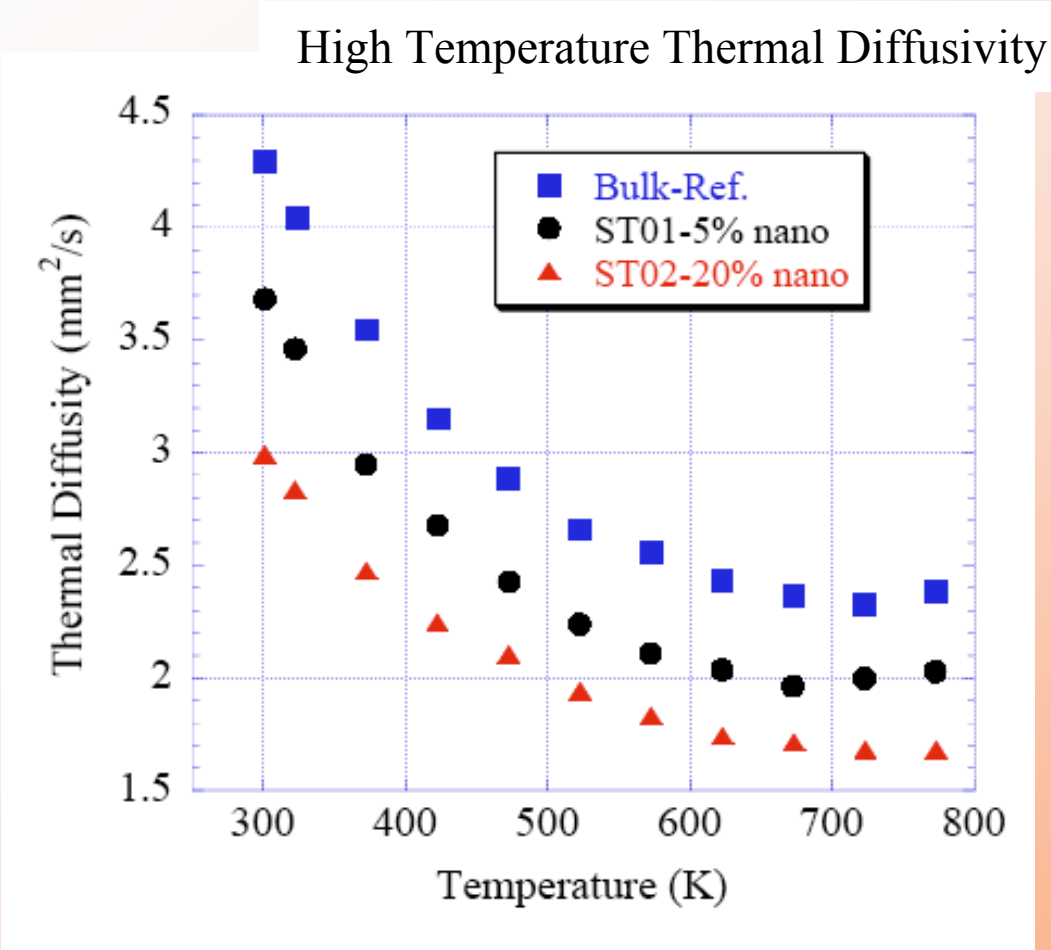
Composite
Bulk & Nano



1/2” diameter
≈ 3/8” Long Sample



Hydrothermal Nano-Coating Process for $CoSb_3$ Effect on Thermal Properties



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

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High Temp Thermal Conductivity:

High Temperature DSC
Measure C_P To 1500˚C
Thermal Stability & Heat Capacity

NETZSCH LFA 457
Thermal Diffusivity (*d*)
Or Conductivity (κ)
Temp Range: RT to 1100˚C

$$\kappa = d\rho_D C_V$$

Funded by DOE EPSCoR

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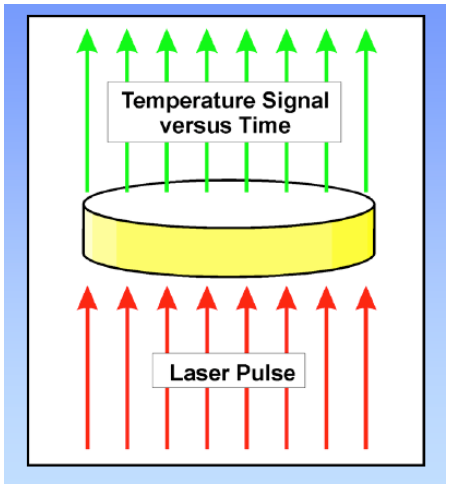
Schematic of the flash method

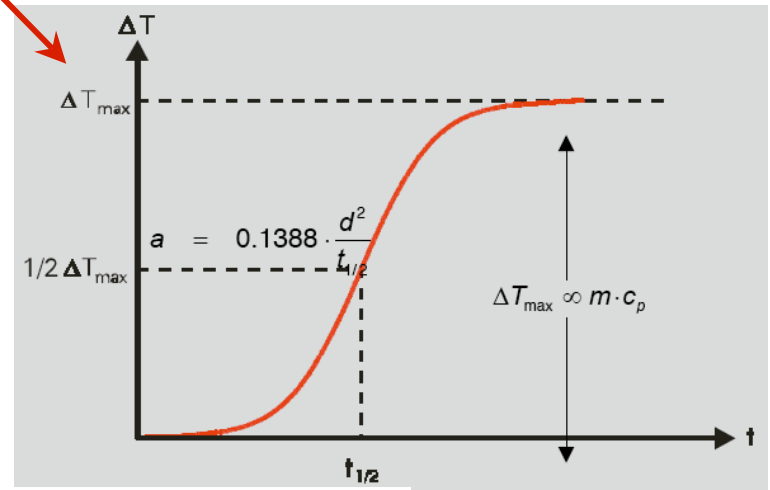
$$d = 0.1388\left(\frac{L^2}{t_{1/2}}\right)$$

$t_{1/2}$ = Rise half time
L = sample thickness

$$\kappa = d\rho_D C_V$$

κ = thermal conductivity
d = thermal diffusivity
ρ_D = density
C_V = Heat Capacity





J. W. Parker et.al., J. Appl. Phys., 32, 1679 (1961)

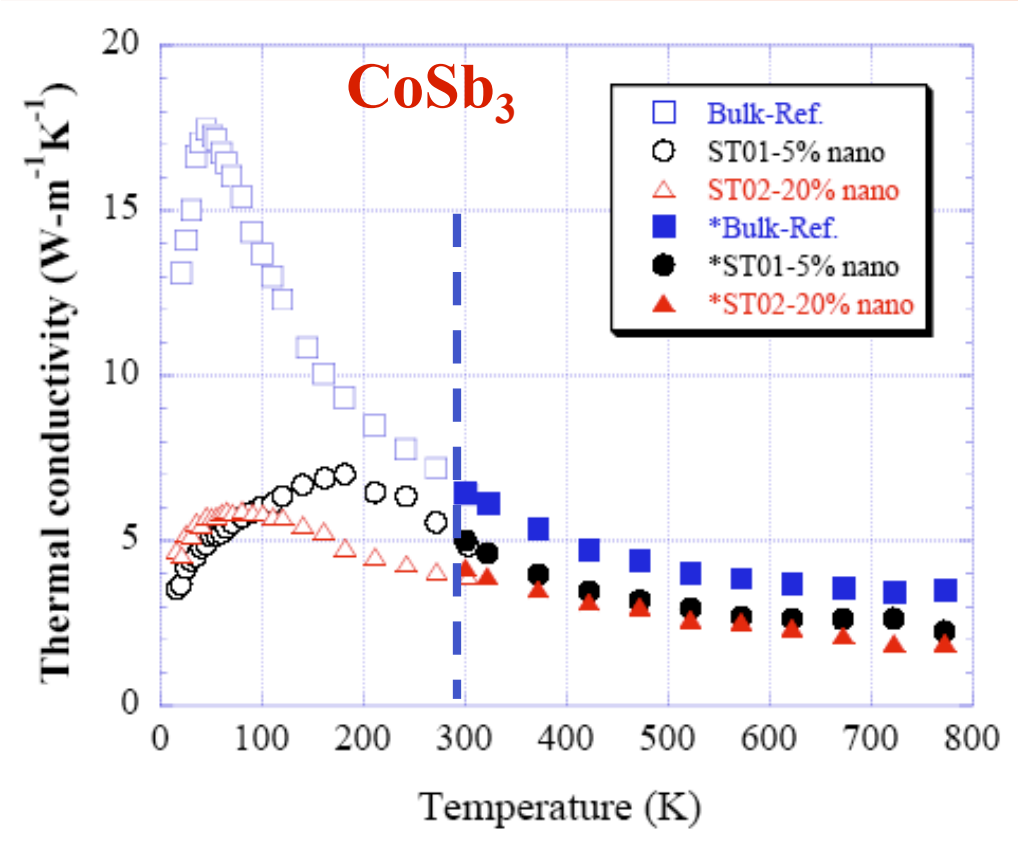
Nano-Coating Process for $CoSb_3$: Effect on Thermal Properties

High & Low Temperature Thermal Conductivity

Low T - Steady State Method (T < 300K)

High T - Laser Flash Method (T > 300K)

See X. Ji. *et.al* , Rap. Res.. Lett., **1**, no.**6**, pp.229-231, (2007)



Major Points:

1.) Very good match high & low temp. measurements!!

2.) Thermal conductivity reduces with addition of nano-coating

3.) More amorphous-like behavior evident at low T

4.) Future Work:
<u>Filled Skutterudites</u>

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Success: Able to grow nanostructures!
Thermal conductivity is reduced!

Issue: When mixing $CoSb_3$ nanoparticles (also PbTe)

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

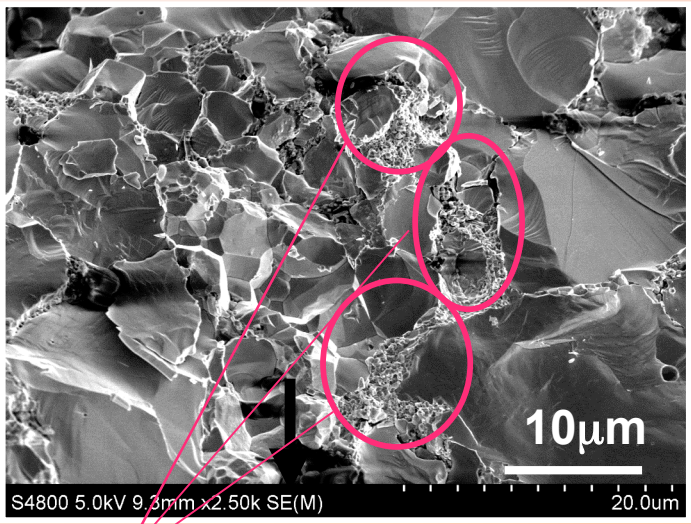
Lower Thermal Conductivity but Typically High Resistivity.

