2011 DOE Vehicle Technologies Program Review

Proactive Strategies for Designing Thermoelectric Materials for Power Generation

PNNL / ONAMI Joint Project on Advanced TE Materials & Systems

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Project ID #PM014

11 May 2011

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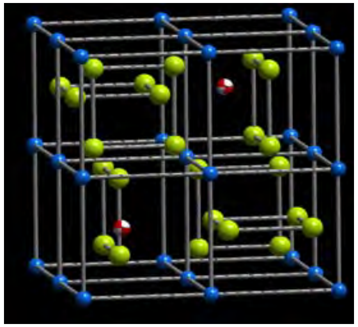
Agenda

- Overview – Timeline, Budget, Technical Barriers, & Collaborations
- Objectives
- Relevance
- Technical Approach
- Project Accomplishments
- Collaborations & Coordination
- Future Work
- Summary

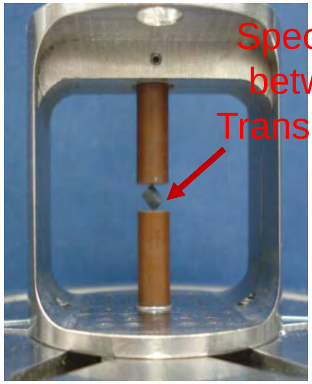
Proactive Strategies for Designing Thermoelectric Materials for Power Generation - Overview

Timeline

- Project Start Date: 15 December 2008
- Project End Date: 15 December 2011
- 75% Complete



$R_xCo_4Sb_{12}$



OVT - Advanced Combustion R&D Goals & Solid State Energy Conversion Barriers A, B

- Improve heavy truck efficiency to 50 percent by 2015
- Achieve stretch thermal efficiencies of 55% in heavy-duty engines by 2018
  - Improve Cost-Effectiveness & Performance of Exhaust Heat Recovery
- Achieve at least a 17 percent on-highway efficiency of directly converting engine waste heat to electricity
  - Fuel Economy Increases of 10% over 2010
- Improve Fuel Efficiency of Light-Duty Gasoline Vehicles by 25% & Light-Duty Diesel Vehicles by 40% (compared to 2009)
- Scaling Up High-Performance Waste Energy Recovery Materials to Integrate into Advanced Engines

Budget

- Total FY 2009 Project Funding $260K
- Total FY 2010 Project Funding $260K
- Total FY 2011 Project Funding $260 K ($130 K To Date)

Partners

- **Lead: Pacific Northwest National Laboratory**
- **Partner: Oregon State University, Corvallis, OR**
- **Tellurex Corporation**
- **ONAMI**

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ONAMI OREGON NANOSCIENCE AND MICROTECHNOLOGIES INSTITUTE

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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

  - **Hybrid Electric Vehicles**

    Move Toward Electrification – Micro, Mild, and Full

    Needs for Power Generation

    Needs for Electric-Driven Cooling

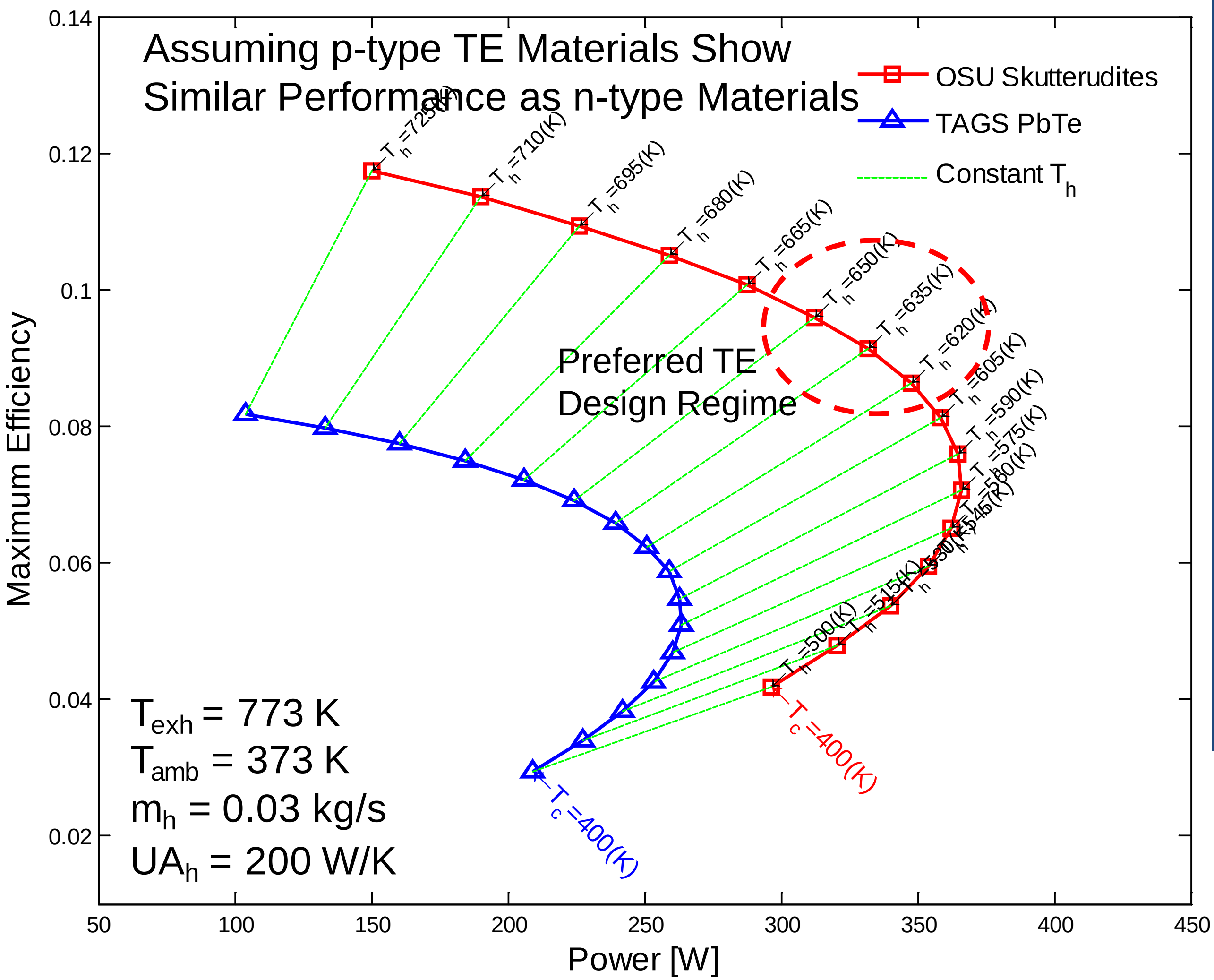
[1]*Transportation Energy Data Book,* 2010, Edition 29, U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicles Technology Program. ORNL-6985, Oak Ridge National Laboratory, Oak Ridge, Tennessee. http://cta.ornl.gov/data/index.shtml.

Relevance - Project Objectives

- Develop new high-performance n-type and p-type thermoelectric (TE) material compositions to enable:
  - 10% fuel efficiency improvements from waste energy recovery in advanced light-duty engines and vehicles.
  - Heavy truck efficiencies to 50% by 2015
  - Stretch thermal efficiencies of 55% in advanced heavy-duty engines by 2018.
  - Achieve 17% on-highway efficiency of directly converting engine waste heat to electricity
- Improve cost-effectiveness and performance of exhaust heat recovery in light- and heavy-duty vehicles. Scaling up to operating TE devices.
- Develop TE materials with operational temperatures as high as 800 K to 900 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.

Relevance - TE Material Impacts on System Design

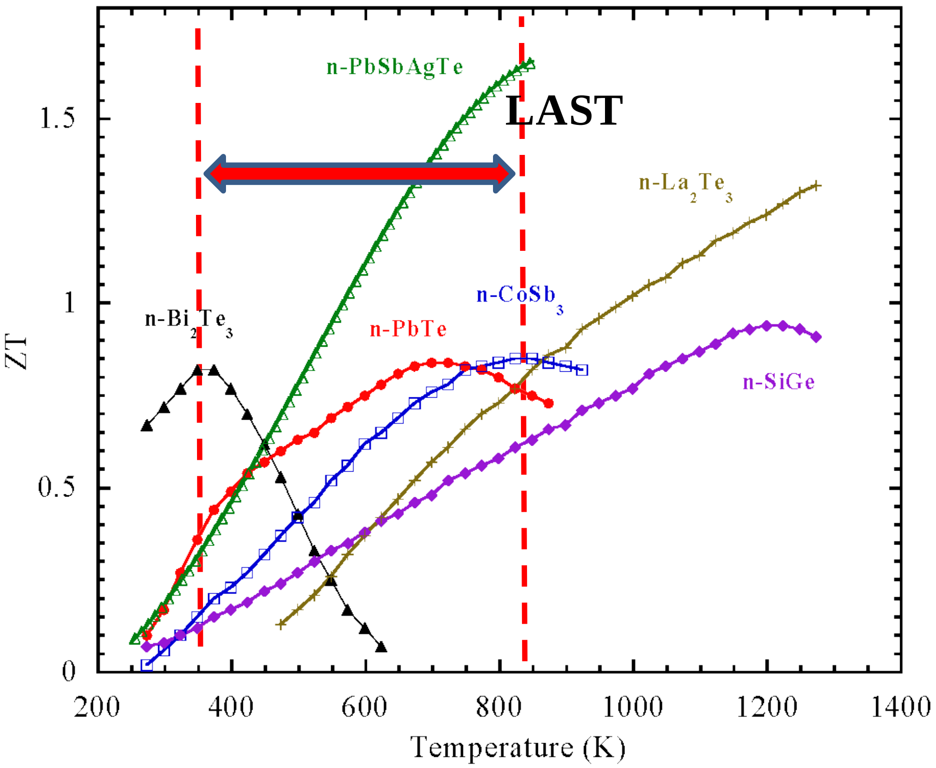
- System-Level Analyses Show OSU/PNNL Skutterudites Potential Superiority Compared to Common High-Performance TE Materials
  - Heavy- & Light-Duty Automotive Exhaust Heat Recovery (EHR) Applications
  - Heavy-Duty Exhaust System Power ~ 2kW, EGR System ~ 1 kW



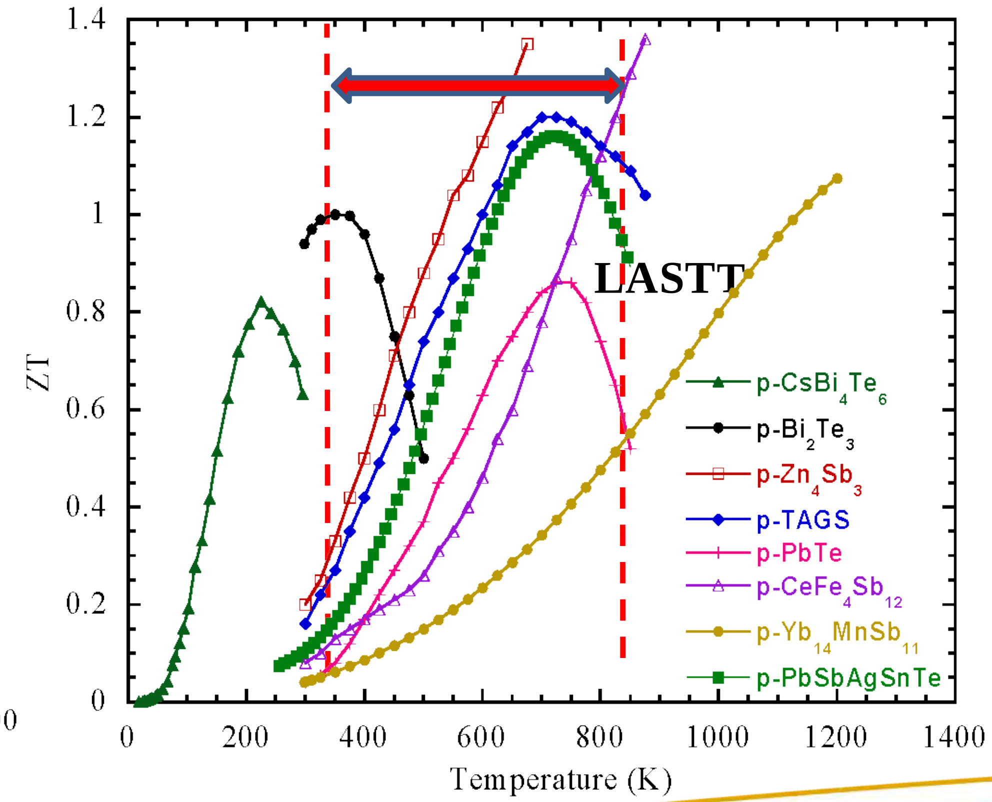
- Benefits Heavy-Duty Engine Performance:
  - 10% Conversion in Exhaust Could Move Heavy Duty Engines Toward 48% Efficiency
  - Additional Benefit from EGR Thermal Recovery
- Benefits Heavy-Duty APU Development to Reduce Idling Fuel Consumption
- Improves Light-Duty EHR Performance to Enhance Light-Duty Fuel Economy

Technical Approach – Current Laboratory-Level SOA

- Power Generation in Light-Duty & Heavy-Duty Applications Requires TE Materials in the 350 K to 820 K Range



Z*T vs. Temperature for Various n-type TE Materials

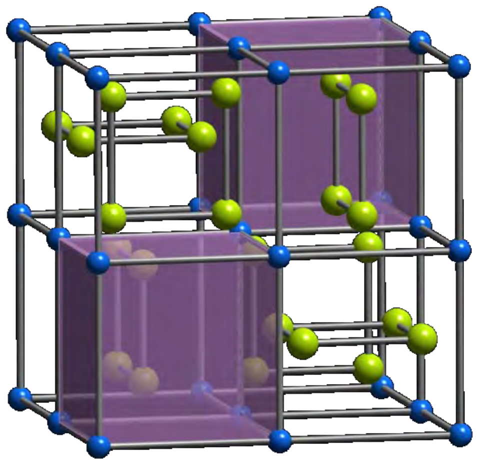


Z*T vs. Temperature for Various p-type TE Materials

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

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



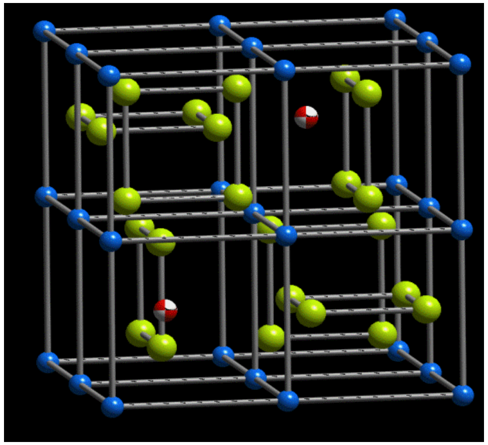
Co_4Sb_{12} (n-type)

