The Challenge of Measuring Thermoelectric Materials and Devices Electrical and Thermal Performance

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Workshop on Quantification of Uncertainties in Materials Science

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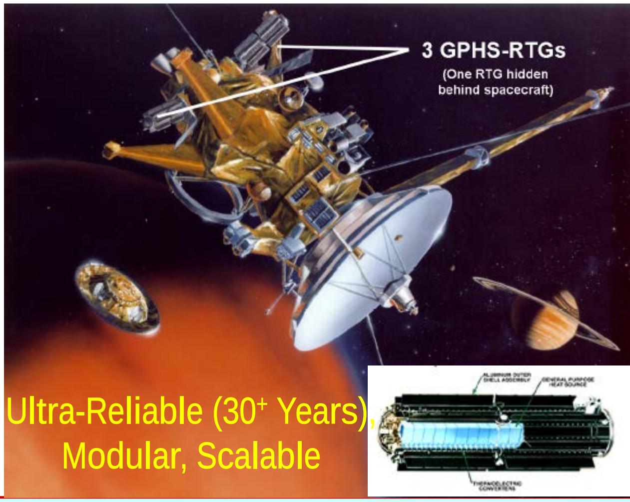
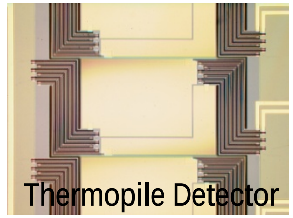
Breadth of Thermoelectric (TE) Applications

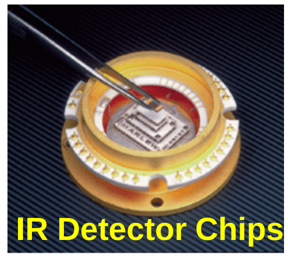
Power, Cooling, Sensing

Cassini - Saturn - NASA



40 years of NASA Investment in High Temperature TE Power Generation Technology for Deep Space Science Exploration