Nanocomposites fabricated by Hydrothermal /solvothermal nano-planting/coating

- Nanoparticles are easy to form aggregates.
- In TE nanocomposites, inhomogeneity may de-base the TE performance.

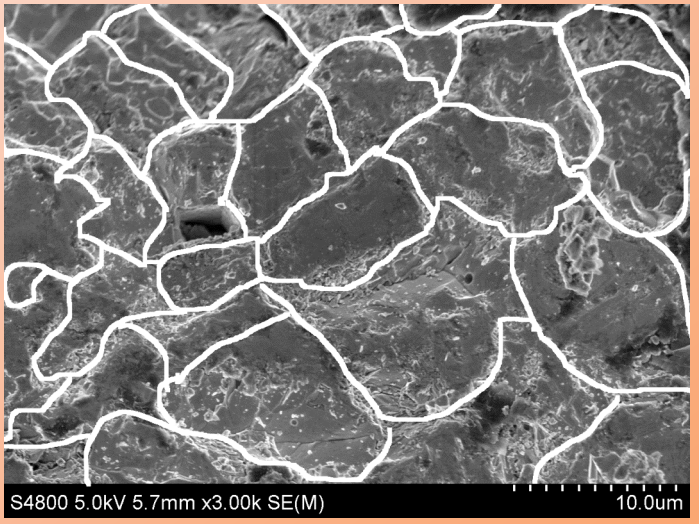
Hot press → **Relatively-homogeneous nanocomposite**

Mechanical mixing



Nanoparticle-clusters

Solvothermal nano-coating



Better homogenous distribution of Nanostructures

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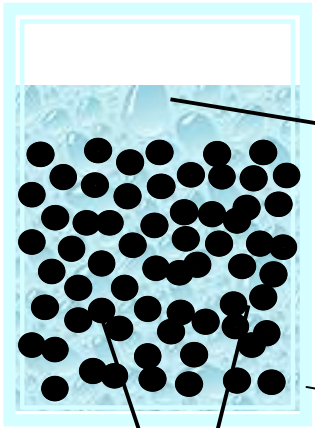
An alkali metal hydrothermal treatment technique



Various alkali metal (Na, K) compounds solution

Hydrothermally treat

Remove powder, wash & dry

Hot press

pellet

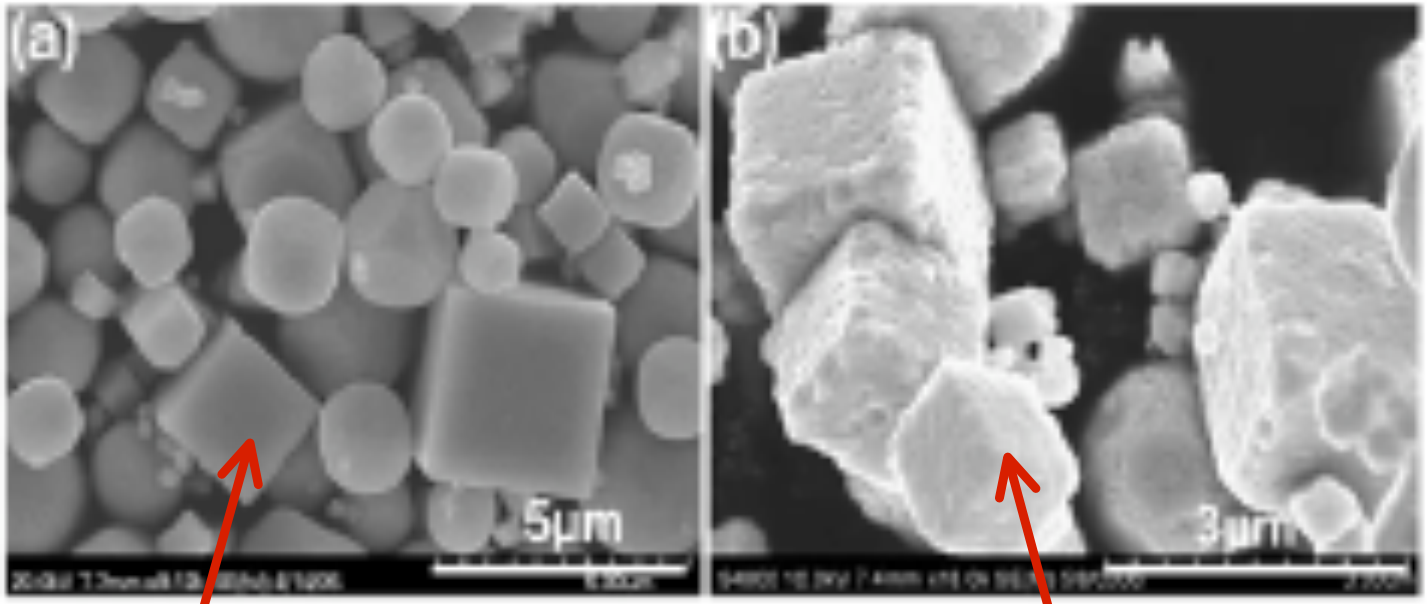
autoclave

Bulk TE raw powder

150°C for 36 hr

alkali metal hydrothermal treatment process,
an admixture of 6 mmol NaOH (KOH),
2 mmol NaF (KF), 3 mmol $NaBH_4$ (KBH_4)
35 ml distilled water,
and ~ 2.5 g $Pb_{0.75}Sn_{0.25}Te$
bulk reference powder were loaded into
a 45 ml Teflon-lined autoclave

Hydrothermal Nano-Coating Process on PbTe



PbTe: As grown via CVD

PbTe: after hydrothermal Treatment with (Pb-Sn)Se -- Notice thin coating

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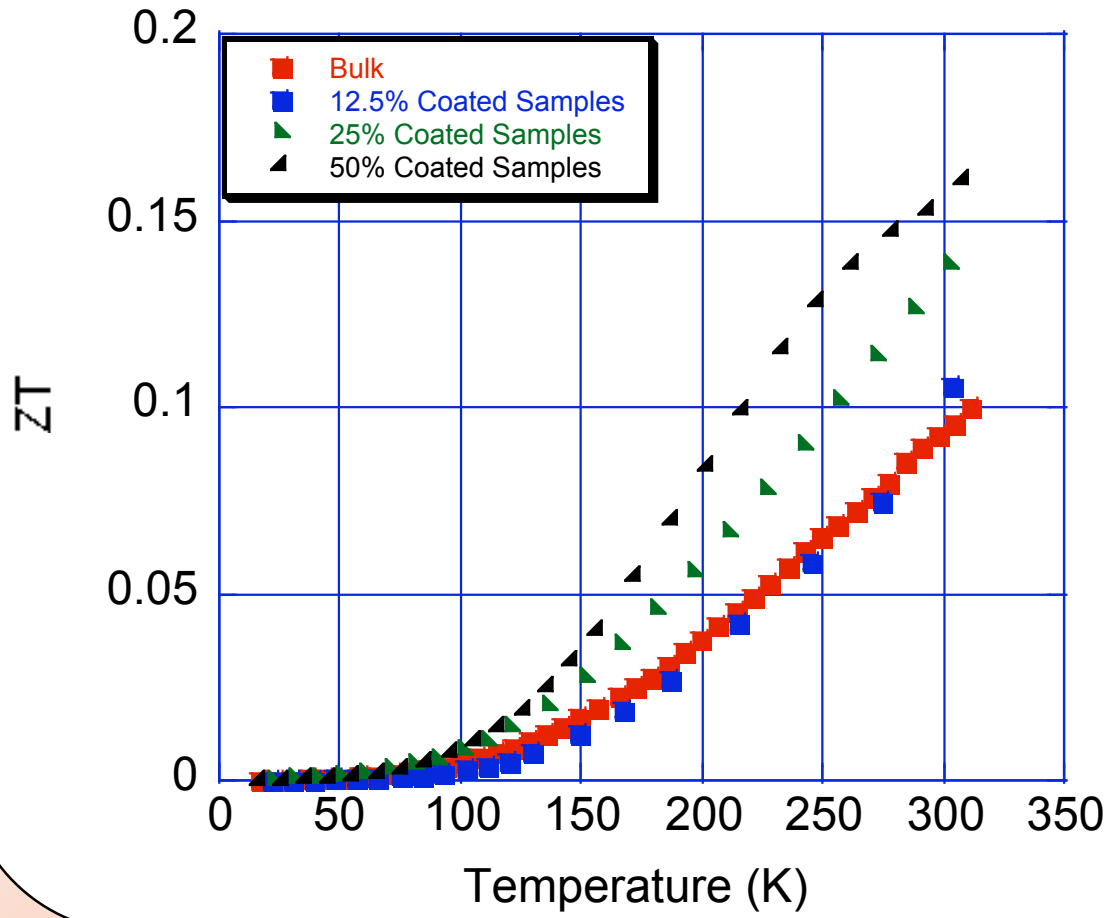
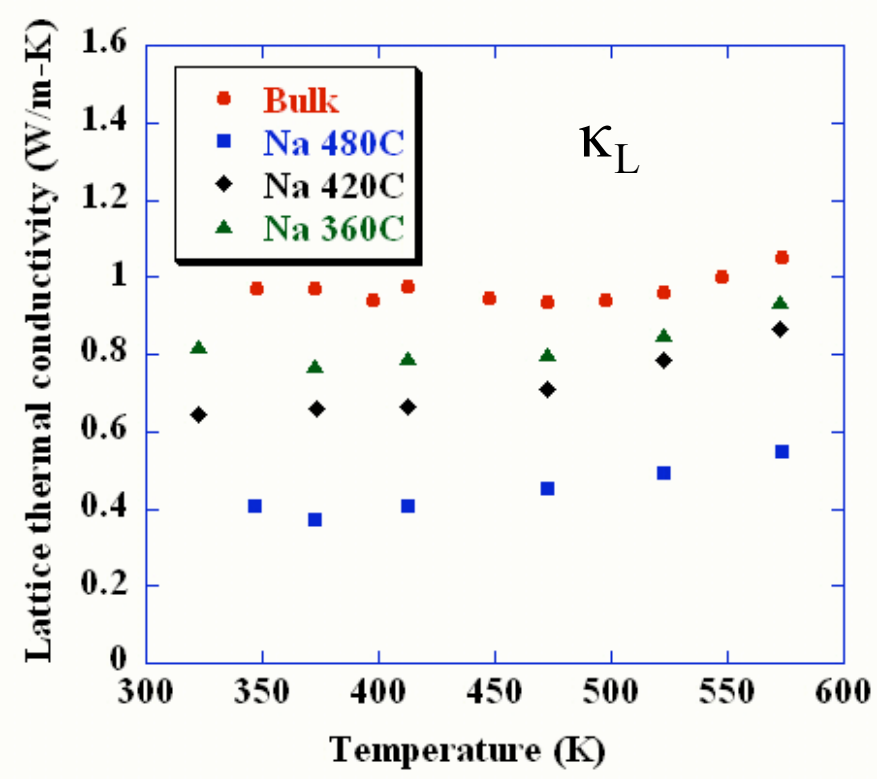
Hydrothermal Coated PbSnTe: Figure of Merit

