Proactive Strategies for Designing Thermoelectric Materials for Power Generation

PNNL / ONAMI Joint Project on Advanced TE Materials & Systems

Project ID #PM014

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Office of Vehicle Technologies 2010 Annual Merit Review
10 June 2010

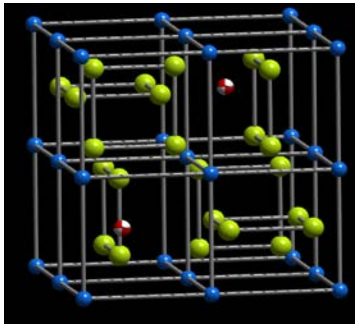
Agenda

- Overview – Timeline, Budget, Technical Barriers, & Collaborations
- Objectives
- Milestones
- Technical Approach
- Accomplishments
- Collaborations & Coordination
- Future Work
- Summary
- Publications/Presentations
- Critical Issues

Proactive Strategies for Designing Thermoelectric Materials for Power Generation - Overview

Timeline

- Project Start Date: 15 December 2008
- Project End Date: 15 December 2010
- 50% Complete



$R_xCo_4Sb_{12}$

OVT Barriers – Advanced Combusion R&D Solid State Energy Conversion

- Improve heavy truck efficiency to 50 percent by 2015
- Achieve stretch thermal efficiencies of 55% in heavy-duty engines by 2018
  - Fuel Economy Increases of 10% over 2010
  - 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
- Improve Light-Duty & Commercial Vehicle Fuel Efficiency up to10%
- High-Performance Waste Energy Recovery Materials to Integrate into Advanced Engines
- Methods for Maintaining Fuel Economy at Light-Load

Budget

- Total FY 2009 Project Funding $260K
- Total FY 2010 Project Funding $260K

Partners

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

Oregon State University OSU

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

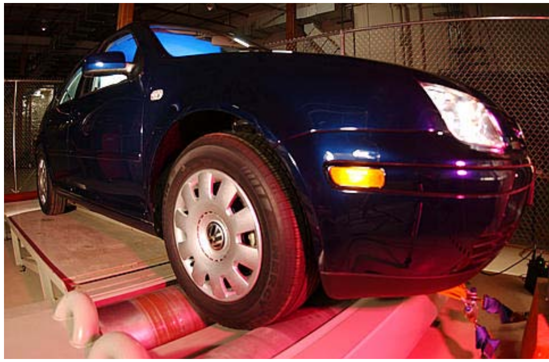
- **60-70% Energy Loss in Most of Today's Processes**
- **Transportation Sector**
  - **Light-Duty Passenger Vehicles + Light-Duty Vans/Trucks (SUVs)**

    2002: 129.8 billion gallons of gasoline

    2004: ~135 billion gallons of gasoline

    ~ 4.5 quads/yr exhausted down the tail pipe

    ~ 5.5 quads/yr rejected in coolant system



  - **Heavy-Duty Vehicles**

    2002: 29.8 billion gallons of diesel

    2004: 32 billion gallons of diesel

    ~1.45 quads/yr exhausted down the tail pipe

    ~1 quad/yr rejected in coolant system (~1 quad)