$Fe_xCo_{4-x}Sb_{12}$ (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



$R_xCo_4Sb_{12}$

$R_xR'_yCo_4Sb_{12}$

- **This Year's Focus:**
  - n-type $In_{0.2}Co_4Sb_{12}$
  - n-type $In_xCe_yCo_4Sb_{12}$
  - n-type $In_xCe_yYb_zCo_4Sb_{12}$

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Technical Approach

- Proactive, Systematic Investigation of Dual- & Tri-Rattler Skutterudites
  - Refine n-type Materials, Characterize at Higher Temperatures & Transition to TE Couple
  - Systematically Investigated p-type Materials
- TE Property Measurements @ OSU Laboratories
  - Seebeck Coefficient Measurements vs. T
  - Electrical Conductivity Measurements vs. T
  - Thermal Conductivity Measurements vs. T

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

- Engaging Third-Party Validation
  - ORNL – See ORNL Measurements in Technical Backup Slides
- Structural / Thermal Property Measurements @ PNNL
  - Resonant Ultra Sound Techniques (E, ν) Up to 300 °C
  - CTE Up to 400 °C
- Recognition That Structural Properties Just as Important as TE Properties
- PNNL to Characterize System-Level Benefits of Material Compositions in Waste Energy Recovery Applications (See Reviewer Only Slides)
- Demonstrate High-Performance TE Couples for Transition to Waste Energy Recovery Applications

Technical Approach - Schedule / Milestones

Month/Year	Milestones:
Dec. 2009–Dec. 2010	P-type and n-type Thermoelectric Development & Testing. Optimize Compositions for TE Performance. Measure TE Properties (Seebeck Coefficient, Electrical Resistivity, & Thermal Conductivity). On-going throughout the year due to third-party validation. ORNL n-type Material Tests Completed January 2011.
Jan. 2010 – Oct. 2010	Select p-type and n-type TE Materials for Structural Testing. Criteria Will Be Selecting the Best TE Materials Properties (ZT vs. T.). Selected and Continued Refining n-type $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ and $In_{0.2}Co_4Sb_{12}$ for Reproducibility. p-type LASTT Materials Selected in October 2010.
Dec. 2009 – Dec. 2010	Continue Measuring & Categorizing Room Temperature Structural Properties of p-type & n-type TE Materials. Measured E, ν, CTE in Several Compositions to Date.
September 2011	Measure High Temperature Structural Properties of n-type TE Materials.
December 2011	Develop and Measure TE Couple Performance Using In n-type $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ and/or $In_{0.2}Co_4Sb_{12}$ materials coupled with p-type LASTT TE materials. Tellurex Corporation As Commercialization Partner

Technical Approach - TE Properties Characterization

LFA 457 MicroFlash® :
thermal diffusivity
(150 – 1000 K)

1

Density measurements

2

TE Sample

3

3

Uncertainties:
S ±5%; ρ ±5%;
λ ±10 %

Specific Heat Capacity:
Mettler DSC820
(RT – 800 K)

Standards:
Constantan
n- & *p*-Bi_2Te_3

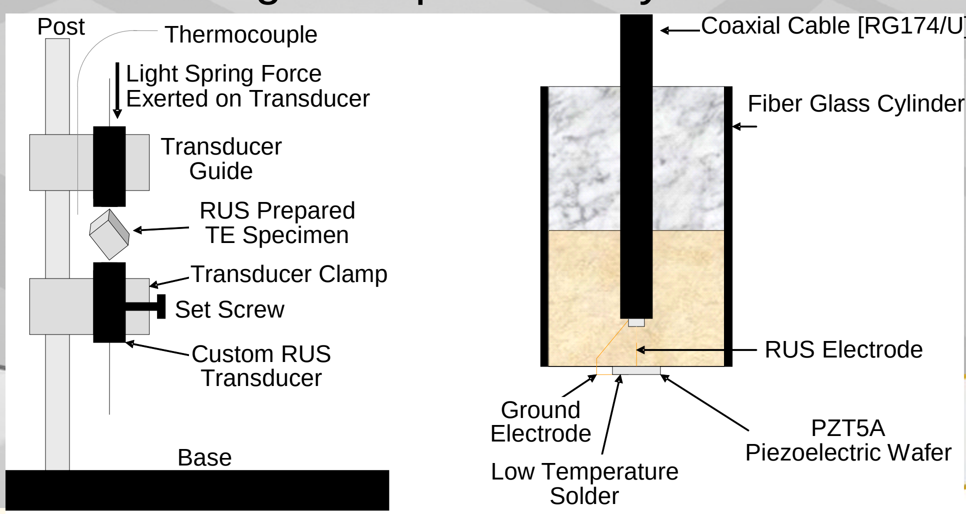
ZEM 3 (ULVAC)
Seebeck coefficient/electrical resistance measurement (RT-800K)

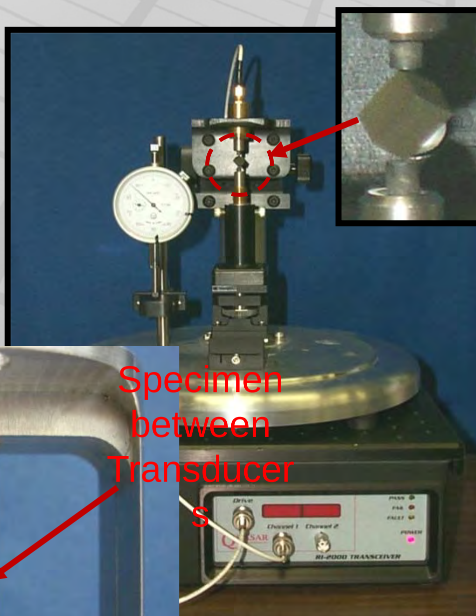
QD - PPMS(5-300K)

X-ray data from another sample prepared from the same batch

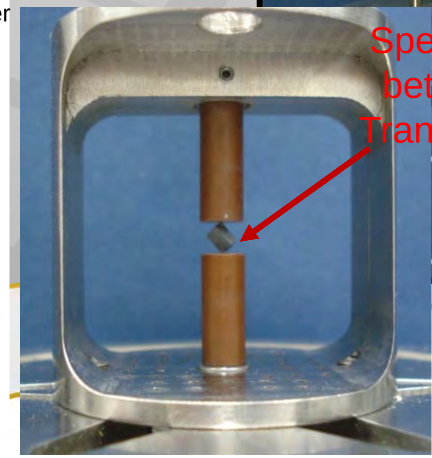
Technical Approach-Structural Property Measurements

- 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
    - Currently Measuring E and *v* at Multiple Temperatures Spanning Room Temperature to 300 ºC
- RUS Systems
    - Room Temperature Shown Right & Below
    - High-Temperature System in Reviewer Charts





Specimen between Transceivers



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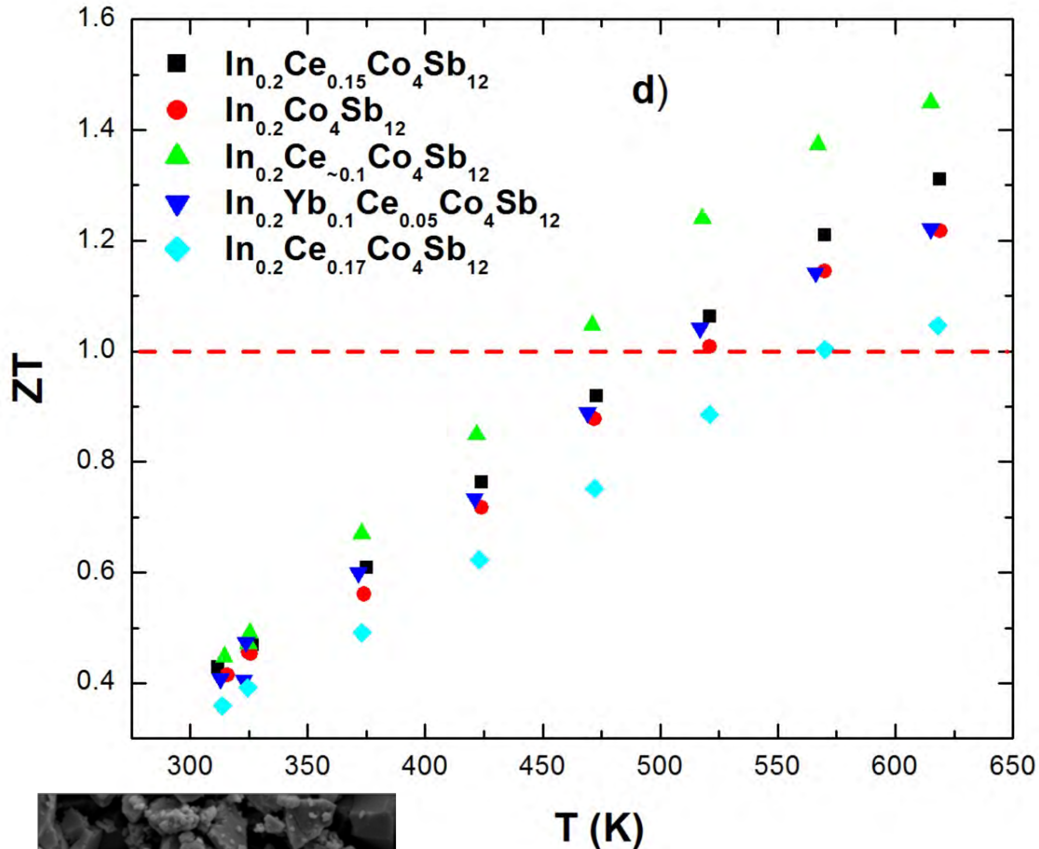
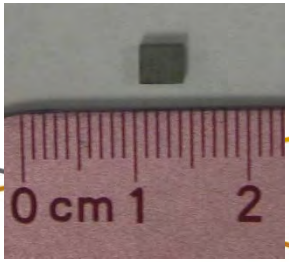
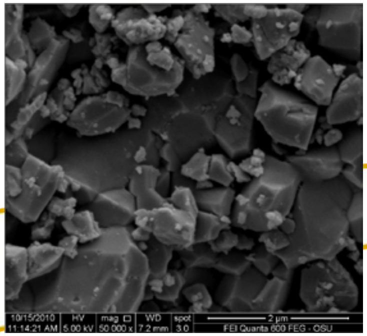
Project Accomplishments
n-Type $In_xCe_yCo_4Sb_{12}$ TE Properties

- $In_{0.2}Co_4Sb_{12}$ 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.
- Last year one $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ sample showed ZT ~ 1.5 – 1.6 around 500 K. Working on reproducing it. (See reviewer only slides)







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

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n-type Structural and TE Properties

Specimen Label and Comments	ρ, density (g/cm³)	υ, Poisson's ratio	*CTE* *(10^{-6} / C)* *(298 – 673 K)*	*E*, Elastic Modulus (10^{11} 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 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 and 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

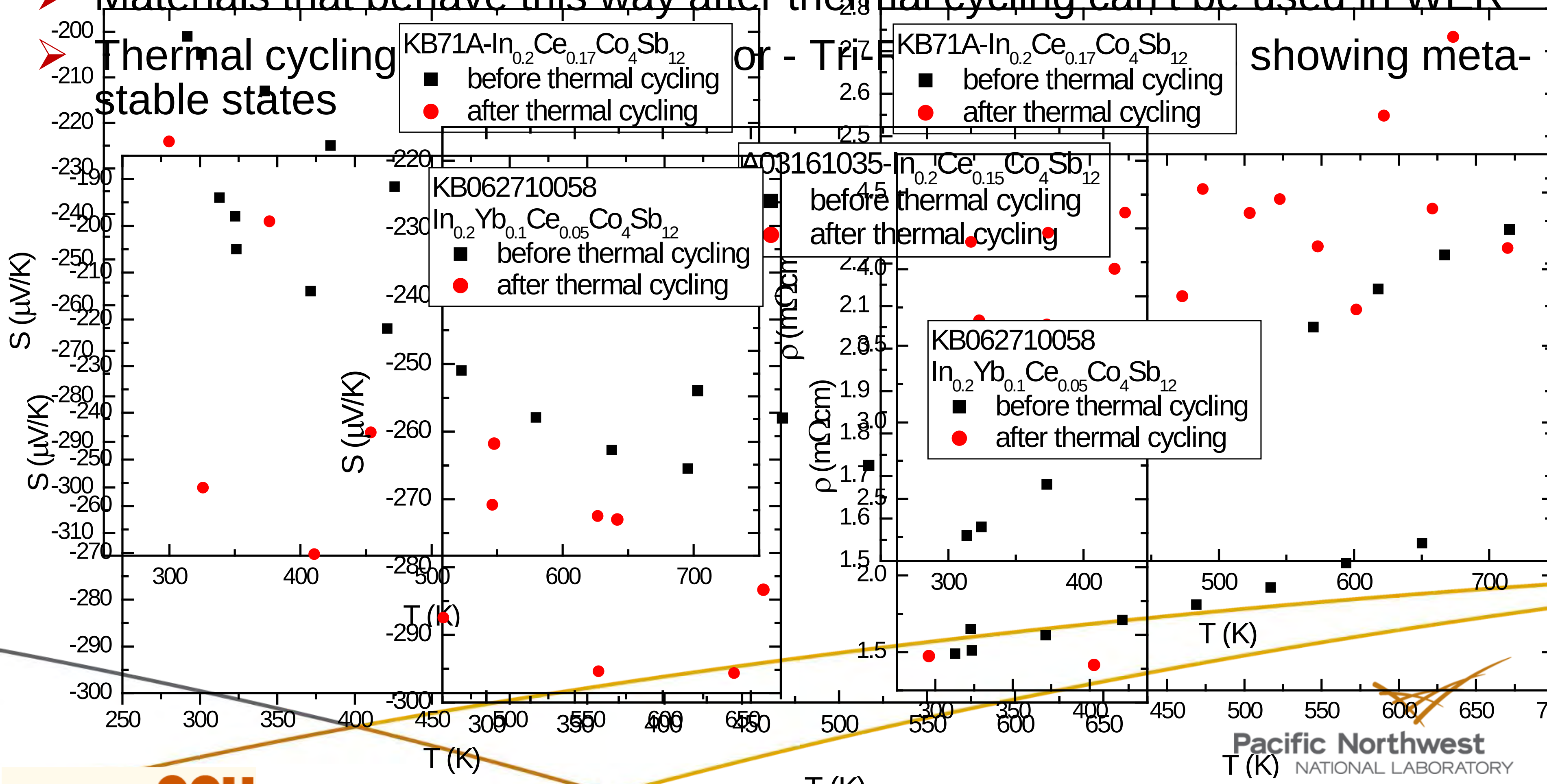
Thermal Cycling Impacts on Power Factor

- $In_{0.15}Ce_{0.1}Co_4Sb_{12}$ 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 [$\mu W/cm\text{-}K^2$]	Seebeck Coefficient [μV/K]	Electrical Resistivity [mΩ-cm]	Power Factor [$\mu W/cm\text{-}K^2$]
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (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%)