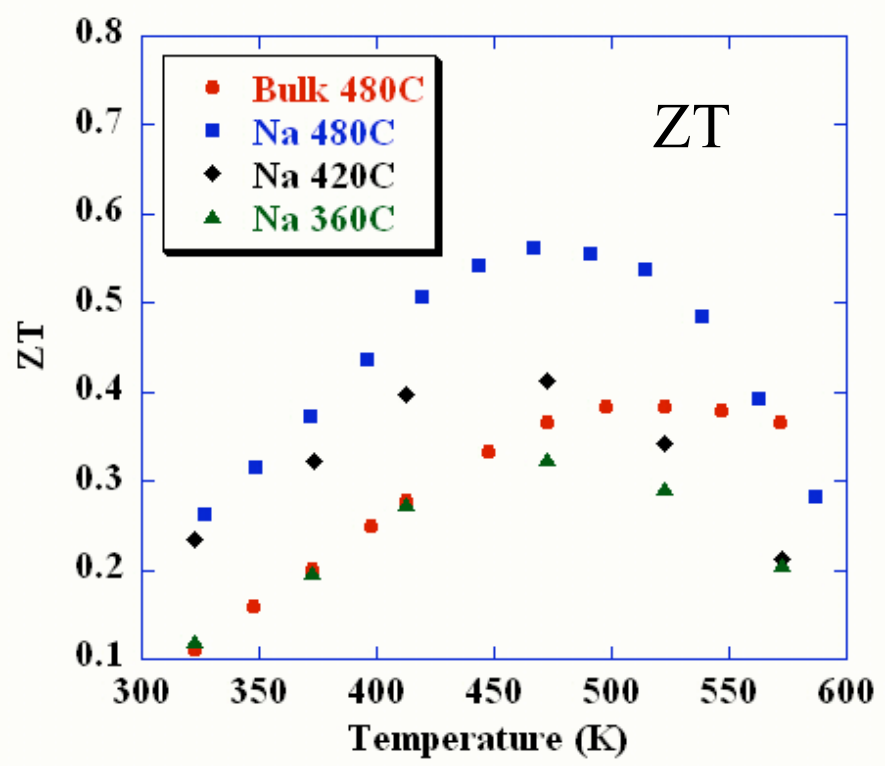


ZT is enhanced in the coated samples By about 50%

Note: Bulk means uncoated seed particles.

κ_L and ZT of the Na-treated nanocomposites hotpressed at different temperatures





κ_L is decreased and ZT increased as the Hot press temperature is increased!

Novel Nanostructures and High ZT in Melt Spun p-type $Bi_{0.52}Sb_{1.48}Te_3$

Collaboration with Prof. X. Tang and student Wenjie Xie
Wuhan Univ. of Tech:
W.Xie *et.al*, Applied Phys Letters, **94**, 102111-09

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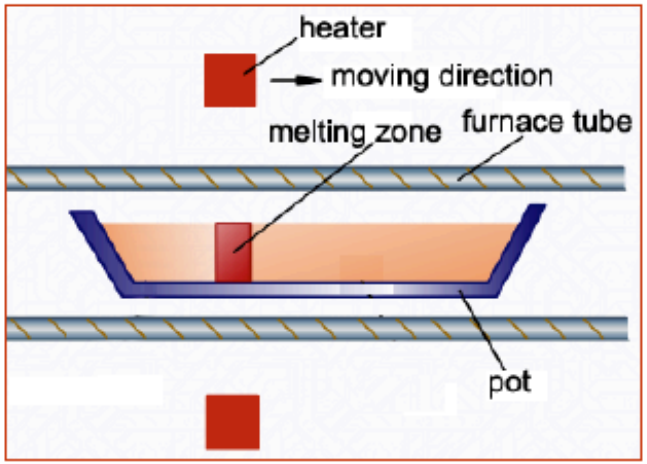
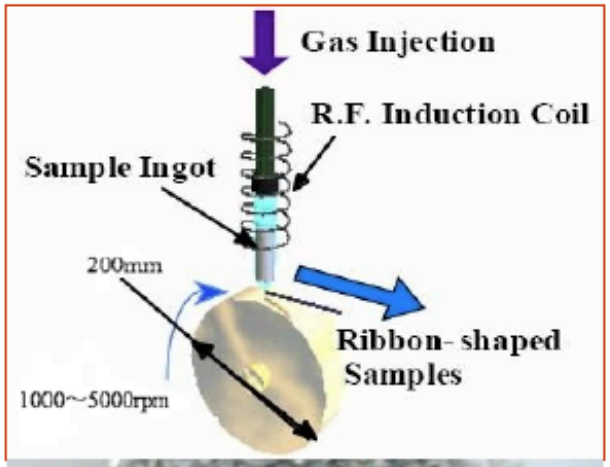
Novel Nanostructures in Melt Spun p-type $Bi_{0.52}Sb_{1.48}Te_3$

Zone Melted Ingot



Melt Spun Ribbons



Collaboration w. Prof. X. Tang and student Wenjie Xie
Wuhan Univ. of Tech:
W.Xie *et.al*, Applied Phys Letters, **94**, 102111-2009

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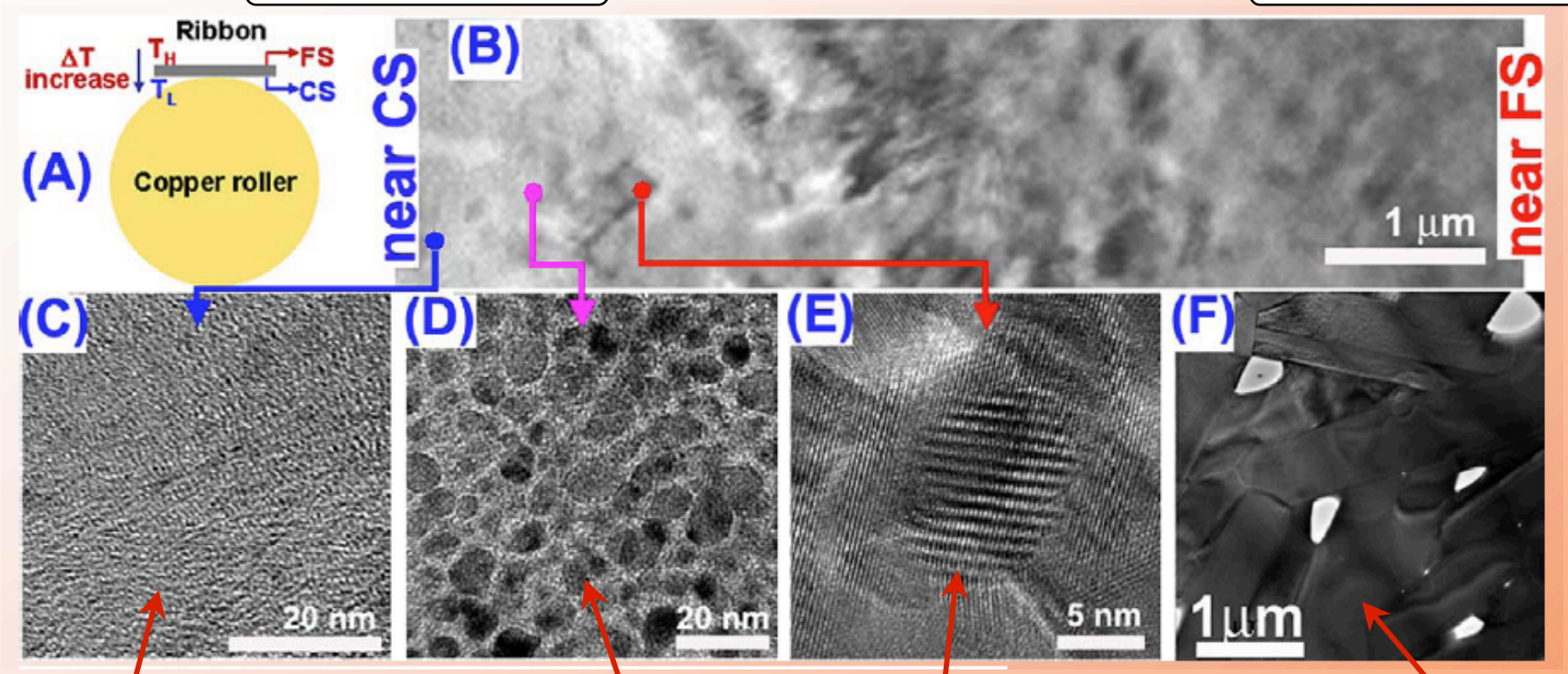
Novel Nanostructures in Melt Spun p-type $Bi_{0.52}Sb_{1.48}Te_3$

Contact Surface

Free Surface



Amorphous Microstructure near Contact surface

5-15 nm Nanocrystalline Regions or grains near CS

Large dendritic regions near free surface

Collaboration w. Prof. X. Tang and student Wenjie Xie
Wuhan Univ. of Tech:
W.Xie *et.al*, Applied Phys Letters, **94**, 102111-2009

