Analysis of Advanced Thermoelectric Materials and Their Functional Limits

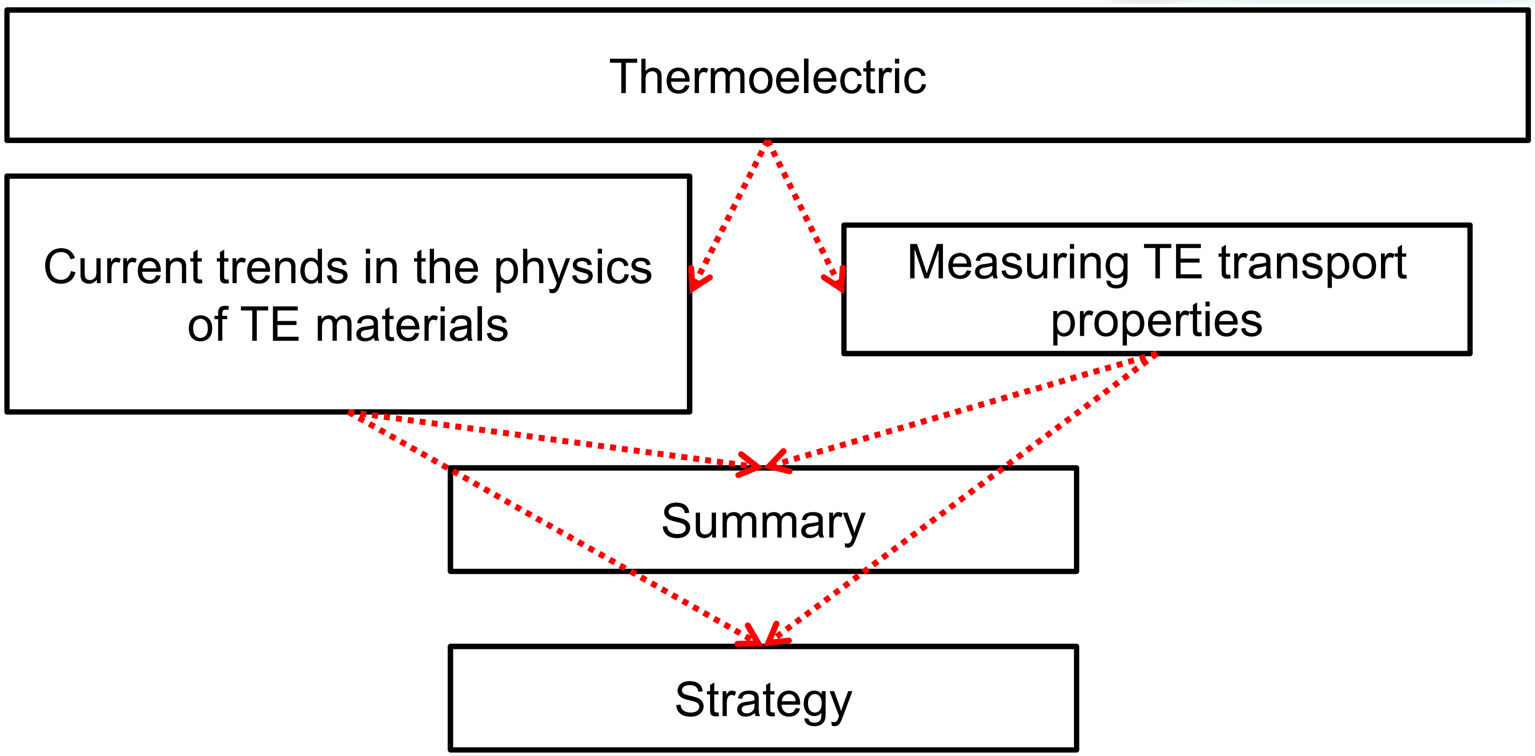
Hyun Jung Kim
(Hyunjung.kim@nasa.gov)

Senior Research Scientist
National Institute of Aerospace

March 09, 2015

Presentation Goal & Outline

- Help audience to establish a strong foundation in fundamental concepts of Thermoelectric
- Share NIA / NASA Langley Research Center TE research



National Institute of Aerospace

- An Independent Non-profit Research and Graduate Education Institute formed in 2002 by a Consortium of Research Universities and the AIAA Foundation
- Conceived by NASA Langley Research Center and established to serve as LaRC's Collaborative Partner
- Conducts Collaborative ***Research*** in Engineering and Science relevant to Aerospace
- Offers Full- and Part-time Resident ***Graduate Education*** in Engineering and the Sciences from Member Universities
- Leads and Participates in a wide range of ***Outreach*** Programs to enhance the nation's Science and Technology Workforce

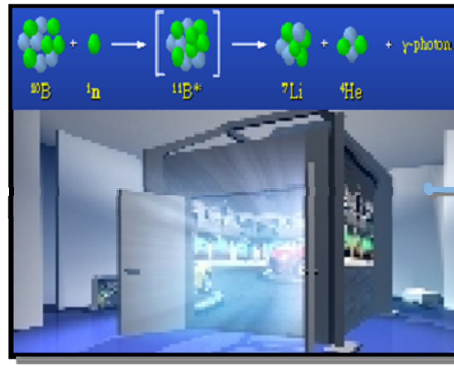
Virginia Business Best Places to Work 2014
2014 WINNER
The National Institute of Aerospace

NPT's Best Nonprofits to Work For ★2014★
WINNER U.S. COMPANIES
The National Institute of Aerospace

Structures, Materials, Measurement Sciences

Aerodynamics, Hypersonics, Acoustics
Flight Dynamics, Aviation Safety and Aerospace Operations
Planetary Exploration, Atmospheric Science, and Global Environmental Change

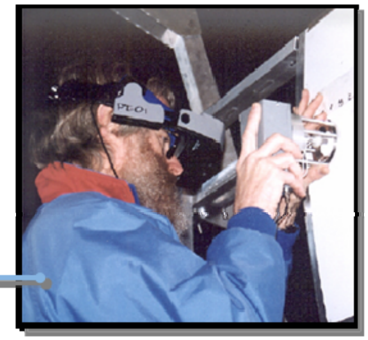
Materials Synthesis & Processing



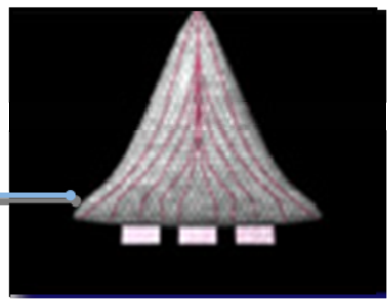
Analytical & Computational Methods

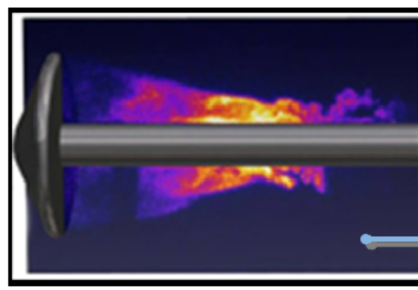
Durability & Damage Tolerance

Nondestructive Evaluation



Structural Health



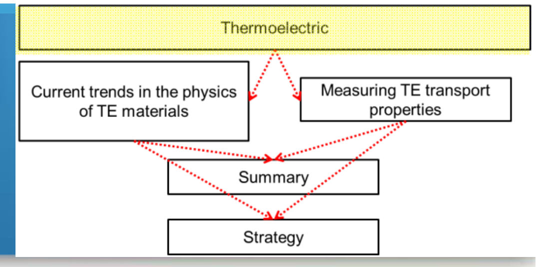


Advanced Sensing & Optics

Structural Concepts

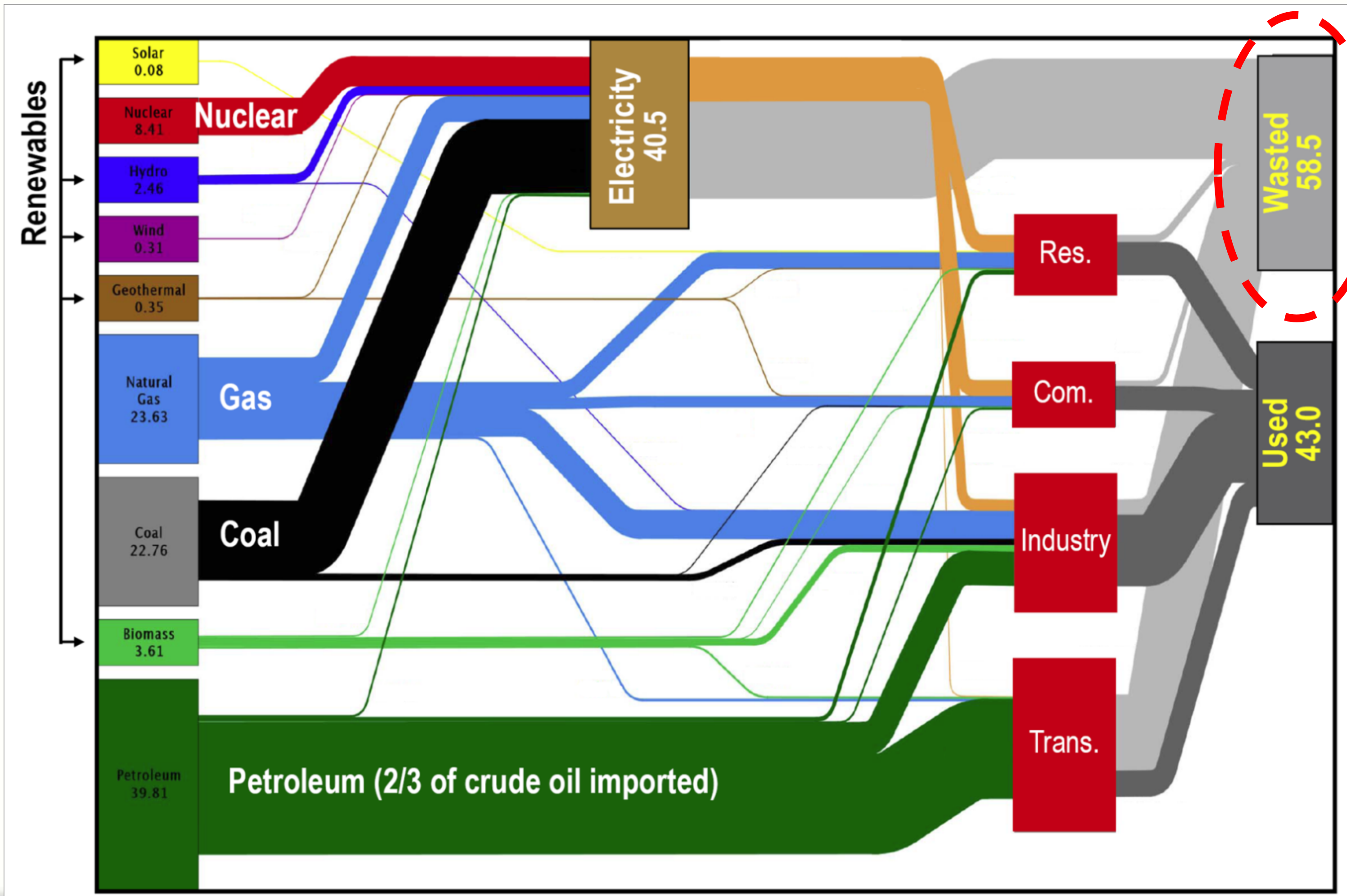
All images credit: NASA

Energy and Thermoelectric
(Potential of TE)



U.S. Energy Consumption ~ 102 Quads (2007)

"Waste Heat" Can Be Utilized Using Thermoelectrics



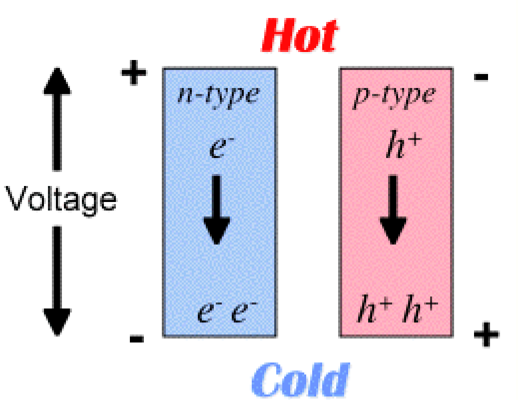
Source: LLNL 2008, data from DOE/EIA -0384 (2006)

Thermoelectrics (TE) and background physics

Thermoelectric materials are a group of electronic materials which can interconnect gradients in electrical potential and temperature.