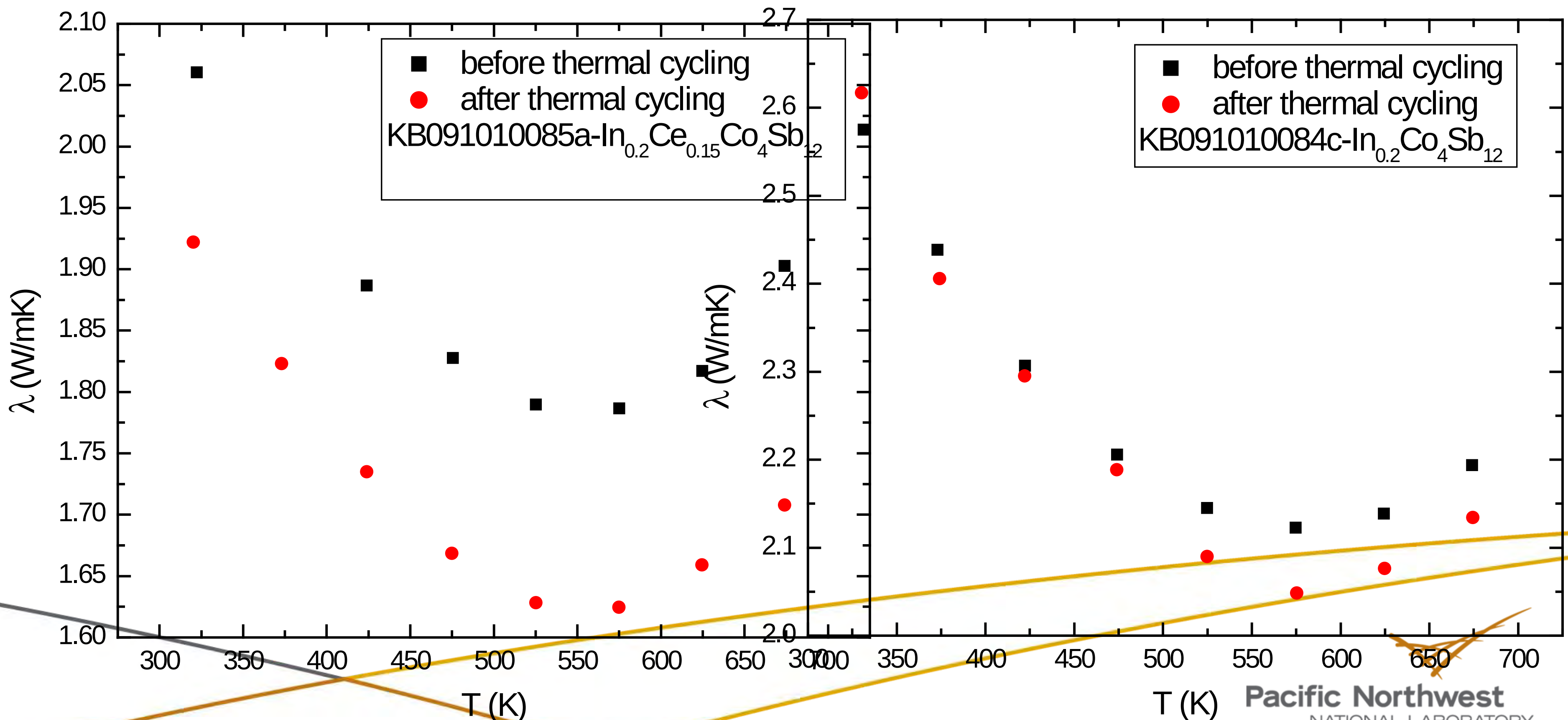
Thermal Cycling Impacts on Power Factor

- $In_{0.2}Ce_{0.17}Co_4Sb_{12}$ 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% <u>decrease</u> in PF @ 525 K
- Materials that behave this way after thermal cycling can't be used in WER
- Thermal cycling … or - Tri-F… showing meta-stable states



Thermal Cycling Impacts on Thermal Conductivity

- Major Discovery – 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



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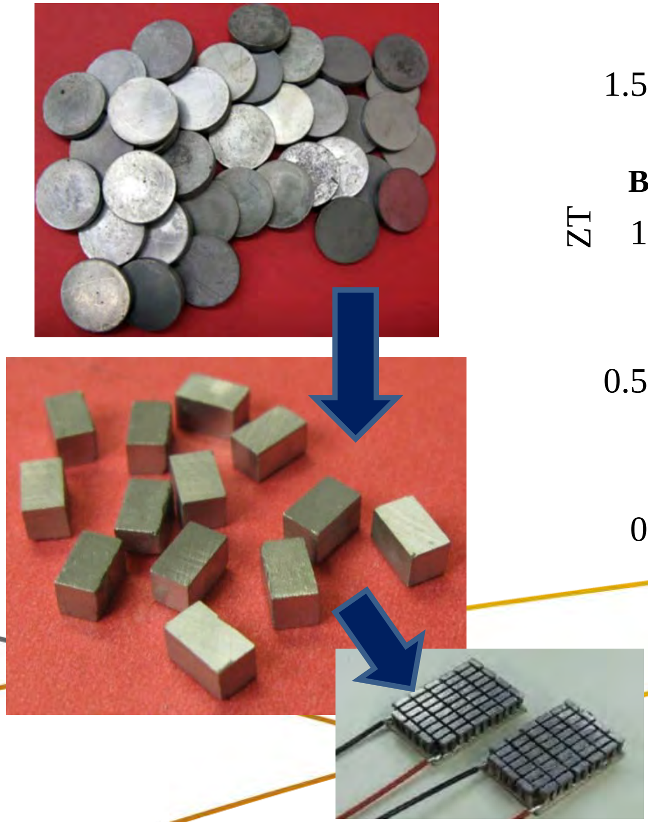
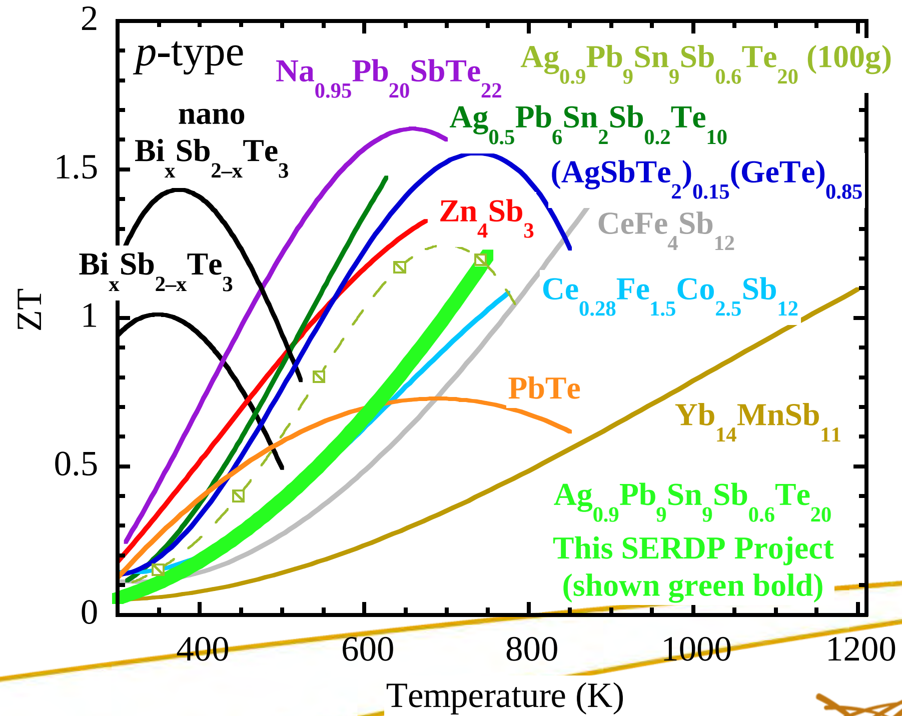
p-Type Skutterudites To Date

- ZT of ~0.48 is obtained for $In_{0.2}Yb_{0.1}Ce_{0.05}Co_3FeSb_{12}$ & $In_{0.2}Yb_{0.05}Ce_{0.1}Co_3FeSb_{12}$ at 710 K (See Reviewer Only Slides)
- Current Plan is to Combine n-Type In-Ce Based Skutterudites with p-Type LASTT Materials to Demo TE Couple
  - Well-Developed Thermoelectrically & Structurally (Tellurex Corp., 2009)
  - Demonstrated in TE Modules (Tellurex Corp., 2009)
  - ZT = 1.2 @ 750 K





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Collaboration and Coordination with Other Institutions

- Partners
  - Oregon State University, MicroProduct Breakthrough Institute
  - Oregon Nanoscience & Microtechnology Institute
  - Oak Ridge National Laboratory – Validation Testing
- Technology Transfer
  - Tellurex Corporation
  - ZT Plus (Part of Amerigon, Inc.)
- Coordination with *Advanced Combustion R&D Solid State Energy Conversion Sub-Program*
  - OVT Waste Heat Recovery & Utilization Project

Microproducts Breakthrough Institute

ONAMI
OREGON NANOSCIENCE AND MICROTECHNOLOGIES INSTITUTE

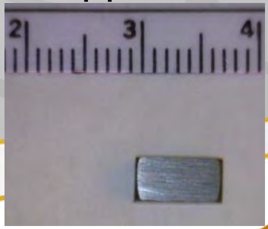
TELLUREX CORPORATION

Future Work & Path Forward

- Optimize Synthesis Procedures for *n*-type (In,R)Co_4Sb_{12} Compositions
  - Focus on $In_{0.2}Co_4Sb_{12}$ and $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ n-type Materials
  - Good Reproducibility
  - Fabricating Highly Dense Samples
- Integrate with *p*-Type LASTT Materials to Create TE p / n Couple
  - TE Couple Completed By October 2011
- Complete High-Temperature Structural Transducer Fabrication
- Characterize Structural Properties at High Temperature – Up to 300°C
  - Young's Modulus, E(T)
  - Poisson's Ratio, ν(T)
  - CTE(T) - Already Have this One
  - High-Temperature Structural Measurements by September 2011

Summary

- **Results**
  - n-type Skutterudite TE Materials Showing Excellent TE Properties (See Publications)
  - $In_{0.2}\,Ce_{0.15}\,Co_4\,Sb_{12}$ and $In_{0.2}\,Co_4\,Sb_{12}$ Selected as n-Type Materials in TE Couples
  - Room Structural Properties & High-Temperatture CTE Testing Completed
  - Good Structural Stability Upon Thermal Cycling
  - Thermal Cycling Has Quite Positive Impacts on TE Properties: $(\alpha^2/\rho)\uparrow$ $\kappa\downarrow$
  - High Temperature Structural Test Equipment Operational & Calibrated
- **Challenges**
  - Batch to Batch ZT Reproducibility and Consistent Properties, Sintering to Highly Dense Samples
  - High Temperature Structural Properties
  - Integrating n-type and p-type Materials into TE Couple – Diffusion Barriers & Interconnects
- **Benefits**
  - System-Level Analyses Show OSU/PNNL Skutterudites Superiority (See Supplements)
  - TE Conversion Efficiencies Can Be High
    - 9-10% in Automotive Applications in Preferred TE Design Regions
    - 11-12%+ in a Direct-Fired APU System
    - Potential Superiority to Other Materials in Automotive TE Systems
  - Bulk TE Materials for Easy Integration into TE Module / System Designs



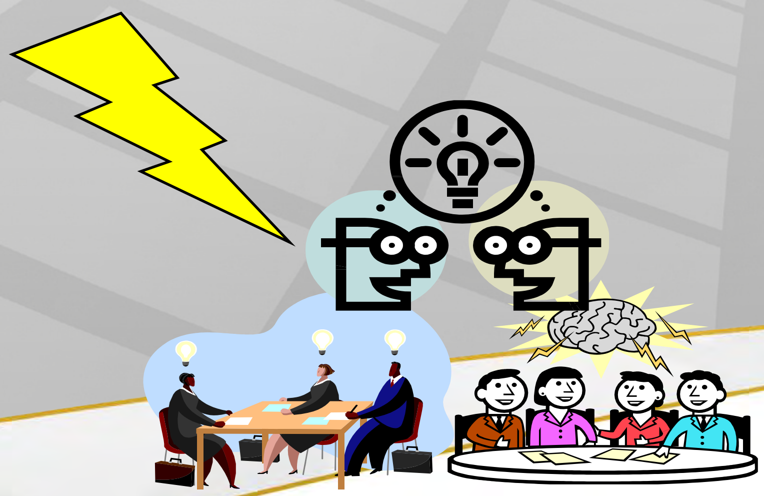
We are What We Repeatedly do. Excellence, Then, is not an Act, But a Habit.