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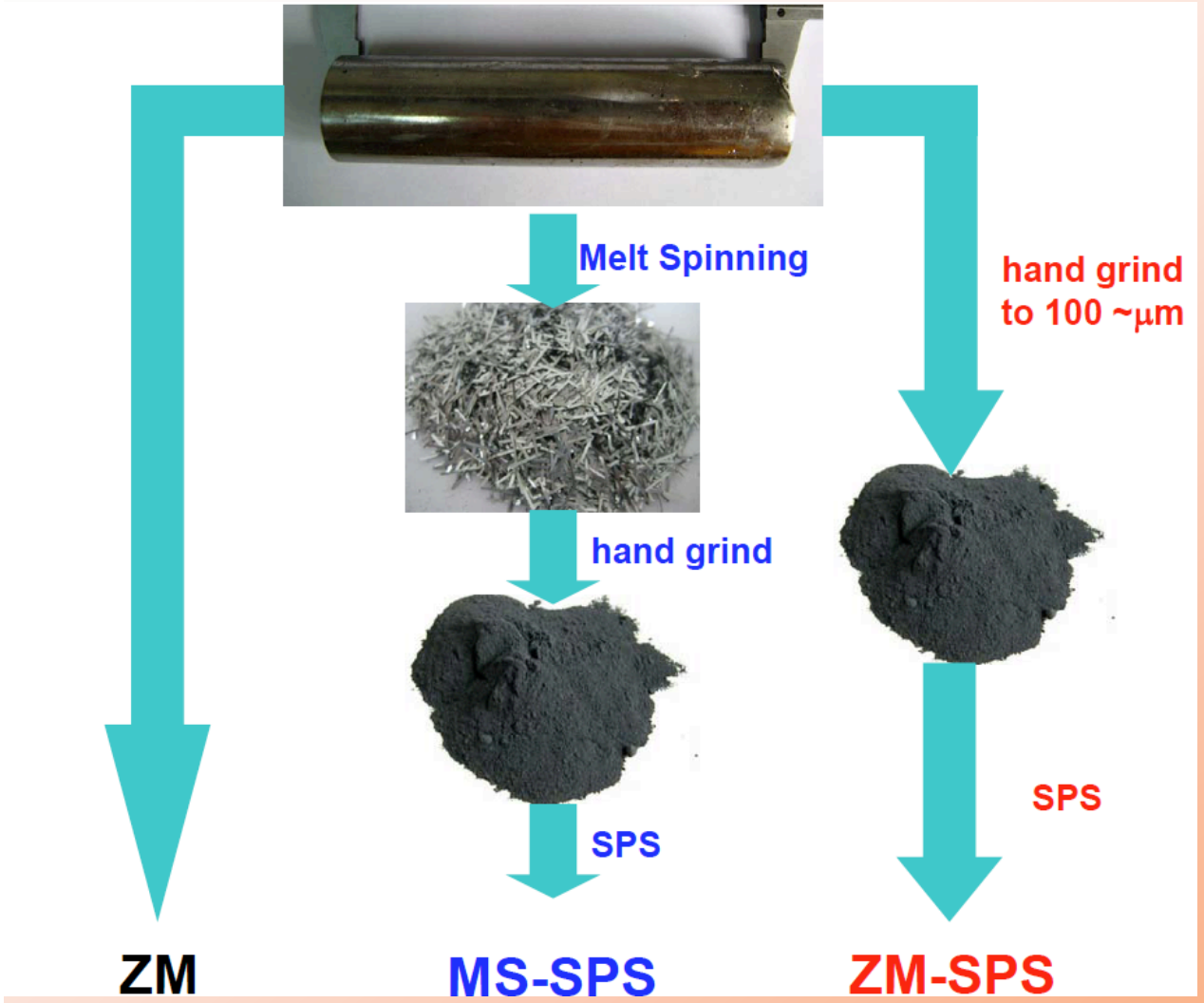
Novel Nanostructures in Melt Spun p-type $Bi_{0.52}Sb_{1.48}Te_3$



Spark Plasma Sintering Conditions

300- 400 ˚C
For several minutes

Force ≈ 3-5 KN

Collaboration w. Prof. X. Tang and student Wenjie Xie
Wuhan Univ. of Tech:
W.Xie *et.al*, Applied Phys Letters, **94**, 102111-2009

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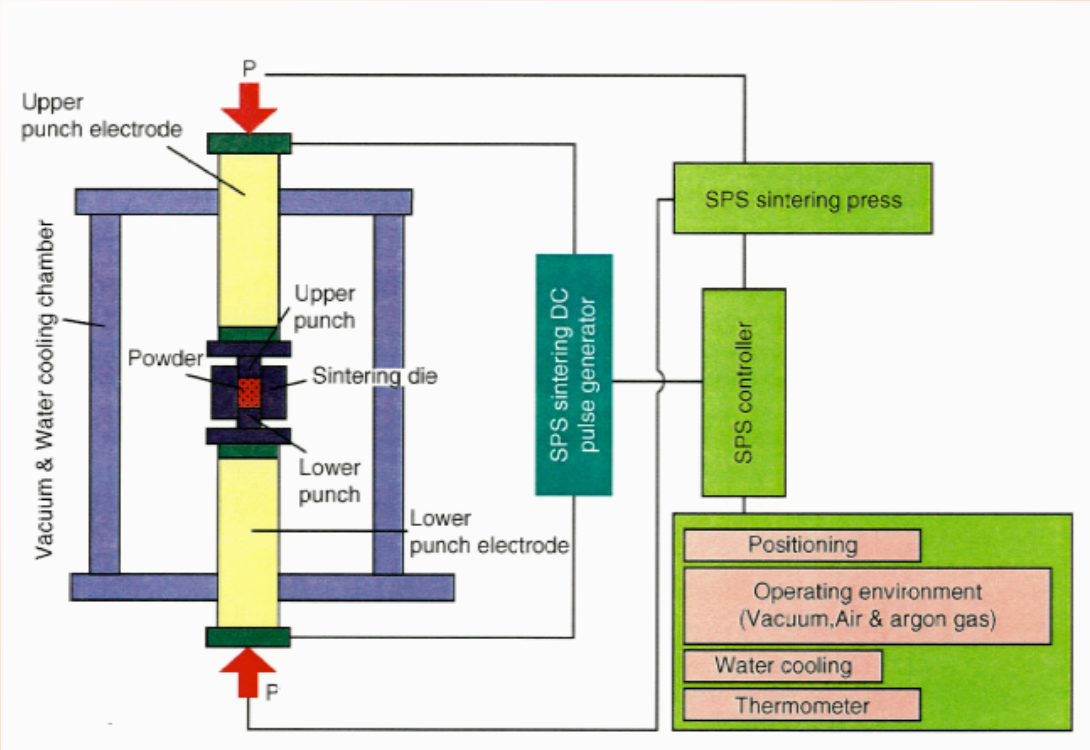
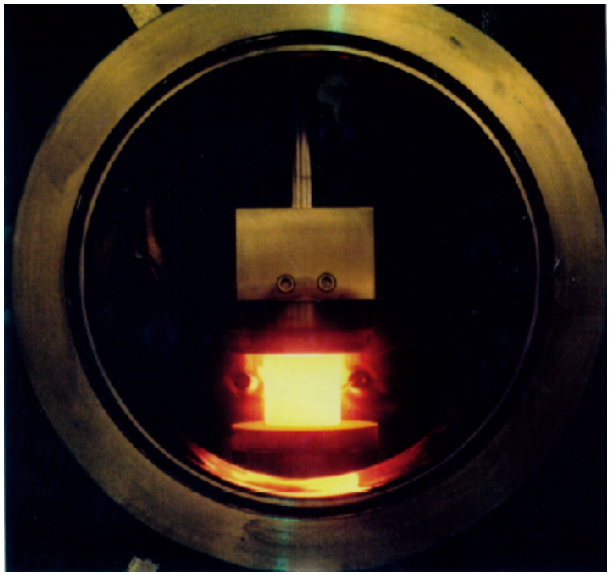
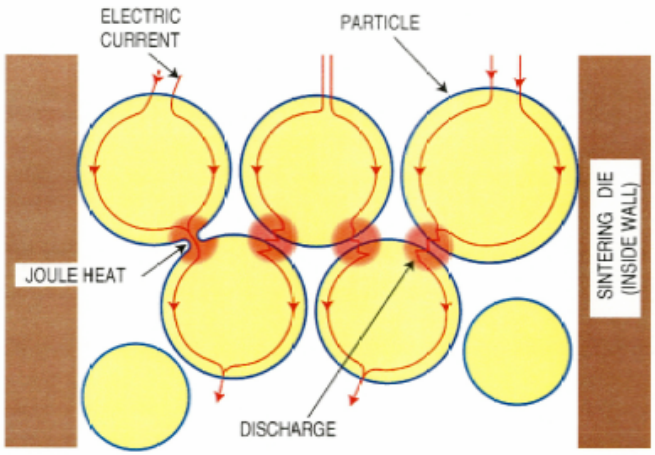
Spark Plasma Sintering (SPS):
ON-OFF DC pulsed current
Temperature & Pressure
Rapid Solidification
Preserve Nanostructures







Pulsed current flow through powder particles

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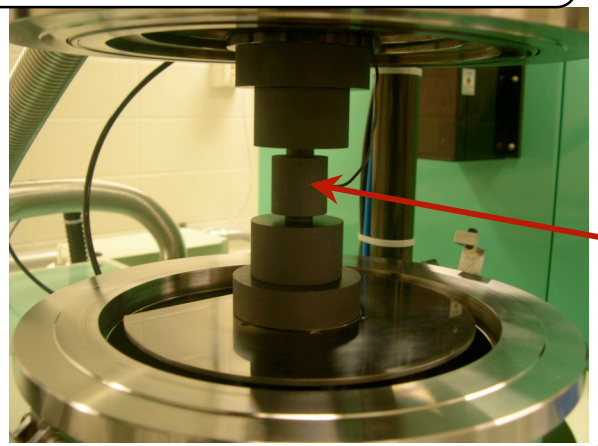
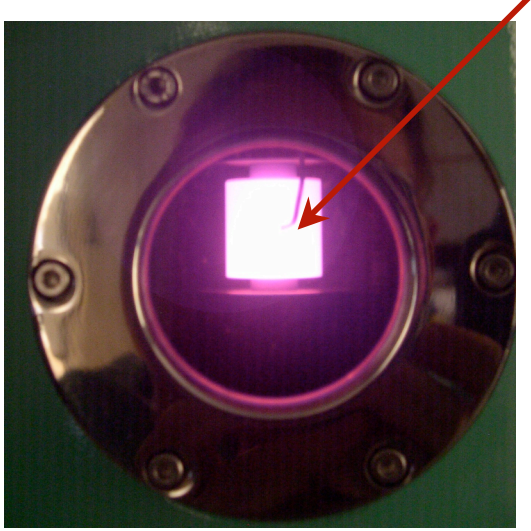
Spark Plasma Sintering System: 1500 Amps

