DOE-EERE Thermoelectric Applications Workshop

Thursday, Oct. 1st 2009

Lattice Thermal Conductivity and Stability of "TE Nano-Composites"

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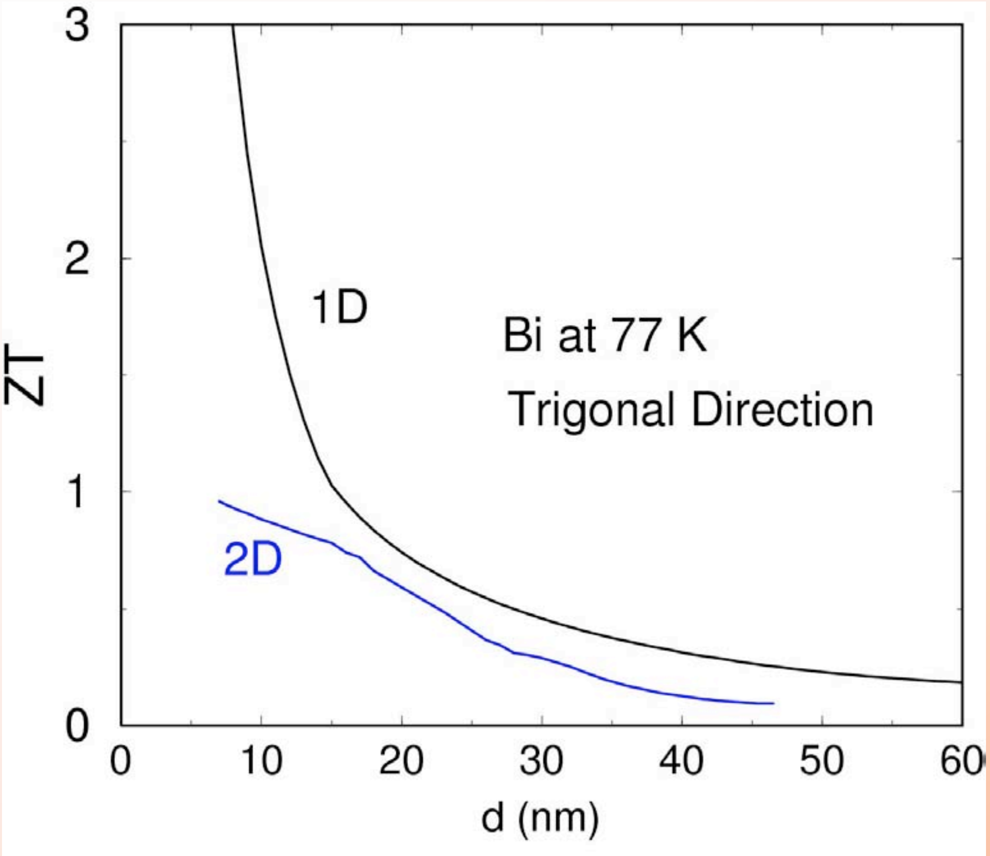
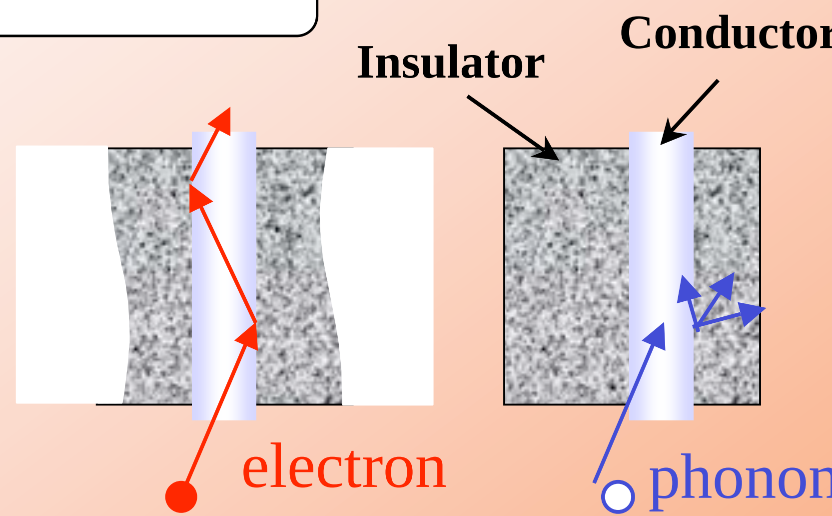
Motivation for Low Dimensional TE Materials:





Hicks & Dresselhaus, PRB 1993
Dresselhaus, Plenary Talk - ICT 05, Adv. Mats 07

Quantum Enhancement
Increase Seebeck

Interface Scattering
Large Kapitza Resistance
Reduce κ_L

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Relative Importance of α^2/ρ and κ

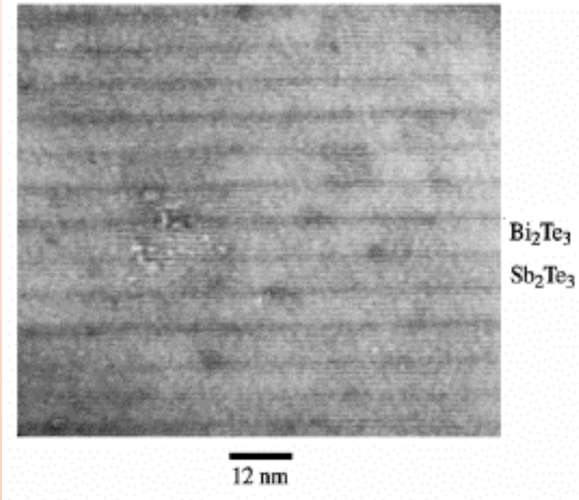
Bi_2Te_3 / Sb_2Te_3	Nano	Bulk
α^2/ρ ($\mu W/cm\text{-}K^2$)	40	51
κ ($W\text{-}m^{-1}K^{-1}$)	0.6	1.45
ZT (T =300K)	2.4	1.0

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

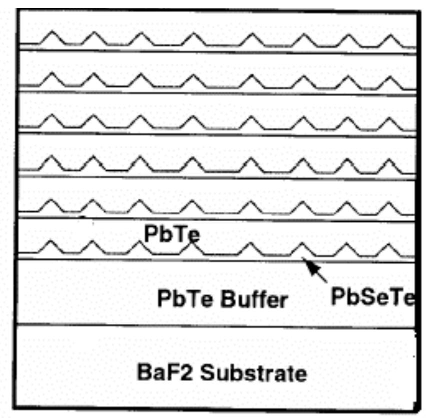
PbTe/PbSeTe	Nano	Bulk
α^2/ρ ($\mu W/cm\text{-}K^2$)	32	28
κ ($W\text{-}m^{-1}K^{-1}$)	0.6	2.5
ZT (T =300K)	1.6	0.3

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**
ZT (T =300K)	2.4	1.0

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

PbTe/PbSeTe	Nano	Bulk
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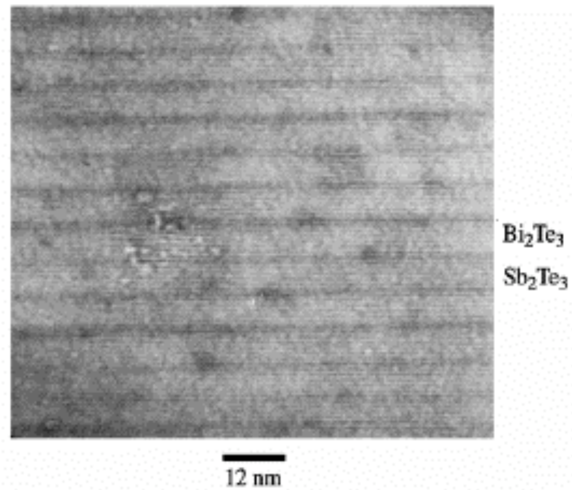
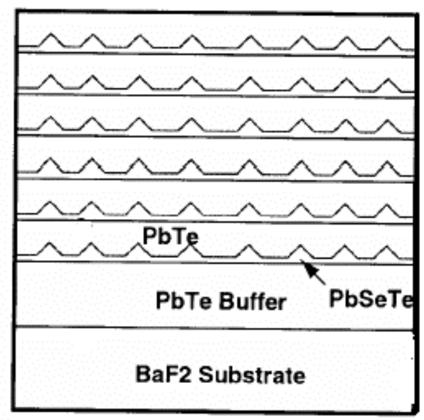
Bi_2Te_3/Sb_2Te_3 Superlattice