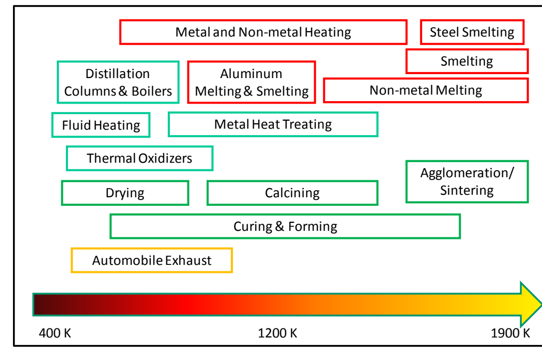




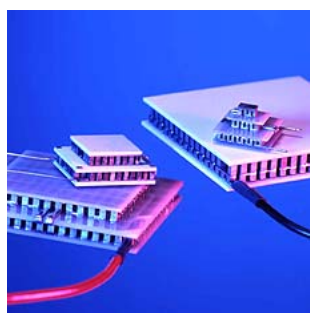
IR Sensing

All-Solid-State Refrigeration

1 kW$_e$ Thermoelectric Generator Installed in Place of Muffler



Energy Harvesting & Waste Heat Recovery



Solid-State TE Device
A Key Enabling Technology Component

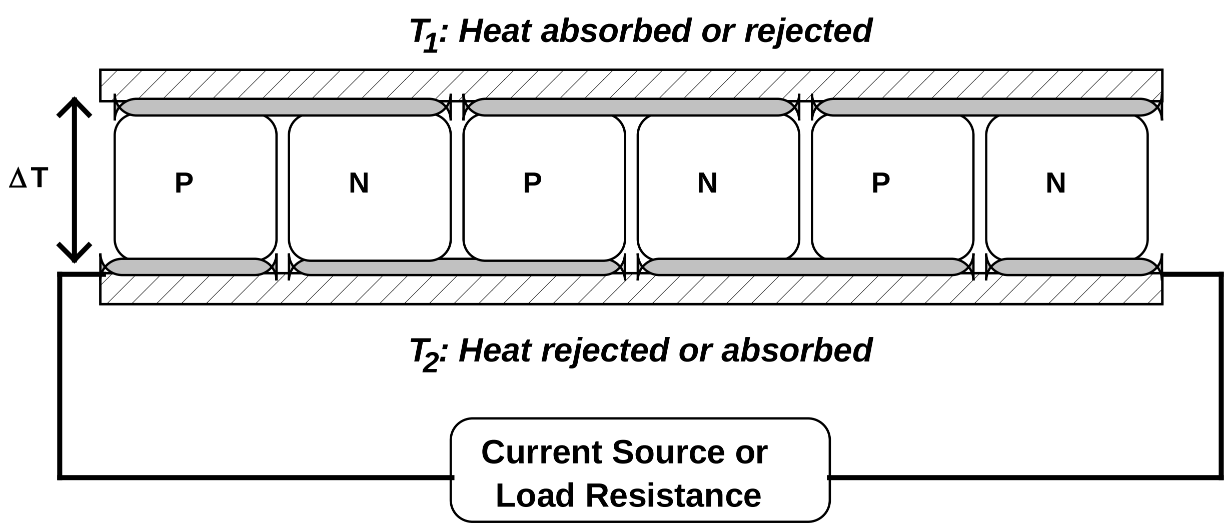
Autonomous Remote Power Generator

Active heated and cooled seating system

Thermoelectric Transport

Thermoelectric effects

- Thermoelectric devices are based on two transport phenomena: the Seebeck effect for power generation and the Peltier effect for electronic refrigeration.
- If a steady temperature gradient is applied along a conducting sample, the initially uniform charge carriers distribution is disturbed as the free carriers located at the high temperature end diffuse to the low temperature end. This results in the generation of a back emf which opposes any further diffusion current. The open circuit voltage when no current flows is the Seebeck voltage.
- The complementary Peltier effects arises when an electrical current I passes through the junction and a temperature gradient is then established across the junctions



Thermoelectric Transport Coefficients

- Electrical (σ) and thermal (λ) conductivities are direct effects connecting electrical and heat current with the related force

- The Seebeck (S) and Peltier (Π) coefficients are cross effects connecting respectively an electrical response to a thermal force and a heat current to an electrical force

Thermoelectric Property	Definition	Under Condition	Type
Electrical Conductivity	$i = \sigma E$	$\nabla T = 0$	Direct
Thermal Conductivity	$Q = -\lambda \nabla T$	$i = 0$	Direct
Seebeck Coefficient	$E = S \nabla T$	$i = 0$	Cross
Peltier Coefficient	$Q = \Pi i$	$\nabla T = 0$	Cross

Thermoelectric Figure of Merit

- Thermoelectric effects are defined by a coupling between the electrical and thermal currents induced by an electric field and a temperature gradient

$$\bar{i} = \sigma(\bar{E} - S\bar{\nabla}T)$$

$$\bar{Q} = ST\bar{i} - \lambda\bar{\nabla}T$$

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

- ZT is representative of the relative strength of this cross-coupling

- S, Seebeck coefficient
- σ, ρ electrical conductivity and resistivity
- λ, thermal conductivity
- zT is a true transport property

$$\frac{\rho_{Q=0}}{\rho_{\nabla T=0}} = 1 + ZT$$

$$\frac{\lambda_{E=0}}{\lambda_{i=0}} = 1 + ZT$$

What is a Good Thermoelectric Material?

- General considerations for the selection of materials for thermoelectric applications involve:
  - High figure of merit
  - large Seebeck coefficient S (or α)
  - low electrical resistivity ρ
  - low thermal conductivity λ
  - Possibility of obtaining both n-type and p-type thermoelements
    - No viable superconducting passive legs developed yet

$$Z = \frac{S^2 \sigma}{\lambda} = \frac{S^2}{\rho \lambda}$$

- Good mechanical, metallurgical and thermal characteristics
  - Capable of operating over a wide temperature range
    - Especially true for high temperature applications
  - To allow their use in practical thermoelectric devices

General Thermoelectric Properties of Metals, Semiconductors and Insulators at 300K

- The Seebeck coefficient is much too low in metals
- The electrical conductivity is much too low in insulators
- Only semiconductors possess the right combination of high power factor $PF = S^2\sigma$ and relatively low thermal conductivity λ
  - Degenerate semiconductors and semi-metals are most attractive

Metals	Semiconductors	Insulators
S ~ 5 μVK-1	S ~ 200 μVK-1	S ~1000 μVK-1
$\sigma \sim 10^8\ \Omega^{-1}m^{-1}$	$\sigma \sim 10^5\ \Omega^{-1}m^{-1}$	$\sigma \sim 10^{-10}\ \Omega^{-1}m^{-1}$
$\lambda_{tot} = \lambda_L+\lambda_{el} \sim \lambda_{el}$	$\lambda_{tot} = \lambda_L+\lambda_{el}$; $\lambda_{el} < \lambda_L$	$\lambda_{tot} = \lambda_L+\lambda_{el} \sim \lambda_L$
~ 10-1000 $Wm^{-1}K^{-1}$	~ 1-100 $Wm^{-1}K^{-1}$	~ 0.1-1 $Wm^{-1}K^{-1}$
$ZT \sim 10^{-3}$	$ZT \sim 0.1 – 2.0$	$ZT \sim 10^{-14}$