First System in Southeast
1 of ≈10 in the US

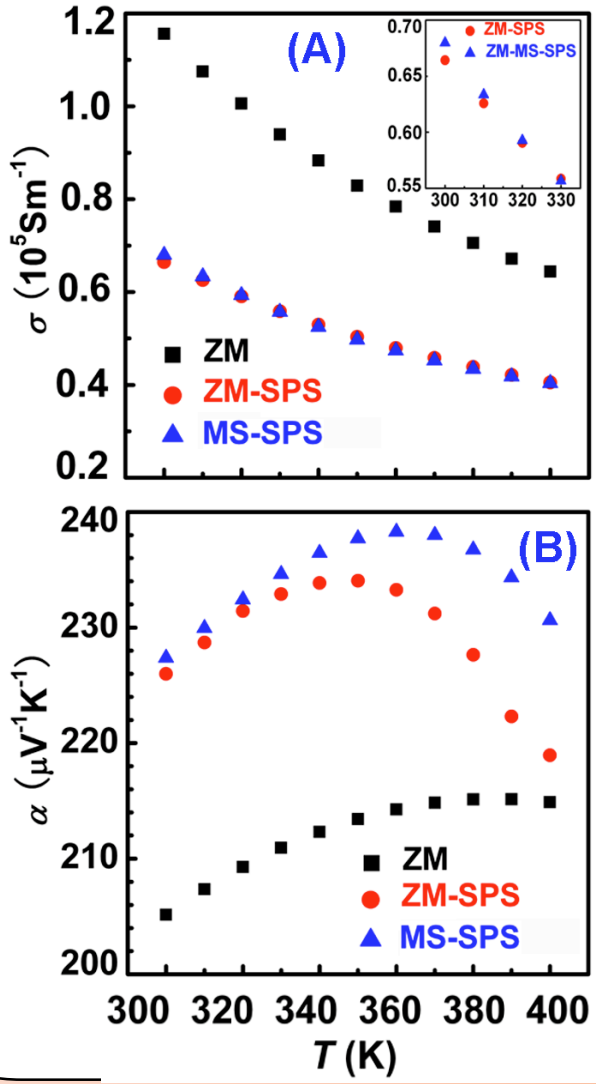
Funded by DOE EPSCoR

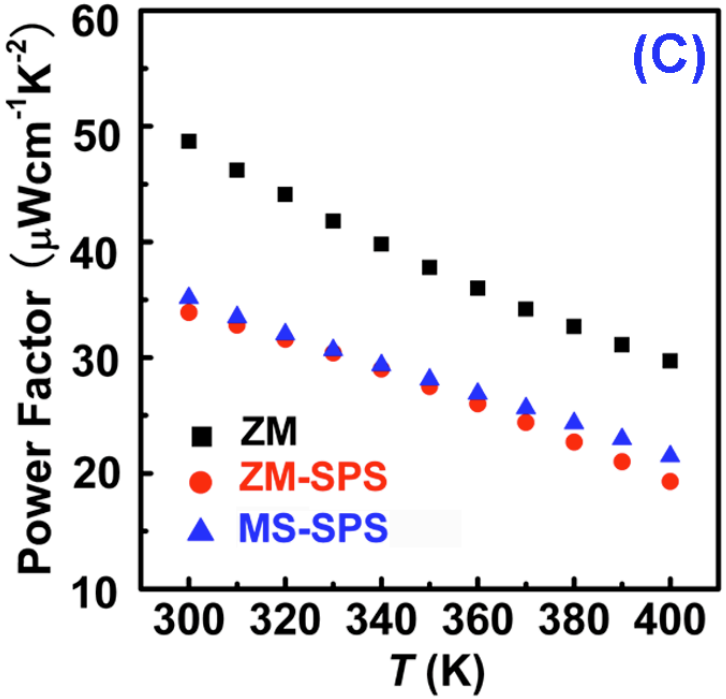




Sample
In Mold

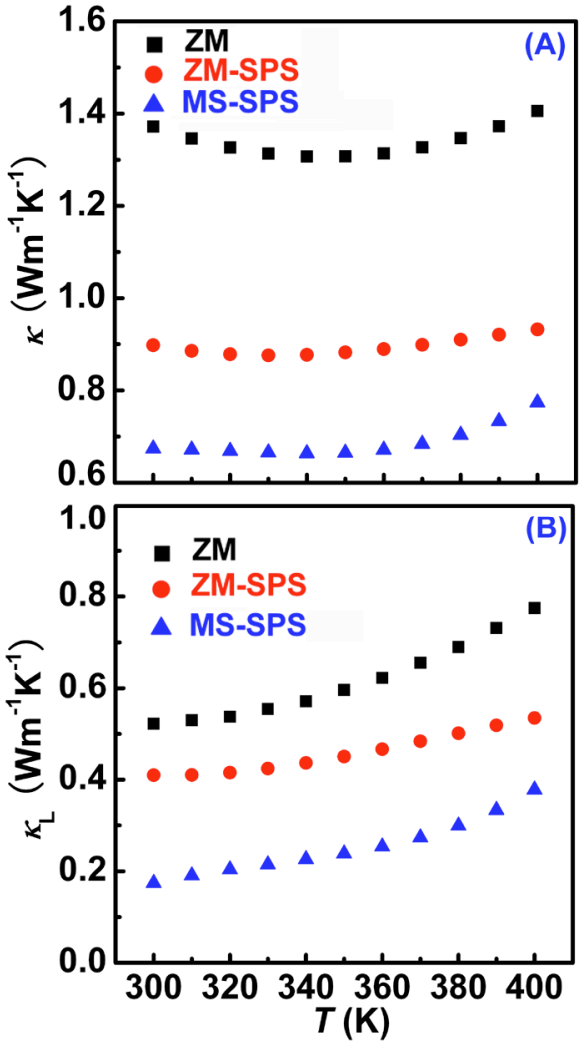
TE Properties of Melt Spun p-type $Bi_{0.52}Sb_{1.48}Te_3$

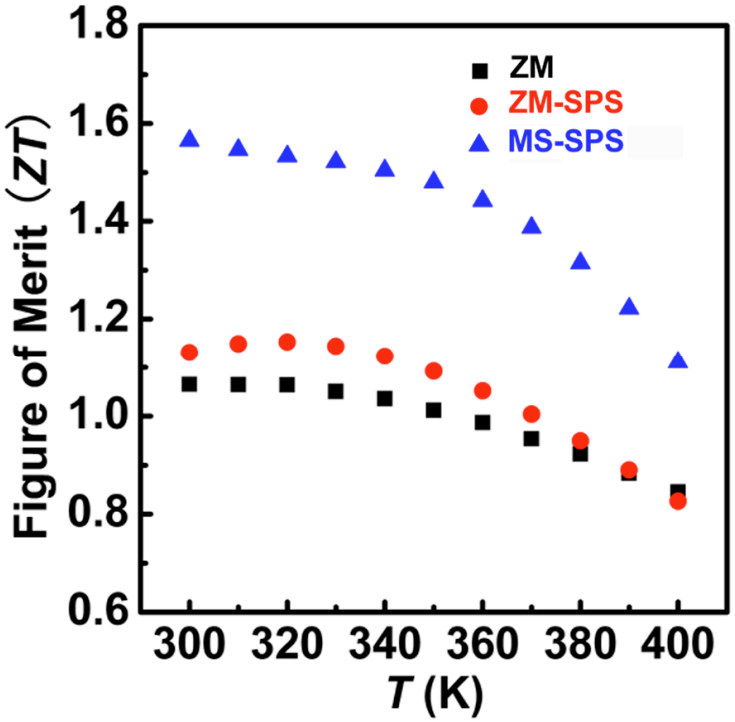




Zone Melted Sample Exhibited Better electronic Properties than the MS-SPS Sample (esp. higher σ)

TE Properties of Melt Spun p-type $Bi_{0.52}Sb_{1.48}Te_3$





But the **MS-SPS Sample** Exhibited lower κ_L and thus Higher ZT (ZT ≈ 1.5) Than other samples

Collaboration w. Prof. X. Tang and student Wenjie Xie
Wuhan Univ. of Tech:
W.Xie *et.al*, Applied Phys Letters, **94**, 102111-2009

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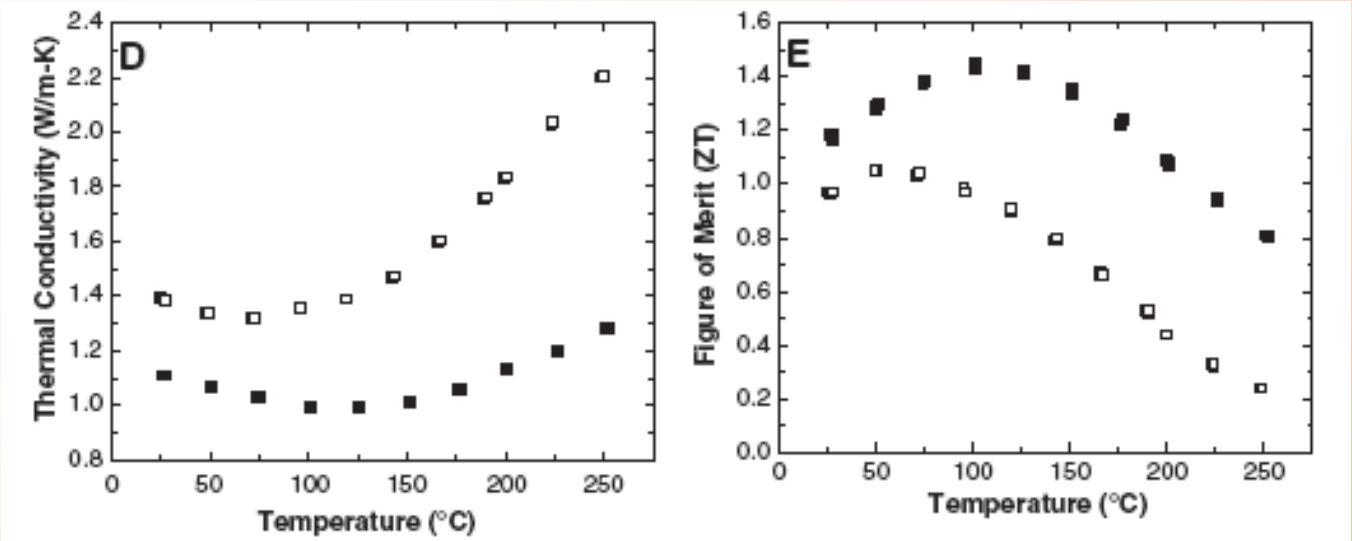
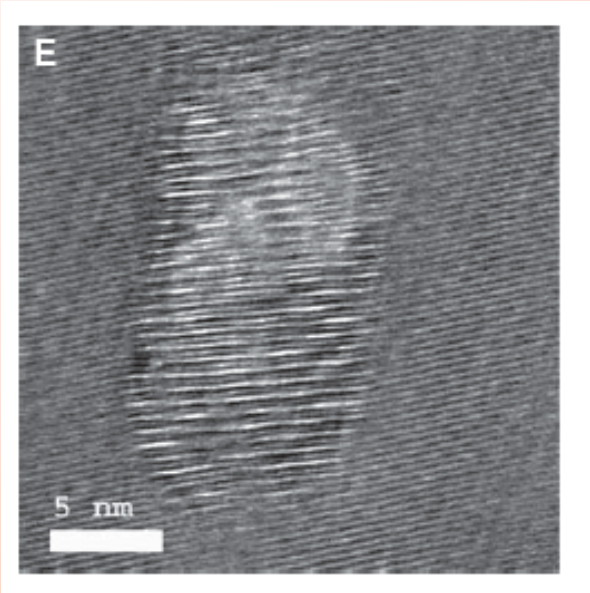
MIT Results: Hot Pressed Nanopowders