PbTe/PbSeTe Quantum Dots



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

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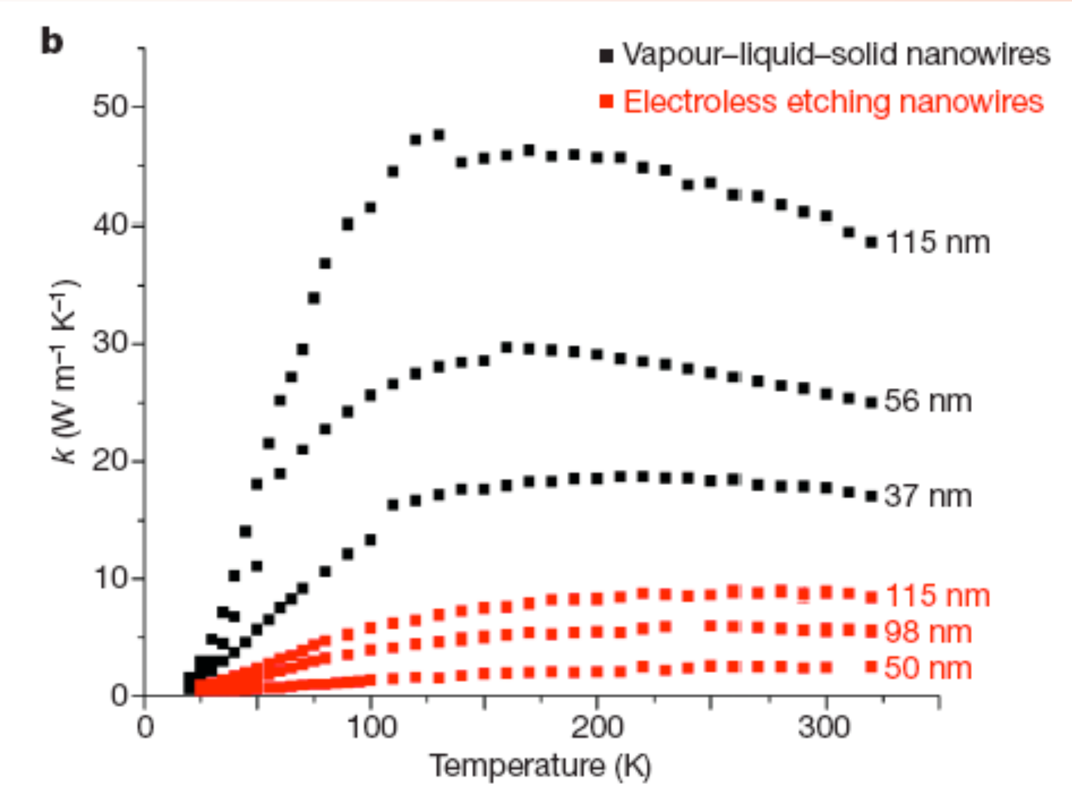
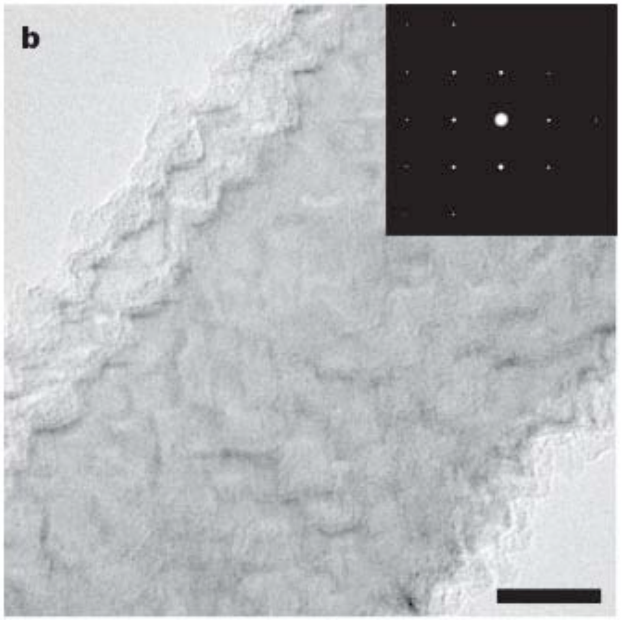
TE Enhancement of Roughened Si Nanowires

A. Hochbaum et.al., Nature, 451-p 163 (2008)
Jan 2008 -- LBNL & Berkeley Groups





Surface Roughness Above

Leads to Reduction in Thermal Conductivity (Left)

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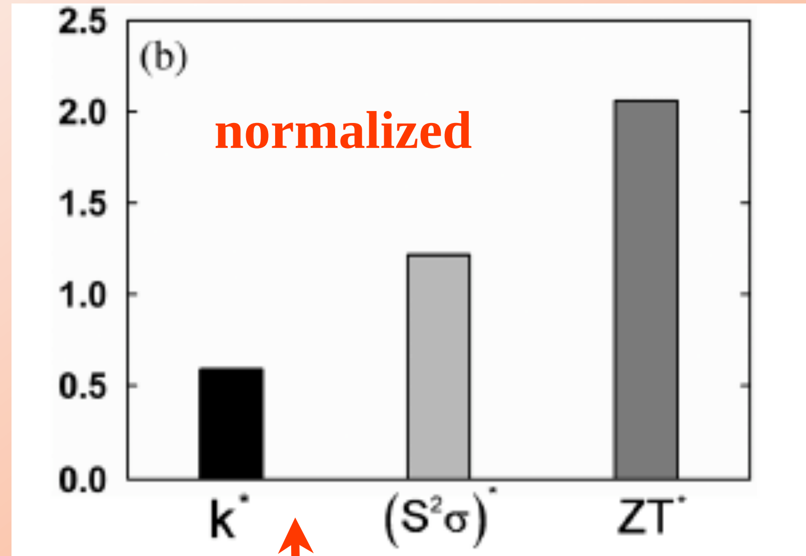
Embedding Nanoparticles in Crystalline Semiconductors

ErAs nanoparticles in $In_{0.53}Ga_{0.47}As$ 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
- <u>Theoretical analysis</u> 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 !

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TE Nanomaterials Growth,
TE Nanocomposites &
Grain Boundary Engineering

But First,
Discussion on TE Measurements!

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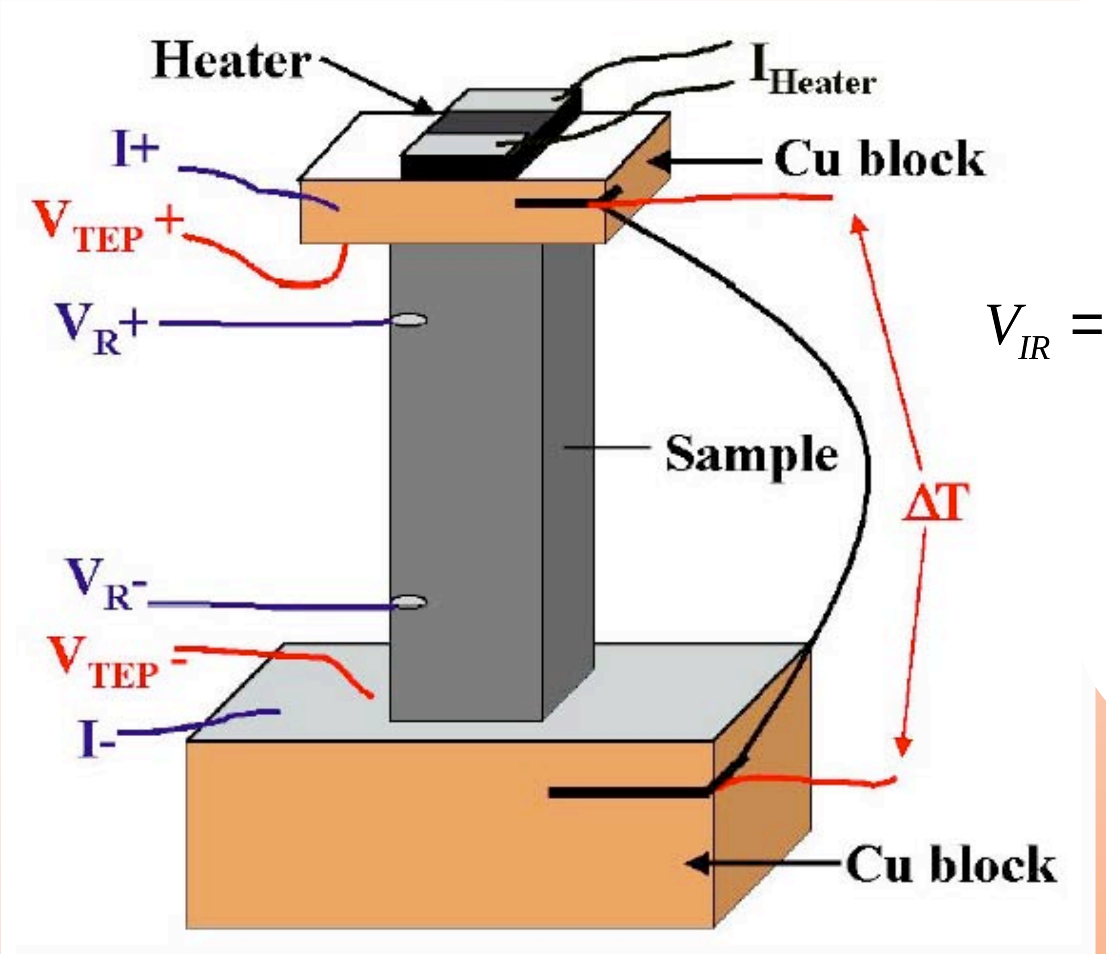
Resistivity and Seebeck Measurement Description:



$$V_{Total} = V_{IR} + V_{TE}^{*}$$

$$V_{IR} = \frac{[V(I^{+}) + V_{TE}^{*}] - [V(I^{-}) + V_{TE}^{*}]}{2}$$

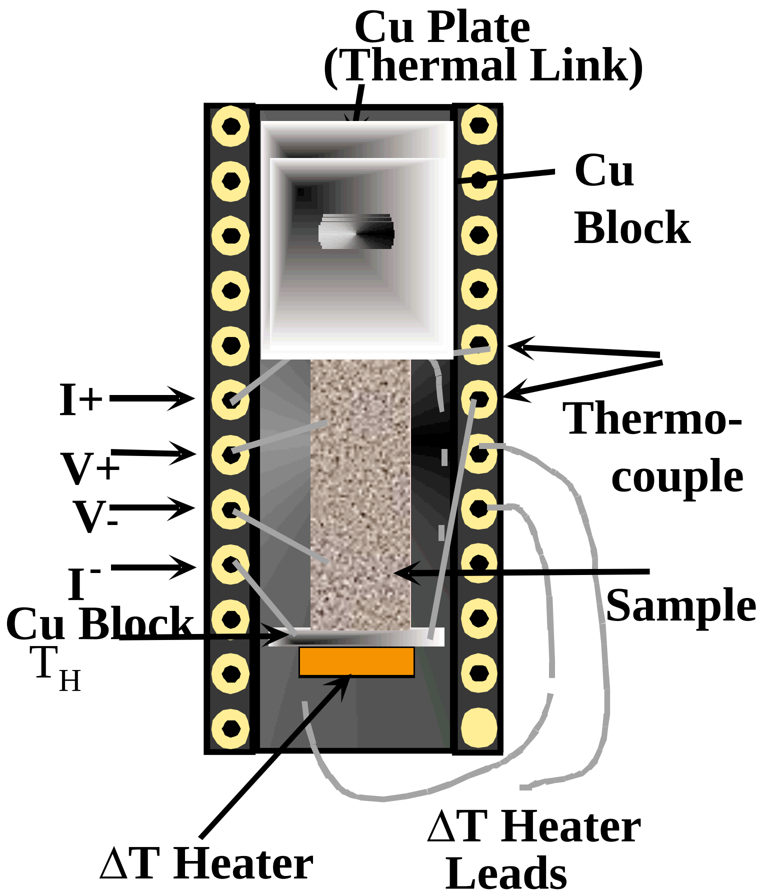
$$\alpha_{AB} = \frac{\Delta V}{\Delta T} = \frac{(V_H - V_L)}{(T_H - T_L)}.$$

Measure all Properties on Same Sample!

