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Baltimore, MD

Thermoelectric Couple Demonstration of (In, Ce)-based Skutterudite Materials for Automotive Energy Recovery

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DOE Office of Vehicle Technology Project

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Agenda

- National & DOE Motivation
- Thermoelectric Properties
- Structural Properties
- TE Couple Demonstration
- Closing Thoughts

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Relevance - National Waste Energy Recovery
Magnitude of the Opportunity – Why Are We Interested?

- **60-70% Energy Loss in Most of Today's Processes**

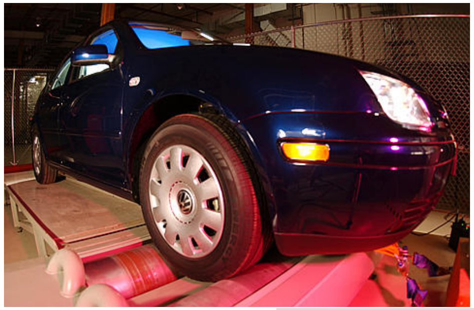
- **Transportation Sector**
  - **Light-Duty Passenger Vehicles + Light-Duty Vans/Trucks (SUVs)[1]**

    2002: 16.27 Quads of Fuel Usage

    2008: 16.4 Quads of Fuel Usage

    2002: ~ 5.7 quads/yr exhausted down the tail pipe

    ~ 5 quads/yr rejected in coolant system



  - **Medium & Heavy-Duty Vehicles[1]**

    2002: 5.03 Quads of Fuel Usage

    2008: 5.02 Quads of Fuel Usage

    ~1.5 quads/yr exhausted down the tail pipe

- **Industrial Process Sector**
  - 10 Quads of Waste Energy Flows in Industrial Processes
    - Aluminum. Glass
    - Paper
    - Petroleum
    - Chemical
  - 1.8 Quads Recoverable

[1] *Transportation Energy Data Book,* 2010, Edition 29, U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicles Technology Program. ORNL-6985, Oak Ridge National Laboratory, Oak Ridge, Tennessee. http://cta.ornl.gov/data/index.shtml.

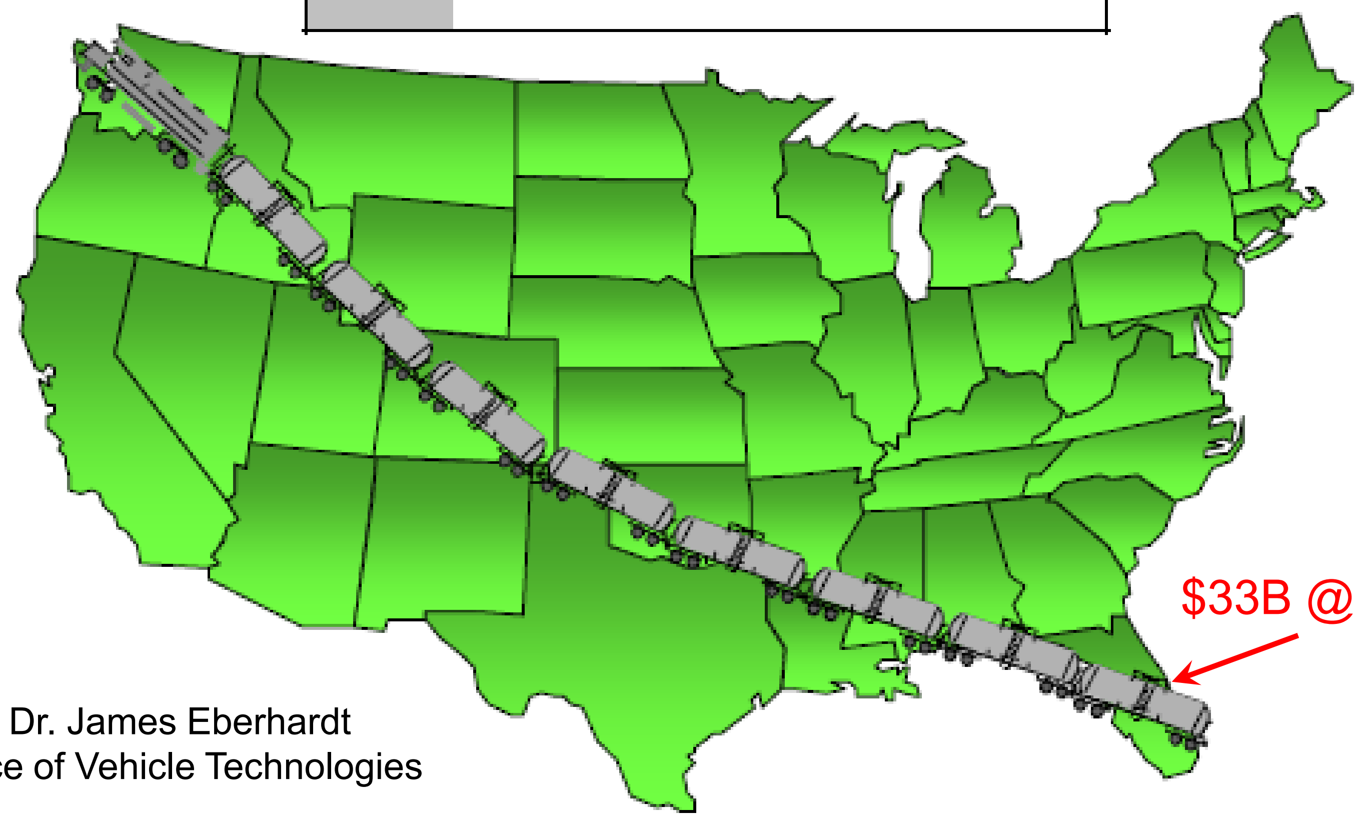
The Magnitude of Our Energy Problem

Office of Heavy Vehicle Technologies

	1973	1997
U.S.	74 Quads	91 Quads
World	225 Quads	365 Quads

2007
102 Quads

$33B @ $100/Barrel



Reference - Dr. James Eberhardt
DOE – Office of Vehicle Technologies

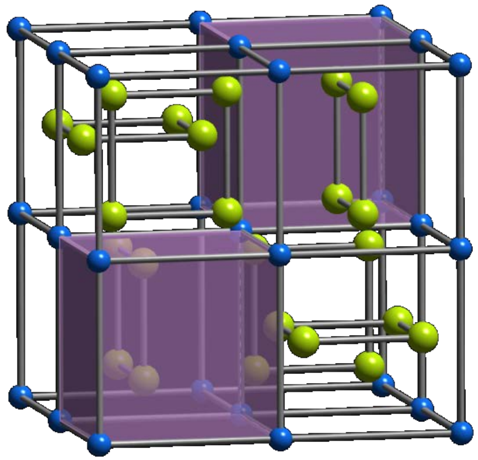
1 Quad of energy is equivalent to 340,000 tank cars of crude oil stretched from Miami to Seattle (3,300 miles).