Hot Pressed Nanopowders
From **Ball milled ingots**

Nanodots in Bulk structure
of Bi_2Te_3 (5-20 nm)

ZT ≈ 1.4 due primarily to
Reduction in κ

Poudel et.al Science, 320, 634 (2008)

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Concluding Scientific 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 Properties
  Challenges in Theory, Synthesis & Characterization
- Low Dimensional TE Materials - - High ZT
  Due primarily to reductions in lattice thermal conductivity
- Many Opportunities in Nanocomposites, "Grain Surface Engineering" or Nanoscaled Bulk TE Materials **ZT ≈ 1.4**
  or Nanocomposites (Future-Spark Plasma Sintering)
- More Theoretical Modeling & Insight Needed

Impact of DOE EPSCoR Implementation Award

- 4 New Faculty Members
- Extensive Expansion of Equipment and Capabilities
- Education & Training of Graduate Students,
  Undergraduate Students & Postdocs
- Expanded Collaborations through Outreach Program
- eg. Over 35 refereed publications in last reporting period.

Approach To Strengthen TE Cluster: Phase I

- **Develop High Temperature Thermal Transport Capabilities**
  - Laser Flash & High Temp DSC Systems (Thermal Conductivity)
  - Build High Temp. Resistivity & Seebeck Systems (Rev. Sci. Instrm.)
  - Commercial System R & α - Ulvac ZEM-2: Delivery Dec. 2006

- **Establish Extensive Expertise & Capabilities in Materials Synthesis**
  - New Hire (Drymiotis) & Postdocs (**He**, Ponns and Ji)

- **Expand Sample Synthesis & Characterization**
  - Highly Densified Sample Synthesis (HIP) Capabilities
  - Over 10 new High Temp. Synthesis Furnaces, Arc Melter (2), etc.
  - Build Materials Synthesis Lab (Drymiotis)
  - Nano-Materials & Bulk Materials (He, Ponns and Ji)

- **Expand Collaborative Effort with ORNL**
  - **Jian He** (former Mandrus student joins Clemson as Postdoc -- Faculty)
  - S. Bhattacharya (former Tritt student joins Univ. of TN as Postdoc)
  - Students / Faculty travel to ORNL - sample synthesis

Approach To Strengthen TE Cluster: Phase II

Expand Expertise & Capabilities in Synthesis & Characterization

New Hire (Fivos Drymiotis, Summer of 2005)
New Hire (**Jian He**, Jan. of 2008)
New Hire (Hye Jung Kang - Neutron Diffraction, Fall 2008)
New Theory Hire (Sumanta Tewari, Fall 2008)

Expanded Collaborations

Univ. of Waterloo, Kleinke (Outreach Program)
New Collaborations (Zhejiang University, Wuhan Univ. of Tech.)
Student Exchange & Visitation Program
Develop New Collaboration & Funding -- (Air Force Mats. Lab.)

Expand Sample Synthesis & Characterization Capabilities

Expanded Highly Densified Sample Synthesis
Spark Plasma Sintering (SPS) Capabilities
More New High Temp. Synthesis Furnaces, Arc Melter, etc.
Optical Floating Zone Furnace (He)
Nano-Materials & Bulk Materials (Tritt, He and Ji)

DOE-EPSCoR Educational Participants:

Postdoctoral Researchers Supported by DOE & SC EPSCoR

Dr. V. Ponns (1/2) (Feb. 04 - High Temp Measurements)
Dr. Xiaohua Ji* (Sept. 05, Hydrothermal Synthesis of TE nanostructures)
Dr. X. Gao* (July 05; Theory; Band Structure Calculations)

Graduate Students with Support from DOE & SC EPSCoR Funds

Bo Zhang (CVD Synthesis of PbTe & Bi_2Te_3 nanostructures)
Nick Gothard (CVD Synthesis of PbTe & Bi_2Te_3 nanostructures)
(Hot Pressing Bulk Pellets & measurements)
Paola Alboni* (Synthesis & measurements of skutterudite nanocomposites)
Su Zhe (CVD Synthesis of PbTe & Bi_2Te_3 nanostructures)
Sloan Lindsey (High Temp R & α Measurements - at Zhejiang Univ.)
Tim Holgate (TE Chalcogenides - Kleinke Collaboration)
Daniel Thompson (Fall 2005 - SiGe and PbTe nano)
Jason Reppert (Raman Spectroscopy - *Attended Nobel Laureates Conf.*)
Anil Jian *(Web page Design & Support)*
Jen Hubbard* (Synthesis & measurements of skutterudites)

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DOE-EPSCoR Visibility and Awards:

Terry M. Tritt:

Edited Materials Research Society Bulletin on TE's (March 2006)
SC Governor's Research Prof. of the Year: 2008
Clemson University Alumni Award for Research: 2008
Materials Research Society Meeting Chair - Spring 2009
(Over 5000 attendees at this meeting)
Vice Pres. and Fellow of International TE Academy (2008 -)
Led EFRC and MRSEC Proposal Teams as PI - *Unsuccessful*

Apparao Rao:

Elected Fellow of the American Physical Society (2009)

Jian He:

Nominated for Outstanding Young Investigator in TE (2009)

Fivos Drymiotis:

Outstanding Teaching Award in CoES (2009)
Awarded NSF Grant beginning Fall 2009

Acknowledgements:

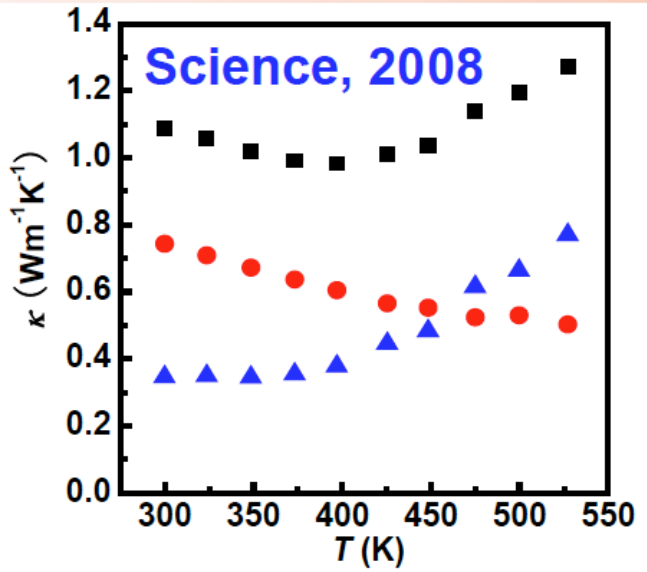
Dept. of Energy: DOE EPSCoR Implementation Grant (DOE #: DE: FG02-04ER-46139)

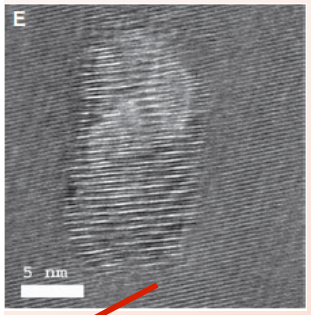
Thank You!

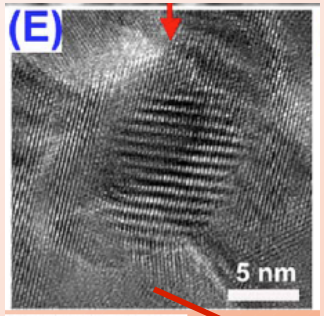
Questions??

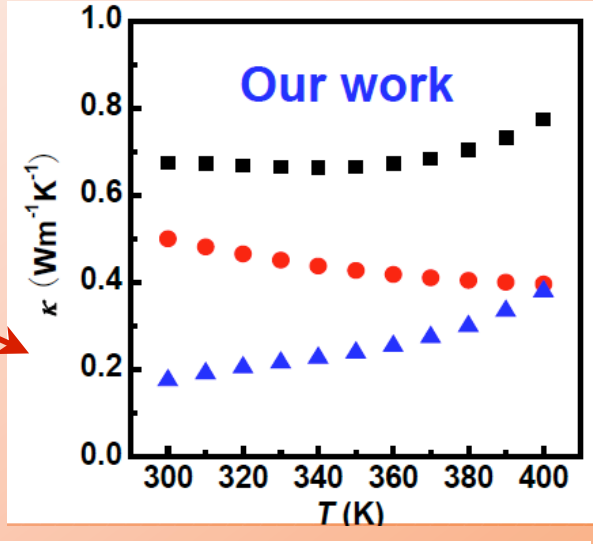
Slides for Questions!