Important to measure ΔT Correctly where ΔV_{TE} is measured

Crycooler Head for R & α Measurements System (3 Systems):

Typical Size: 2 x 2 x 8 mm^3
6-10K < T < 320 K



•A. L. Pope, R. T. Littleton, IV and **Terry M. Tritt,** Rev. Sci. Instrum., **72**, 3129 (2001)

Measures
two samples
Simultaneously
6 K < T < 320 K

IC Chip
receptacle

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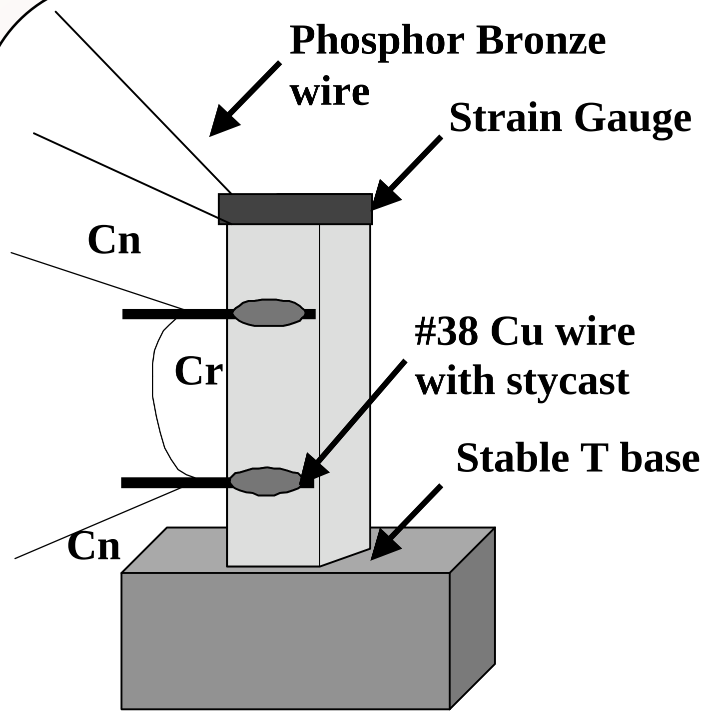
Thermal Conductivity -Bulk Samples



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

Pope et.al Cryogenics, **41**, 725 (2001)

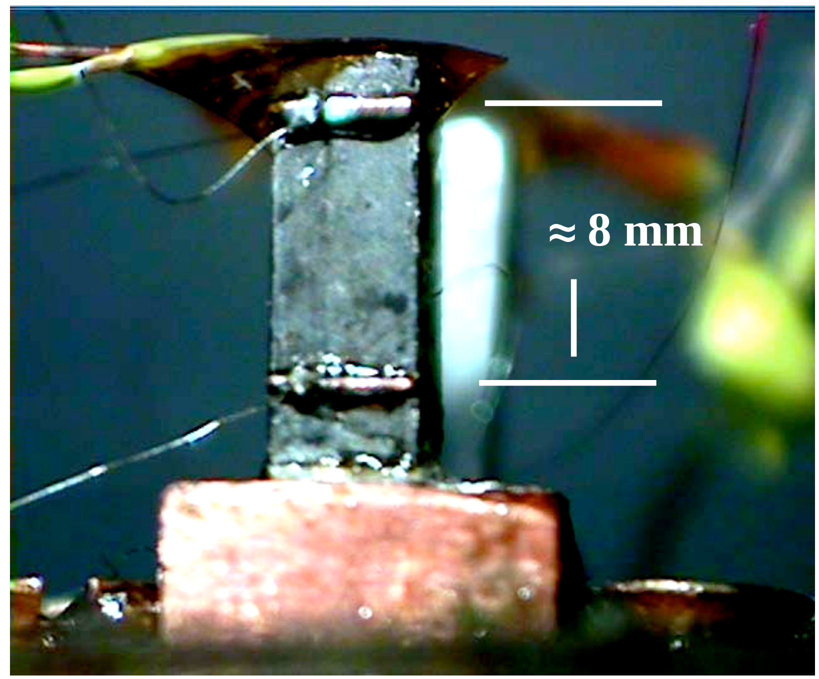
Low Temp Thermal Conductivity:

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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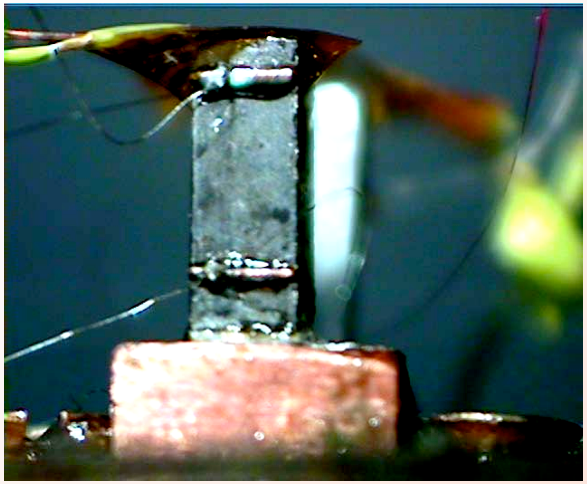
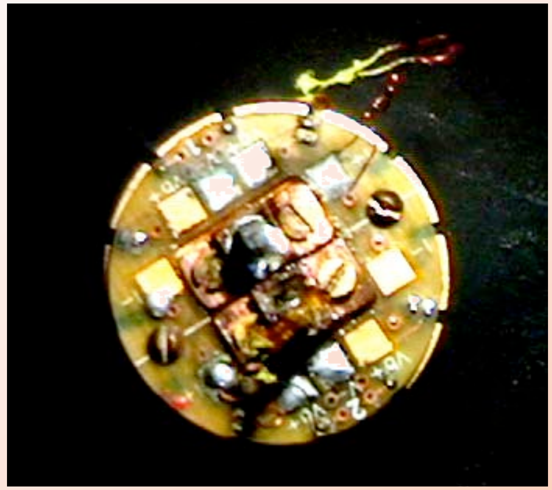
Thermal Conductivity -Bulk Samples





Absolute steady state technique

Two samples may be mounted simultaneous

Dismountable puck

The puck socket attached on a Cryocooler

Three Separate Systems

Thermal conductivity measured from 6 K to 300 K

A. L. Pope, B. M. Zawilski and Terry M. Tritt
Cryogenics, **41**, 725 (2001)

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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

$$\kappa = d\rho_D C_V$$

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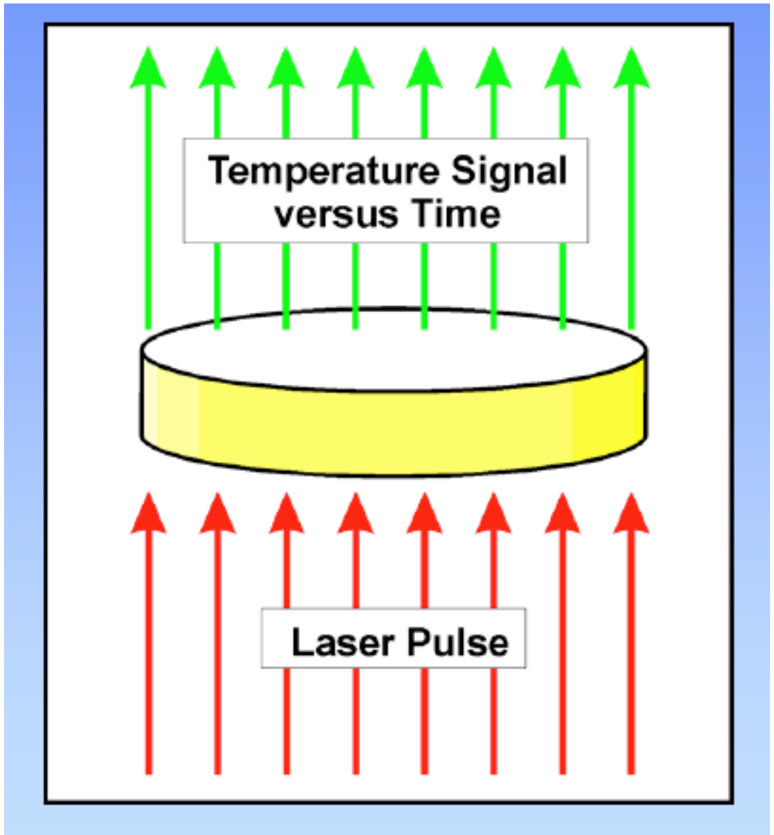
Schematic of the flash method

$$\kappa = d\rho_D C_V$$

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



NETZSCH

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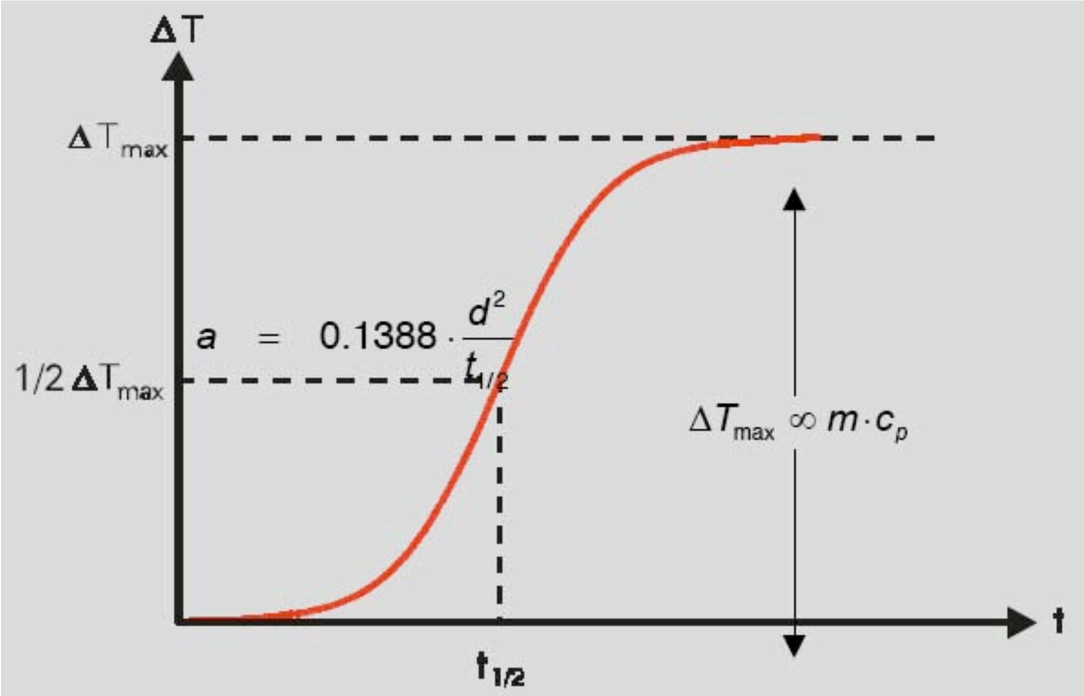
Temperature increase for various experimental conditions