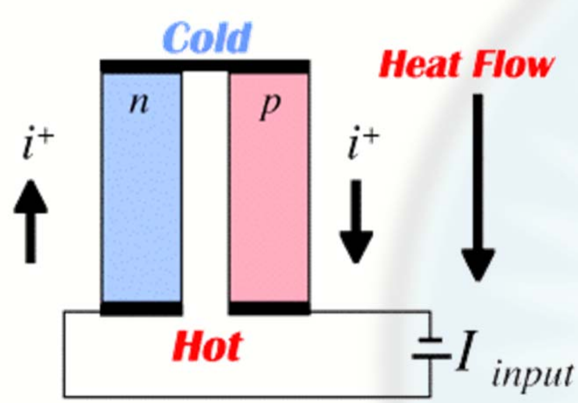
Physics of TEs are governed by **three thermodynamics effects**

Seebeck effect (1822)
Heat → electric current



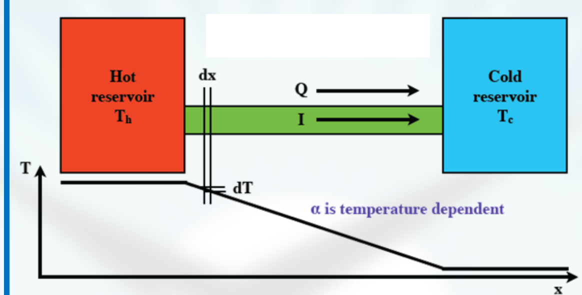
$V = \alpha \Delta T$
V = Voltage
α = **Seebeck coefficient**
ΔT = Temperature difference

Peltier effect (1834)
Current → cooling



Peltier coefficient is the energy carried by each electron per unit charge & time

Thomson effect (1850s)

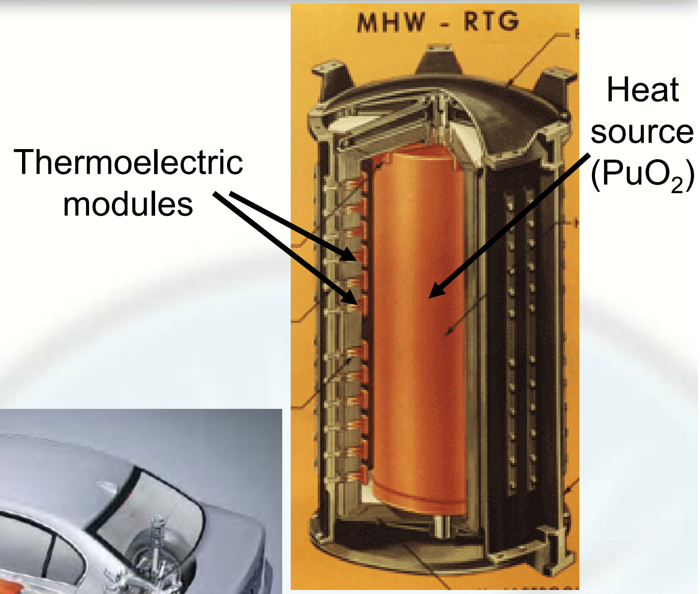


Released or absorbed internally in a material if the Seebeck coefficient depends on temperature, balancing for the flowing Peltier heat.

All effects are related to heat being transported by the charge carriers.

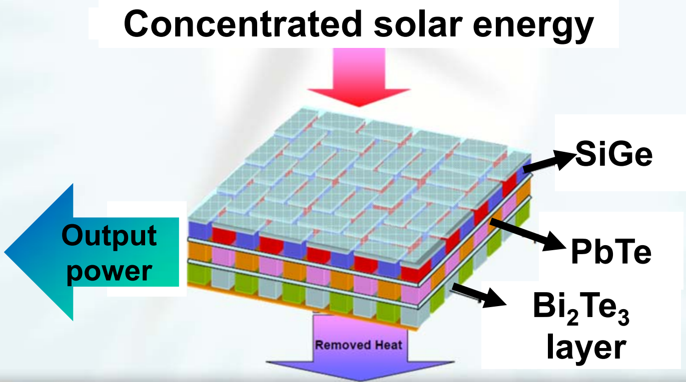
Historic development of TE materials based on applications

- RTG power system for deep space exploration



- VW and BMW announced TE on exhaust in 2008
  : 24 Bi_2Te_3 modulus
  : 600W under motorway driving →
  30% of car's electrical requirement
  : 5% reduction in fuel consumption through
  removing alternator

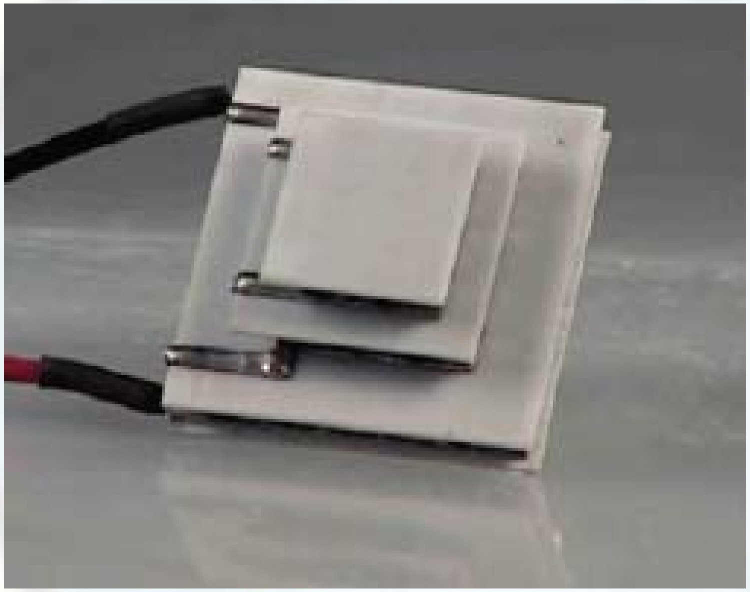
- Hybrid low cost power sources
  - Advanced TE system in tandem mode
  for high gain of cascade efficiency
  - Solar thermal applications(Photovoltaic + TE)



Shakouri and Zhang, IEEE trans. 28, 65 (2003); Sang H. Choi, SPIE Newsroom. DOI: 10.1117/2.1200604.0234 (2006)

Why use Thermoelectrics?

- No moving part → no maintenance
- Peltier Coolers: fast feedback control mechanisms → $\Delta T < 0.1^{o}C$
- Scalable to the nanoscale → physics still works (some enhancement) but power ∝ area



- Most heat sources are "static"
- Waste heat from many systems could be harvested

home, Industry, background

Efficiency of the TE materials and conversion efficiency

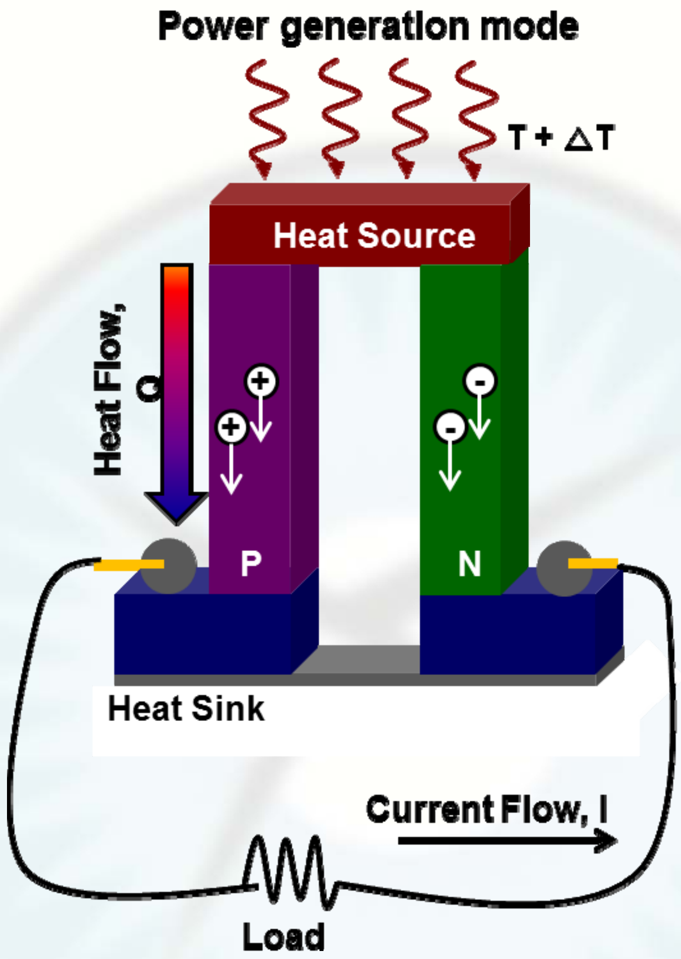
- Efficiency determined by Dimensionless figure of merit

$$ZT = \frac{\sigma S^2}{\kappa} T$$

S = seebeck coefficient
σ = electrical conductivity
κ = thermal conductivity
ε = efficiency of a TE device for electricity generation

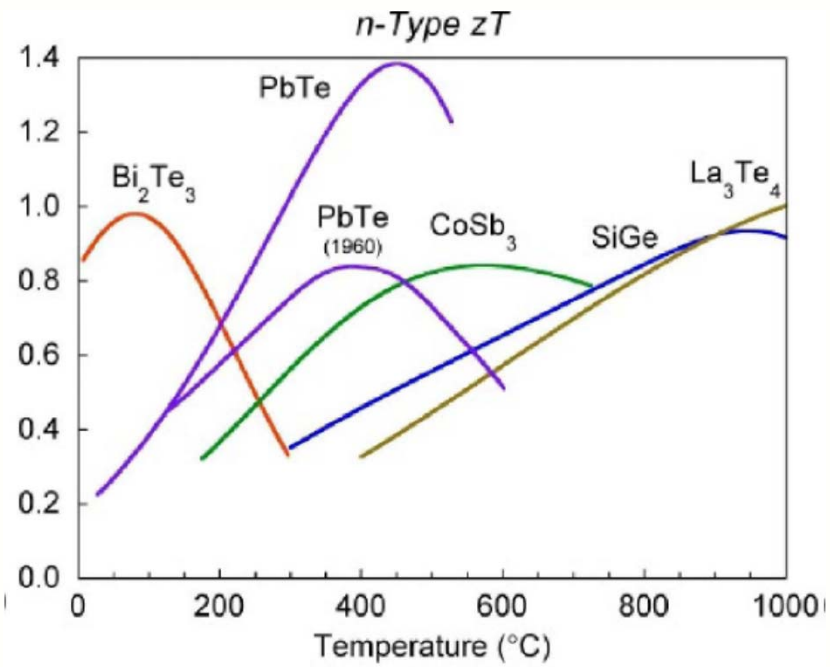
$$\varepsilon = \frac{T_H - T_C}{T_H} \cdot \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + \frac{T_C}{T_H}}$$