Aristotle

Acknowledgement

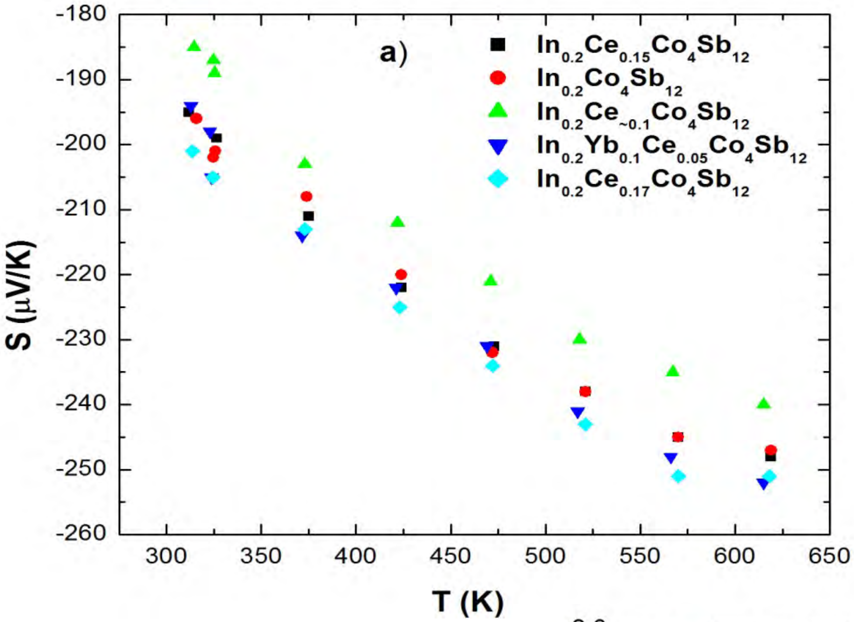
We sincerely thank Jerry Gibbs, Office of Vehicle Technologies Propulsion Materials, for his support of this project.

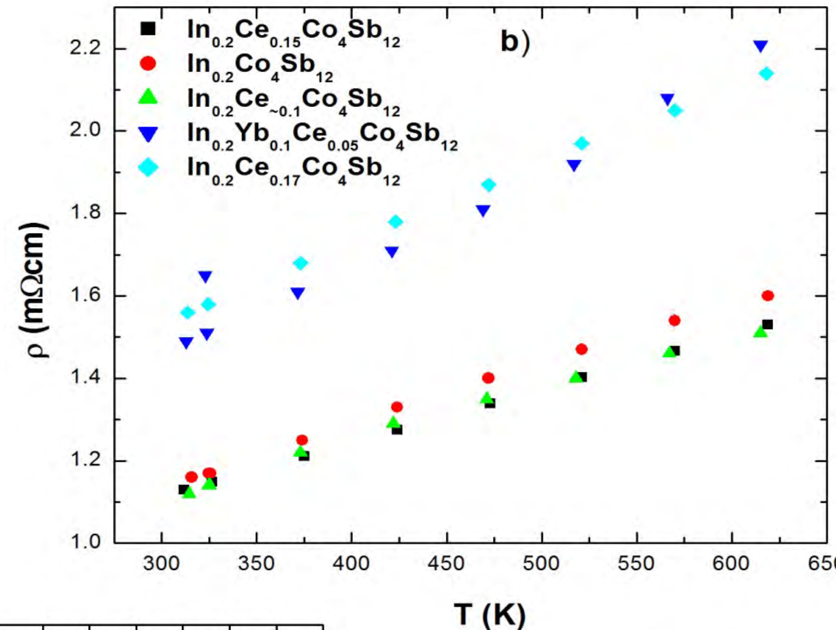
Questions & Discussion

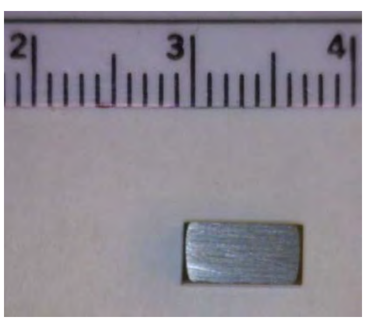


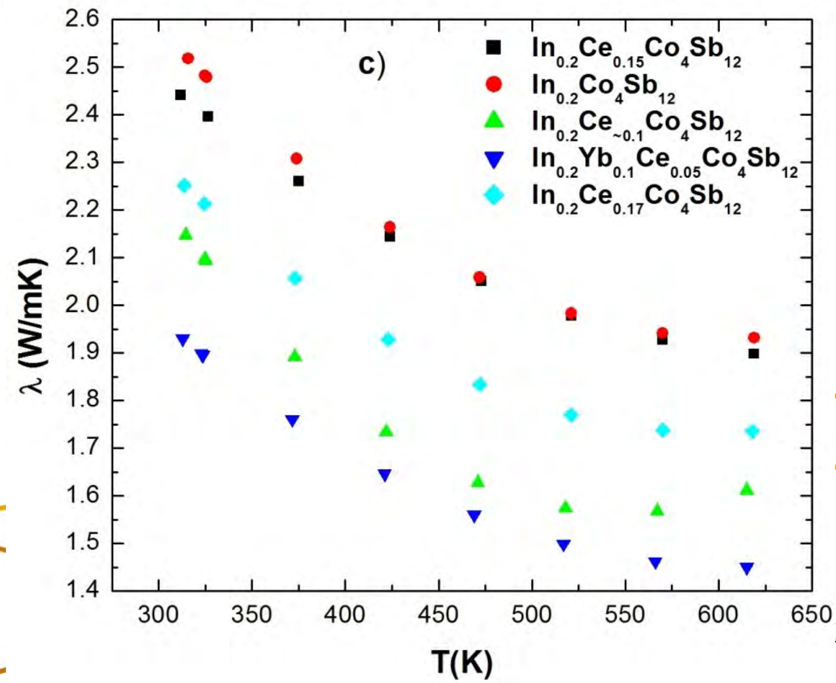
Technical Backup Slides

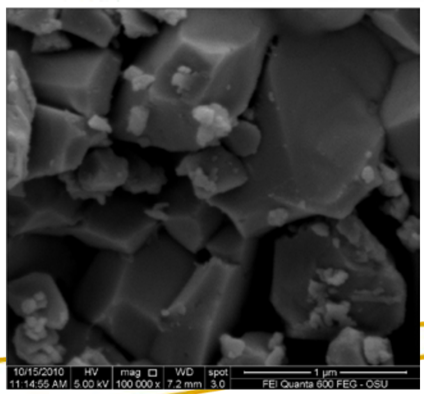
(InCe)-based Compounds - Seebeck Coefficient, Electrical Resistivity, Thermal Conductivity vs. Temperature











$In_{0.2}Ce\sim_{0.1}Co_4Sb_{12}$ SEM
1 um Resolution

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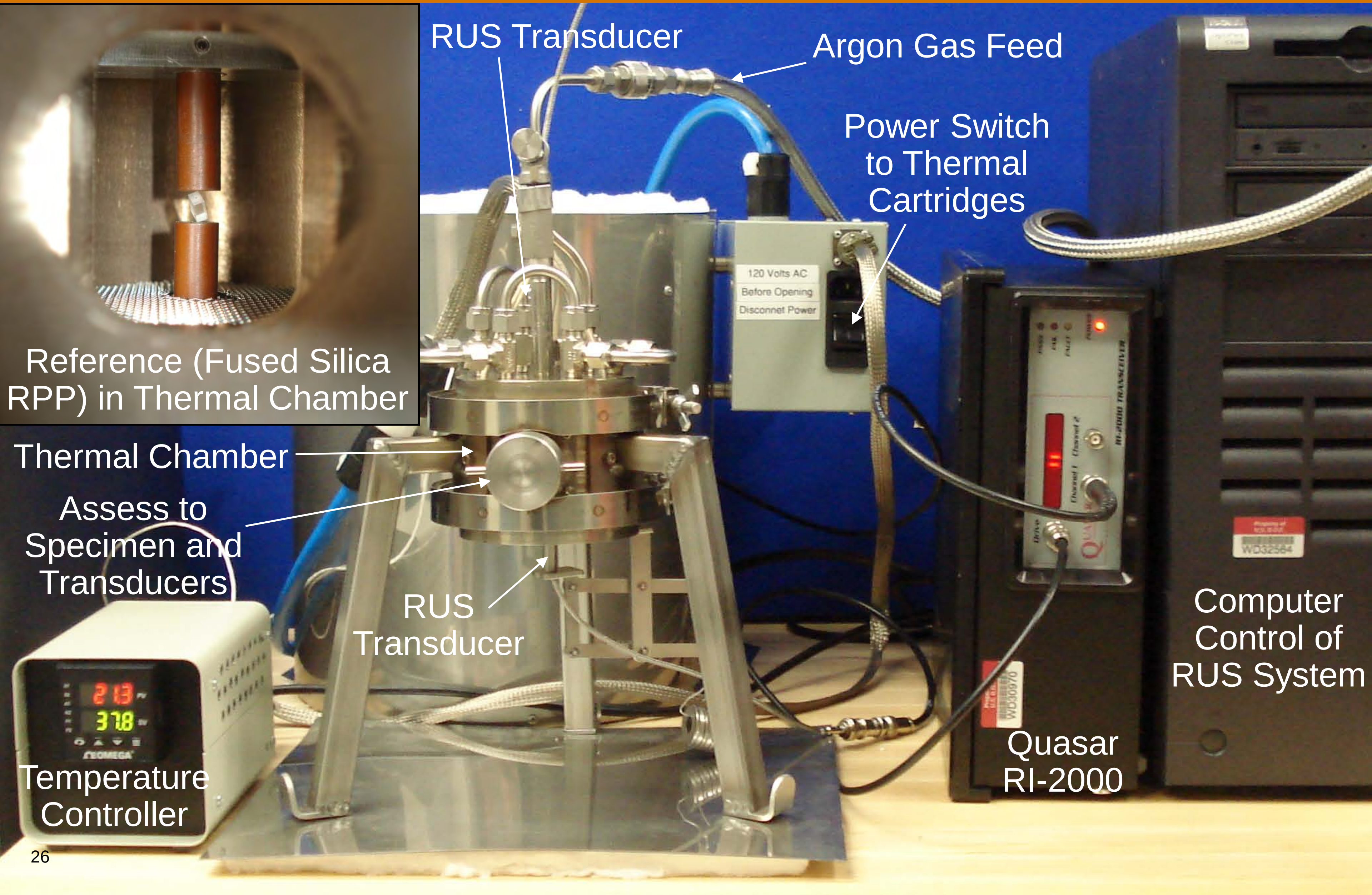
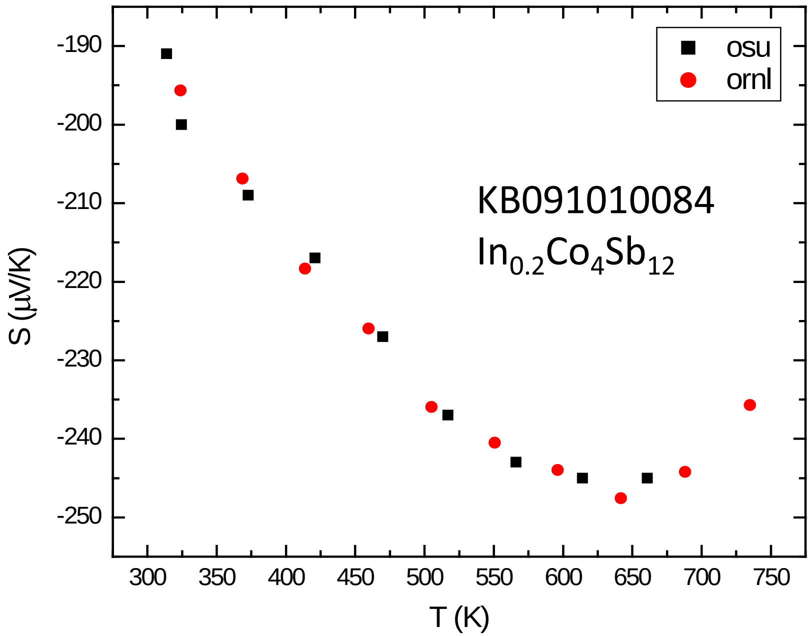
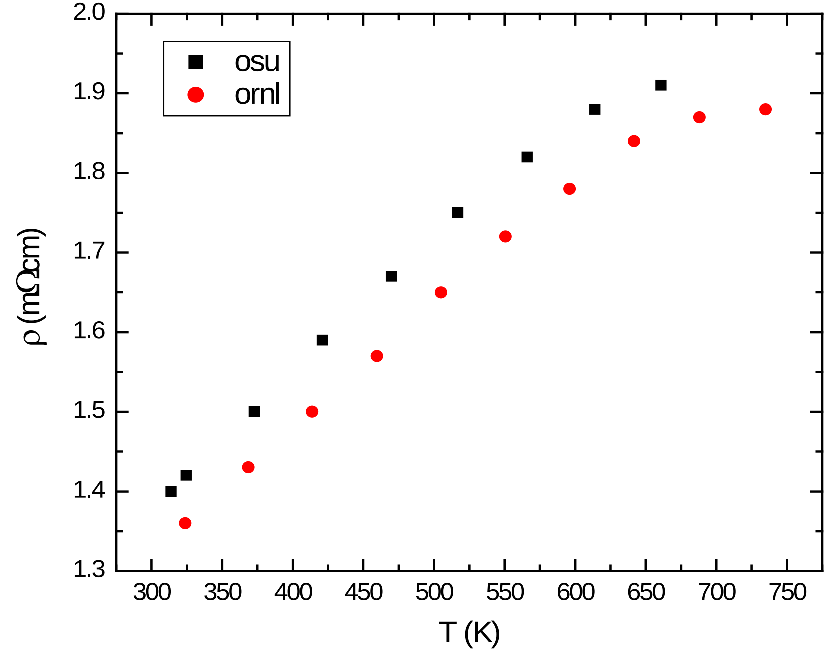
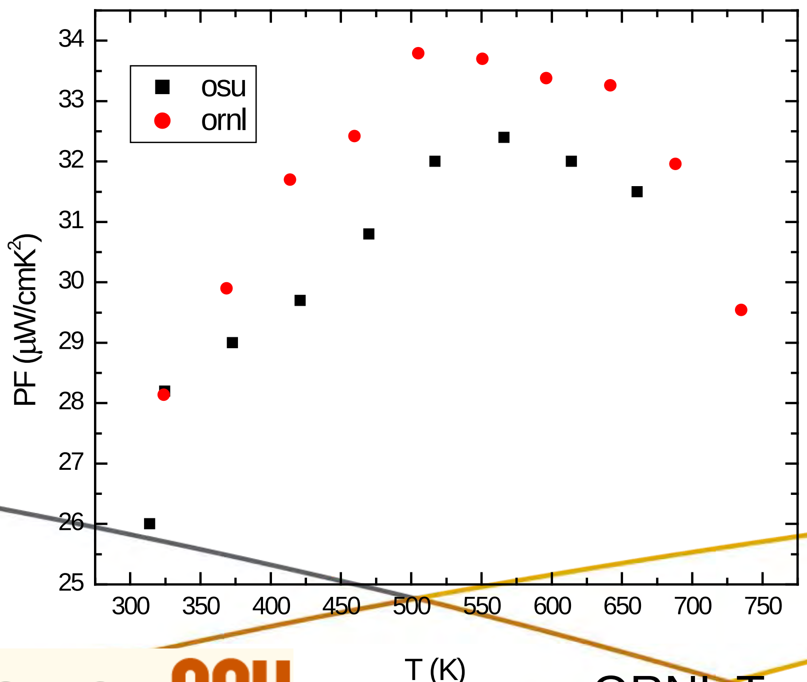
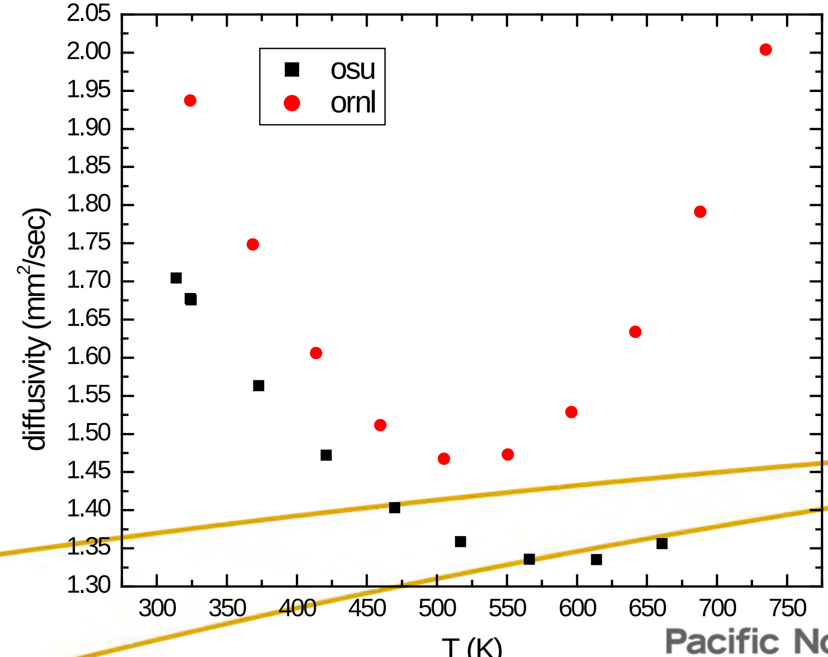
RUS High Temperature Measurement System