Good Thermoelectrics – Implications for Transport Property Measurements

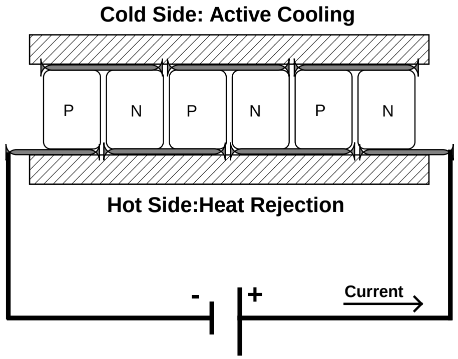
- Good TE materials have:
  - Thermal conductivity like glass
  - Large thermopower values – order of magnitude higher than Type K TC
    - Strong voltage response to changes in temperatures
    - Strong Peltier effect means strong temperature response to changes in applied current
  - Good electrical conductivities – only 10-50 times higher than metals

➢ The larger the zT, the higher the potential for erroneous measurements

  - However need to recognize that for a given material electrical properties typically vary in tandem (high resistivity and high Seebeck vs. low resistivity and low Seebeck)

Power Generation and Cooling

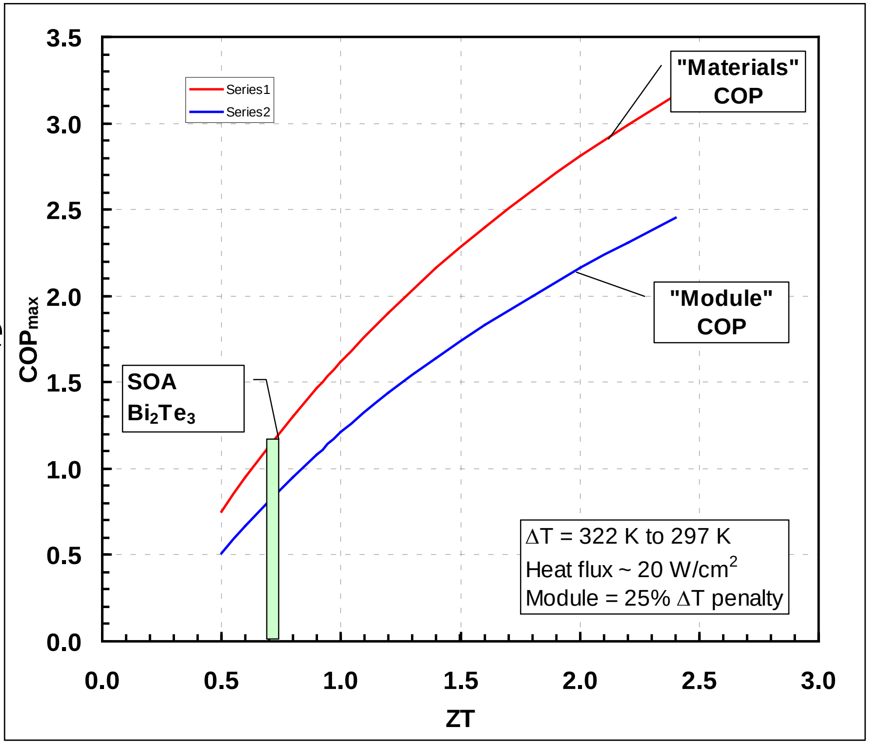
Thermoelectric Cooling



$$COP_{max} = \frac{Q_{max}}{P_{max}} = \frac{T_{cold}}{T_{hot} - T_{cold}} \frac{\sqrt{1+ZT} - \frac{T_{hot}}{T_{cold}}}{\sqrt{1+ZT} + 1}$$