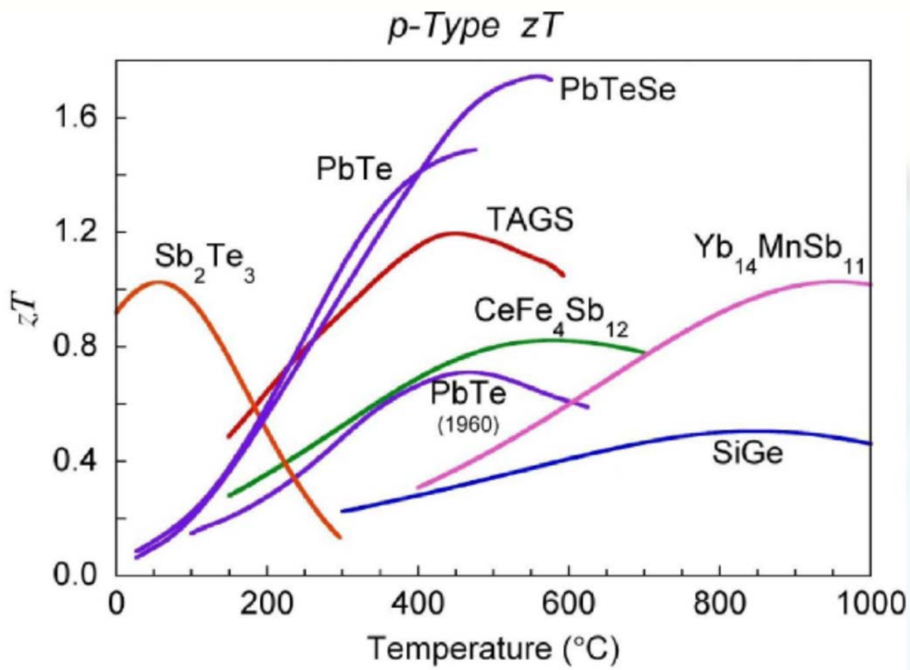
= Carnot X Joule losses and irreversible processes



ZT versus Temperature range

Different material harvest optimally at different temperature ranges

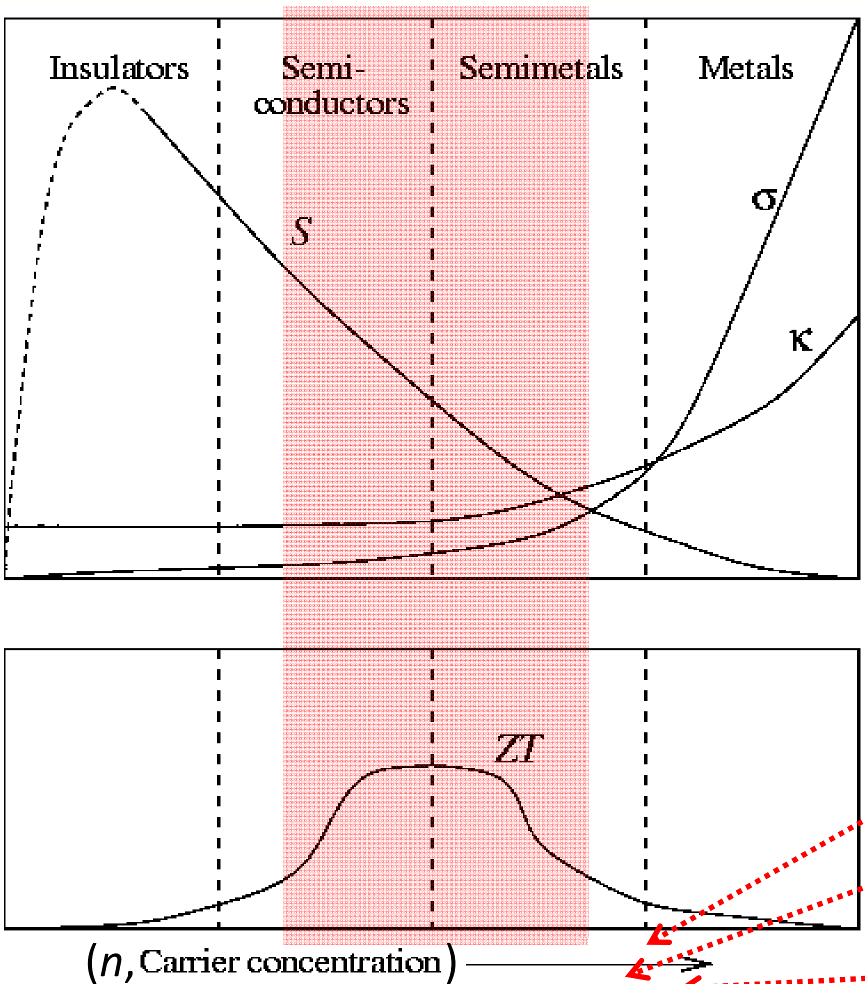




- Bulk n-Bi_2Te_3 and p-Sb_2Te_3 used in most commercial Peltier coolers
- Bulk $Si_{1-x}Ge_x$ (x~0.2 to 0.3) used for high temperature satellite applications

G. J. Snyder et al., Nature Mat., 7, 105, 2008

TE properties of conventional materials



Conflicting Materials Requirements

S (Seebeck coefficient)
Need small n, large m*
- Semiconductor (valence compound)

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{\frac{2}{3}}$$

σ (Electrical conductivity)
Need large n, high μ, low m*
- Metal

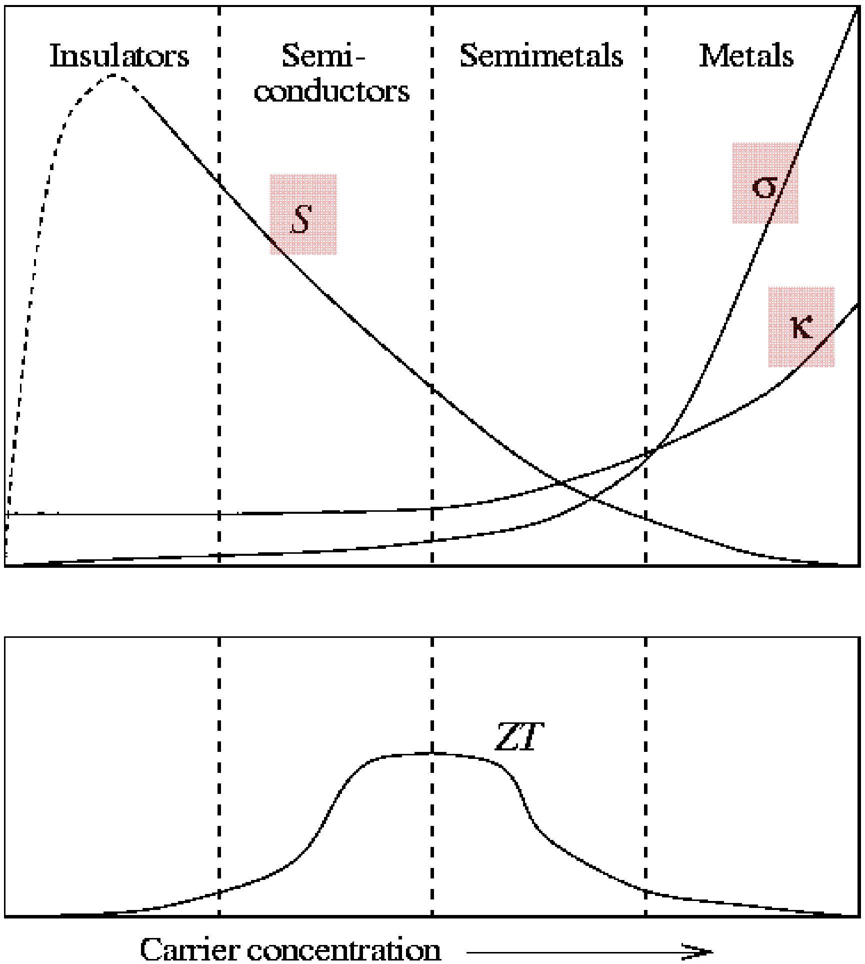
$$\sigma = ne\mu$$

k (Thermal conductivity)
Desire small k_{ph}, small *n*

$$k = k_{ph} + LTne\mu$$

L: Lorentz constant, K_e and K_{ph} correspond to carrier and phonon contribution to thermal conductivity, respectively. m*: carrier effective mass

TE properties of conventional materials (Cont.)



For most bulk materials…

$$ZT = \frac{S^2\sigma}{\kappa}T = \frac{S^2\sigma}{\kappa_e + \kappa_{ph}}T = \frac{S^2}{L + (\kappa_{ph}/\sigma T)}$$

To increase *ZT*, we want

$S\uparrow,\ \sigma\uparrow,\ \kappa\downarrow$ but $S\uparrow \Leftrightarrow \sigma\downarrow$

$\sigma\uparrow \Leftrightarrow \kappa\uparrow, S\downarrow$

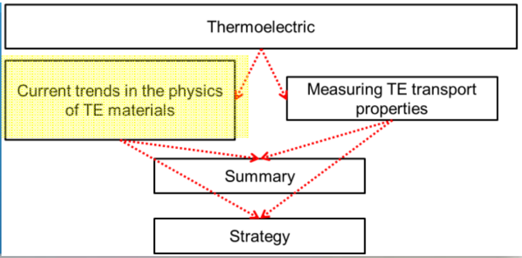
- Empirical law from experimental observation that

$$\frac{k}{\sigma T} = \text{constant for metals}$$

- For low carrier densities in semiconductors, $k_e << k_{ph}$
- For high carrier densities in semiconductors, $k_e >> k_{ph}$
- Good TE materials should ideally have $k_e << k_{ph}$

G. J. Snyder et al., Nature Mat., 7, 105, 2008

Current trends in the physics of TE materials
(Main strategies for optimizing ZT)



$$ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_{ph}} T$$

"Electron Crystal (crystalline semiconductor) – Phonon Glass (insulator)"

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{\frac{2}{3}}$$

$$= -\frac{\pi^2}{3}\frac{k_B}{e} k_B T \left[\frac{d\ln(\sigma)}{dE}\right]_{E_F}$$

$$= -\frac{\pi^2}{3}\frac{k_B}{e} k_B T \left[\frac{1}{G}\boxed{\frac{dG}{dV_g}\frac{dV_g}{dE}}\right]_{E_F}$$

$$S_i = \frac{1}{(eT)}\left[\frac{<\boxed{E\tau>}}{<\tau>} - E_f\right]$$

$$\sigma = ne\mu$$

- ► Low-dimensional structures:
  - Quantum confinement effect
  - Increase S through enhanced DOS
  - Make S and σ almost independent
- ► Energy filtering

Y. I. Ravich et al., Phys.Stat. Sol (b), 43, 453, 1971

Main strategies for optimizing ZT (cont.)

$$ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_{ph}} T$$

"Electron Crystal (crystalline semiconductor) – **Phonon Glass (insulator)**"

$$k = k_{ph} + LTne\mu$$

► Reducing thermal conductivity faster than electrical conductivity

- Skutterudite structure: filling voids with heavy atoms

► Low-dimensional structures:

- Reduce k through numerous interfaces to increase phonon scattering

► In metals, the thermal conductivity is dominated by k_e

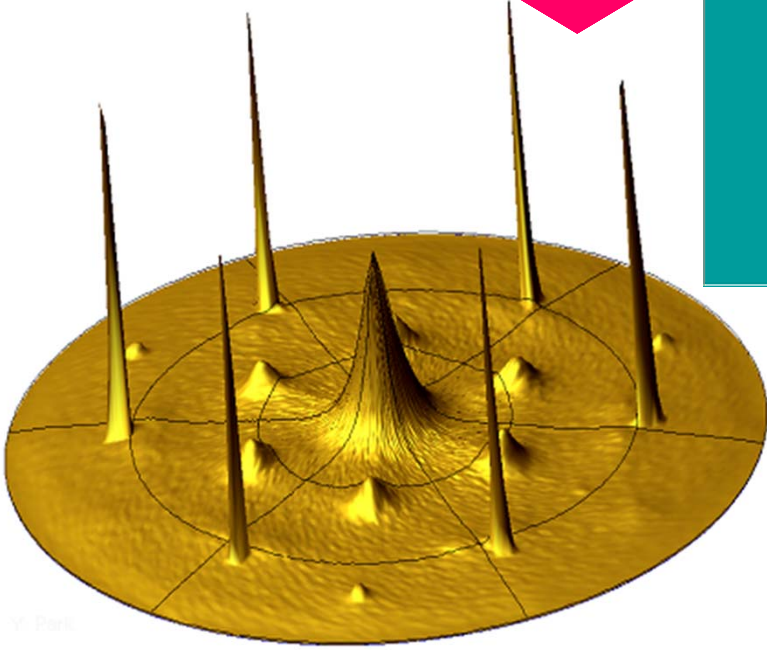
- Exceptions
  - some pure metals at low temperatures
  - certain alloys where small k_e results in significant k_{ph} contribution
  - certain low dimensional structures where k_{ph} can dominant

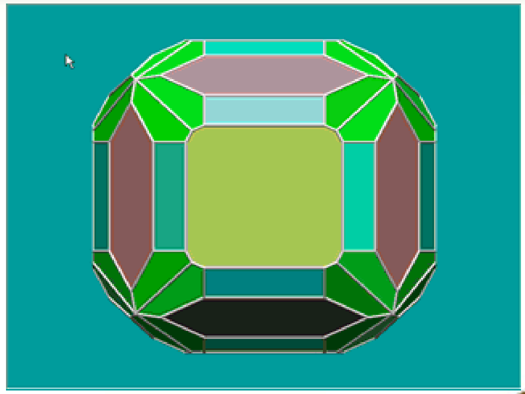
NIA / NASA Results

1st Approach:
SiGe twin crystal for high temperature application

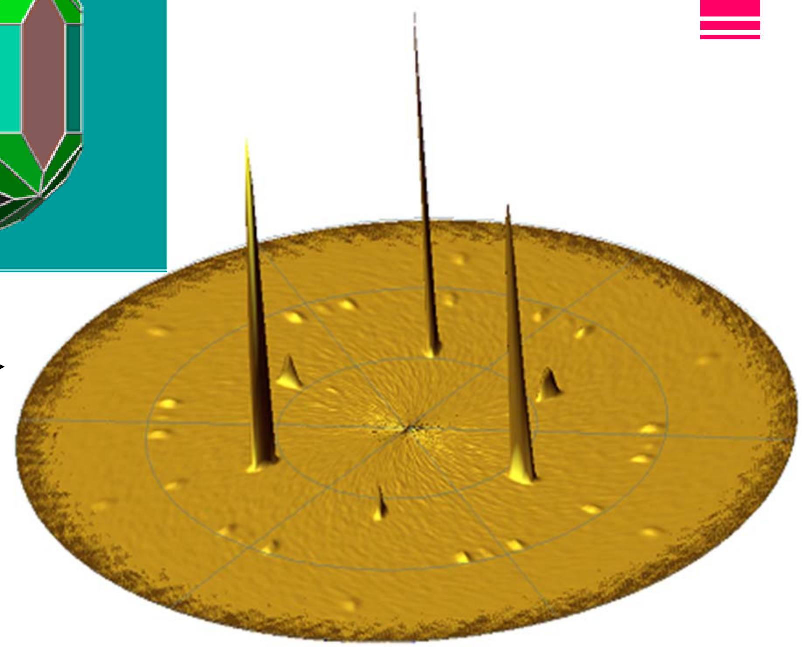
σ, k

Thermal conductivity ↓





Electrical conductivity ↑



↔ Material Design

Highly Twinned SiGe Layer

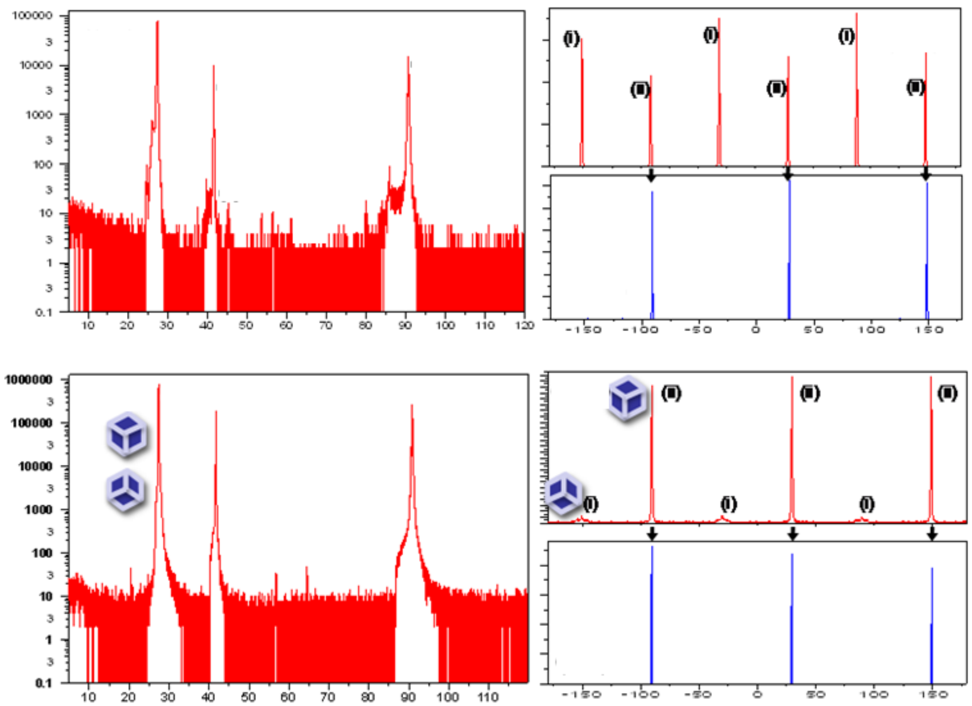
Phonon-scattering for Thermoelectric Material Application

85% Single-Crystalline SiGe Layer

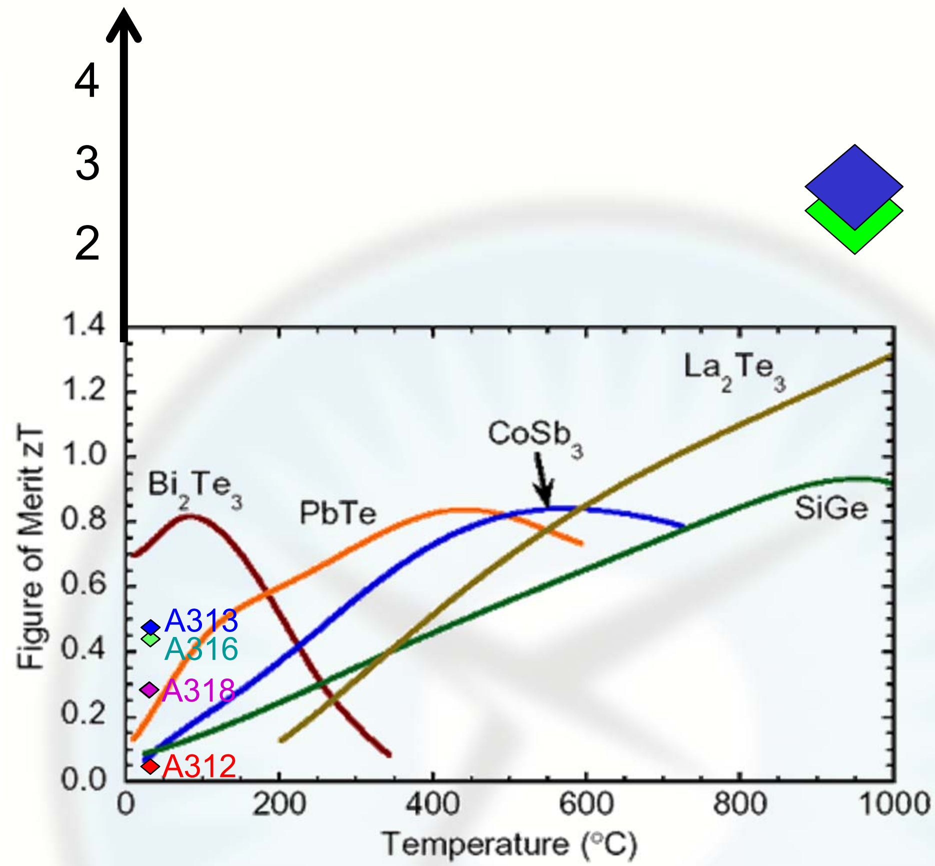
High-Mobility Semiconductor Device Application

{220} pole-figures of [111]-oriented SiGe on trigonal substrate

Figure of merit results



X-ray diffraction measurement on two-samples- (1) grown at 820°C and (2) 850°C.