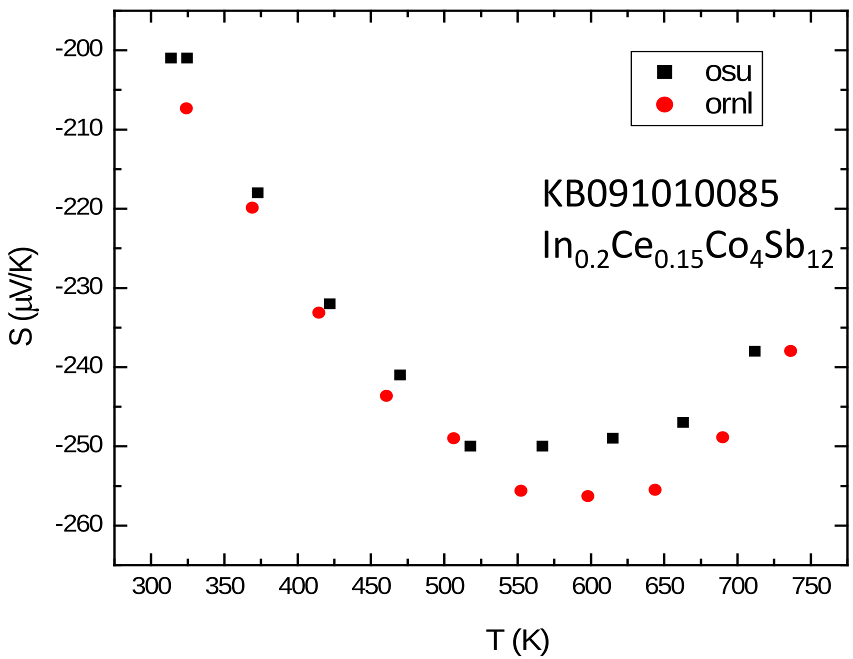


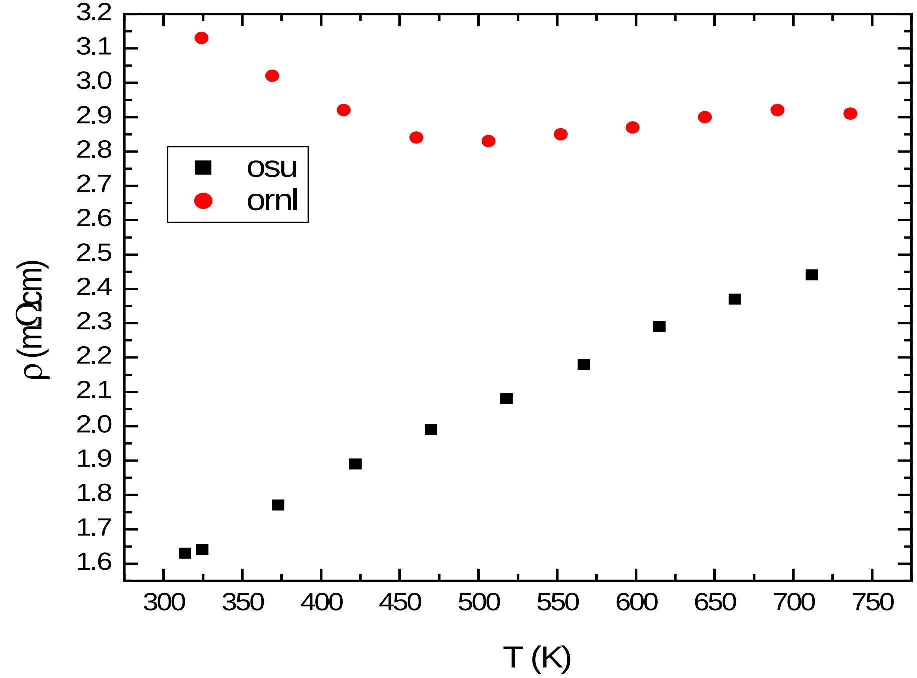


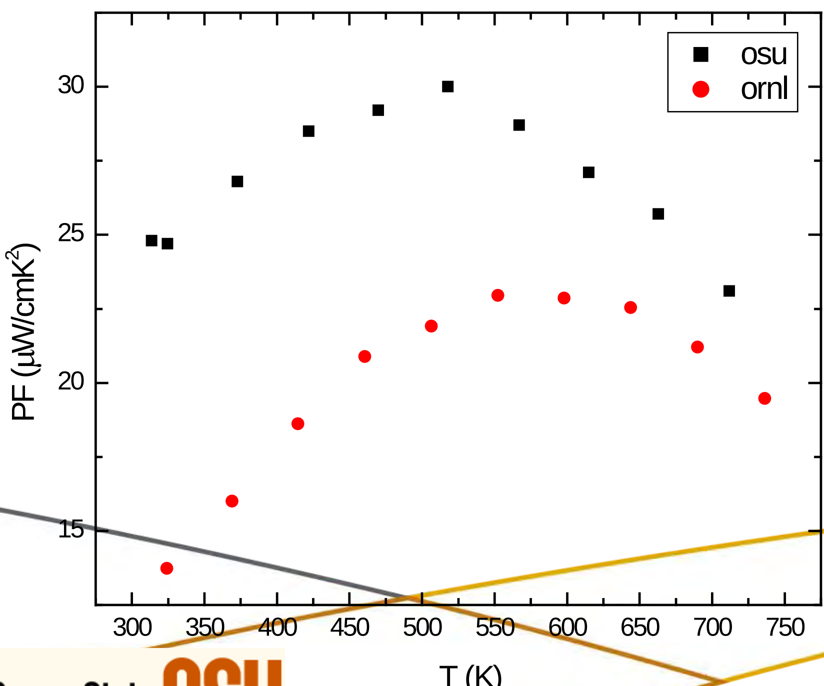


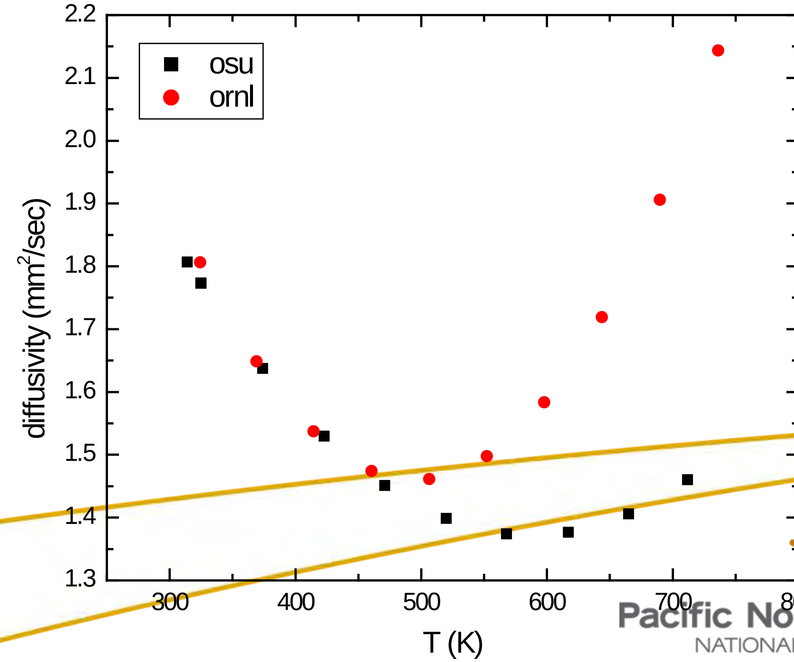


ORNL Test Data Comparisons



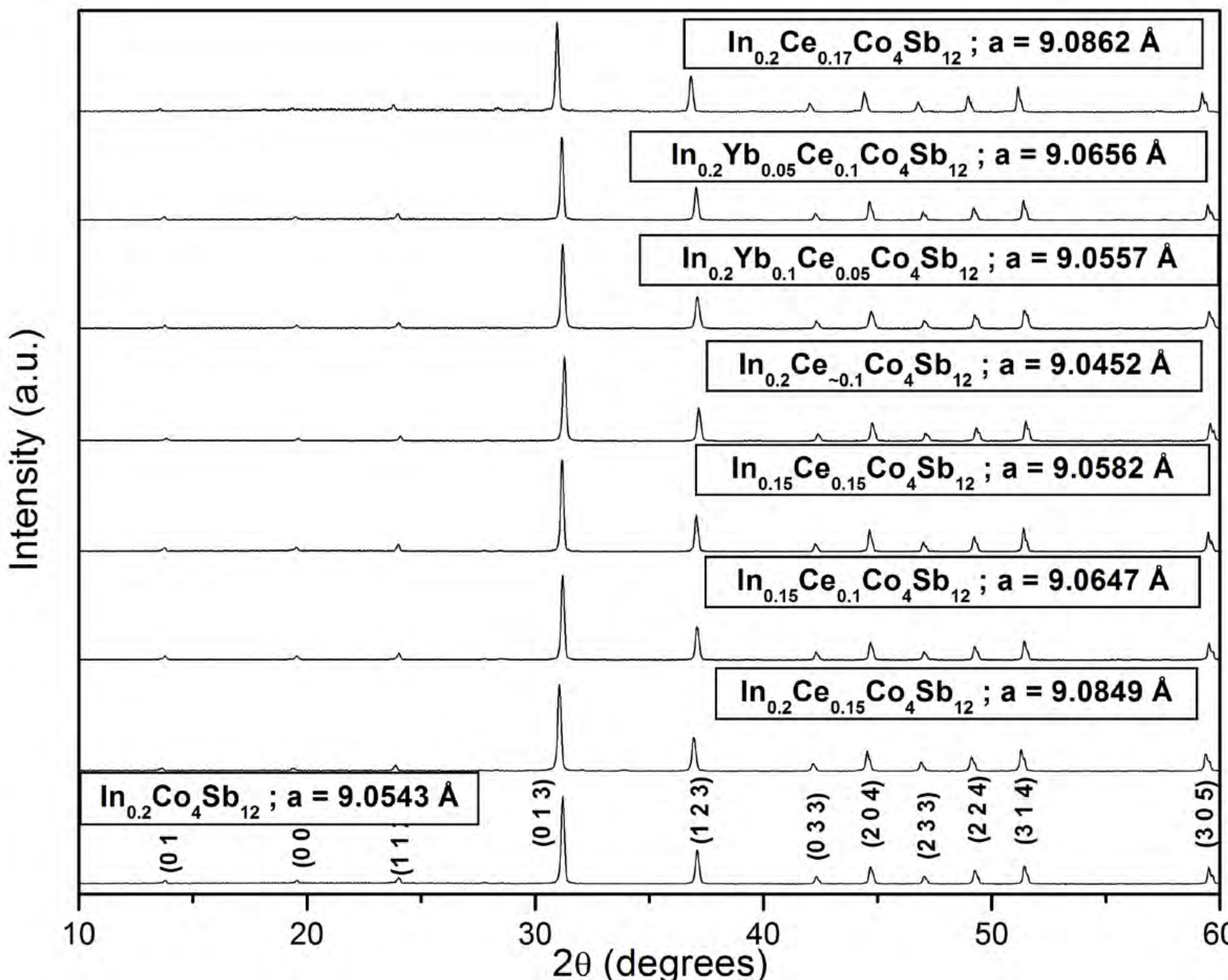






ORNL Test Data Comparisons

XRD Analysis Results Show Pure, Single-Phase Crystal Structures



Reviewer Only Slides

Responses to OVT AMR 2010 Reviewer Comments

- Review Comment:
  - One Reviewer Had A Cost Concern On Use of In and Ce in TE Materials
  - *Response:* Only small amounts of each are used in the two selected compositions - $In_{0.2}$ $Ce_{0.15}$ Co_4 Sb_{12} and $In_{0.2}$ Co_4 Sb_{12} . After discussions with our industrial partner, Tellurex Corporation, we believe the cost per couple will be slightly lower than other skutterudite compounds (<$0.30/couple), especially in large volumes. In and Ce are less expensive than Yb for example.
- Review Comment:
  - One Reviewer Was Not Clear What Relevance the High-Temperature Structural Measurements Had to These Materials for Waste Heat Recovery
  - *Response:* The high temperature structural properties are critical to determining and governing the TE material and device internal stresses during high-temperature operation. The properties are critical to establishing crucial design techniques and materials to mitigate and minimize these stresses.
- Review Comment:
  - One Reviewer Suggested Cross-Referencing of Our Data with Other Groups
  - *Response:* This year we had ORNL measure the TE properties and specific heat of our *(InCe)-based skutterudites*