Goals & New Frontiers

- Develop new high-performance n-type and p-type thermoelectric (TE) material compositions to enable:
  - Fuel efficiency improvements from waste energy recovery in advanced light-duty engines and vehicles.
  - Improved heavy truck efficiencies by 2015
  - Stretch thermal efficiencies of 55% in advanced heavy-duty engines by 2018.
  - Improve efficiency of directly converting waste heat in industrial processes
- Develop high-performance TE materials with operational temperatures as high as 850 K
  - Advanced n-type and p-type bulk TE materials that have peak ZT (Figure of Merit x Temperature) of approximately 1.6 or higher at 600 K
  - Minimize temperature-dependency in properties to achieve high performance in the 350 K to 820 K range
- Measure Structural Properties & Characterize Thermal Cycling Impacts
- Improve cost-effectiveness and performance of exhaust heat recovery in transportation / industrial applications. Scaling up to operating TE devices

Strategies in Designing *n*-type and *p*-type Skutterudites: $R_xR_y'Co_{4-x}M_xSb_{12}$

- Multiple Rattler Systems Dramatically Reduce Thermal Conductivity While Maintaining Electrical Conductivity & Seebeck Coefficient
  - Single Rattler Systems
  - Multiple Rattler Systems



Co_4Sb_{12} (n-type)

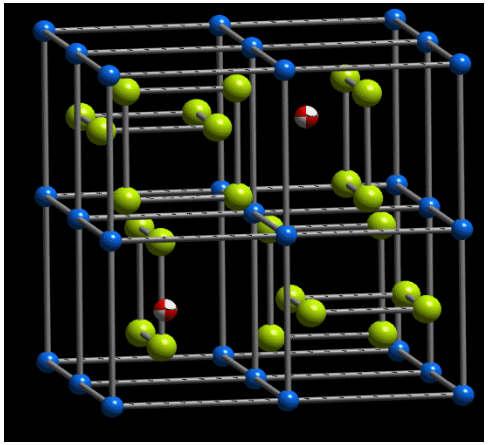
$Fe_xCo_{4-x}Sb_{12}$ (p-type)

Single and Multiple Rattlers

↓

R^{2+}: Ba, Ce, Sr, Ca, Ag, Pd,

R^{3+}: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, In, Sc



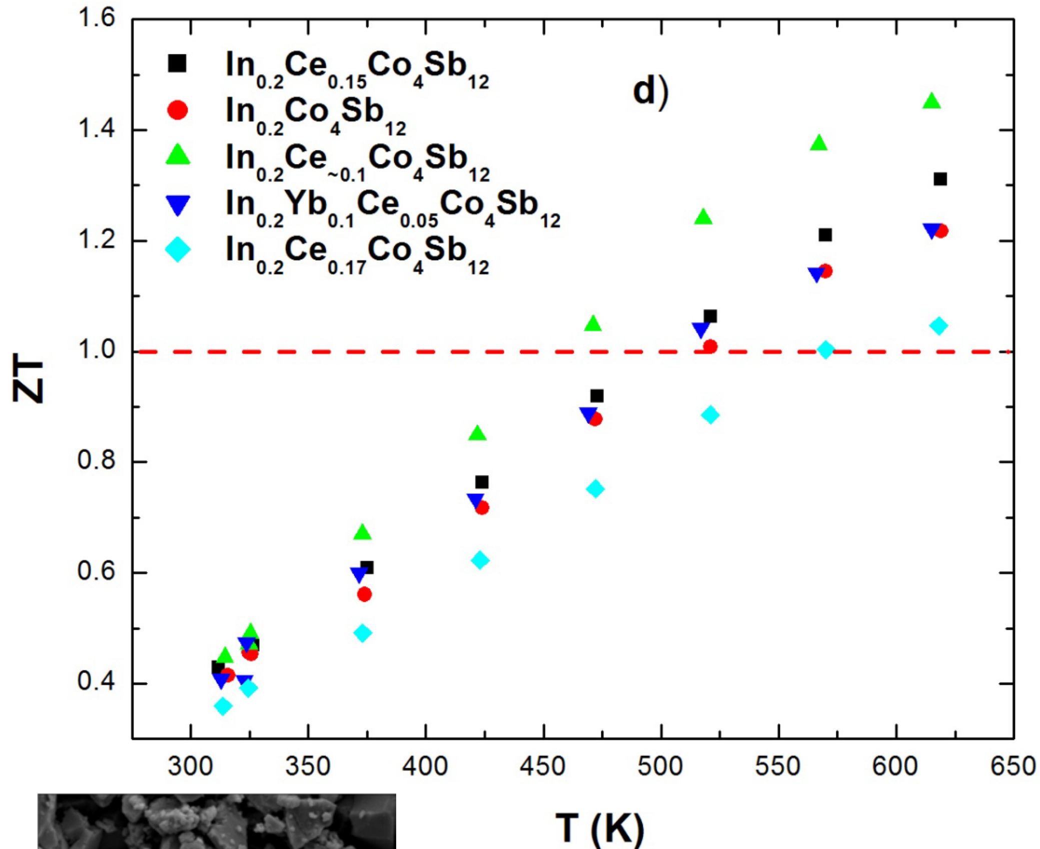
$R_xCo_4Sb_{12}$

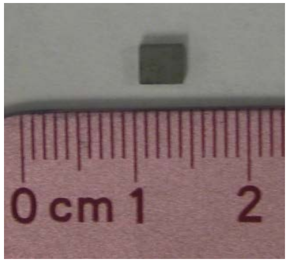
$R_xR'_yCo_4Sb_{12}$

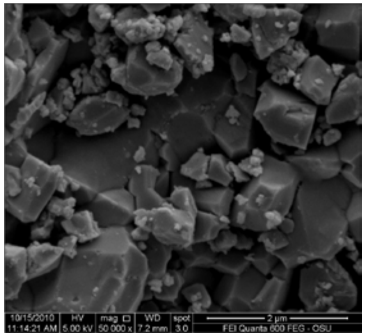
- **Most Recent Focus:**
  - n-type $In_{0.2}Co_4Sb_{12}$
  - n-type $In_xCe_yCo_4Sb_{12}$
  - n-type $In_xCe_yYb_zCo_4Sb_{12}$