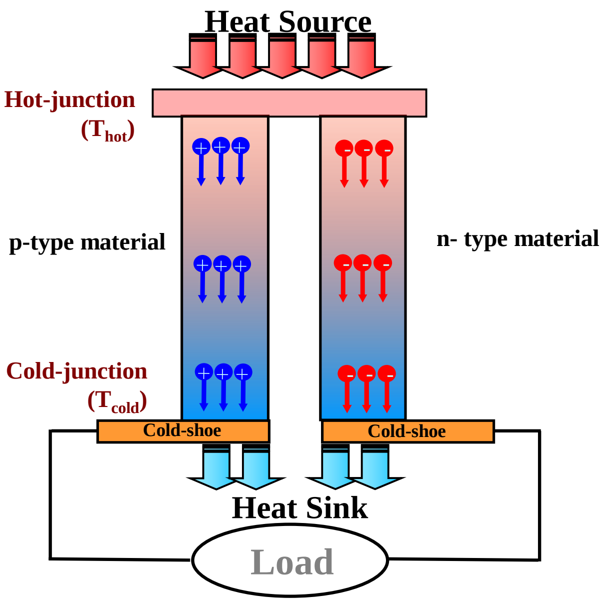
$$\Delta T_{max} = \frac{ZT_{cold}^2}{2}$$

- Two important design conditions
  - Maximum cooling power (ΔT=0)
  - Maximum cooling temperature (P=0)
- Both conditions directly proportional to ZT
- Coefficient of performance (COP) for some typical thermal management conditions
  - 297 K at 323 K ambient
  - State-of-practice: ZT ~ 0.7
    - Bulk and thin film devices
    - ZT ~ 2.0 reported on thin film superlattices but no validation at the device level yet



Thermoelectric Power Generation

Thermoelectric Couple



Thermoelectric effects are defined by a coupling between the electrical and thermal currents induced by an electric field and a temperature gradient

Dimensionless Thermoelectric Figure of Merit, ZT

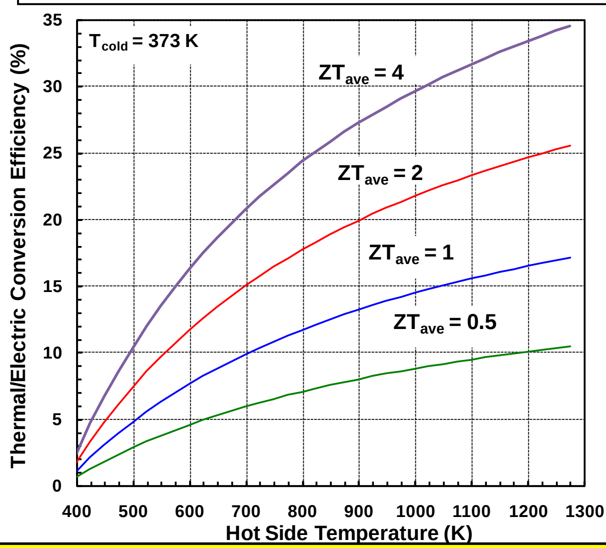
$$ZT = \frac{\sigma S^2 T}{\lambda} = \frac{S^2 T}{\rho \lambda}$$

Seebeck coefficient S
Electrical conductivity σ
Electrical resistivity ρ
Thermal conductivity λ
Absolute temperature T

Carnot *TE Materials*

$$\eta_{max} = \frac{T_{hot} - T_{cold}}{T_{hot}} \cdot \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + \frac{T_{cold}}{T_{hot}}}$$

Conversion Efficiency



Power generation
(across 1275 to 300 K)
State-Of-Practice materials:
$ZT_{average}$ ~ 0.5

State-Of-the-Art materials:
$ZT_{average}$ ~ 1.1

Best SOA materials:
ZT_{peak} ~ 1.5 to 2.0

Conversion efficiency is a direct function of ZT and ΔT

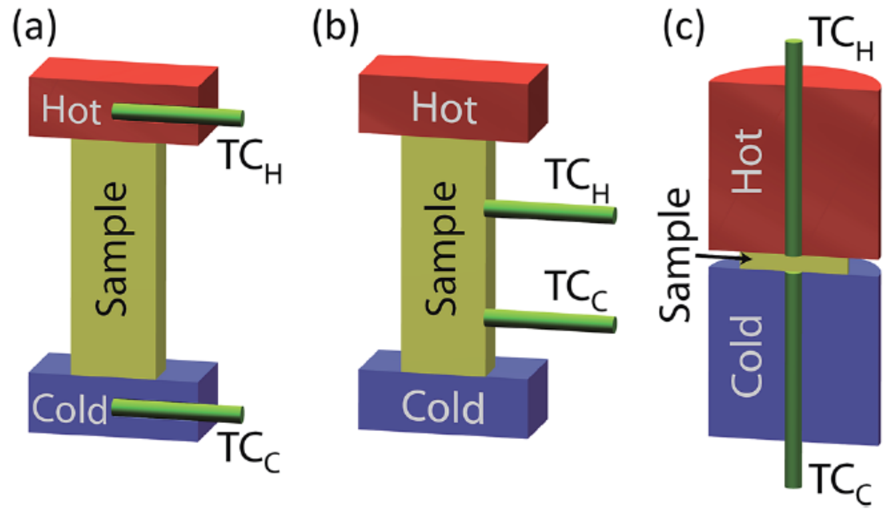
Good Thermoelectric Devices – Implications for Characterization and Validation of TE Materials Performance