Publications and Presentations

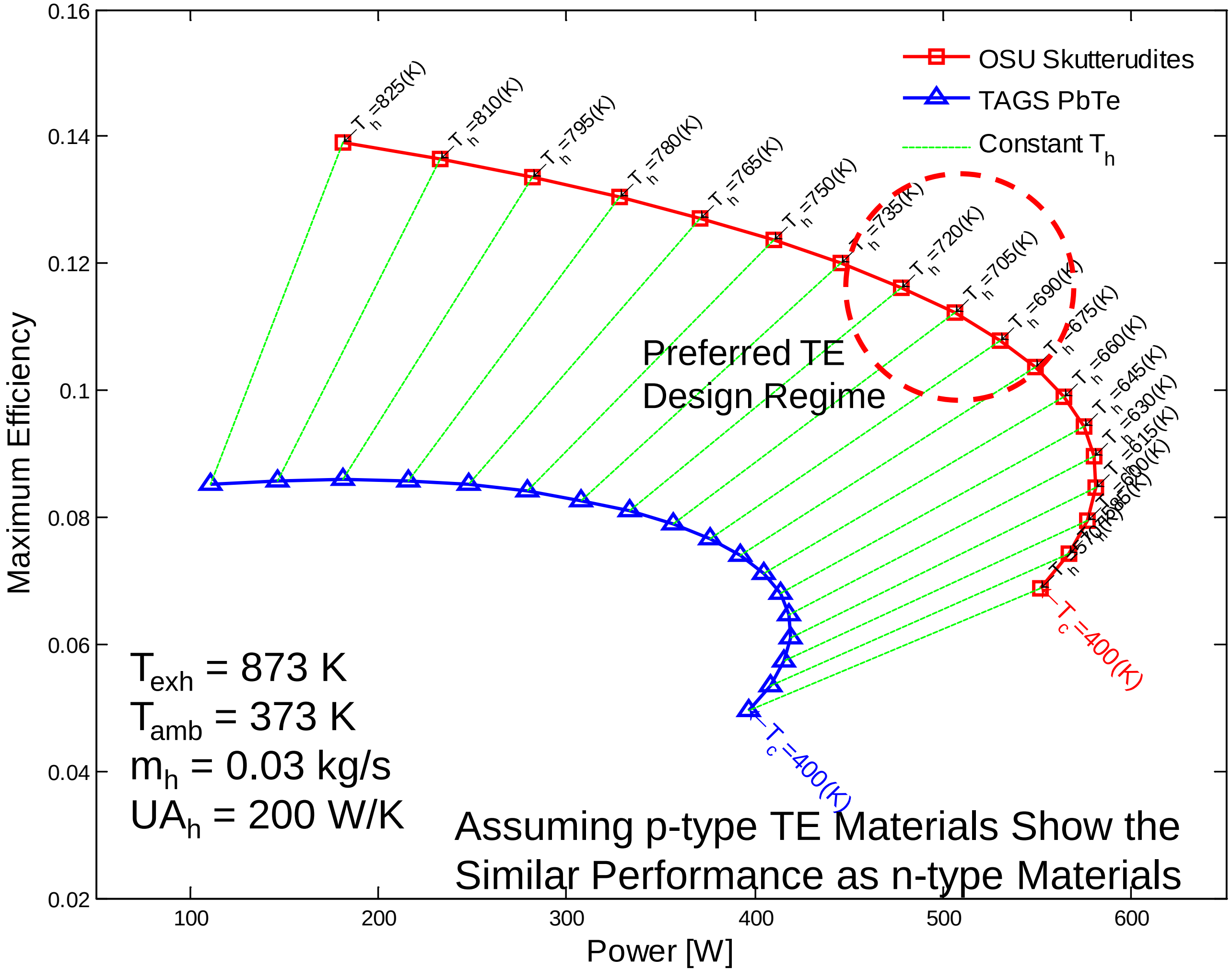
- **Journal Article**, Biswas, K., Roberts, K., Good, M. Subramanian, M.A., Hendricks, T.J., "Thermoelectric and Structural Properties of High-Performance In-Based Skutterudites for High-Temperature Energy Recovery", Manuscript #JMR-2010-0700, *Journal of Materials Research - Focus Issue: Advances in Thermoelectric Materials*, (Under Review at this Time).
- **Invited Presentation,** European Materials Research Society, Nice, France
- **Invited Presentation**, DOE 2011 Thermoelectric Applications Workshop, Title: "Proactive Design of *n*-Type (In,Ce) Filled Skutterudites Enabling High-Temperature Waste Heat Recovery", Thermoelectric Materials II Session, San Diego, CA, January 2011.
- **Invited Presentation**, Advanced Concepts in Semiconductor Materials and Devices for Energy Conversion, U.S. Army Research Laboratory and RDECOM Workshop, Title: "Characterizing Thermoelectric & Structural Properties of Materials Enabling Portable Thermoelectric Power Systems", Beltsville, MD, December 2010.
- **Invited Presentation**, 2010 Materials Research Society Fall Meeting, Title: "Thermoelectric and Structural Properties of High-Performance In-based Skutterudites for High-Temperature Energy Recovery", Symposium LL, Boston, MA, December 2010.
- **Invited Presentation**, DOE 2009 Thermoelectric Applications Workshop, Title: Proactive Strategies for Designing Thermoelectric Materials for Power Generation", San Diego, CA, September 2009.
- **Invited Presentation**, Subramanian, M.S., Eilertson, J., Hendricks, T.J., and He, T., "Thermoelectric Properties of Skutterudites Filled With Duel Rattlers", *2008 International Conference on Thermoelectrics*, Corvallis, OR, August 2008.

Critical Issues

- p-Type Skutterudites Slow in Developing
  - p-type LASTT Materials Are The Best Alternative for Couple Demo
- Structural Measurements Can Be Quite Tedious and Time-Consuming for Some Samples

TE Material Impacts on System Design

- System-Level Analyses Show OSU/PNNL Skutterudites Potential Superiority Compared to Common High-Performance Materials
  - Direct-Fired APU Applications Create Higher Power Due to Higher Temperatures



- Benefits Heavy-Duty Engine Performance:
  - 10% Conversion in Exhaust Could Move Heavy Duty Engines Toward 48% Efficiency
  - Additional Benefit from EGR Thermal Recovery
- Benefits Heavy-Duty APU Development to Reduce Idling Fuel Consumption

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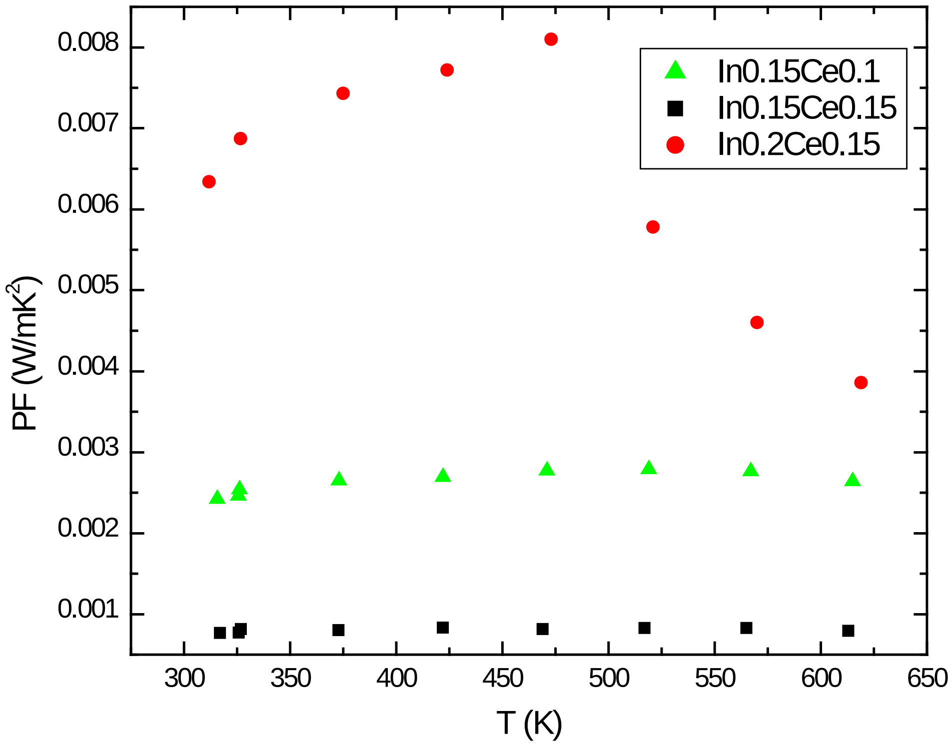
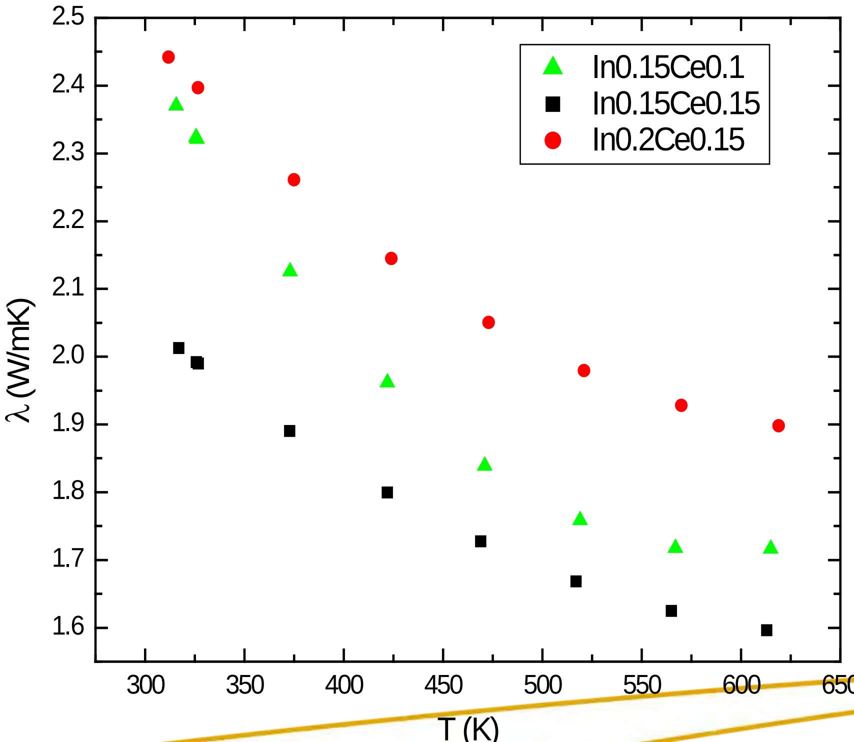
n-Type $In_xCe_yCo_4Sb_{12}$ TE Properties

- Ultimately Led to ZT ~ 1.5 – 1.6 at 425 – 525 K for $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ Compounds
- Once Again – Bulk Materials Easily Integrated into TE Device
- Must Monitoring MicroCracking





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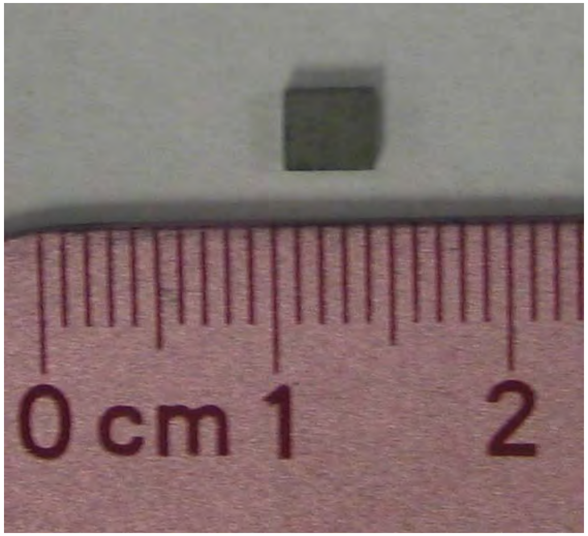
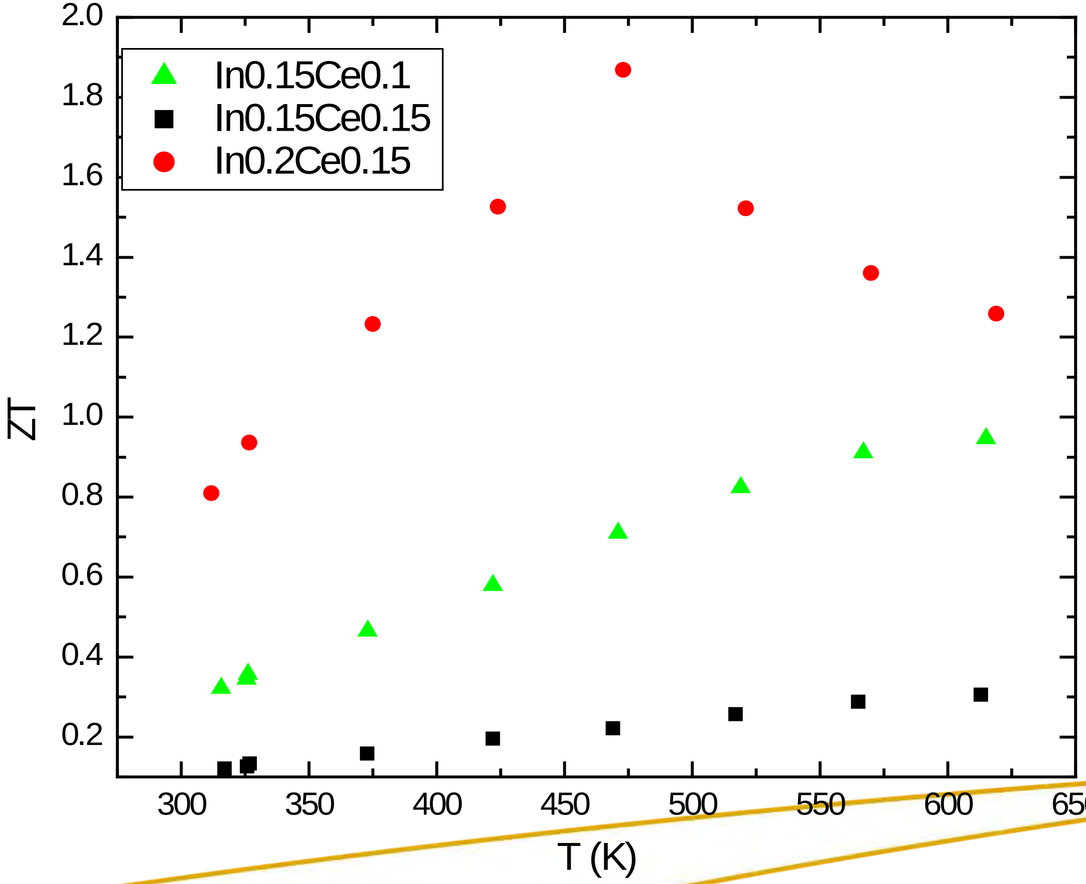
ZT vs. Temperature Presented at FY 2010 AMR