Recent Accomplishments n-Type $In_xCe_yCo_4Sb_{12}$ TE Properties

- $In_{0.2}Co_4Sb_{12}$ ZT ~ 1.2 @ 600 K (highly reproducible).
- Several $In_{0.2}Ce_yCo_4Sb_{12}$ Showed ZT = 1.2-1.45 at 625 K
- There is an enhancement of ZT when Ce is co-filled with In
- Cerium (Ce^{3+}, Ce^{4+}) mixed valiancy may play a role. - Enhancement of Seebeck values.
- In 2010, $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ sample showed ZT ~ 1.5 – 1.6 around 500 K. Working on reproducing it







$In_{0.2}Ce_{\sim 0.1}Co_4Sb_{12}$ SEM
2 um Resolution

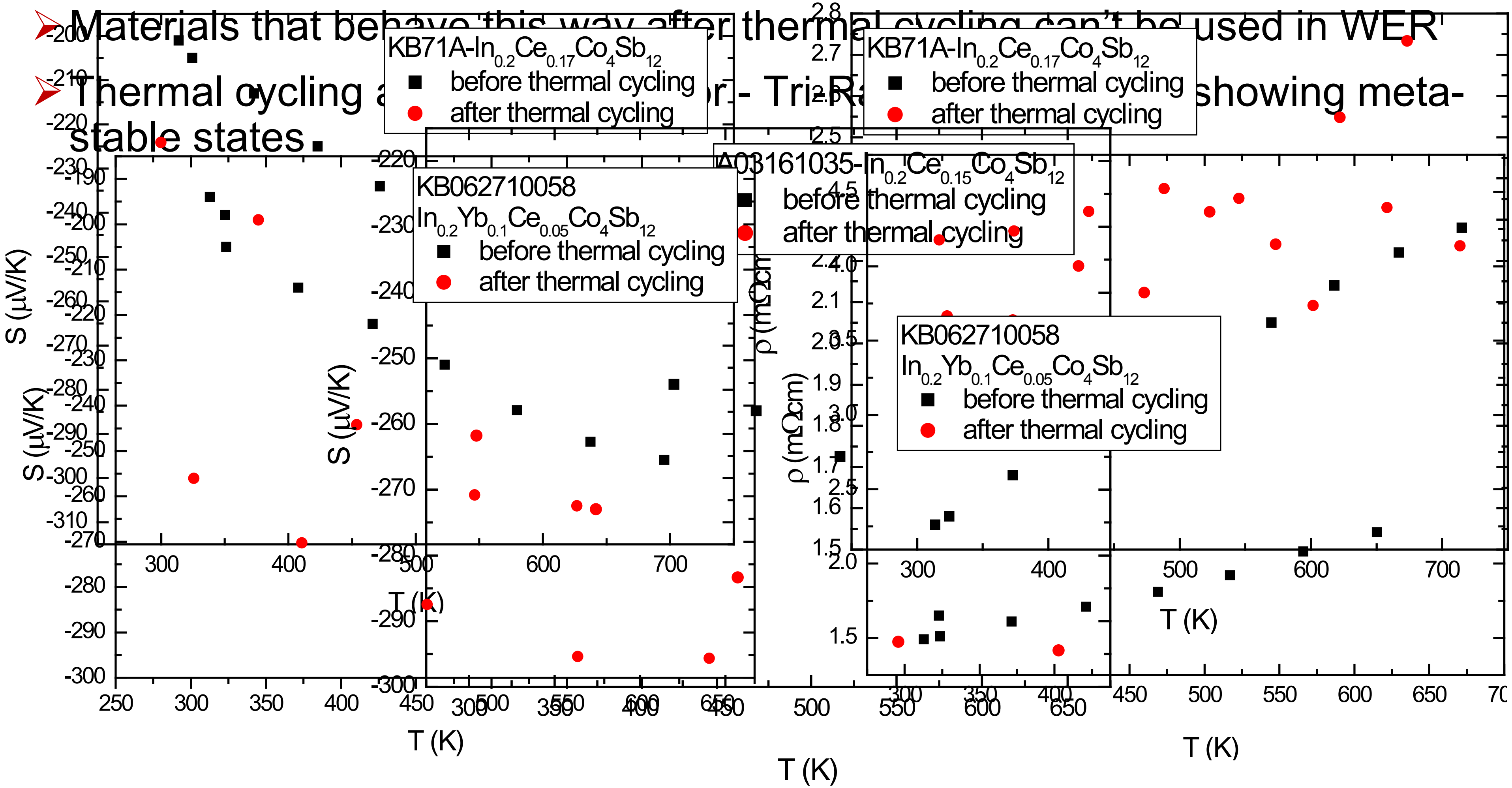
Thermal Cycling Results

- Materials howing Good Stability Upon Thermal Fatigue Cycling
  - 200 Cycles ; 40 °C to 400 °C
- Minimal thermal cycling impact on structural properties
- Indicates little or no microcrack growth or initiation
- Thermal stability critical to transitioning into operating TE devices & systems

	Temperature [°C]	Before Thermal Cycling		After Thermal Cycling	
		Young's Modulus, E 10^9 [N/m^2]	Poisson's Ratio, ν	Young's Modulus, E 10^9 [N/m^2]	Poisson's Ratio, ν
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (LBL1) – n-type	20-22	134.8	0.215	134.4	0.204
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (LBL2) – n-type	20-22	132.6	0.204	131.9	0.200
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (PNNL3-G1B) n-type	20-22	133.9	0.185	135.8	0.194
$In_{0.2}Ce_{0.15}Co_4Sb_{12}$ n-type	20.6	124.5	0.213	125.7	0.214
$In_{\sim 0.2}Ce{\sim}_{0.1}Co_4Sb_{12}$ – n-type	20.5	123.1	0.197	125.1	0.217
$In_{0.2}Ce_{0.17}Co_4Sb_{12}$ – n-type	19.9	109.5	0.213	108.5	0.210
$In_{0.2}Ce_{0.05}Yb_{0.1}Co_4Sb_{12}$ n-type	20-22	89.5	0.208	85.9	0.207