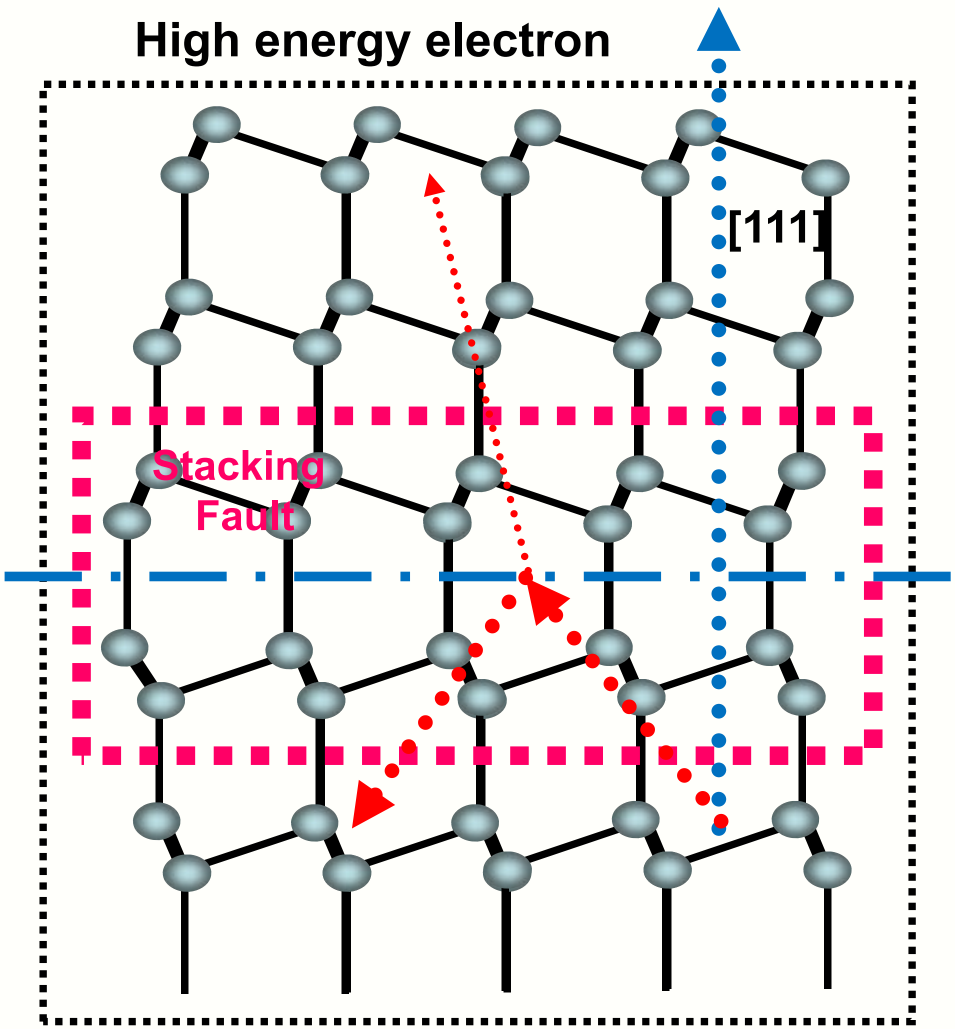


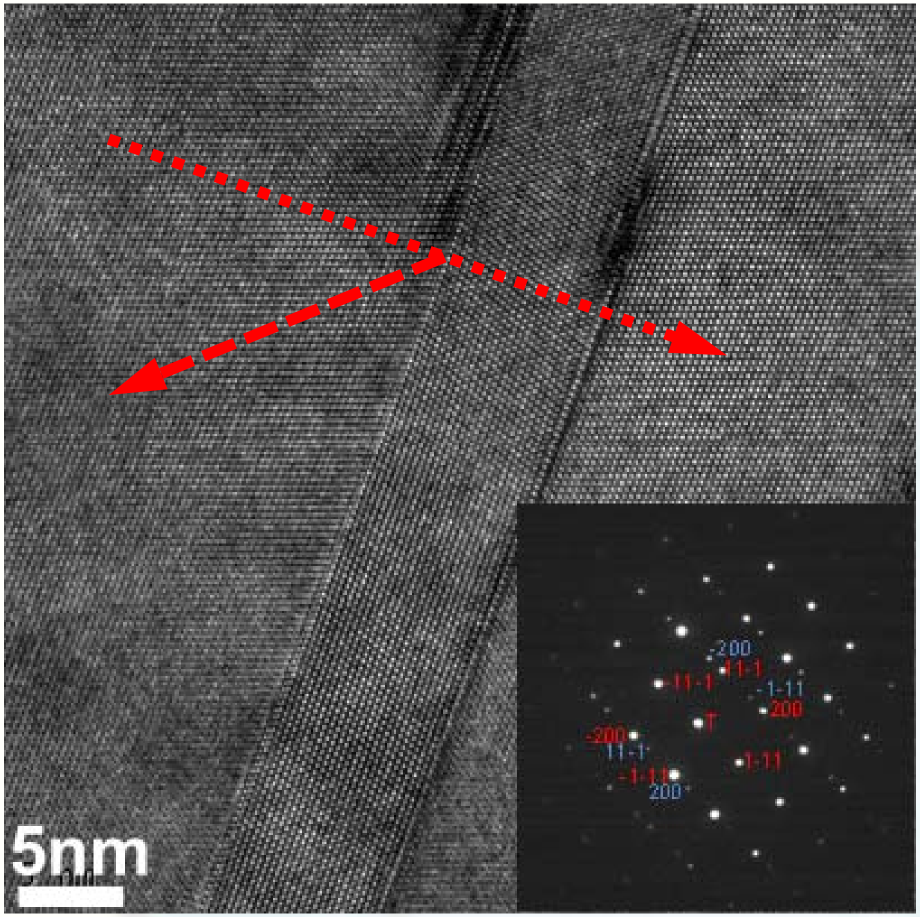
SiGe – TE performance at 300K and 1000K

http://www.its.caltech.edu/~jsnyder/thermoelectrics/index.htm

2^{nd} **Approach**:
SiGe twin crystal for high temperature application

S





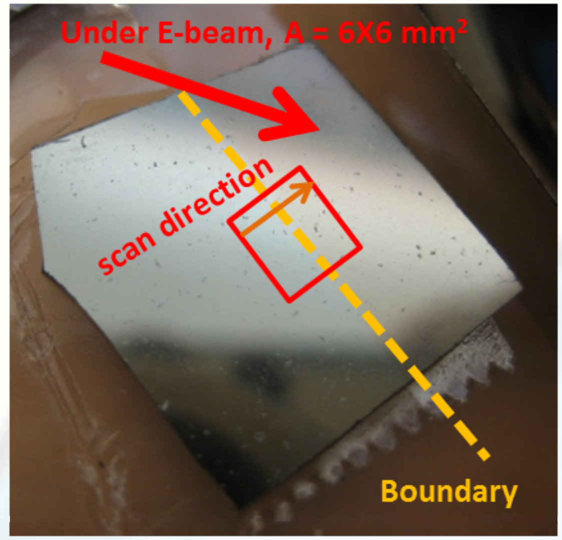
Scanned Seebeck coefficient results

(a)

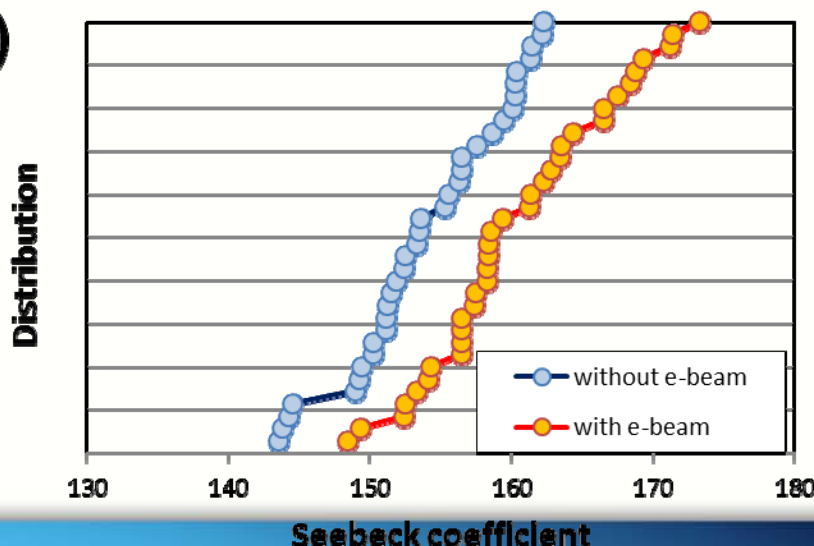
130 — 180

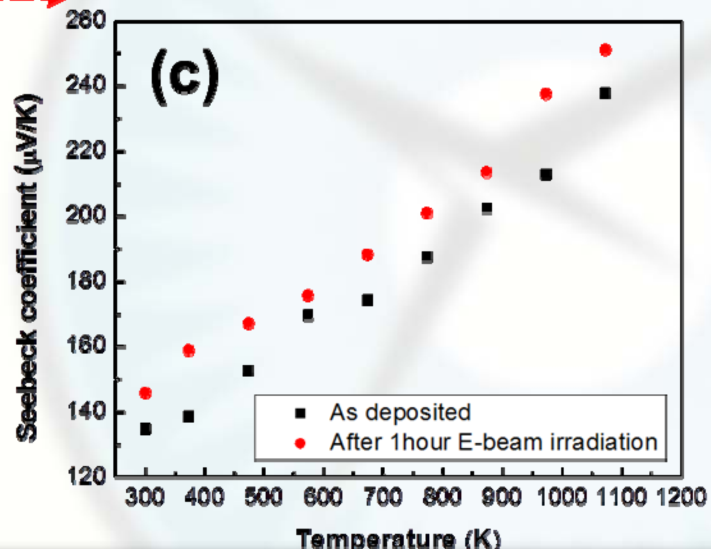
143.5	156.2	151.8	156.4	144.2	164.3	153.3	154.1	161.3	171.1
163.3	162.3	140.4	162.1	155.2	179.4	139.3	146.3	180.4	169.2
151.1	151.2	158.6	150.2	152.5	166.4	132.4	163.5	167.4	168.7
160.0	162.2	167.2	161.4	163.2	179.5	152.5	148.4	178.3	168.3
159.5	162.4	160.2	153.5	141.2	179.4	163.4	142.5	180.2	166.4
167.2	151.5	153.3	161.4	152.3	161.2	157.4	156.4	162.2	162.8
160.2	148.9	157.5	162.4	162.3	158.4	149.3	145.4	158.2	152.4
153.5	142.4	150.2	155.5	149.3	158.5	178.3	179.5	156.4	156.4
143.4	143.2	151.1	143.8	149.2	158.3	173.2	171.3	156.5	154.2
142.5	144.5	156.4	143.3	160.3	159.3	147.4	144.2	157.3	158.2

Not irradiated — Irradiated



(b)