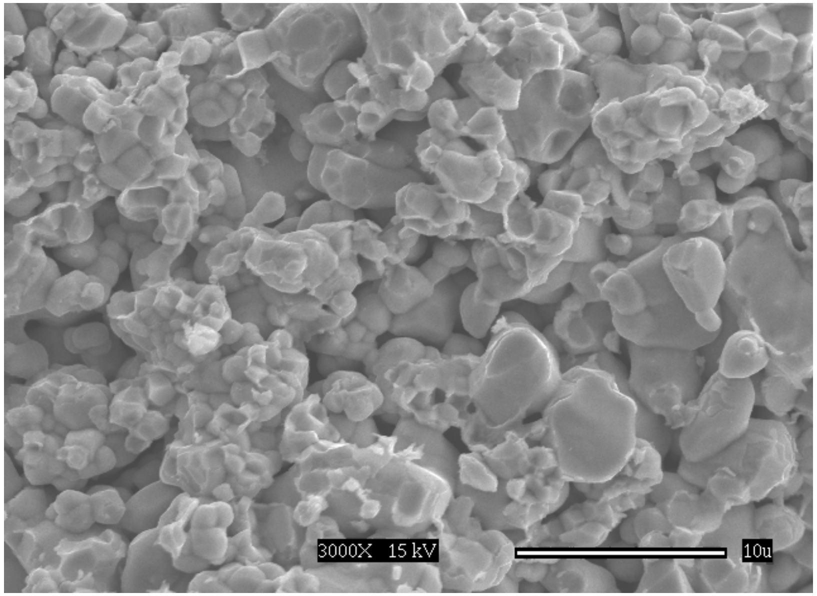
- Ultimately Led to ZT ~ 1.5 – 1.6 at 425 – 525 K for $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ Compounds





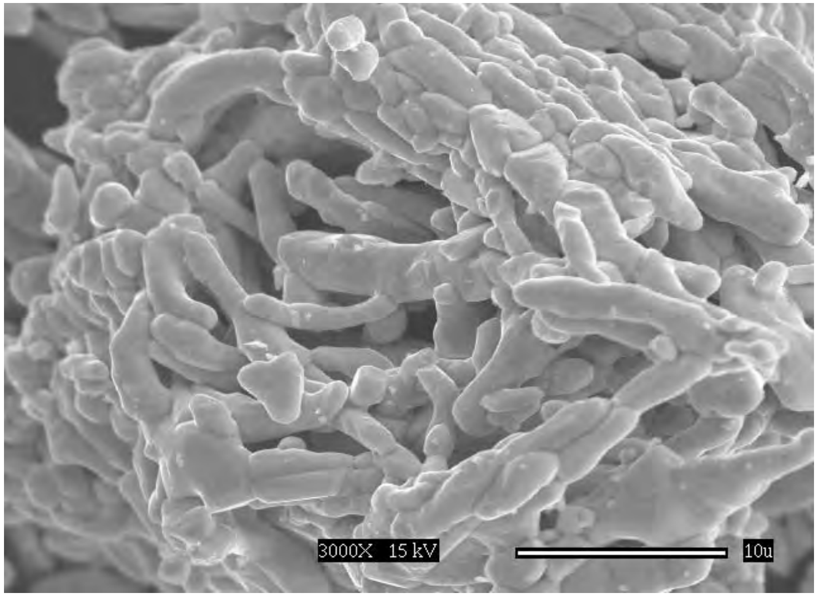
ZT Dependence on Microstructure ($In_{0.15}Ce_{0.10}Co_4Sb_{12}$)

ZT ~ 1.4 @ 600 K



Synthetic Method - 1

ZT ~ 1.1 @ 600 K



Synthetic Method - 2

- **In addition to chemical composition and crystal structure, for ceramic samples, the ZT also depends on microstructure, grain-morphology etc.**

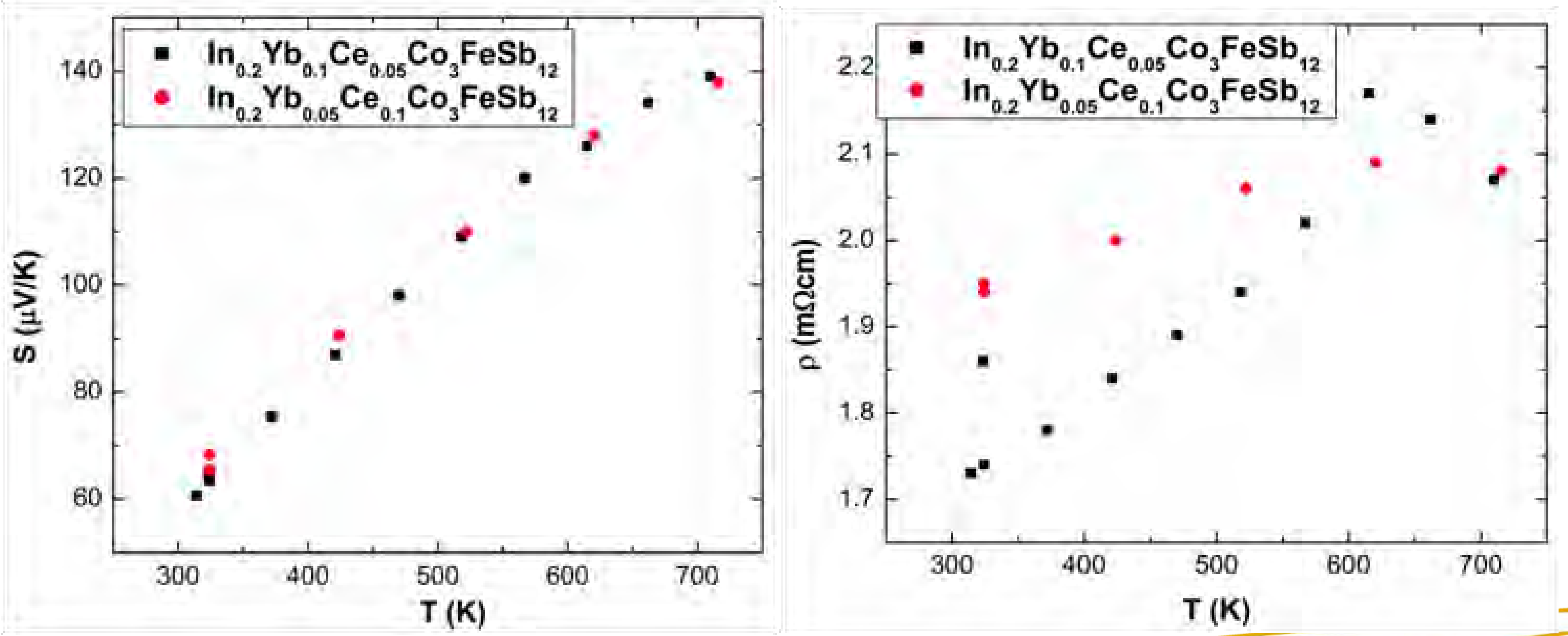
RUS Measurement System Calibration

- RUS Measurement System Checked With Known Fused Quartz
- RUS Measurements Show Very Good Correlation With Literature and Manufacturer's Data on Fused Quartz
- Some High-Temperature Structural Data Also Obtained on Quartz

Specimen Label and Comments	Temperature (ºC)	ρ, density (g/cm³)	υ, Poisson's ratio	*E*, Modulus of Elasticity (10^{11} N/m²)	rms error
Fused Quartz Reference (Manufacturer's Data)	---	2.203	0.17	0.725	---
Fused Quartz Reference #1 (RUS Estimated)	---	2.122	0.156	0.7216	0.32
Fused Quartz Reference #1 (RUS Estimated)	20.8 - 21.0	2.122	0.155	0.7242	0.42
Fused Quartz Reference #1 (RUS Estimated)	89.2 -90.8	2.122	0.156	0.7343	0.45

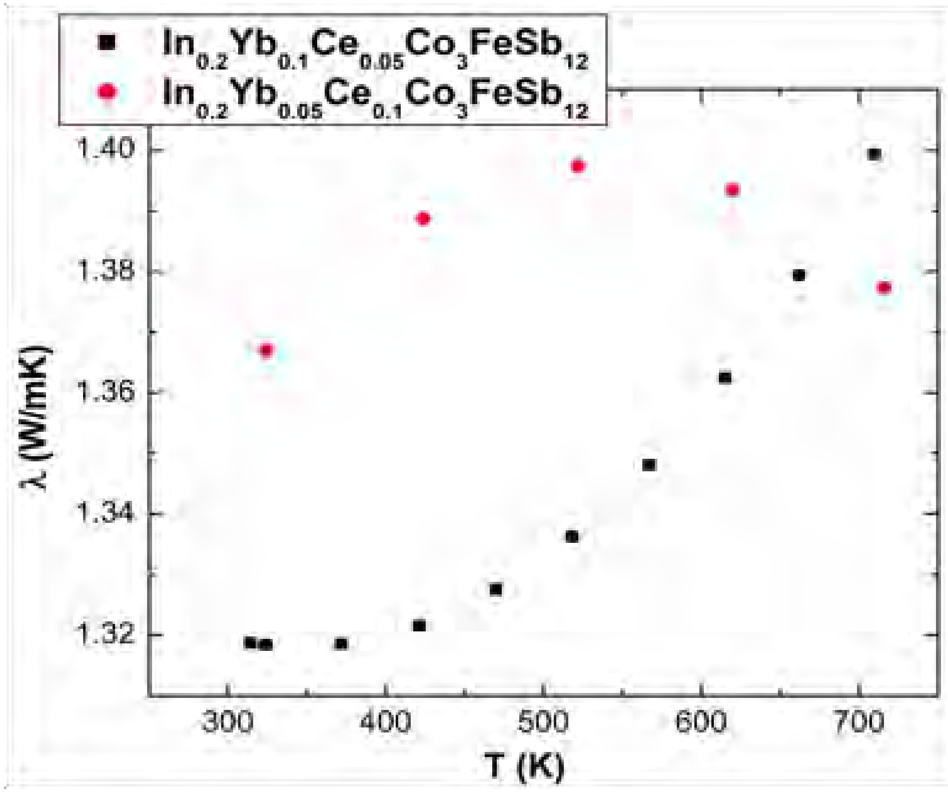
p-Type $In_{0.2}Yb_xCe_yFeCo_3Sb_{12}$ Materials – TE Properties

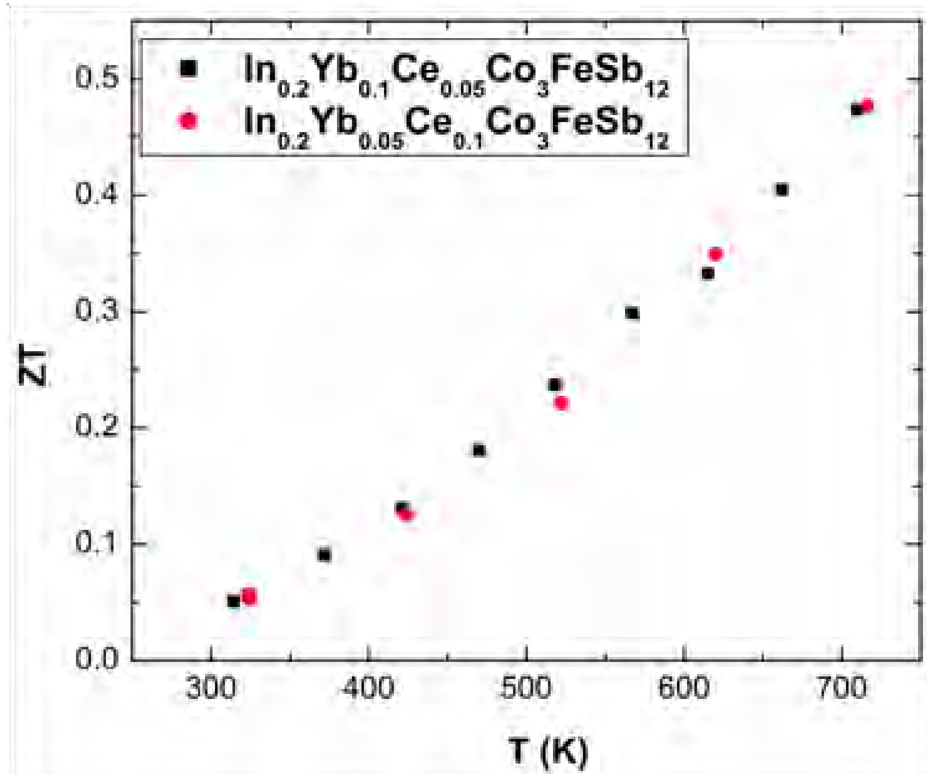
- Seebeck Coefficients are Low



p-Type $In_{0.2}Yb_xCe_yFeCo_3Sb_{12}$ Materials – TE Properties

- Relatively Low Thermal Conductivity
- However, Seebeck Coefficient Limiting ZT ~ 0.48 @ 710 K