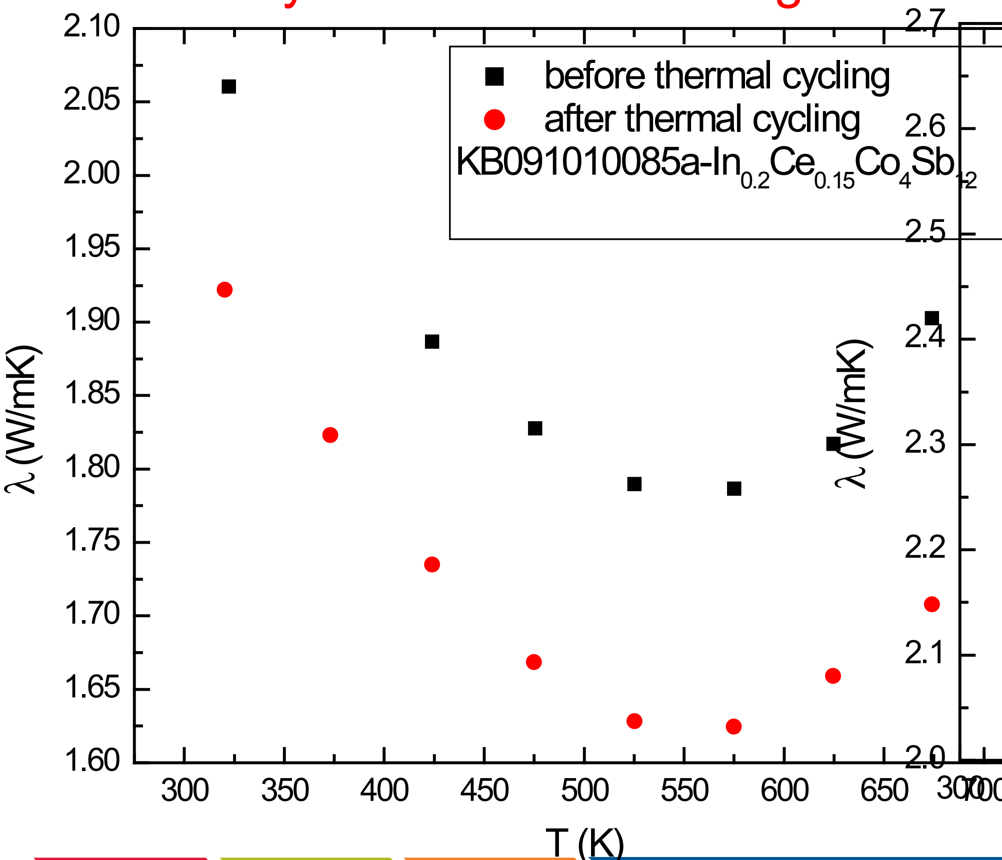
Thermal Cycling Impacts on Power Factor

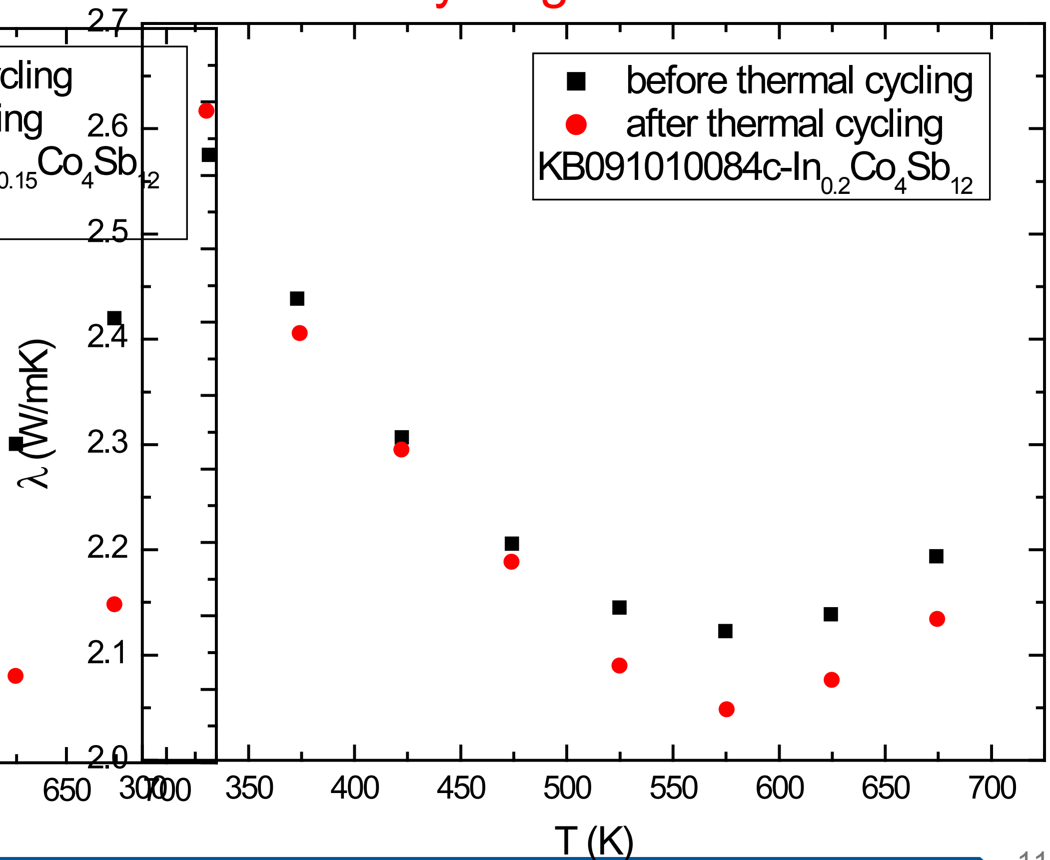
- $In_{0.2}Ce_{0.17}Co_4Sb_{12}$ showed 36% increase in PF @ 525 K
- $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ showed similar increases in Seebeck coefficient
- HOWEVER, $In_{0.2}Ce_{0.05}Yb_{0.1}Co_4Sb_{12}$ showed 36% decrease in PF @ 525 K
- Materials that behave this way after thermal cycling can't be used in WER
- Thermal cycling a r - TriRa showing meta-stable states.