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

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

assumes ideal conditions of adiabatic sample and instantaneous pulse heating



$$\kappa = d\rho_D C_V$$

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

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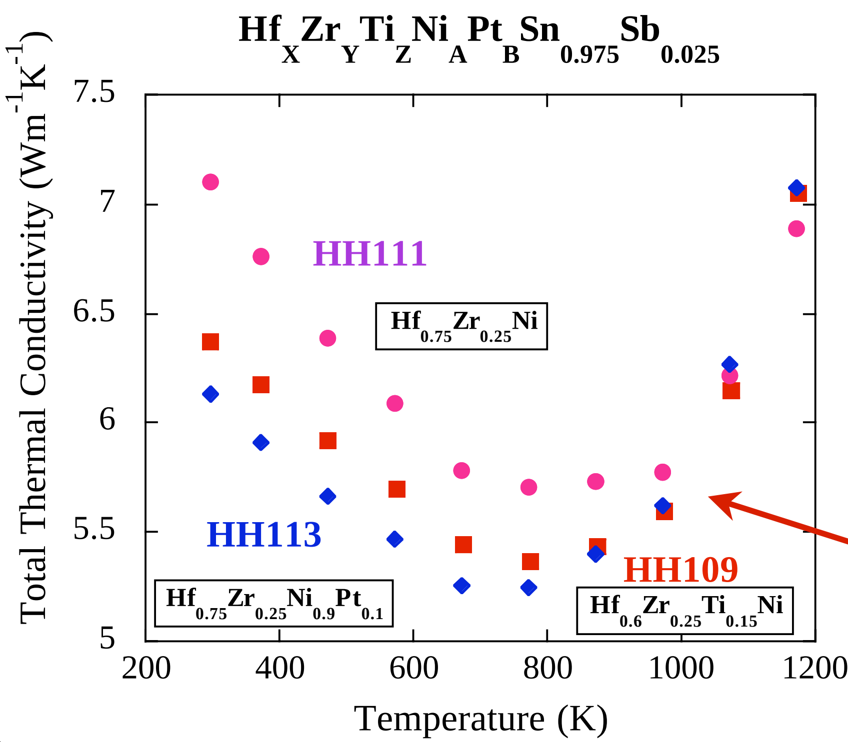
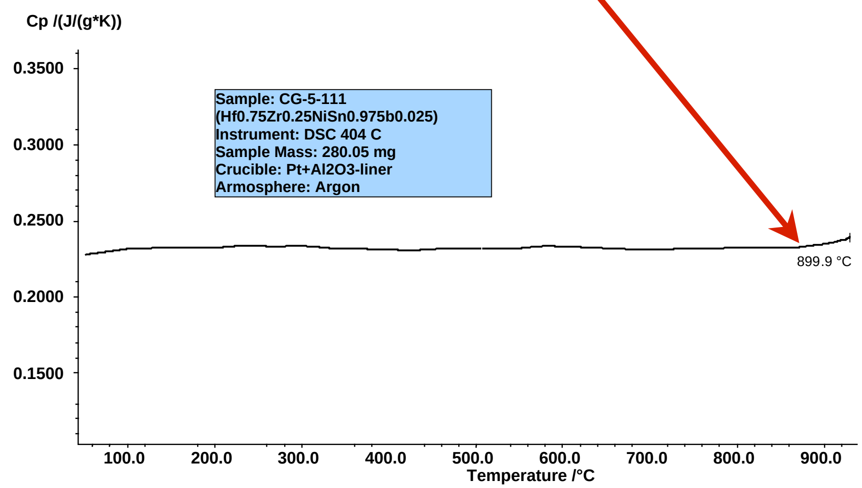
Thermal Analysis Systems:

High Temp DSC in conjunction with Laser Flash
--- **Shows Thermal Stability** of Half Heusler Alloys to 900˚C

UVA & Clemson Results

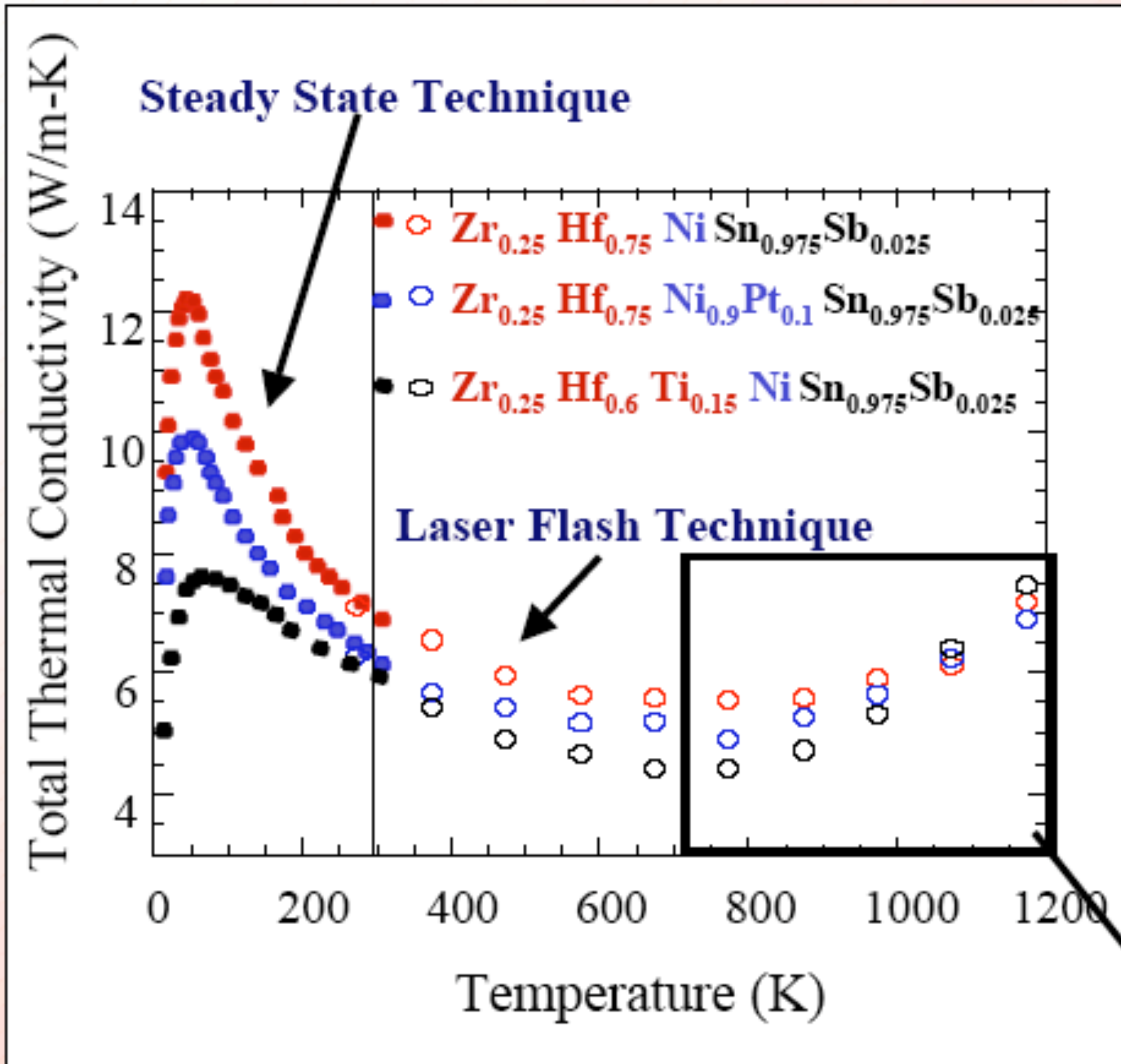




S. Culp, S. J. Poon & T. M. Tritt: APL, 2006

Derived Thermal Conductivity
Half Heusler Alloys to 900˚C

$Ti_{1-x-y}Zr_xHf_yNi\ Sn_{0.975}Sb_{0.025}$



Good Agreement From the Two Systems

Very Different Techniques

Two Carrier Heat Conduction

Acquisition of Commercial High Temperature R & α System

Thermal Analysis/Thermal Measurement

ULVAC-RIKO, INC.