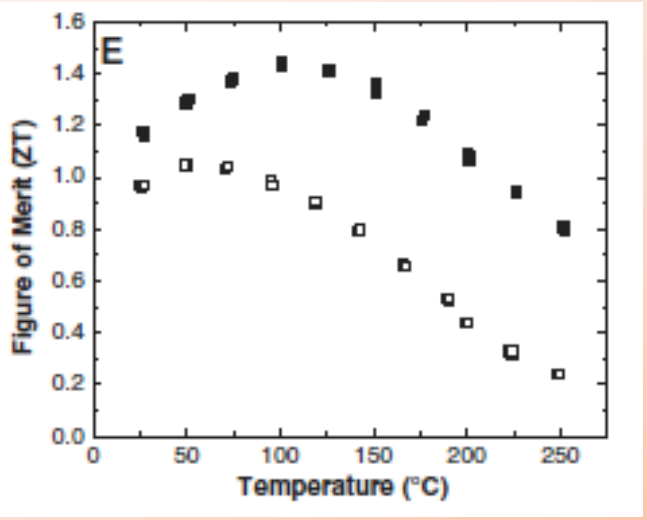
Novel Nanostructures lead to High ZT in p-type $Bi_{0.52}Sb_{1.48}Te_3$









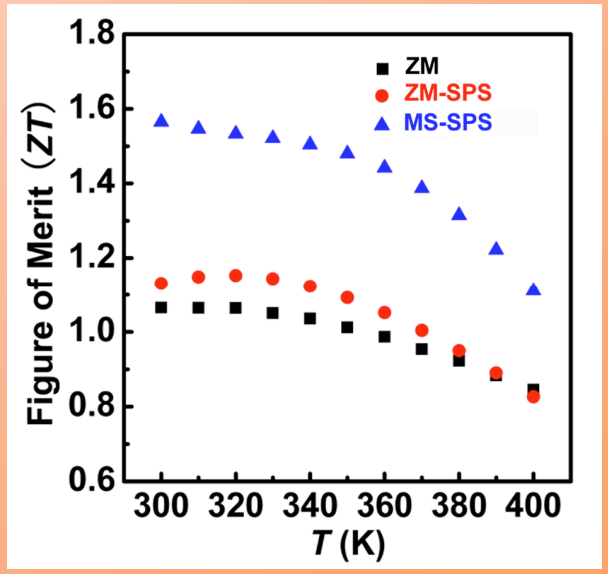


Wuhan/Clemson (right)
& the
MIT Results (left)

High ZT in
p-type $Bi_{0.52}Sb_{1.48}Te_3$

ZT ≈ 1.4

Presence of novel
nanostructures in the bulk
Leading to a low κ_L



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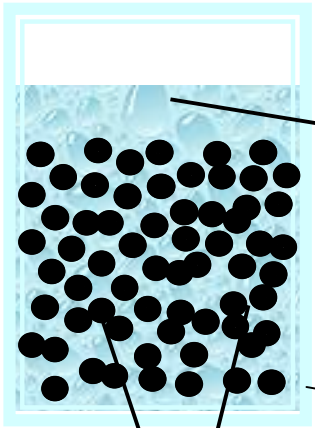
An alkali metal hydrothermal treatment technique



Various alkali metal (Na, K) compounds solution

Hydrothermally treat

Remove powder, wash & dry

Hot press

pellet

autoclave

Bulk TE raw powder

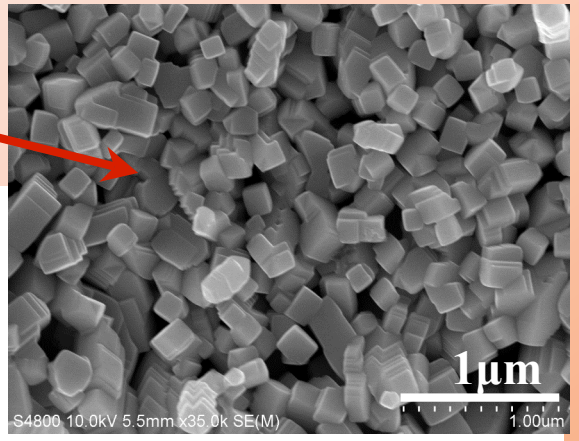
150°C for 36 hr

alkali metal hydrothermal treatment process,
an admixture of 6 mmol NaOH (KOH),
2 mmol NaF (KF), 3 mmol $NaBH_4$ (KBH_4)
35 ml distilled water,
and ~ 2.5 g $Pb_{0.75}Sn_{0.25}Te$
bulk reference powder were loaded into
a 45 ml Teflon-lined autoclave

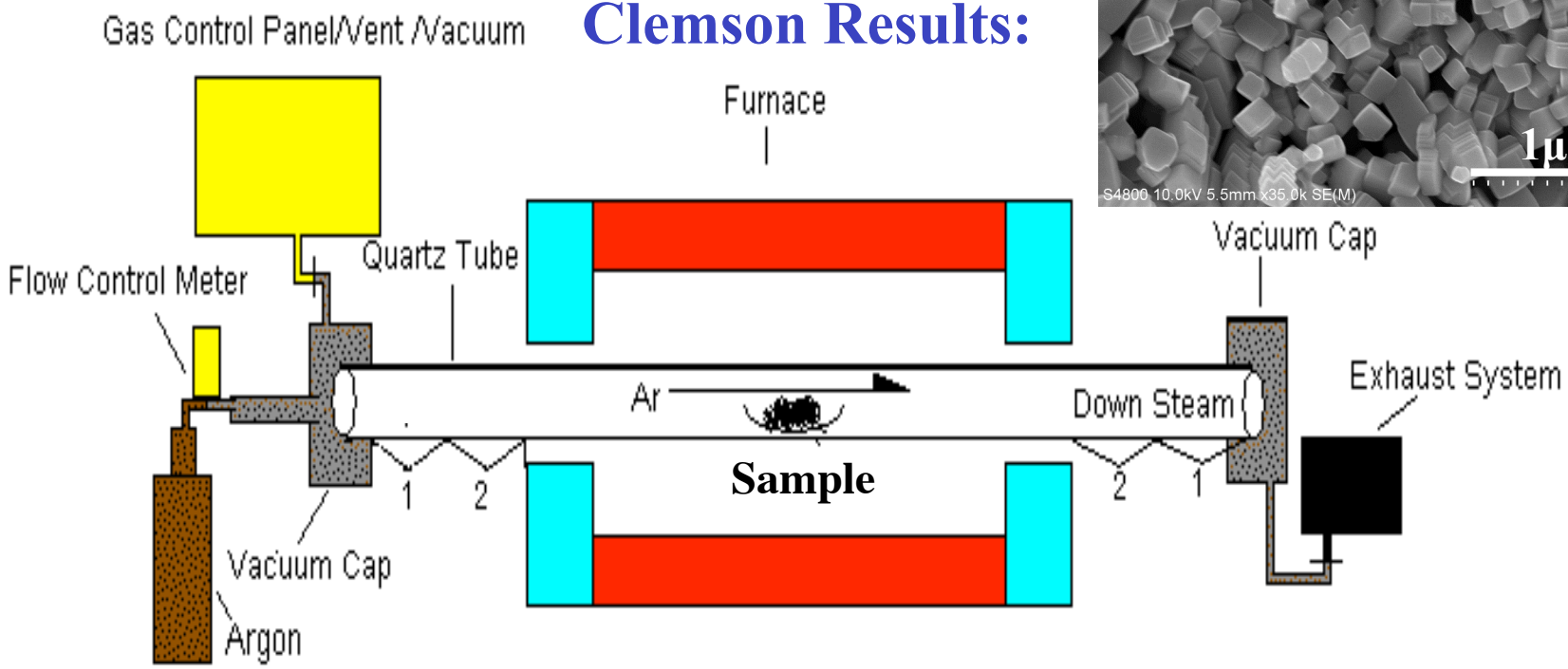
Chemical Vapor Deposition: Synthesis of Nanoscale TE Materials

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

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



Clemson Results:



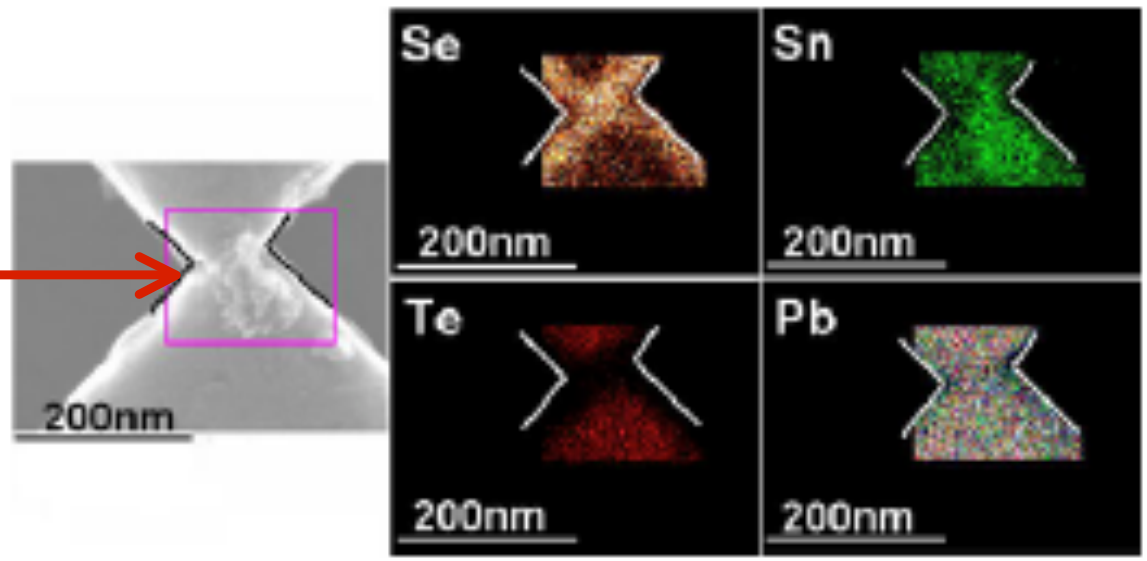
Hydrothermal Nano-Coating Process on PbSnTe

Start with (Pb-Sn)Te Seed particle (several μm)
Hydrothermal Nano-Coating (Pb-Sn)Se