Thermal Cycling Impacts on Thermal Conductivity

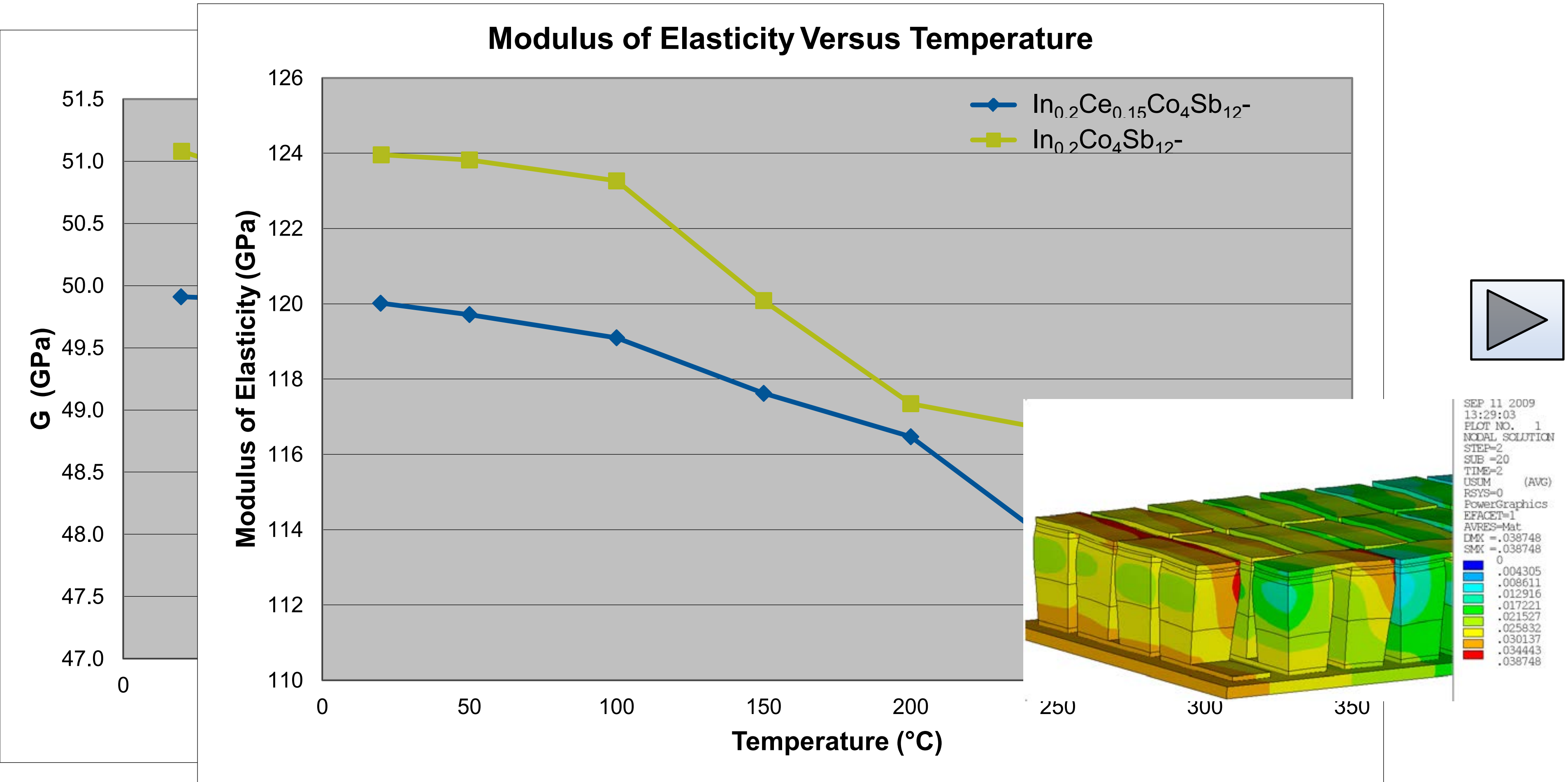
- Major Finding – Thermal Conductivity Decreases After Thermal Cycling in These Materials
  - $In_{0.2}Co_4Sb_{12}$ - λ Decreases By ~ 3% or Stays Approximately the Same
  - $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ – λ Decreases By ~8%
- Coupled with Increases in Power Factor (α^2/ρ) → Increases ZT by 1.4X
- XRD Analysis Shows No Changes After Thermal Cycling





Shear & Elastic Moduli Vs. Temperature

- First Measurements of Temperature-Dependent Structural Properties in These Skutterudite Materials (Reported in Journal of Electronic Materials 2012)
- Temperature-Dependent Structural Properties Critical to TE Device Design



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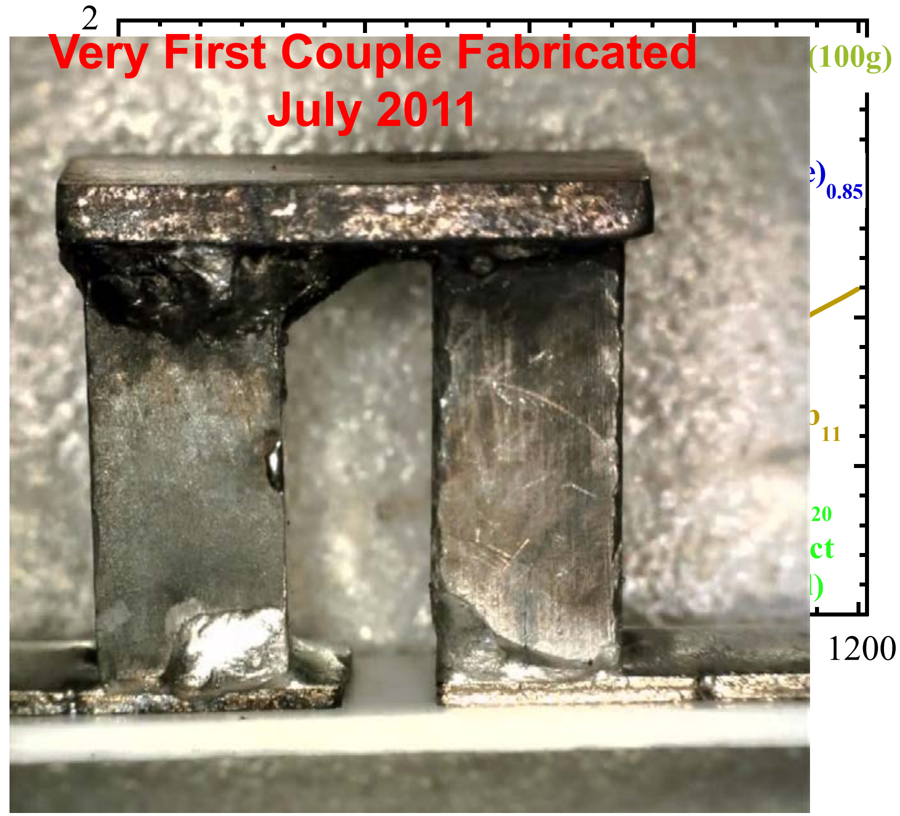
TE Couple Fabrication & Testing

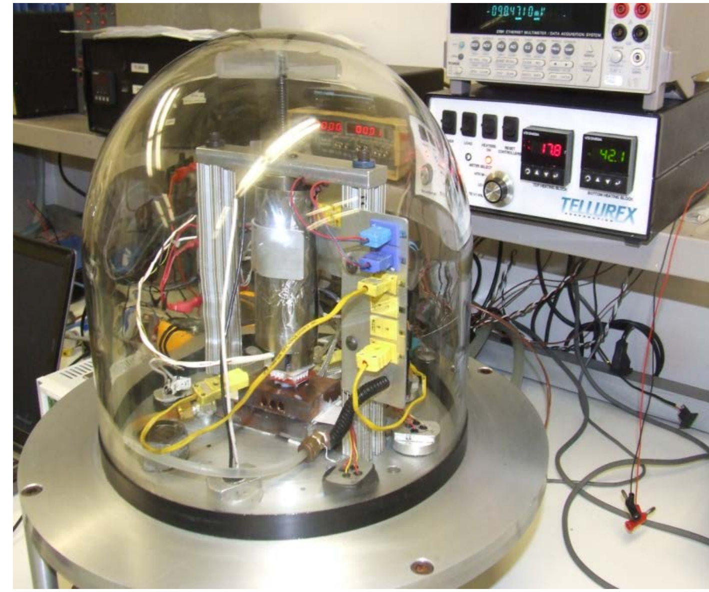
p-Type LASTT / n-Type $In_{0.2}\,Ce_{0.15}\,Co_4\,Sb_{12}$ Couple