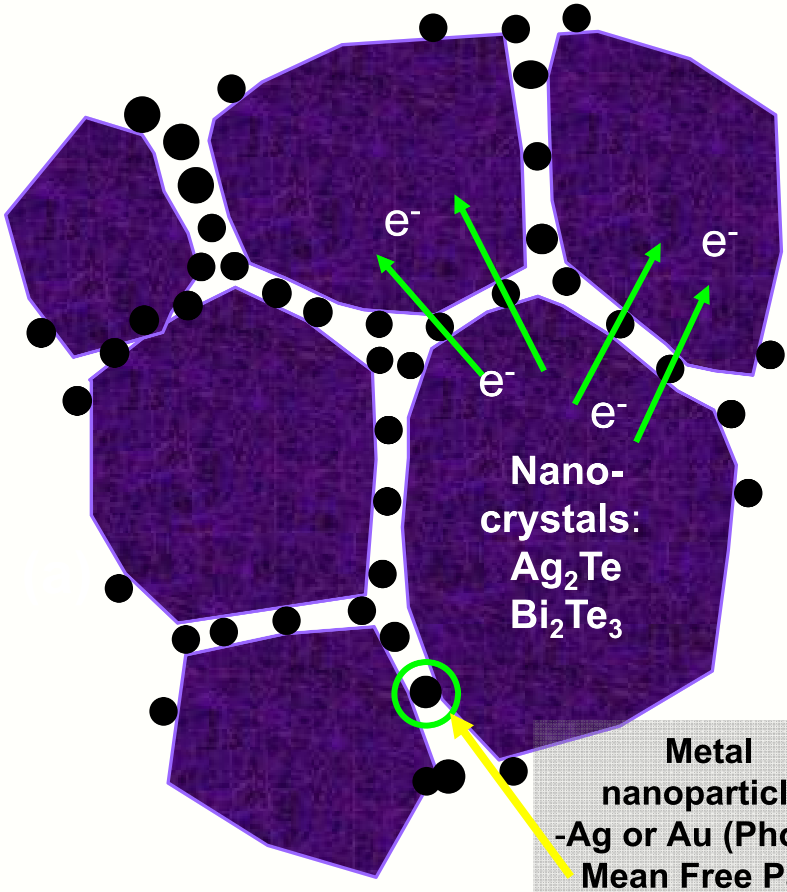




Hyun Jung Kim *et al.*, *RSC Advances*, C2RA21567E, 2012

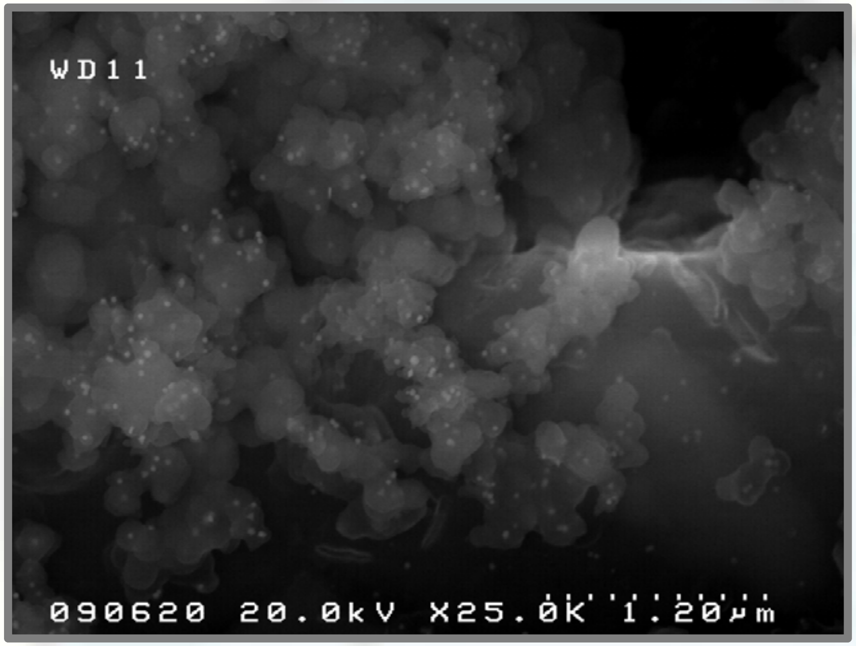
Bi_2Te_3 and Ag_2Te nano-bridge for intermediate / low temperature application

K_{ph}

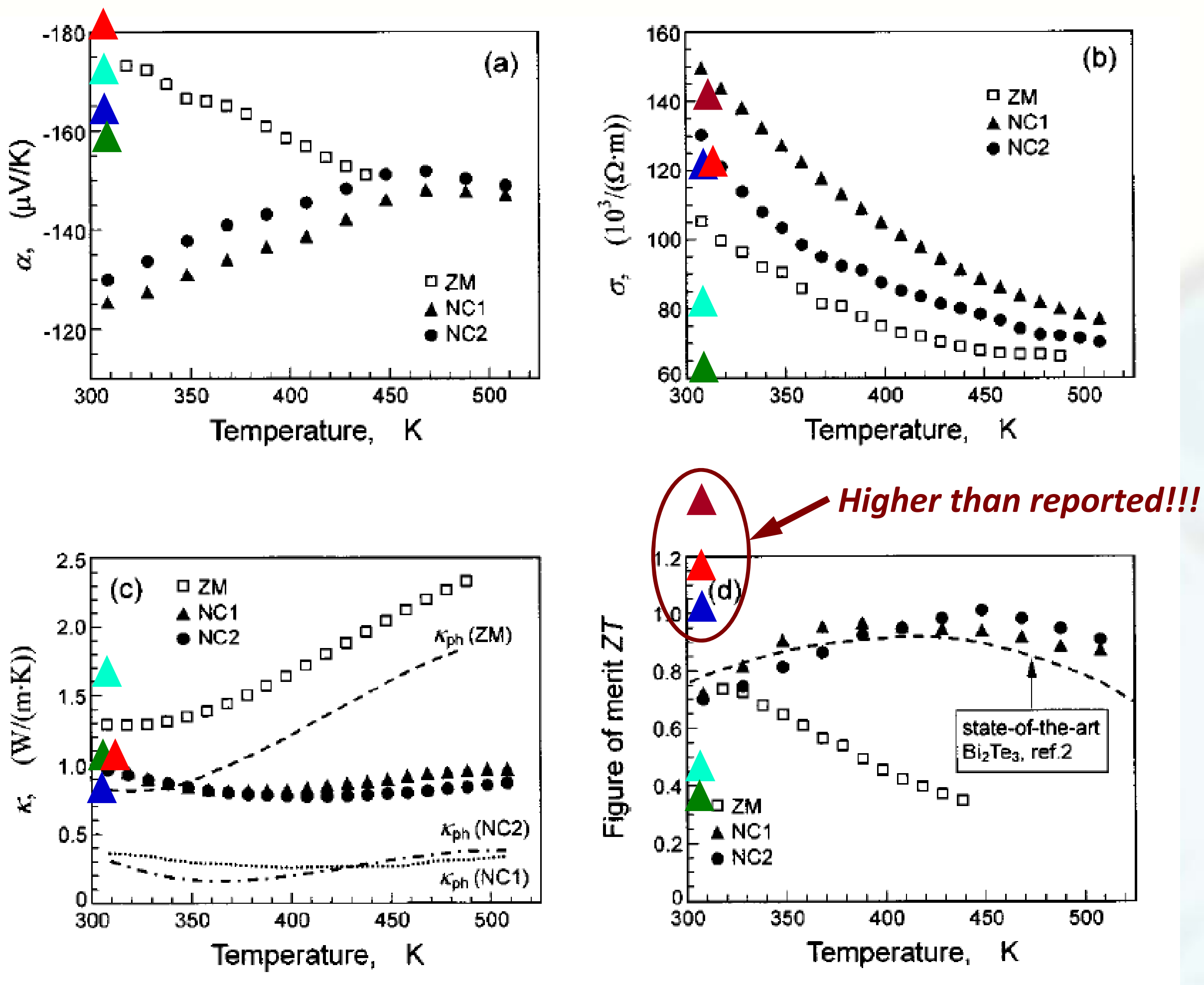


:

0.5 wt% Ag / BiTe



Test results and comparison of Bi_2Te_3

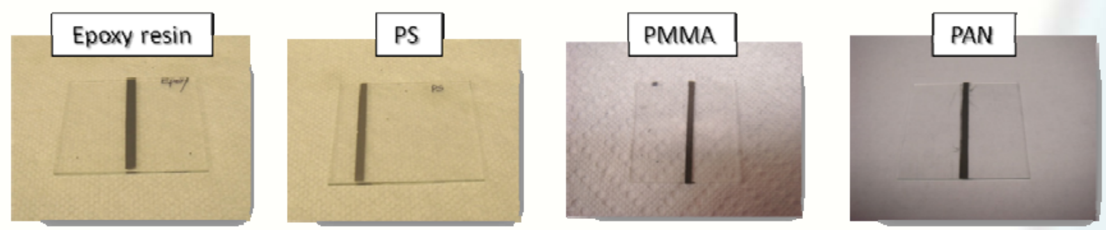


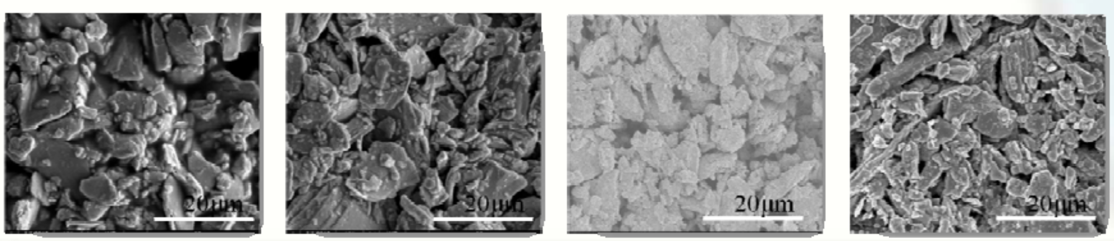
- Bi_2Te_3, no Au particles
- Bi_2Te_3, 0.001 wt% Au particles
- Bi_2Te_3, 0.05 wt% Au particles
- Bi_2Te_3, 0.05 wt% Au particles
- Bi_2Te_3, 0.05 wt% Au particles

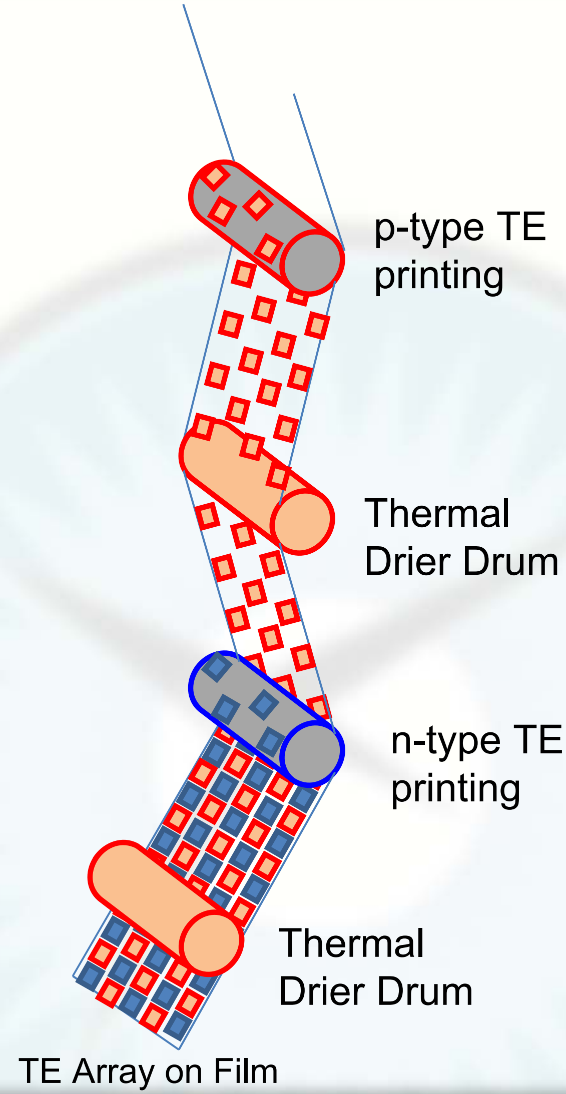
Zhao et al., Appl. Phys. Lett. **86**, (2005)

TE Inks for roll-to-roll process

Mass production
Inexpensive
Solar-tandem mode

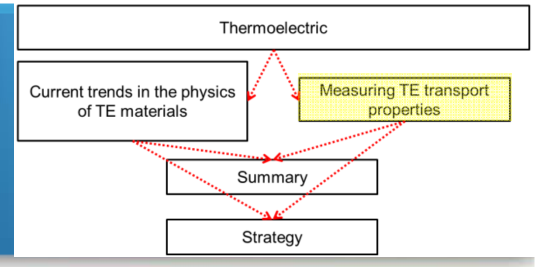






Hyun Jung Kim et al., Proc. SPIE 8691, 2013

Measuring TE transport properties of materials



"In order to direct material development, high precision measurement of ZT as well as good estimates of error is necessary"

Consideration
- No standard reference material (Round-Robin project)
- Density of samples (>97% density)
- Sample homogeneity (scanning system)
- Geometry factor and coating

Parameter	**S**	**σ**	**k**	**ZT**
• Scatter (maximum spread in data / the average)	**5%** (at 300K)	**10%** (at 500K)	**15%** (specific heat) **5%** (density) **7%** (Thermal diffusivity, at 300K)	**12%** (at 300K) **21%** (at 475K)
Note (comparing the data on the same material measured at several labs)		Geometry error Twice that in Seebeck coefficient		Above 475K, higher variation can be expected