- Good TE Devices have:
  - Good TE materials
  - Low electrical and thermal interface resistances
  - Effective thermal coupling to hot side and cold side external interfaces
- ➢ Good TE device performance characterization should be capable of validating TE materials performance
- Moreover:
  - TE devices are often used in long life applications where a high level of performance prediction reliability is essential
  - Prediction reliability depends most on individual property spread in values and associated uncertainties

Measuring Thermoelectric Transport Properties

**Used recent paper by Borup et al., "Measuring Thermoelectric Transport Properties of Materials" Energy Environ. Sci., 2015, 8, 423*

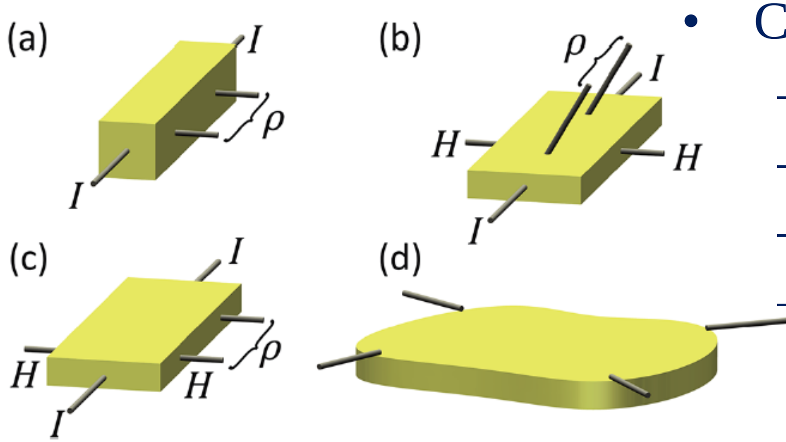
Seebeck Coefficient Measurement



- Common Seebeck measurement configurations
  - Measuring $\Delta V/\Delta T$ through various methods
  - (a) 2-probe end-to-end
  - (b) 4-probe off-axis
  - (c) 4-probe axial

- Measurement methodologies and some common potential issues
  - Sample sizing
  - Small vs. large ΔT
  - Steady-state vs quasi steady-state “ambient” temperature
  - Simultaneous voltage and temperature measurements
  - Single versus multiple measurements
  - Interface thermal and electrical resistance
  - “cold finger” effects
  - Reactivity of probes with thermoelectric material

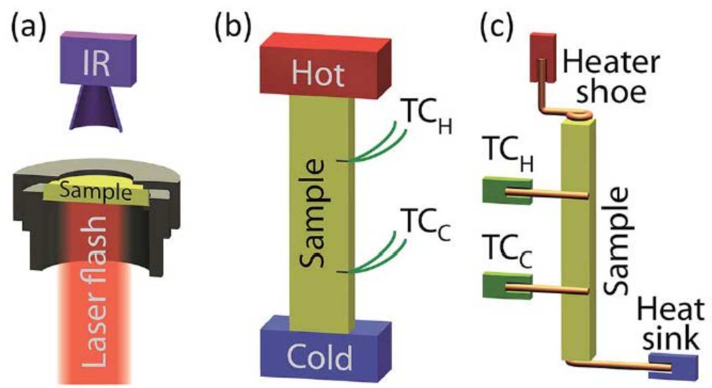
Electrical Resistivity/Hall Effect Measurement



- Common resistivity measurement configurations
  - Measuring R*A/l through various methods
  - (a) 4-probe resistivity only bar shape
  - (b and c) 6 and 5-probe resistivity and Hall effect
  - (d) 4-probe Van der Pauw for resistivity (and Hall effect)