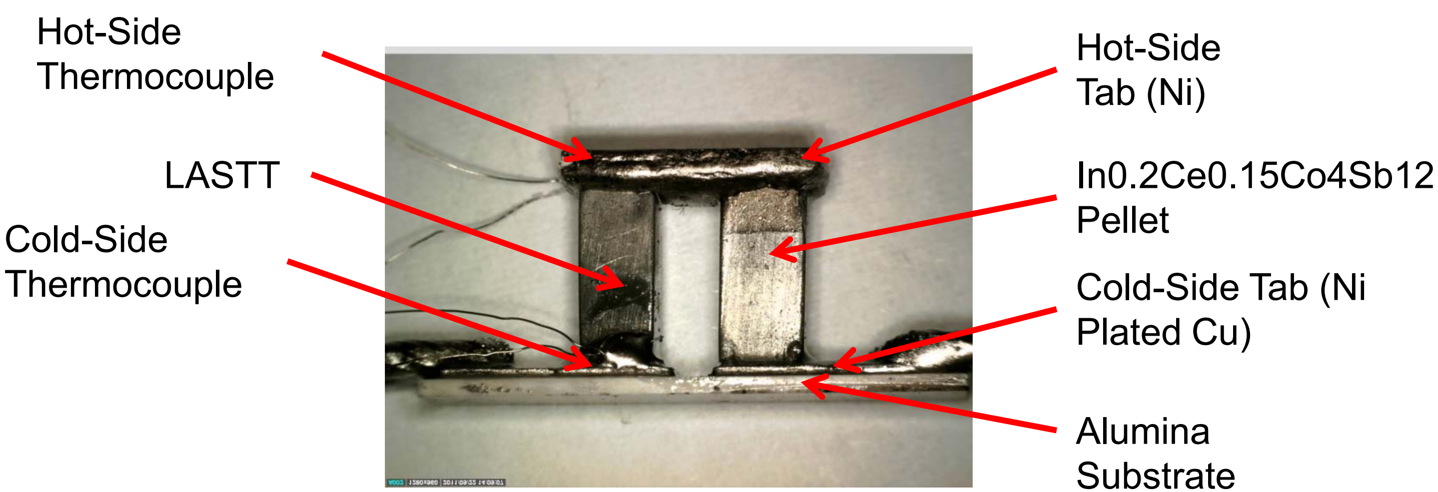
- **n-Type In-Ce Based Skutterudites with p-Type LASTT Materials in Operating TE Couple**
  - **p-Type LASTT Well-Developed Thermoelectrically & Structurally (Tellurex Corp., 2009)**
  - **Demonstrated in TE Modules (Tellurex Corp., 2009)**
  - **ZT = 1.2 @ 750 K**



TELLUREX
CORPORATION

TE Couple Test System





TE Couple Test Results

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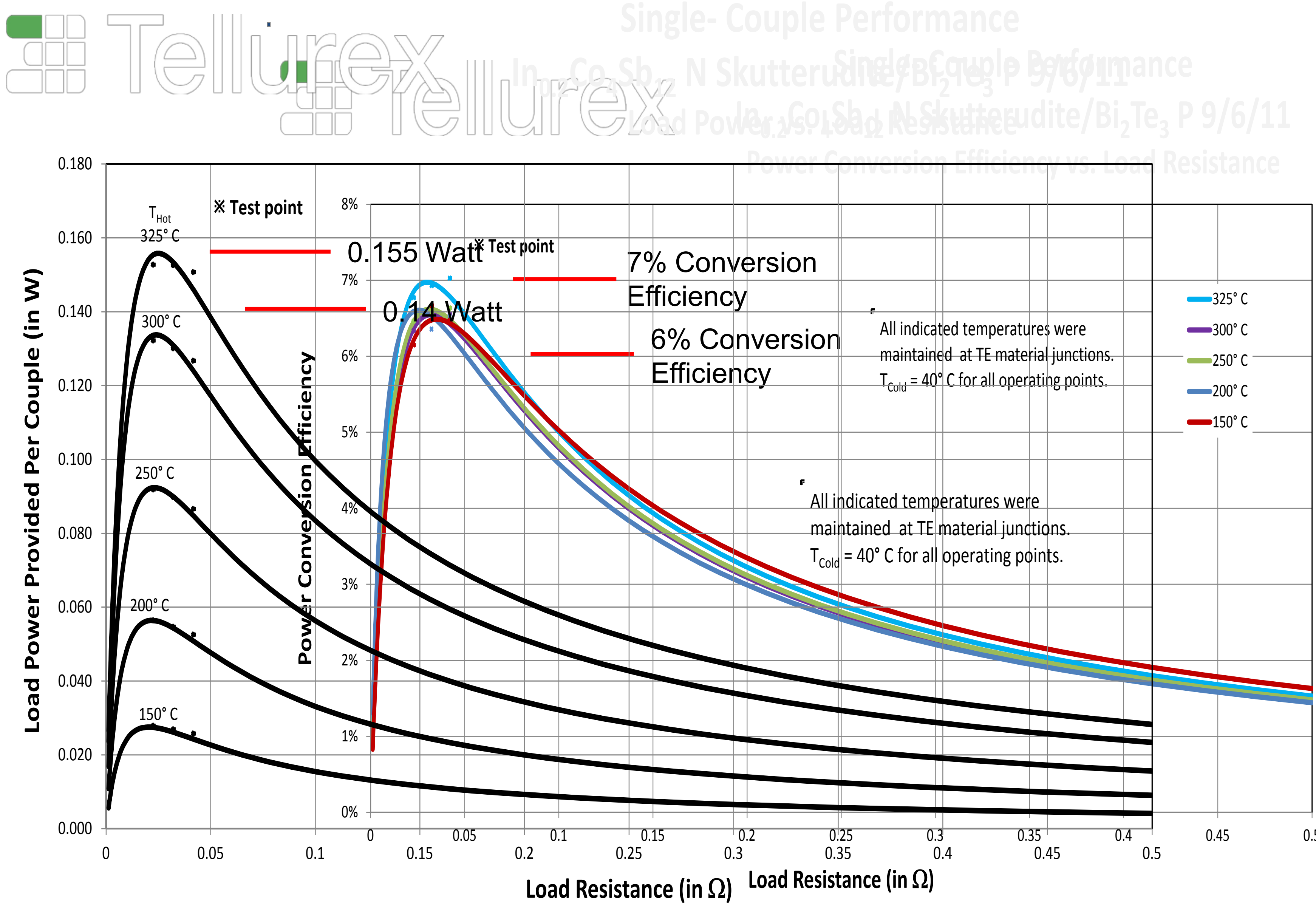