Seebeck Coefficient and Electric Resistance Measuring System **ZEM-2 Series**

Commercial
High Temperature
R & α System

25˚C to 800˚C

Automated

Enhanced Through put

Less Down Time

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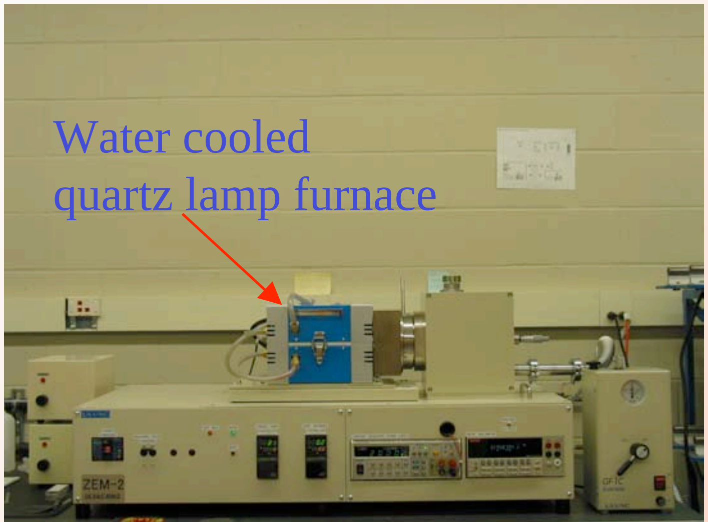
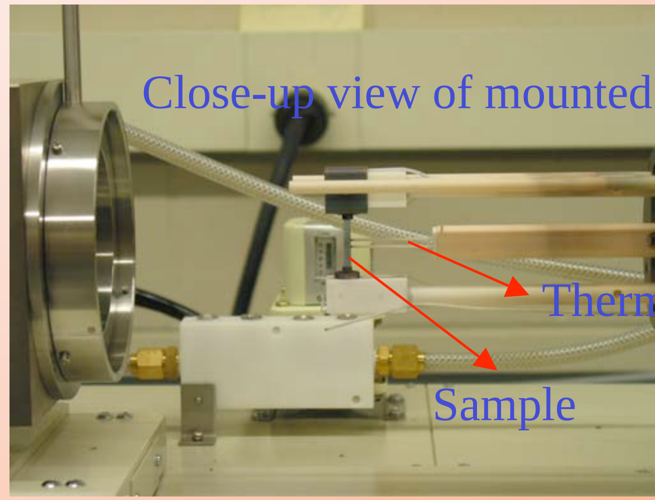
ULVAC (ZEM-2)
Commercial high temp.R & S system





- Temp. range:- 30 to 800°C
- Sample size: 2mm x 2mm x 7mm min.
- Both rod & bar samples can be mounted
- R & S data collected simultaneously
- Completely automated system
- Design allows rapid data collection

See also- V. Ponnalbalam et. al., Rev. Sci Instrum., 2006

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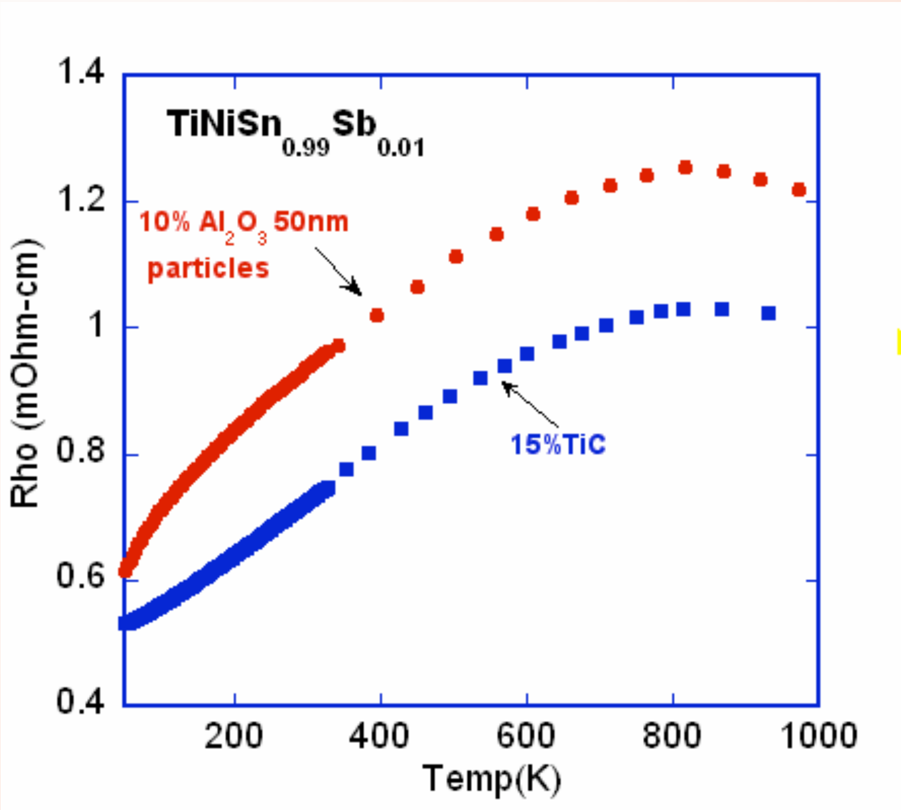
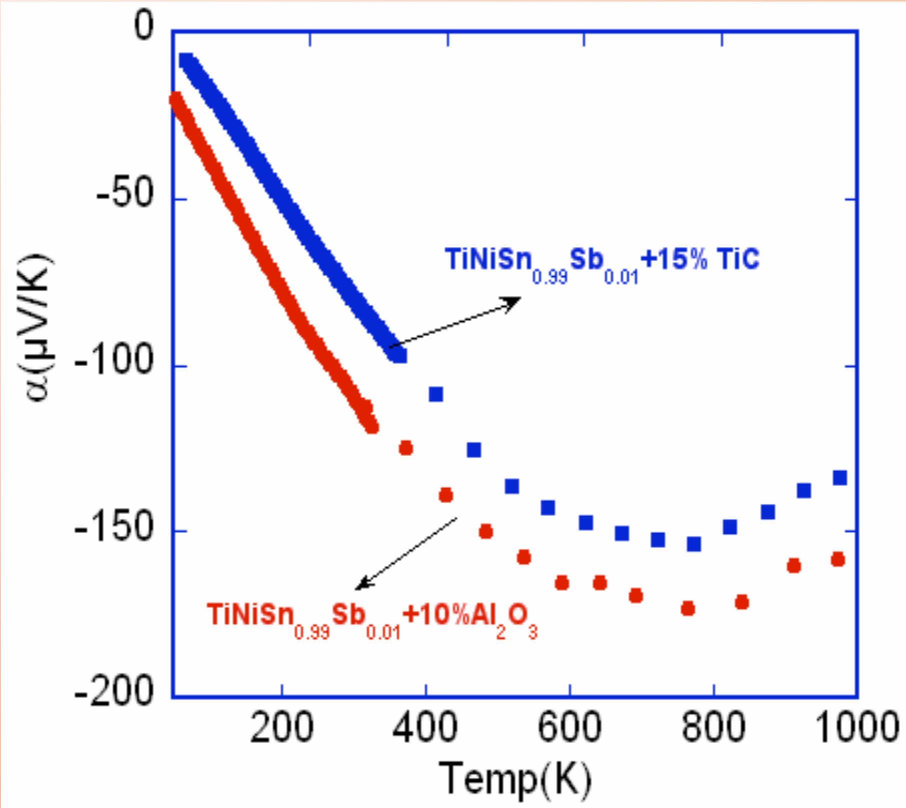
R & S data of $TiNiSn_{0.99}Sb_{0.01}$ nano-composites





Data collected using both low temp. setup and ULVAC (ZEM-2) high temp. system
Data matched well at RT

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Elementary Error Propagation

$$Q = Q(a,b,c)$$

$$\delta Q = \frac{\partial Q}{\partial a}\delta a + \frac{\partial Q}{\partial b}\delta b + \frac{\partial Q}{\partial c}\delta c$$

$$\frac{\delta Q}{Q} = \frac{\delta a}{a} + \frac{\delta b}{b} + \frac{\delta c}{c}$$

$$\boxed{ZT = \frac{\alpha^2 \sigma T}{\kappa} = \frac{\alpha^2 \sigma T}{\kappa_E + \kappa_L} = \frac{\alpha^2 T}{\rho\kappa}}$$

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

$$\kappa = K\frac{L_{TC}}{A}$$

$$\rho = R\frac{A}{L_V}$$

$$\frac{\delta\rho}{\rho} = \frac{\delta R}{R} + \frac{\delta w}{w} + \frac{\delta t}{t} + \frac{\delta L_V}{L_V}$$

High Temp Measurements
d – (κ) by Laser Flash
& DSC (C_P)

Low Temp Measurements
K – (κ) by Steady State

$$\kappa = d\rho_D C_V$$

$$P = K\Delta T = I^2 R - P_{Loss}$$

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} = \frac{\alpha^2 \sigma T}{\kappa_E + \kappa_L} = \frac{\alpha^2 T}{\rho \kappa}$$

$$\kappa = K \frac{L_{TC}}{A}$$

Measure all on One Sample

$$\rho = R \frac{A}{L_V}$$

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High Temp Measurements
d – (κ) by Laser Flash
& DSC (C_P)

Low Temp Measurements
K – (κ) by Steady State

$$\kappa = d\rho_D C_V$$

$$P = K\Delta T = I^2 R - P_{Loss}$$

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} = \frac{\alpha^2 \sigma T}{\kappa_E + \kappa_L} = \frac{\alpha^2 T}{\rho\kappa}$$

$$\kappa = K\frac{L_{TC}}{A}$$

$$ZT = \frac{\alpha^2 T}{\rho\kappa} = \frac{\alpha^2 T}{R\left(\frac{A}{L_V}\right)K\left(\frac{L_{TC}}{A}\right)}$$

$$\rho = R\frac{A}{L_V}$$

At best ≈ 5-7% uncertainly on ZT!

Same Sample -- A cancels

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TE Nanomaterials Growth,
TE Nanocomposites &
Grain Boundary Engineering

Summary Slide Highlights

Expanded Version at End

Various TE Materials Research @ Clemson:

Skutterudites:

Double-filled $In_xYb_yCo_4Sb_{12}$ Skutterudites; J. Peng *et.al.*
Jour. of Appl. Phys., **105**, 084907 (2009);
Jour. of Appl. Phys., **104**, 053710 (2008)

$La_{0.9}CoFe_3Sb_{12}$-$CoSb_3$ Skutterudite Nanocomposites, P.Alboni, *et.al.*
Jour. of Appl. Phys., **103**, 113707, (2008)

Half Heusler Alloys:

(Zr,Hf)Co(Sb,Sn) half-Heusler phases as p-type thermoelectric materials
Slade R. Culp *et.al.* Appl. Phys Letters, **93**, 022105 (2008)

Boundary scattering on the thermal conductivity of TiNiSn-based HH alloys,

S. Bhattacharya, *et.al.* Phys. Rev. B, **77**, 184203 (2008)

Oxide TE Mats:

In-plane thermal conductivity of $Na_xCo_2O_4$ single crystals
Xiaofeng Tang et. al. Phys. Stat. Sol. A, **205 (5),** 1152 (2008)

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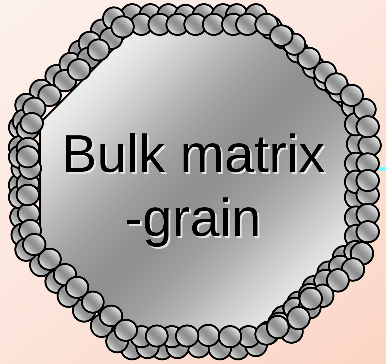
Nanocomposites fabricated by Hydrothermal /solvothermal nano-planting/coating