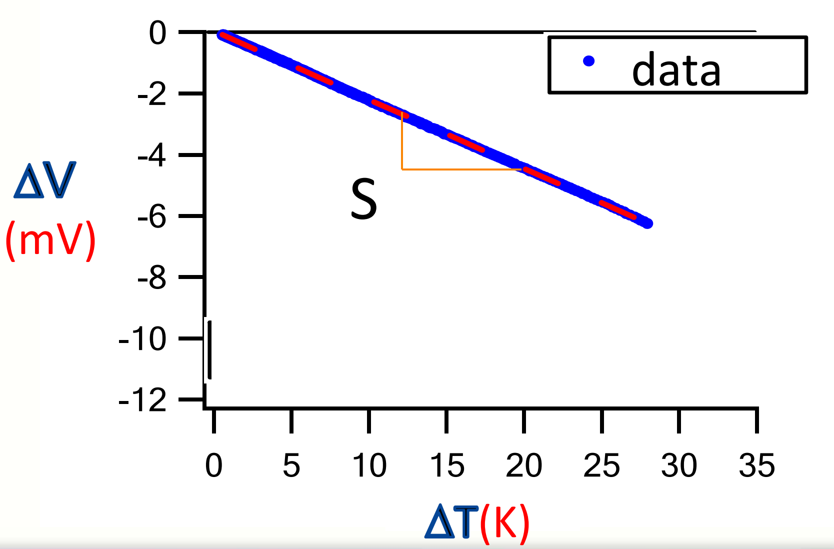
Kasper A. Borup et al., Energy Environ. Sci., DOI: 10.1039/c4ee01320d, 2014

Seebeck coefficient

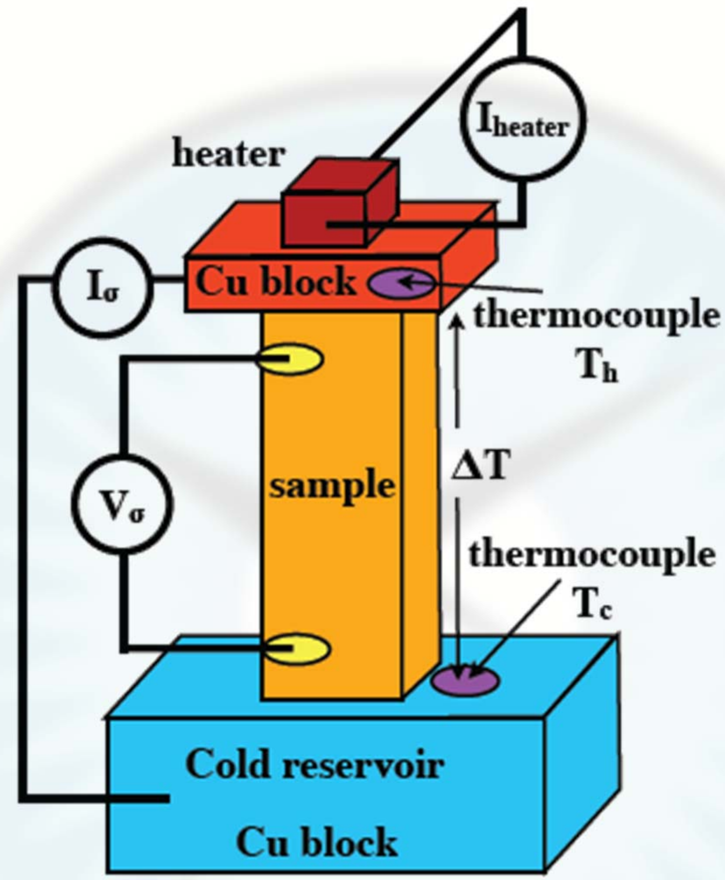
- S>0 for p-type, S<0 for n-type

$$S = -\frac{\Delta V}{T_2 - T_1}$$

- Difficulty and Solution: differences in thermocouple wires, reactive samples, cold finger effect



- Measure T_1, T_2, and ΔV



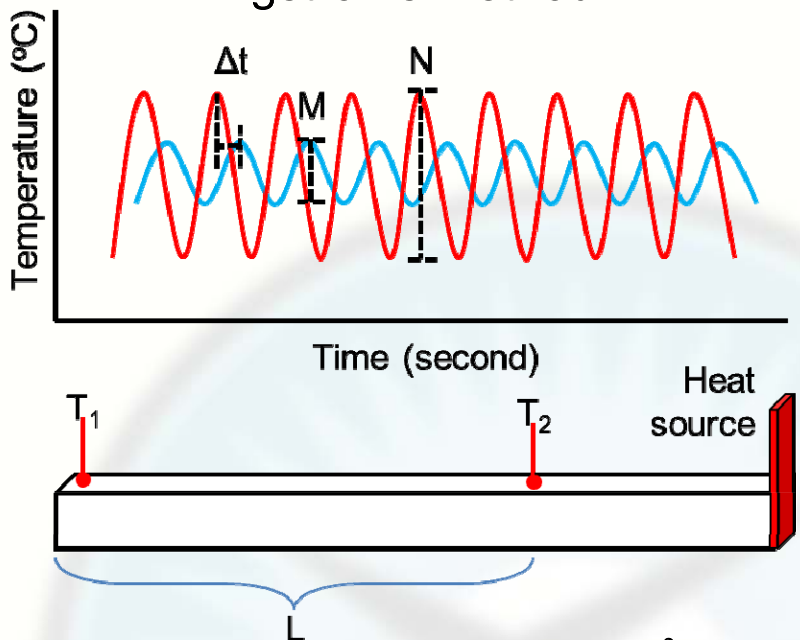
Thermal conductivity

Difficulty: The difficulty in accurately correcting for radiation loss limits the accuracy at higher temperature.

Solution:

- The sample needs to be in good thermal contact with the heater, heat sink, and thermocouples while being thermally insulated from the surroundings
- Apply the radiation correction (heat loss) factor (Cowan, Cape and Lehman, etc. for laser flash method)

Angstroms method



$$\text{Thermal diffusivity, } \alpha = \frac{L^2}{2\Delta t \ln \frac{M}{N}}$$

$$\text{Thermal conductivity, } k = \alpha \rho C$$

ρ = density

C = specific heat

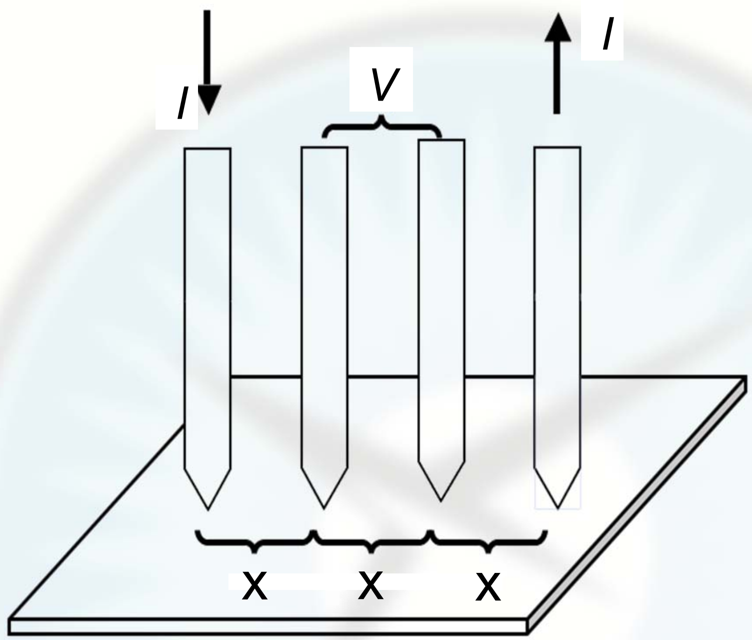
Electrical conductivity

Difficulty:
- Geometry error
- Inaccurate temperature determination

-poor temperature determination
-poor thermal contact between the sample and the thermocouples
-cold or hot finger effect
-varying voltage offset (vacuum, feedthrough, connections)

Solutions:
- Using an insulation shield to reduce the radiation loss from sample surface
- direct attaching the thermocouples to the sample

Linear 4-point method

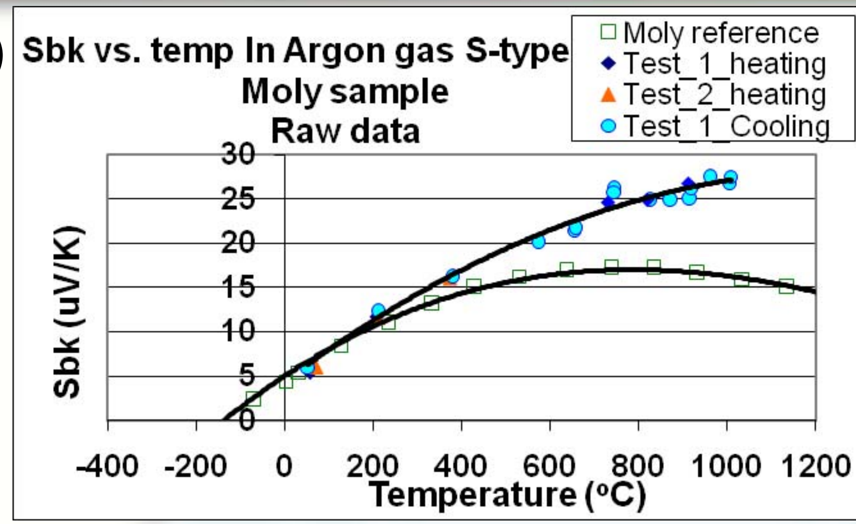


NIA / NASA Results

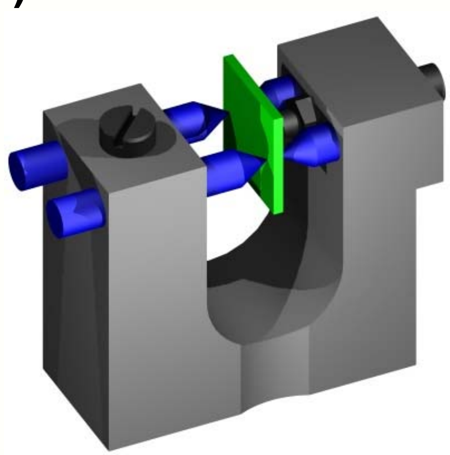
TE Characterization system

(a)

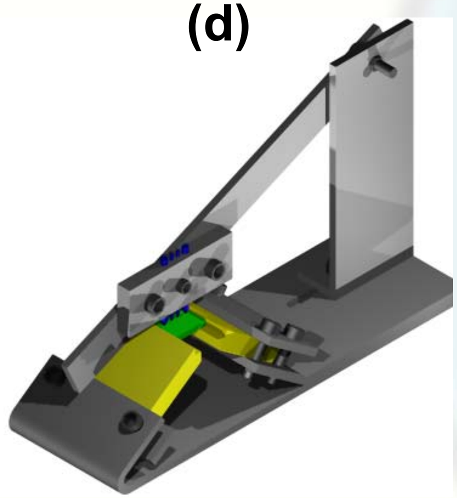
(b)



(c)



(d)