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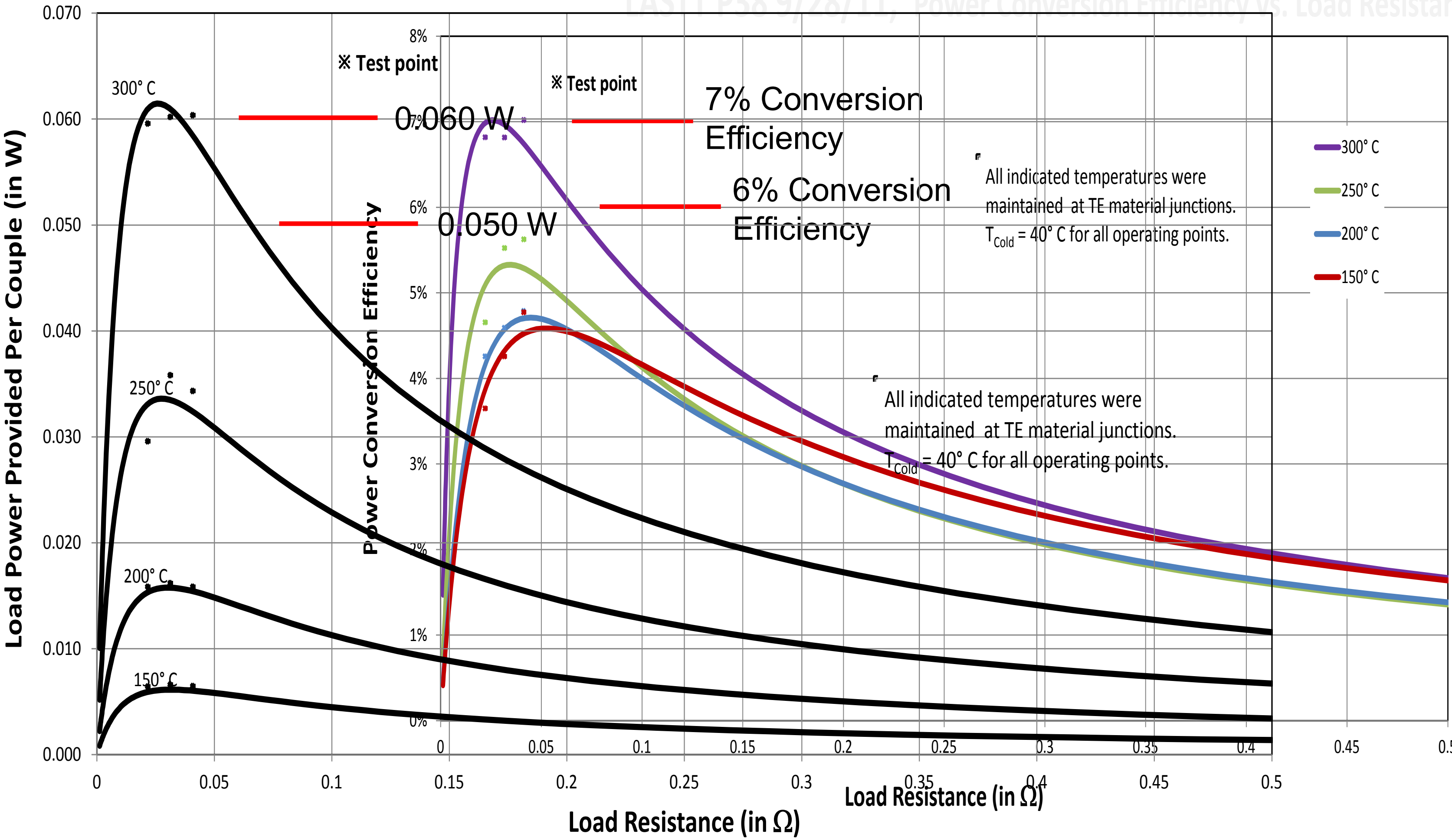
Tellurex

Single- Couple Performance

Single- Couple Performance

$In_{0.2}Ce_{0.15}Co_4Sb_{12}$ N Skutterudite/
Load Power vs. Load Resistance
LASTT P38 9/28/11, Power Conversion Efficiency vs. Load Resistance



Projected 8.1% TE Conversion Efficiency @ T_{hot} = 400°C (673 K)

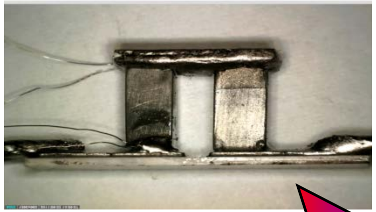
T_{cold} = 40°C (313 K)

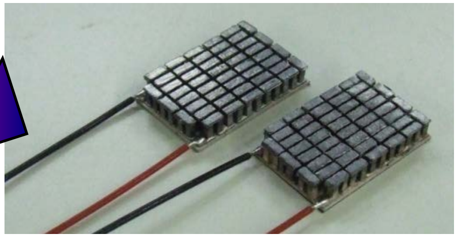
Hot Side Temperature [°C]	TE Couple Efficiency [%]
150	4.75 (Actual Test Data)
250	5.55 (Actual Test Data)
300	7.0 (Actual Test Data)
400	8.1 (Linear Extrapolation of Test Data to Higher Test Temperatures)

- 7% @ T_{hot} = 300°C is an Excellent Conversion Efficiency for an Operating TE Couple at These Temperatures
  - Includes Couple Electrical Contact Resistances & Thermal Contact Resistances
- Creates Numerous Opportunities in Transportation & Industrial Energy Recovery
  - These Couples Are Fully Capable of Environments and Applications Where T_{hot} = ~450°C

Conclusion & Closing Remarks

- p-Type LASTT and n-type $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ Skutterudites Available NOW for Scale-Up
  - Thermoelectric Properties
  - Structural Properties
  - Thermal Cycling





- Highly Manufacturable Materials
  - Excellent Bonding Properties
  - Easy to Handle in Fabricating Couples
  - Very Good Performance Demonstrated in Operating Couple
- Couple Exhibited Very Good Electrical & Thermal Interfaces at Bond Lines
- Additional Development and Scale-Up Funding Now Required

Learn from the mistakes of others. You won't live long enough to make them all yourself.

Yogi Berra

Energy Solutions Needed Now:
If not us, who? It is up to Us!

If not now, when? Urgency is Now!