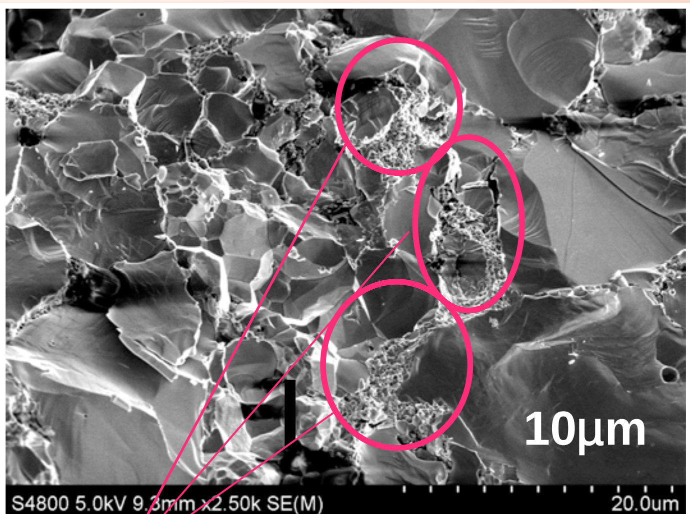
- Nanoparticles are easy to form aggregates.
- In TE nanocomposites, inhomogeneity may de-base the TE performance.



Hot press

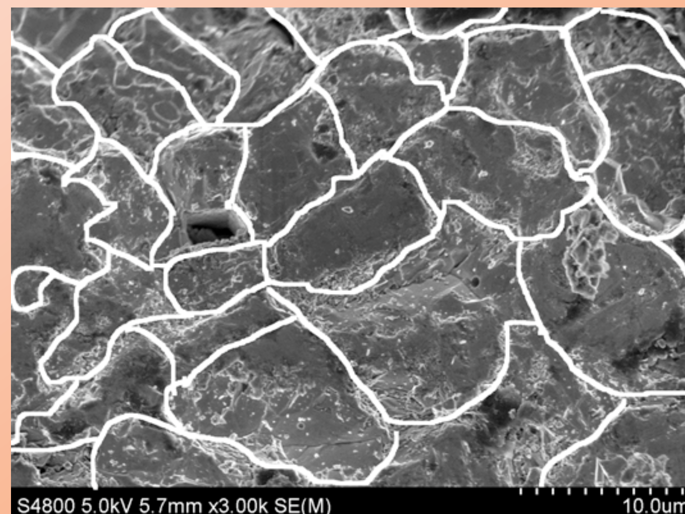
Relatively-homogeneous nanocomposite

Mechanical mixing



Nanoparticle-clusters

Solvothermal nano-coating



Better homogenous distribution of Nanostructures

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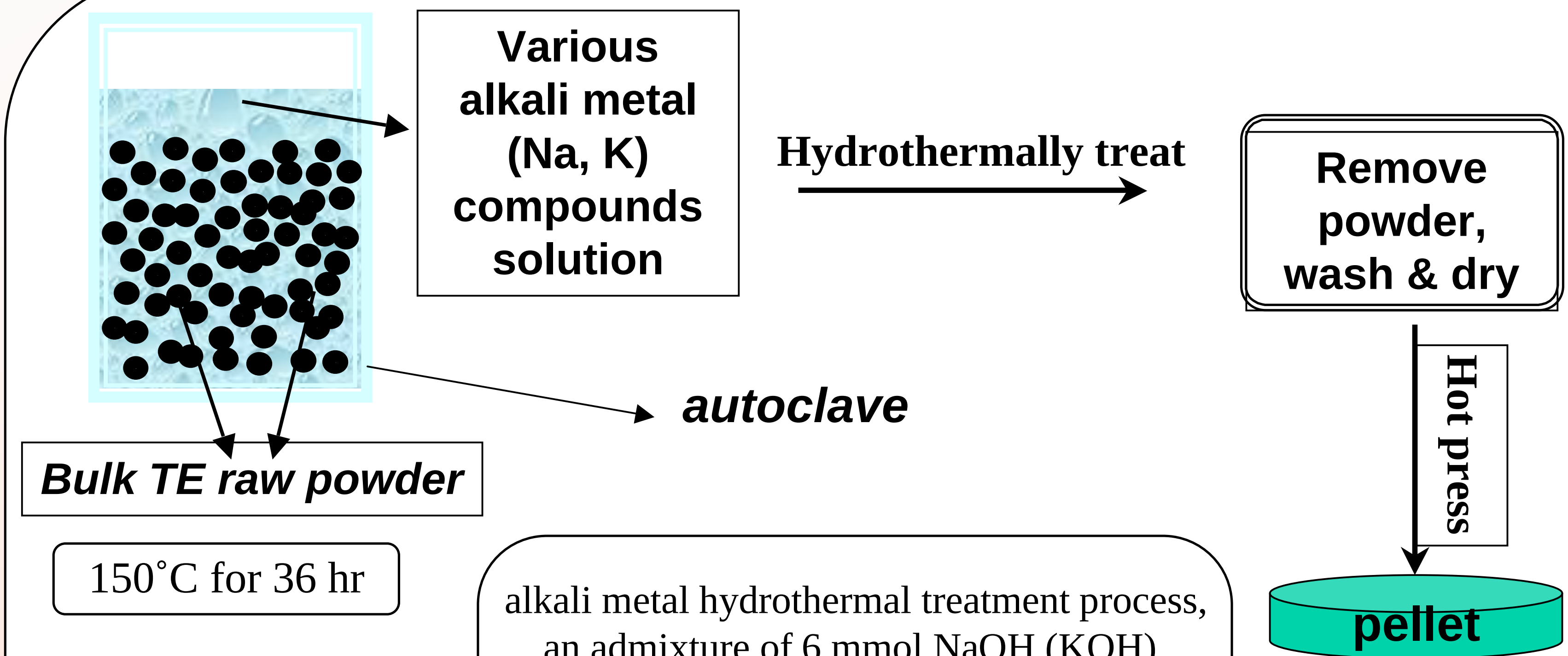
An alkali metal hydrothermal treatment technique

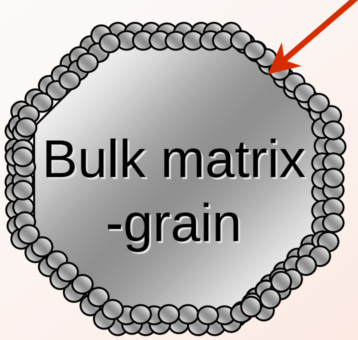


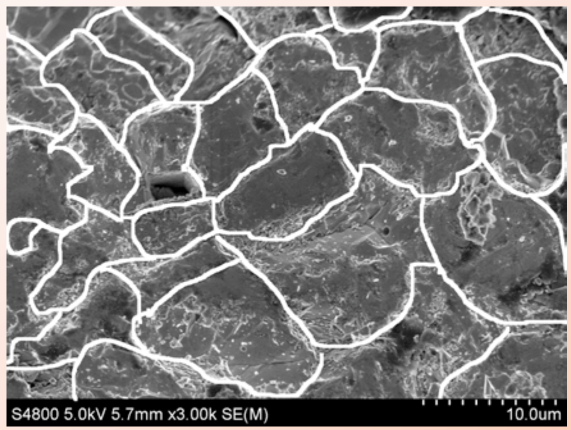
alkali metal hydrothermal treatment process,
an admixture of 6 mmol NaOH (KOH),
2 mmol NaF (KF), 3 mmol $NaBH_4$ (KBH_4)
35 ml distilled water,
and ~ 2.5 g $Pb_{0.75}Sn_{0.25}Te$
bulk reference powder were loaded into
a 45 ml Teflon-lined autoclave

Hydrothermal Treatment of $Pb_{0.75}Sn_{0.25}Te$

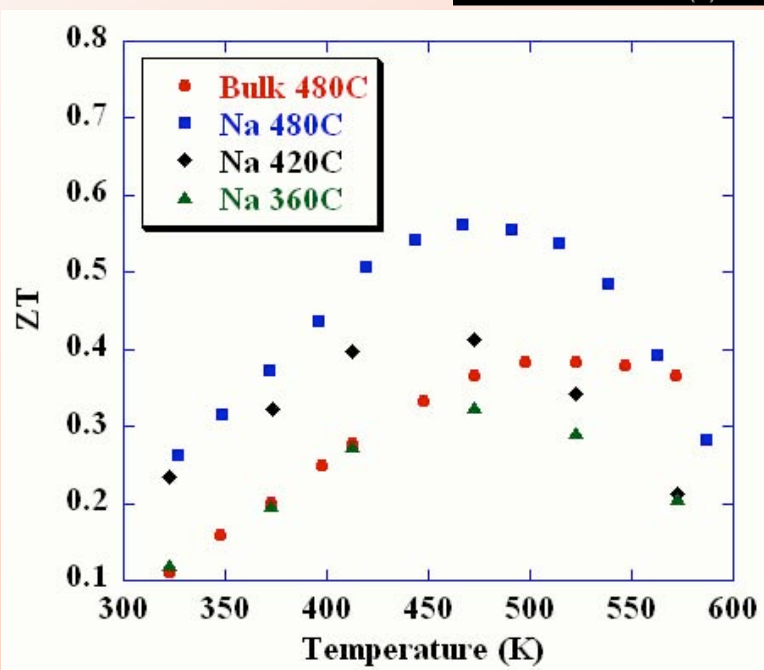
Hydrothermal Treat with NaOH

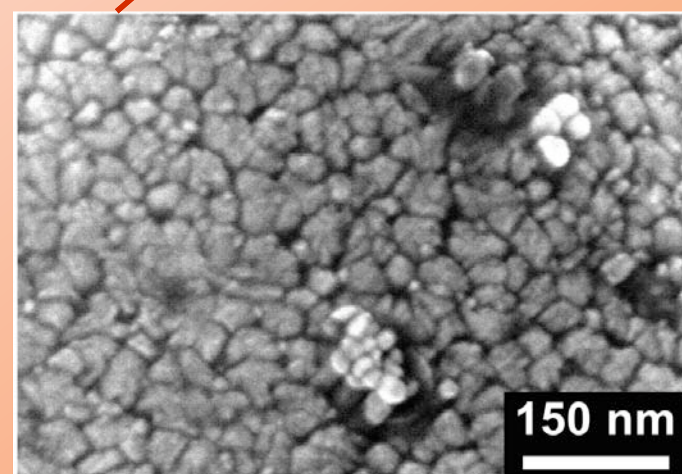
X. Ji. *et.al.*, Phys-Stat-Sol-a-**206**, 221 (2009)