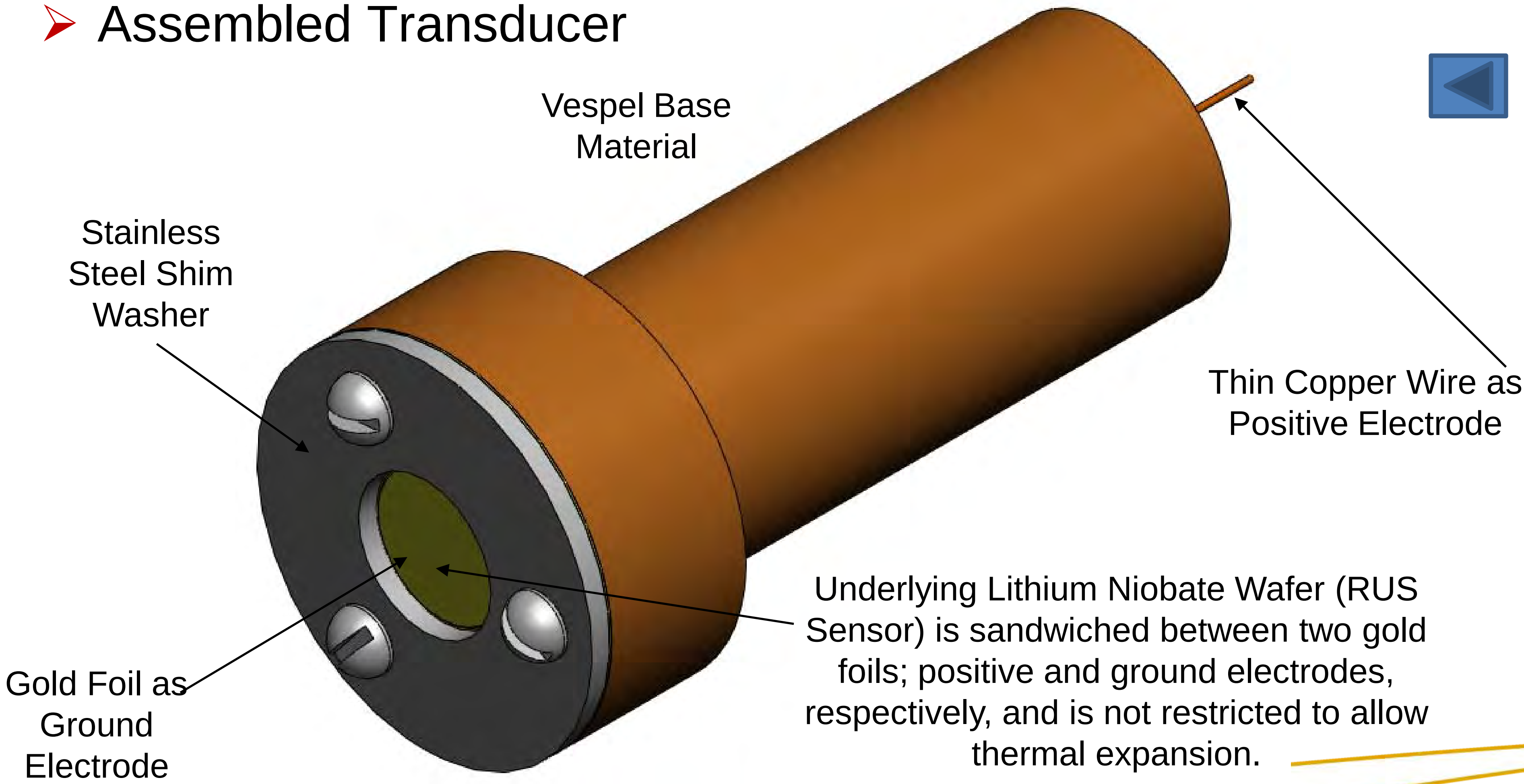
p-Type $In_{0.2}Yb_xCe_yFeCo_3Sb_{12}$ Materials – Structural Properties

- First-Ever Measurement of Structural Properties of These p-type Skutterudites

	Temperature [°C]	**No Thermal Cycling**		
		Young's Modulus, E 10^9 [N/m^2]	Poisson's Ratio, ν	ZT
$In_{0.2}Ce_{0.15}Fe_{0.5}Co_{3.5}Sb_{12}$ p-type	20.3	46.4	0.18	~0.2-0.25 (@673 K)
$In_{0.2}Yb_{0.05}Ce_{0.1}FeCo_3Sb_{12}$ p-type	20.4	99.26	0.210	0.48 (@ 710 K)
$In_{0.2}Yb_{0.1}Ce_{0.05}FeCo_3Sb_{12}$ p-type	20.8	92.38	0.205	0.48 (@ 710 K)

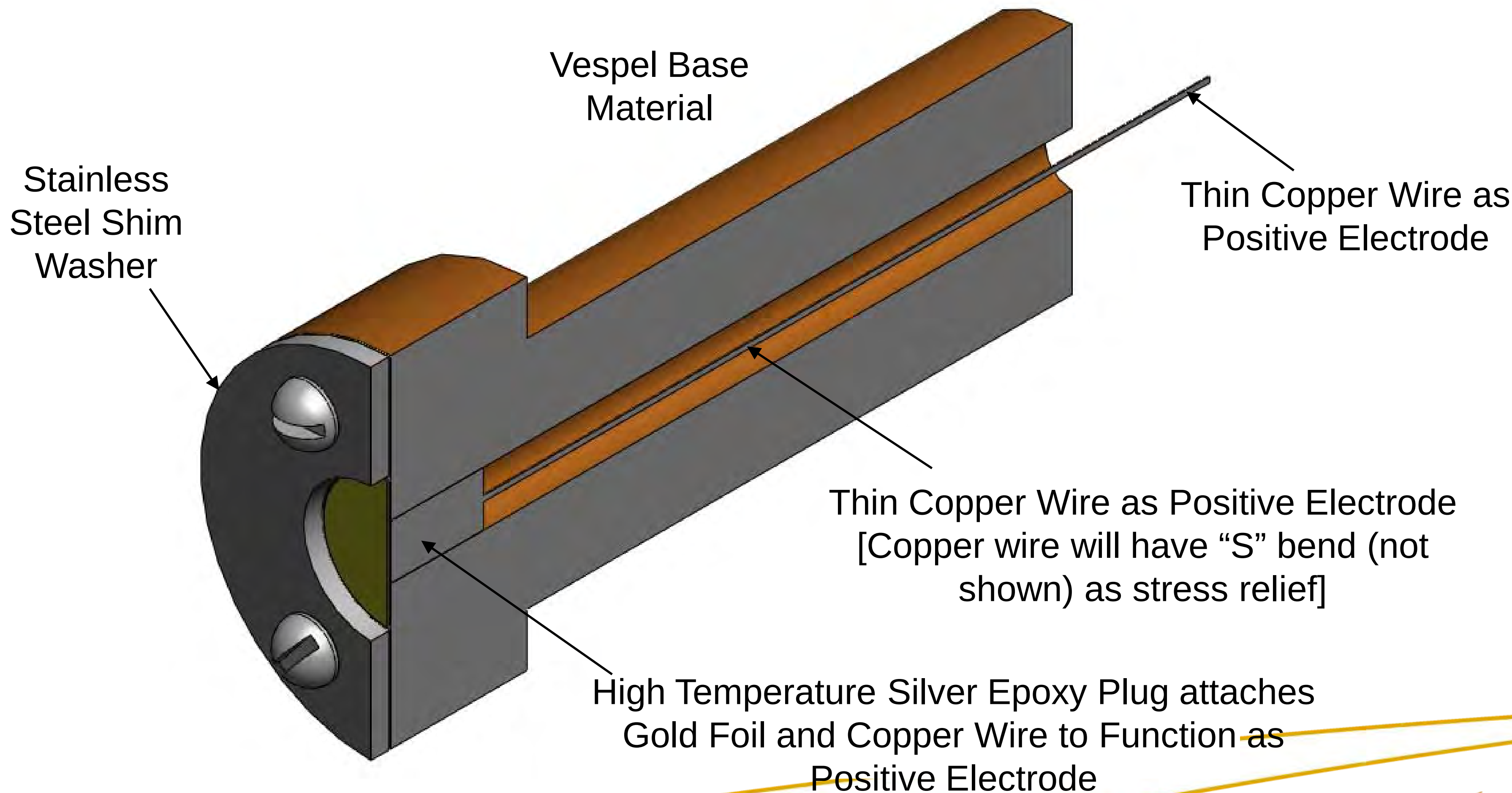
Next Generation of High Temperature Transducer

➢ Assembled Transducer

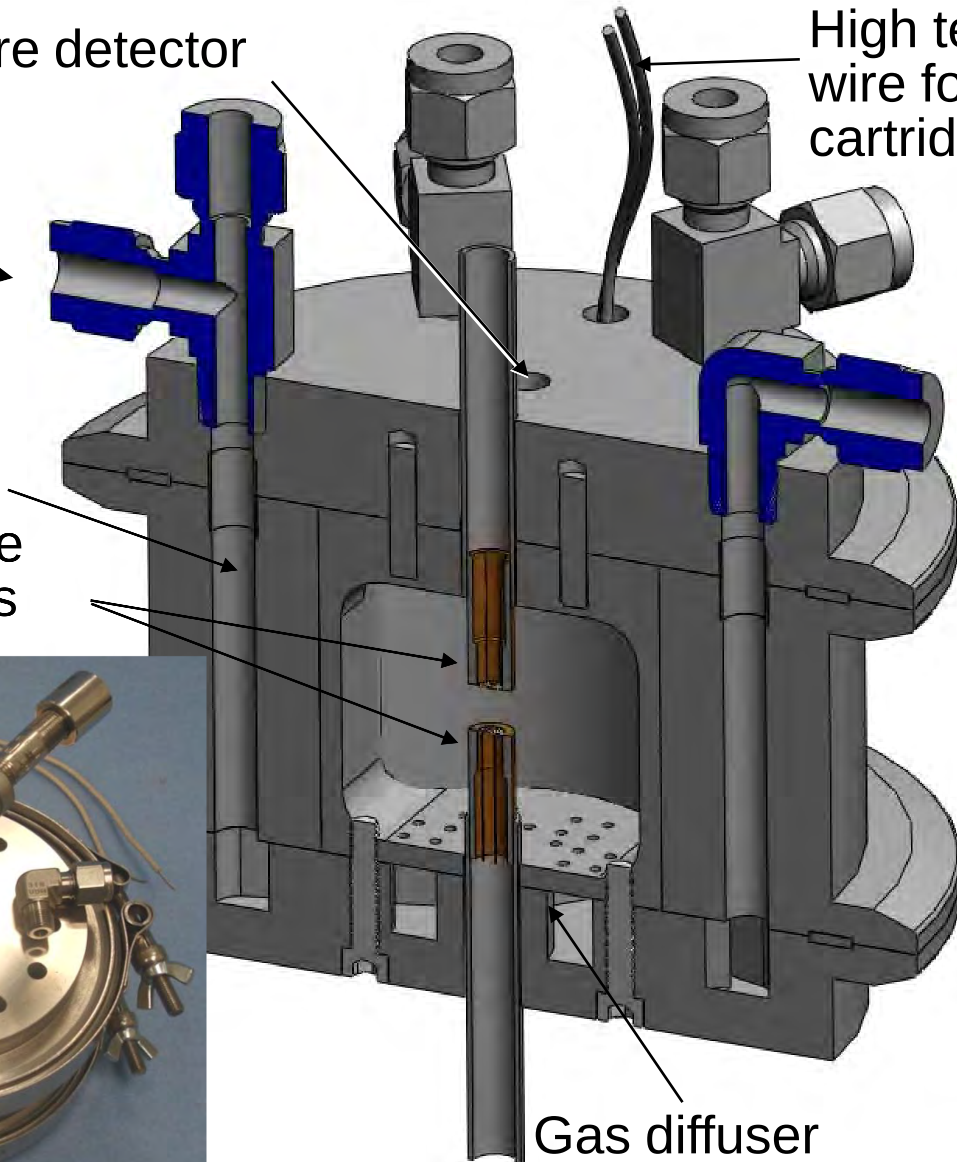


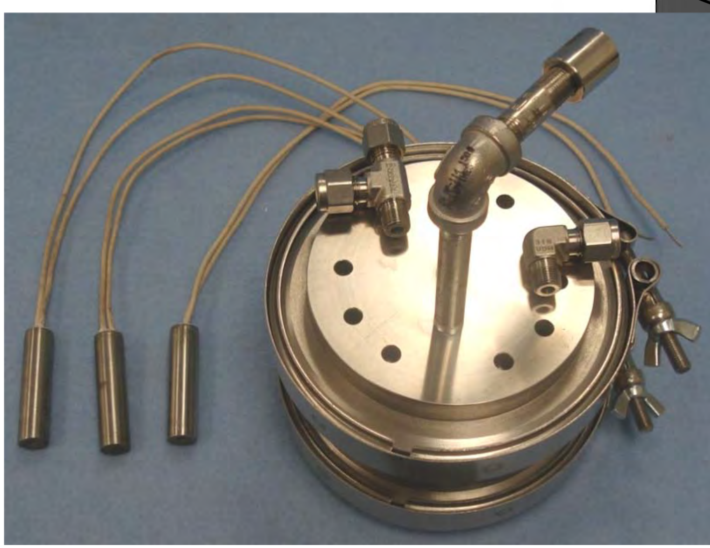
Next Generation of High Temperature Transducer

- Assembled Transducer



Elastic Moduli Estimate by Resonant Ultrasound Spectroscopy: High Temperature Test Chamber





Advanced Thermoelectric System Design

Single Material TE Legs

- System-Level, Coupled Design Analysis
  - Hot Side Heat Exchanger
  - TE Device
  - Cold Side Heat Exchanger
- Single TE Material Legs
- Accounts for Hot/Cold Thermal Resistances
- Accounts for Electrical Contact Resistances
- Optimum Heat Exchanger / TE Design Parameters Determined Simultaneously
- Maximum Efficiency & Maximum Power Density Designs Are Possible
- Off-Nominal & Variable Condition Performance Analysis