- Measurement methodologies and some common potential issues
  - Available sample shape: bar/cylinder versus plate/disk
    - Commonality with other property measurements
  - Sample dimensions and dimensional uniformity (major source of error)
  - Simultaneous current application (pulse DC vs. AC) and voltage measurements
    - Minimize/eliminate extraneous Seebeck voltage effects
  - Uniformity of current flow
  - Location and contact resistance of probes
  - Reactivity of probes with thermoelectric material
  - Temperature measurement and steady-state vs quasi steady-state “ambient conditions”

Thermal Conductivity Measurement



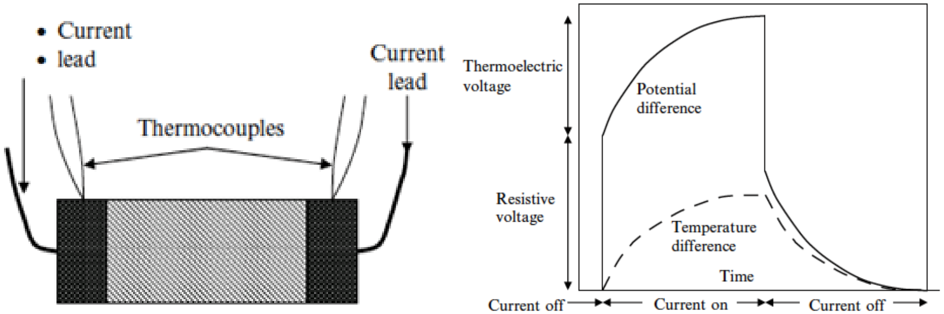
Common measurement configurations

- Measuring Q/ΔT*(l/A) through various methods
- (a) Flash diffusivity (necessitates Cp measurement)
- (b) Direct steady-state measurement
- (c) Direct pulsed heat measurement
- (d) (not shown) comparative measurement

- Measurement methodologies and some common potential issues
  - Available sample shape: bar/cylinder versus plate/disk
    - Plate/disk shape is compatible with other property measurements (Seebeck (c), Van der Pauw)
    - Bar-shape can be used with Seebeck (a,b) and resistivity (a)
  - Sample dimensions and dimensional uniformity
  - Temperature measurements (Sample temperature for flash diffusivity)
  - Heat losses for calculating Q into sample
    - Radiation losses (especially for the direct methods at higher temperatures)
    - Cold fingers for direct measurements
  - Heat capacity calculation or direct measurement required for diffusivity method
    - Calculation requires use of a known standard (C) and surface emissivity coating of unknown
    - "Stand-alone" measurement is difficult, especially at high temperatures

Direct ZT Measurement

Harman Technique

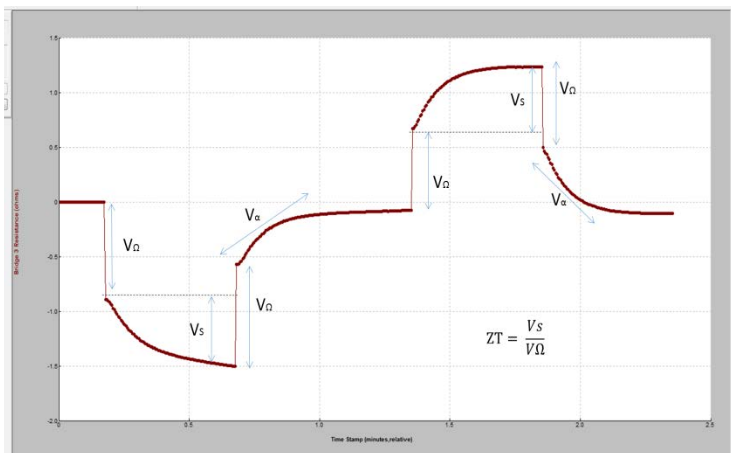


Extracting zT:: Visotermal, Vadiabatic = IR (resistivity)
Va-Vi ~ Seebeck (dV/dT), thermal conductivity inferred

- Harman technique: Direct measurement of ZT via ratio of adiabatic and isothermal voltages
  - (a) 4-probe measurement

$$zT = \left(\frac{V_a}{V_i} - 1\right)\left(1 + \frac{\beta P L^2}{12\lambda A} + \frac{\beta_c A_c L}{2\lambda A} + \frac{K_1}{2\lambda A}\right)$$