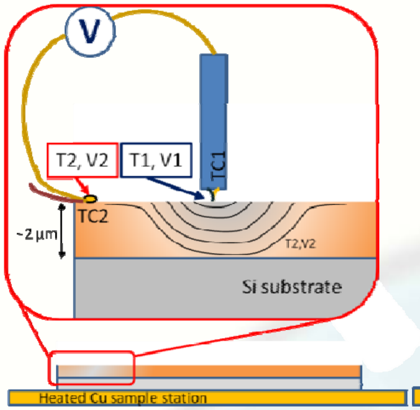
The correction factor

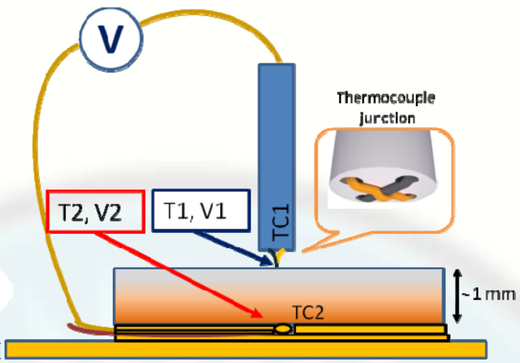
$$ycor = -3.945E - 9 \cdot x^3 + 1.1039E\text{-}5 \cdot x^2 + 0.00428 \cdot x - 0.5843$$

The scanning Seebeck coefficient measurement system

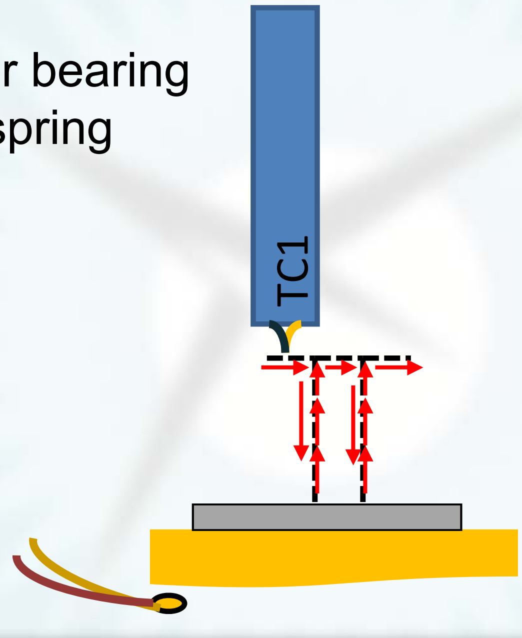
- Motorized XYZ probe head
- Max scan area: 25 x 25 mm
- Min interval: 0.05μm
- LabVIEW interface

- Keithley 740 Scanning voltage meter & DC servo motors

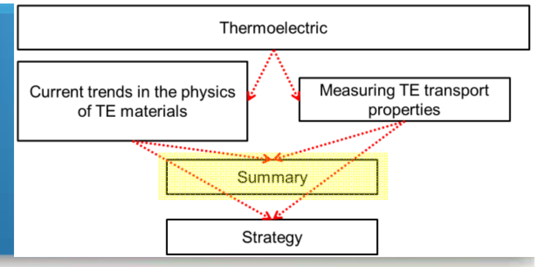




- Linear bearing
- Soft spring



Summary



► Waste heat is everywhere → enormous number of applications

► Seebeck coefficient can be increased by using the low dimensional structures and energy filtering effect

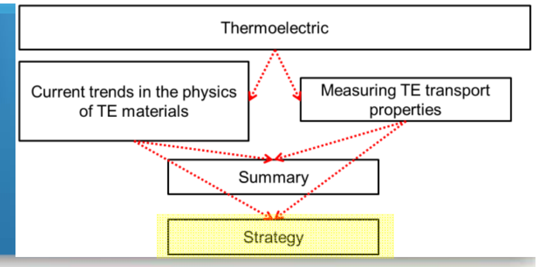
► Reducing k_{ph} faster than σ has been the most successful approach to improve ZT to date

► Heterointerface scattering of phonons has been successful in reducing k

► Need for reliable transport properties measurements
- Simple technique to Seebeck coefficient, Electric conductivity, and Thermal conductivity for bulk, thin film and flexible samples
- Need to solve the thermal contact issue

► TE materials and generators are not optimized → there is plenty of room for innovation

Strategy 1.
(Data driven materials science)



Data + Correlations + Theory = Knowledge Discovery

- Combinatorial experimentation
- Digital libraries & data bases

+

- **Data mining**
- **Dimensionality reduction**

+

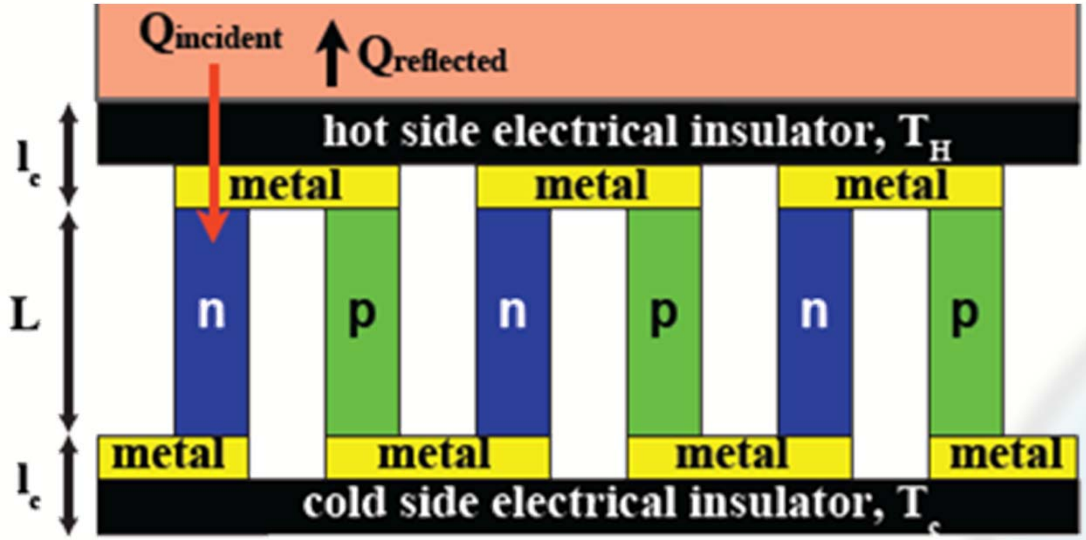
- Atomistic based calculations
- Continuum based theories

=

- Materials discovery
- Structure-property-processing relationships
- Hidden data trends

Information is multivariate, diverse , very large and access / expertise is globally distributed

Strategy 2.
(Heat control for maximum output power)



A = module leg area

L = module leg length

N = number of modules

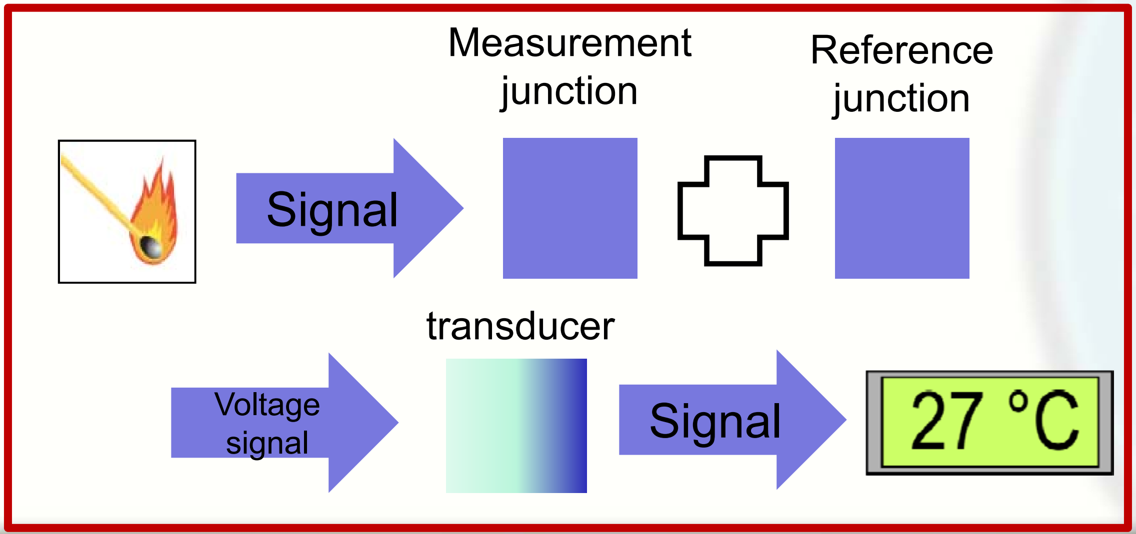
- F = fabrication factor = perfect system – $R_{contact}$ – R_{series} – Lost heat
- Practical system: both electrical and thermal impedance matching is required

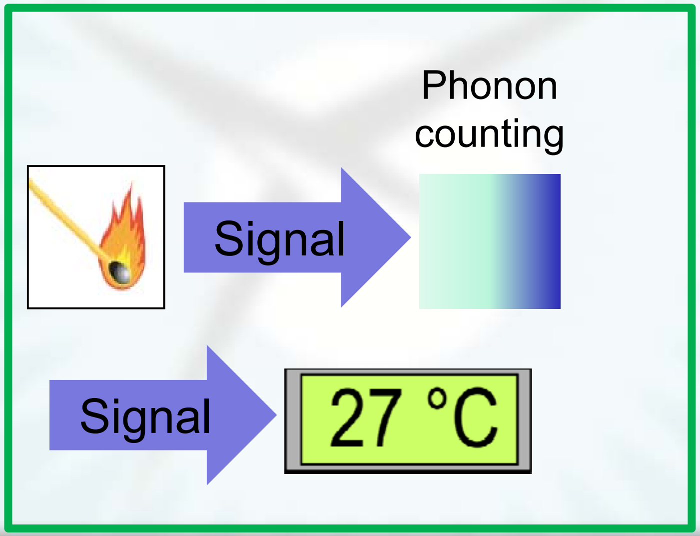
$$P_{max} = \frac{1}{2} FN \frac{A}{L} \Delta T^2 S^2 \sigma$$

Strategy 3.
(New thermal conductivity measurement system)

- Fabricate the thermal conductivity based measurement /management system with a novel nanotube based **phonon waveguide**

- Thermal measurement/management systems are currently very slow and relatively inefficient, particularly when compared to advances in photon (light) transport and photon based measurement system
- Additionally inefficiencies in conversion to and from thermal to electrical, optical or other signals in most thermal measurement/management systems lead to further degraded performance.
- At each of the initial signal conversion steps, measurement accuracy and speed is being lost, while the later processing steps each tends to end to the amount of energy consumed in the process.



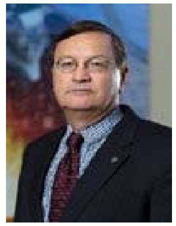


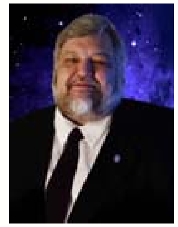
Strategy 4.
(Niche applications abound!)

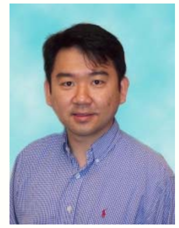
Acknowledgements

NIA


Doug Stanley


Bo Walkley


Karl Drews


Yeonjoon Park


Godfrey Sauti

NASA


Sang H. Choi


Cheol Park


Keith Gordon

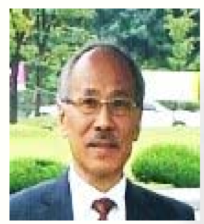

Catharine Fay


Robert Bryant

Caltech

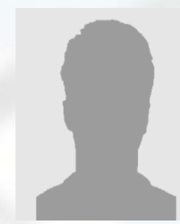

Shiho Iwanaga

DOT/ FHWA


Kunik Lee

University of Arkansas


Vijay Varadan


Jungmin Lee

Funded by

NASA Langley Research Center: C&I, FHWA DOT