Observe 20-50 nm Clusters
On Surface of $Pb_{0.75}Sn_{0.25}Te$
Hot Pressed to T > 400˚C
(Te rich interface)





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Hydrothermal Treatment of $Pb_{0.75}Sn_{0.25}Te$

X. Ji. *et.al.*, Phys-Stat-Sol-a-**206**, 221 (2009)

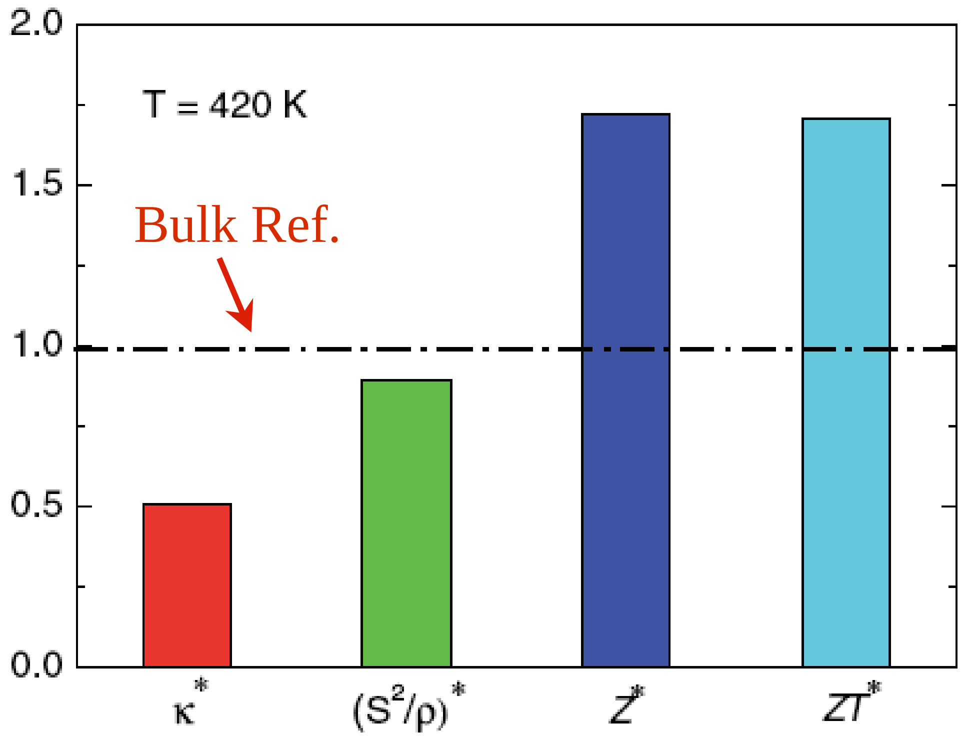

Figure 5 (online colour at: www.pss-a.com) Resulting enhancement of thermoelectric figure of merit at 420 K. Thermal conductivity, power factor, and thermoelectric figures of merit *Z* and *ZT* of Na solution hydrothermally treated $Pb_{0.75}Sn_{0.25}Te$ are normalized by the corresponding values of the bulk reference $Pb_{0.75}Sn_{0.25}Te$. The dash-dotted line shows where the bulk reference is. It is clear that the increases of *Z* and *ZT* are due to

Normalized Properties

Dashed Line -- Bulk reference

Enhancements in ZT Due to Reduction in κ_L!

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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
Also Jour. Appl. Phys., 2009

Supported by China Scholarship Program,
973 Programs and China NSF
US Dept. of Energy EPSCoR

EPSCoR DEPARTMENT of ENERGY

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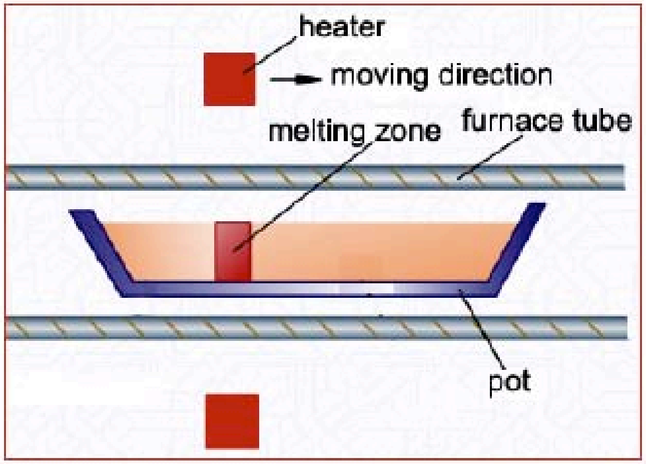
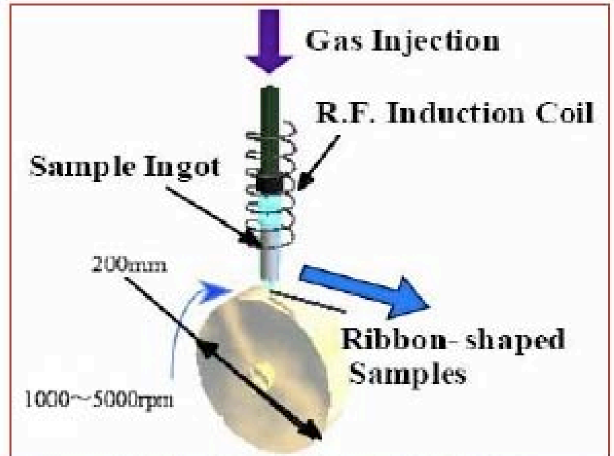
Novel Nanostructures in Melt Spun p-type $Bi_{0.52}Sb_{1.48}Te_3$

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

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

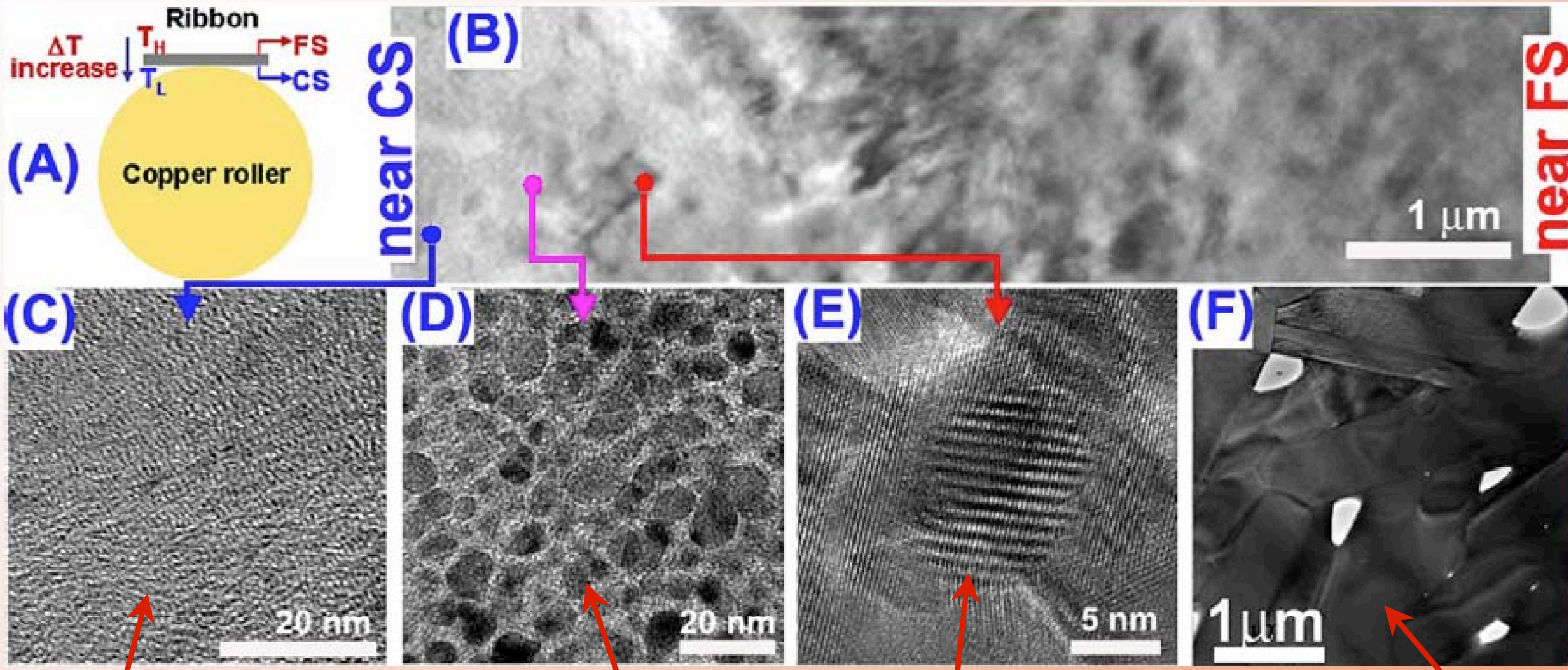
Force ≈ 3-5 KN

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

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

Contact Surface

Free Surface



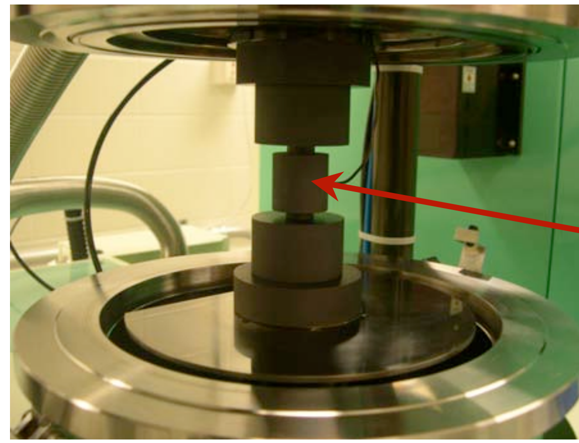
Amorphous Microstructure near Contact surface