Direct ZT — Radiative Effects



Harman ZT measurement redundancy, allows for cross checking/validation

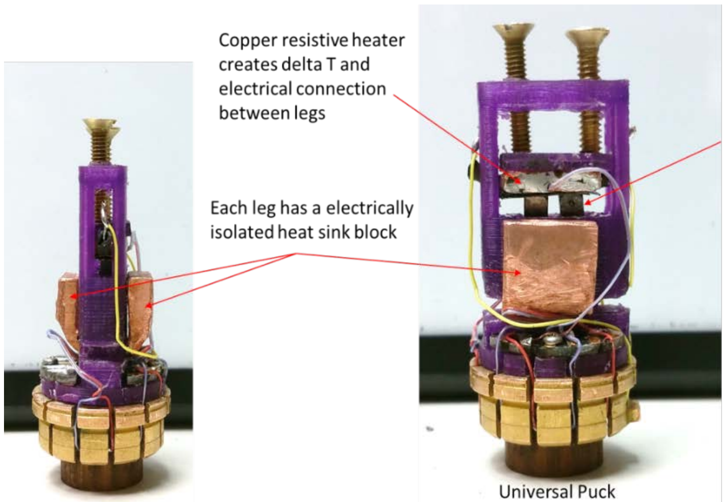
- Methodology and some common potential issues
  - Pulse current through sample
    - Bar/cylinder shape most commonly used
  - Sample dimensions and dimensional uniformity
  - Probe location and temperature measurements
  - Heat losses and heat sinking
    - Radiation losses at higher temperatures
    - Cold finger effects
  - Simultaneous temperature/ voltage measurements
  - Data acquisition rate

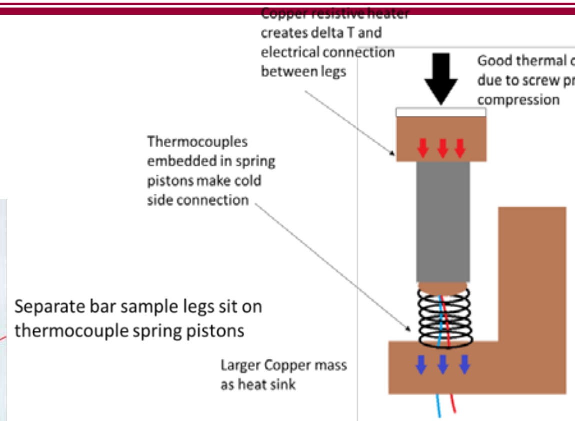
Thermoelectric Devices for Characterization and Validation of TE Material Properties

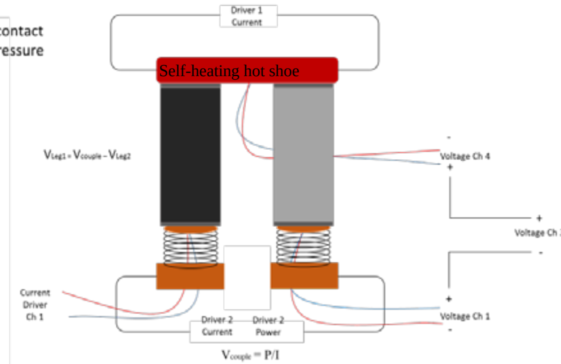
**Used recent paper by Borup et al., "Measuring Thermoelectric Transport Properties of Materials" Energy Environ. Sci., 2015, 8, 423*

Cooling Device-Level Validation of Low Temperature TE Material Performance

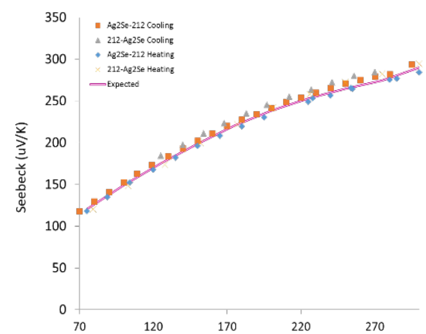
- Single leg and couple test bed (instrumentation/set up)
- Validation of zT of TE materials