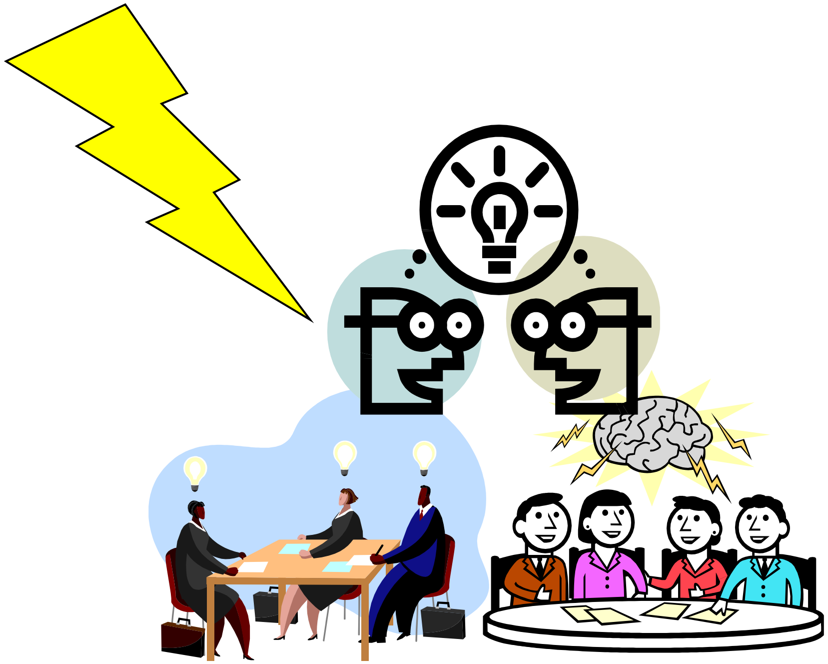
AN ENERGY TSUNAMI AHEAD

Thank you for your interest and attention

We are What We Repeatedly do. Excellence, Then, is not an Act, But a Habit.

Aristotle

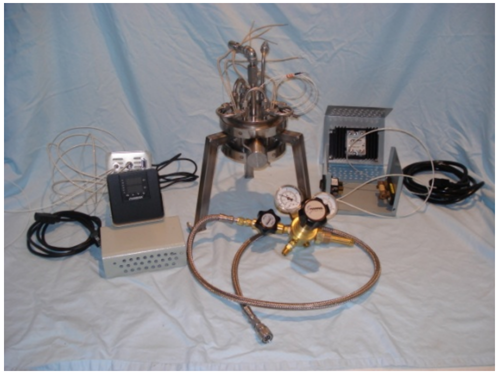
Questions & Discussion

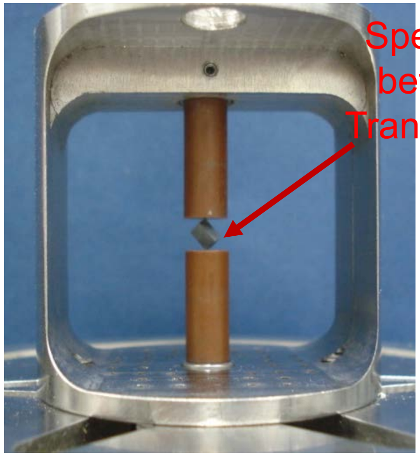


Technical Backup

Structural Property Measurements

- Structural Properties Just as Critical as TE Properties
- Measured Coefficient of Thermal Expansion & Determined Elastic Material Properties Over Elevated Temperatures
  - Measured Coefficient of Thermal Expansion (298 – 673 K)
  - Modified Existing RUS System for Material Property Measurement at Elevated Temperatures
  - Measured E and *v* at Multiple Temperatures Spanning Room Temperature to 300 ºC
- RUS Systems
  - Room Temperature System Shown Right
  - High-Temperature System Shown Below





n-type Structural and TE Properties

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Specimen Label and Comments	ρ, density (g/cm³)	υ, Poisson's ratio	*CTE (10⁻⁶ / C) (298 – 673 K)*	*E*, Elastic Modulus (10¹¹ N/m²)	*ZT (@ 625 K)*
Bi_2Te_3 Alloys		0.21-0.37	14 21 (Anisotropic)	0.40-0.47	0.0-0.1
PbTe		0.26	19.8	0.58	0.7
$CoSb_3$ (literature)		0.222		1.396	0.6
$CoSb_3$ (PNNL)		0.225-0.226	12.8	1.391-1.398	
$In_{0.1}Co_4Sb_{12}$ (PNNL)		0.227	8.37	1.396	
$In_{0.1}Y_{0.1}Co_4Sb_{12}$ (PNNL)		0.247	9.26	1.413	~0.5
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ – PNNL3 2-5-2010 --- REPEAT of 1-21-2010	~7.314	0.185	8.61	1.339	0.95
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ - LB1 2-5-2010	7.304	0.215	8.56	1.348	0.95
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ - LB2 2-9-2010	7.264	0.204	8.26	1.326	0.95
$In_{0.2}Ce_{0.15}Co_4Sb_{12}$ _03161035_3-17-10 6-08-2010 - BNW-60608 – 88(M1-M31)	7.019	0.210-0.214 (2 samples)	8.11-8.44	1.182-1.185 (2 samples)	1.3-1.4 (1.5-1.6 @ 500K)
$In_{0.2}Co_4Sb_{12}$ – A05061030-A 2010-06-09- BNW-60608 – 90(M1-M29 & M31 – No M30)	7.06-7.10	0.208-.218 (2 samples)	8.27-8.34	1.178-1.238 (2 samples)	1.2
$In_{0.2}Yb_{0.1}Ce_{0.05}Co_4Sb_{12}$-KB0627100_7-23-10 2010-08-16-BNW-60608-123 (M1-M27)	6.421	0.207	7.06–9.7	0.895	1.2

Thermal Cycling Impacts on Power Factor

- $In_{0.15}Ce_{0.1}Co_4Sb_{12}$ showed significant increases in power factor after thermal cycling – Table Shows 510 K Properties
- Effect in the right direction – Big impact on Seebeck coefficient
- Required further investigation with other (InCe)-based compounds and with statistically-significant sample numbers

Specimen Label and Composition	Before Thermal Cycling			After Thermal Cycling		
	Seebeck Coefficient [μV/K]	Electrical Resistivity [mΩ-cm]	Power Factor [μW/cm-K^2]	Seebeck Coefficient [μV/K]	Electrical Resistivity [mΩ-cm]	Power Factor [μW/cm-K^2]
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (LB1 sample)	-259	2.33	28.7	-315	2.55	38.9 (+35.5%)
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (LB2 sample)	-259	2.33	28.7	-329	3.32	32.6 (+13.6%)