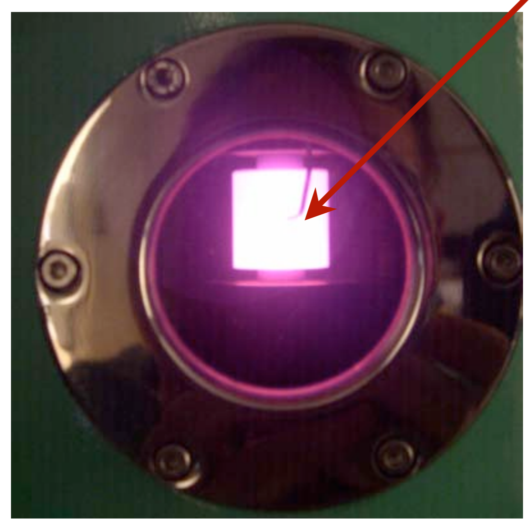
5-15 nm Nanocrystalline Regions or grains near CS

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

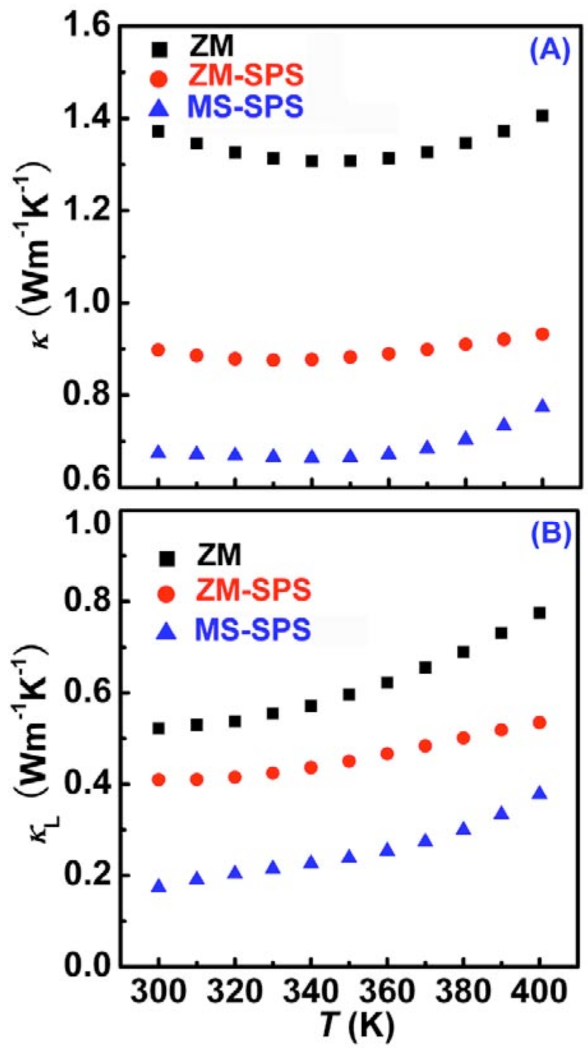
Spark Plasma Sintering System: 1500 Amps

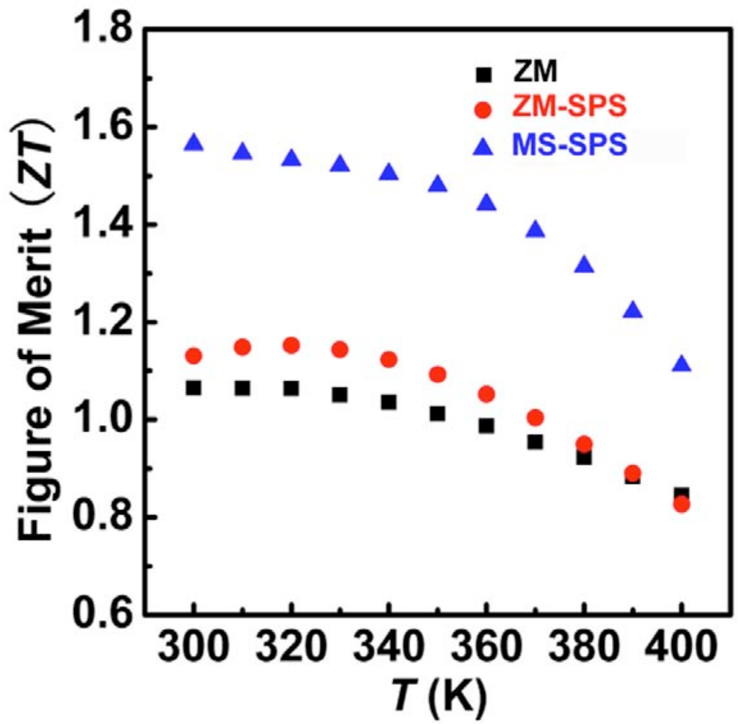




Sample
In Mold

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 ($ZT \approx 1.5$)
Than other samples

Collaboration w. Prof. X. Tang and student Wenjie Xie
Wuhan Univ. of Tech:
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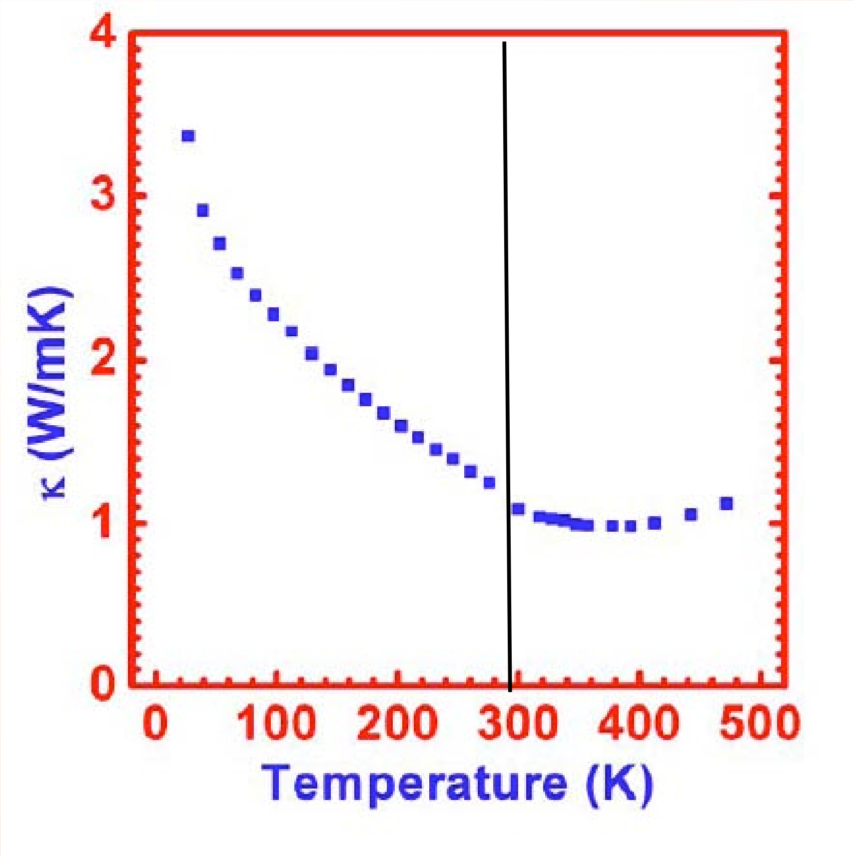
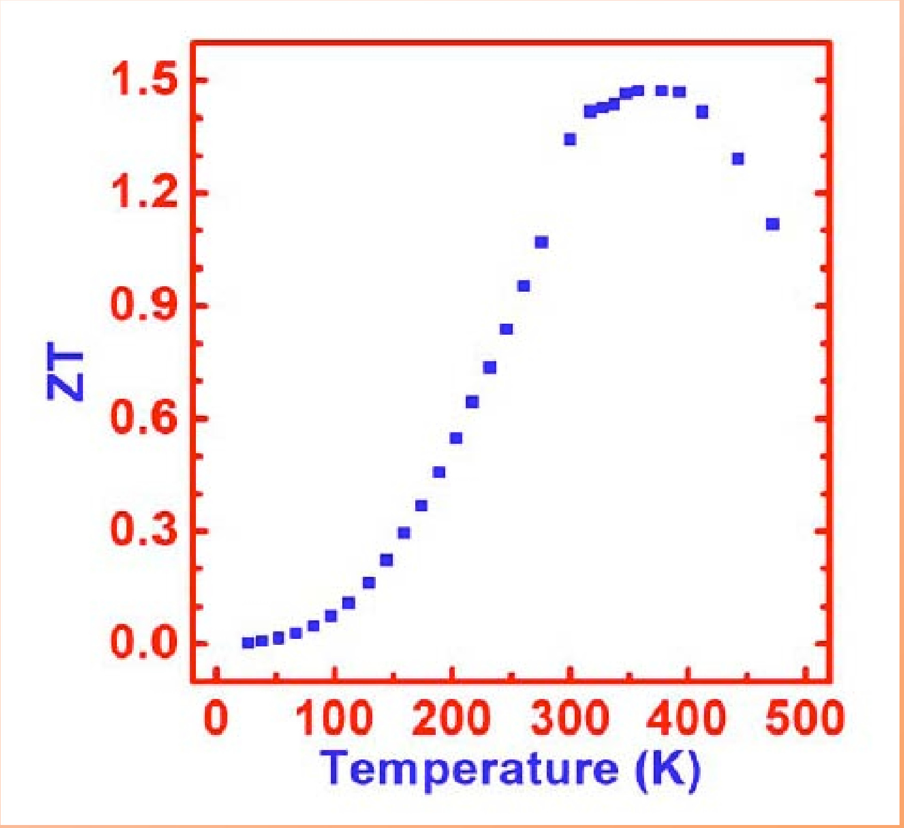
Low Temperature (T < 300K) Properties of MS-SPS -- Bi_2Te_3

Low Temperature (κ) by Steady State Technique
(see Cryogenics- Pope et.al 2000)
High Temp. Using (κ) Laser Flash and DSC





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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 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

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Acknowledgements:

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

SC EPSCoR & Clemson University

DARPA & ONR for Previous Support

Jeff Sharp, Marlow Inds.

Air Force Research Laboratory, Materials and Manufacturing Directorate (AFRL/RXLMD)