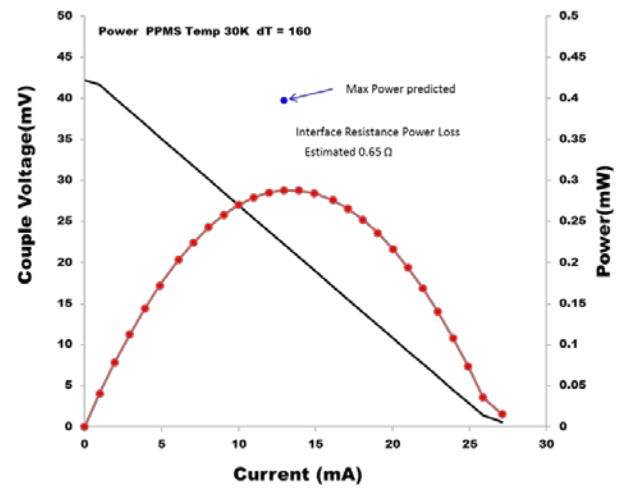






Power Generation
Peltier Effect
Couple Harman Technique

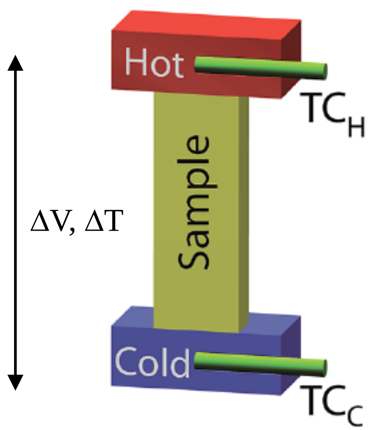




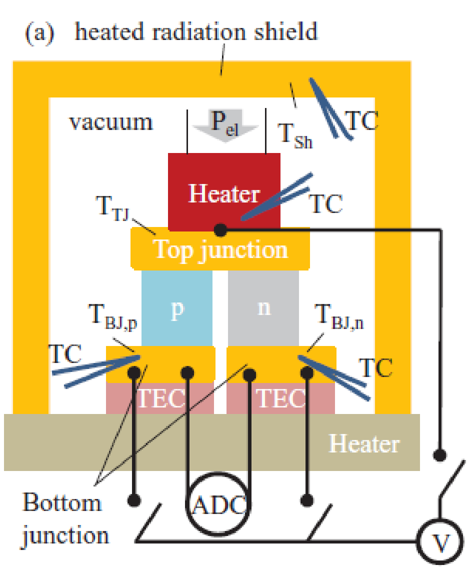
- Utilizing Cu pressure contacted interconnect only
- Multifunctional set up can be used for test bed validation in different modes:
  - Power Generation
  - Peltier Effect
  - Couple Harman Technique

- Methodology has been used for commercial devices based on Bi_2Te_3 alloys
- Simpler devices only available for new TE materials
- Remaining unknown uncertainties mostly related to interface contact resistances

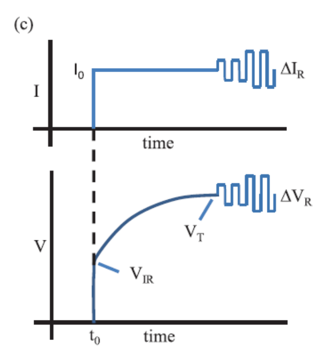
Power Generation Device-Level Validation of High Temperature TE Material Performance

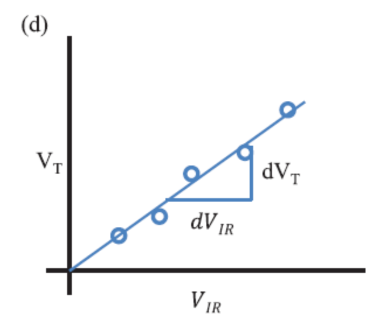


- Various methods exist or under development to provide rapid validation of TE material performance
  - End-to-end single TE device leg performance under large ΔT
    - Open circuit voltage for validating Seebeck
    - Under varying current loads for resistance of TE material and interfaces
  - Full couple under large ΔT
    - ZT measured with differential Harman method
    - Calculated TE transport properties
    - Good agreement with materials property measurements
    - Some limitations related to heat losses, thermal and electrical contact resistances



*Schematic taken from Kraemer and Chen, Rev. Sci. Instruments, 85, 045107 (2014)





Summary

- The TE R&D community has very significantly grown over the past 20 years, and has somewhat been struggling in how materials and device performance are being reported and cross-checked
- Lots of potential for measurement errors in electric and thermal measurements
  - Across a wide range of operating temperatures
  - Typically across significant temperature differentials and/or temperature gradients
- Increased availability of “COTS” materials testing equipment – more difficult to “educate” the TE community on measurement uncertainties and error pitfalls
- Need for cross-checking measurements using multiple techniques, including device level methods
- In addition to obfuscating the pace of materials R&D progress, UQ in thermoelectrics has some significant implications on the generation of high reliability system performance predictions

Acknowlegments

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