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

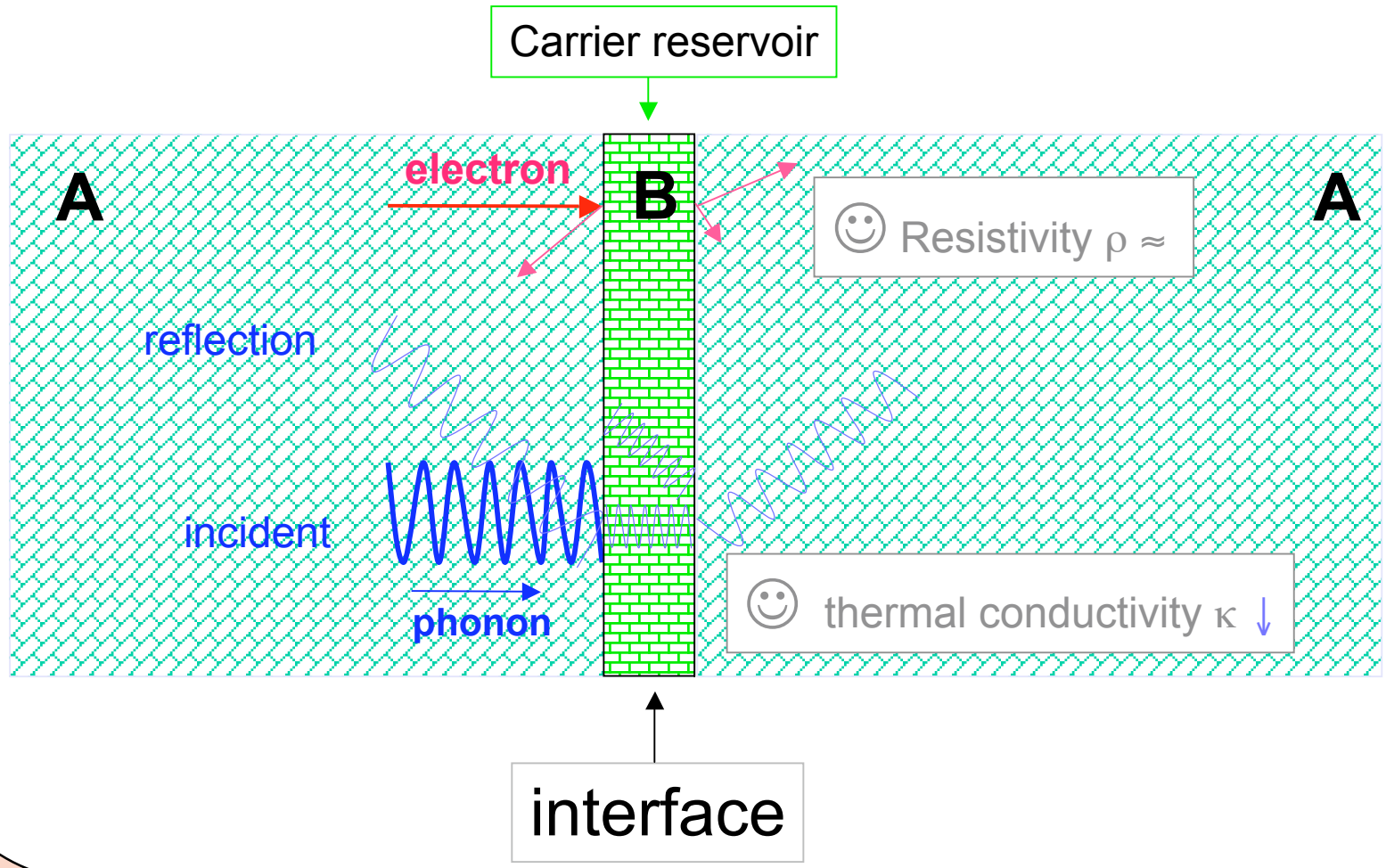
Elemental "Smart Map"

Focus On this area

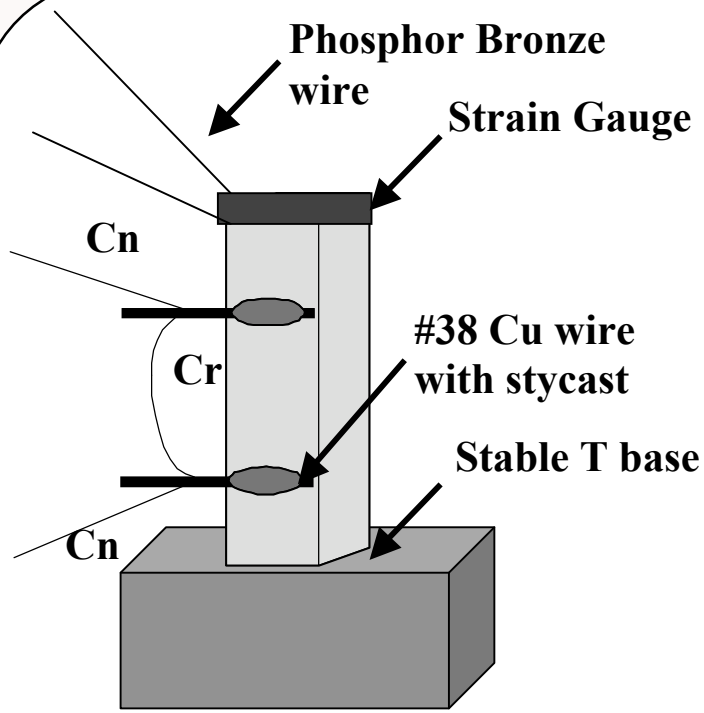


Grain Boundary Engineering Concept

Proof-of-principle study



Thermal Conductivity -Bulk Samples



$$\kappa = \frac{P_s L}{A\,\Delta T}; P_s = I^2 R - P_{loss}$$

Pope. Rev. Sci. Instrum. 72, 3129 (2001).

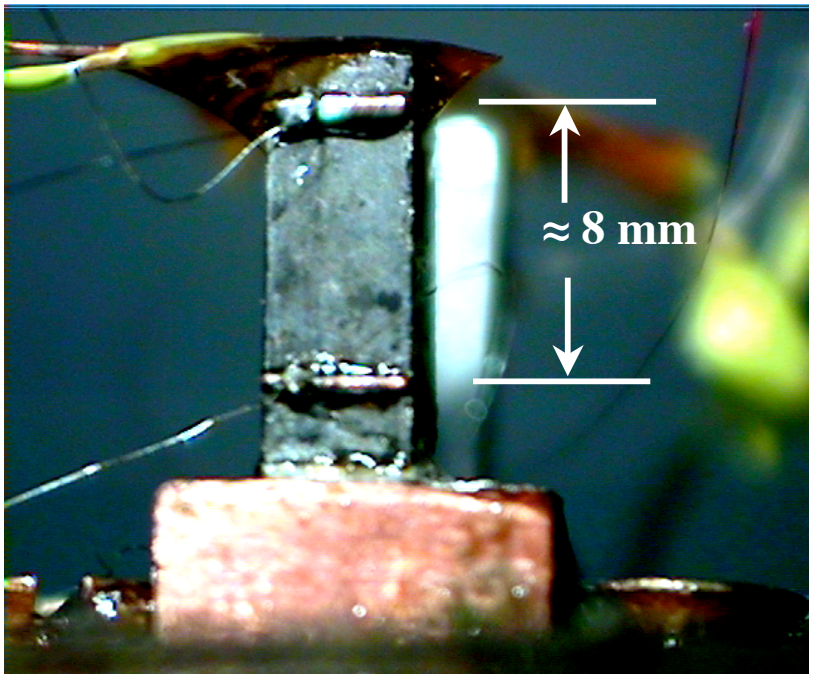
Low Temp Thermal Conductivity:

Steady State Method

(6K to 320 K)

P vs. ΔT Sweeps @ Constant T

$$P_{Sam} = \kappa_{Tot} \frac{A}{L_S} \Delta T$$



Sample Width ≈ 3mm

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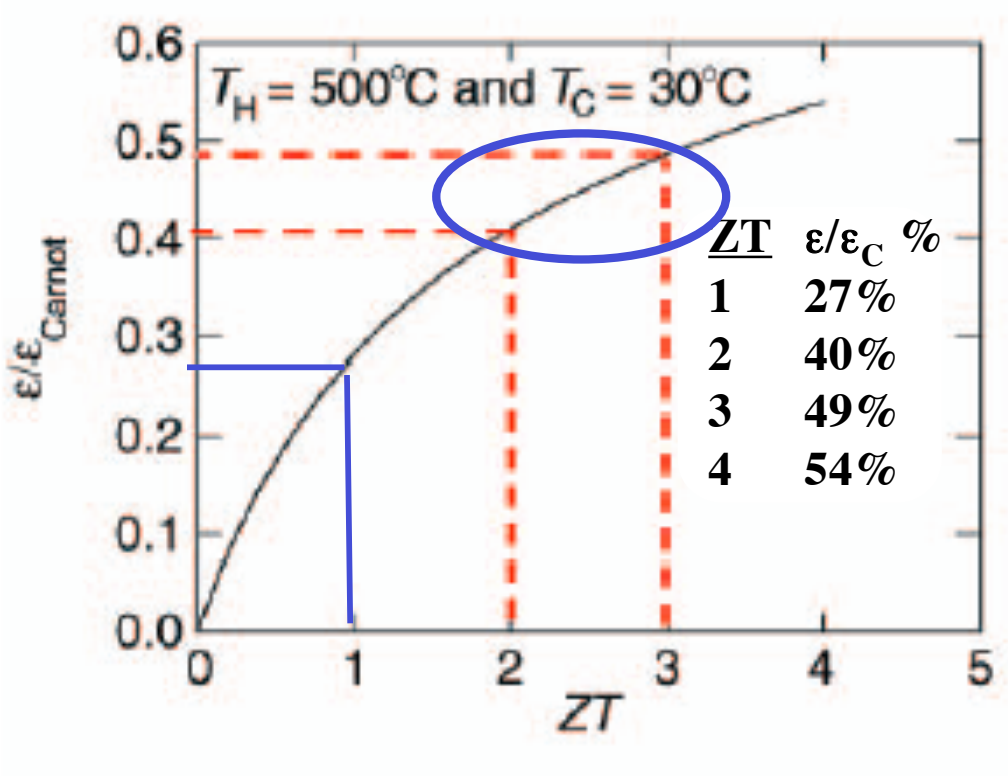
Why a Goal of ZT ≈ 2-3?

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



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

$$\kappa = \kappa_e + \kappa_{ph}$$

Future Material Needs

ZT ≈ 2-3!

➠ η = ε ≈ 15 - 20%

As ZT >> 1 then $\varepsilon \approx \varepsilon_C$ (Carnot efficiency)

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Waste Heat Recovery: TE Power Generation

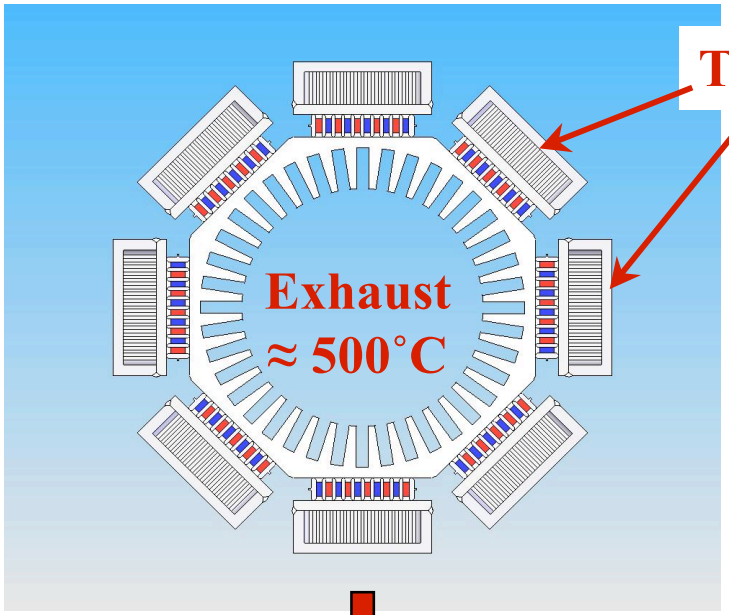
Heat Rejection
Waste Heat > 50%

$T_H \approx 800K$

$T_C \approx 300K$

Carnot Efficiency

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



TE Efficiency

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

Waste Heat Recovery
Goal > 10%

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

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