  - **Hybrid Electric Vehicles**

    Move Toward Electrification – Micro, Mild, and Full

    Needs for Power Generation

    Needs for Electric-Driven Cooling

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Project Objectives

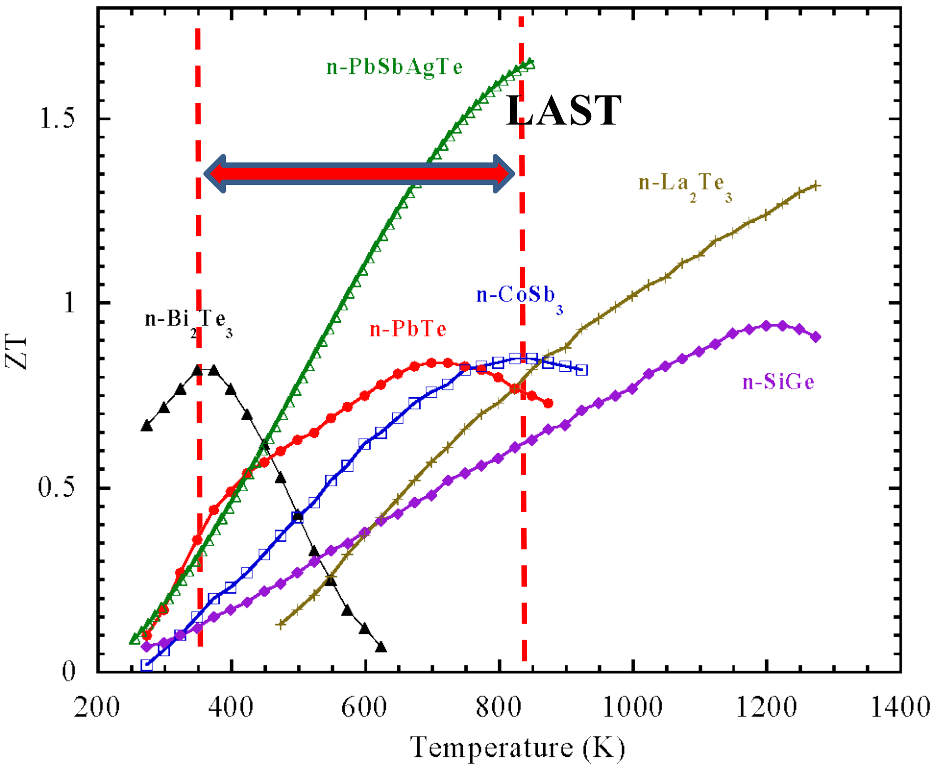
- Develop new high-performance n-type and p-type thermoelectric (TE) material compositions to enable:
  - 10% fuel efficiency improvements from waste energy recovery in advanced light-duty engines and vehicles.
  - Heavy truck efficiencies to 50% by 2015
  - Stretch thermal efficiencies of 55% in advanced 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.
- 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 xTemperature) 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.

Schedule / Milestones

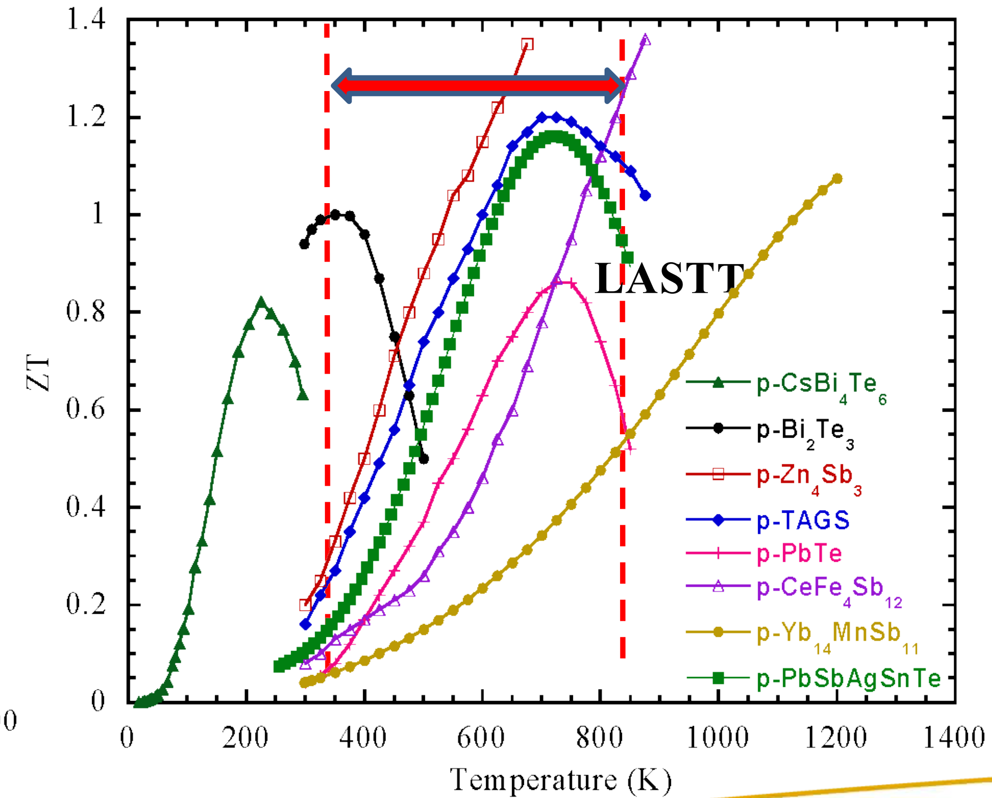
Month/Year	Milestones:
Dec. 2009–Dec. 2010	P-type and n-type Thermoelectric Development & Testing. Optimize Compositions for TE Performance. Measure TE Properties (Seebeck Coefficient, Electrical Resistivity, & Thermal Conductivity). On-going throughout the year due to third-party validation .
July 09	Select p-type TE Materials for Structural Testing. Criteria Will Be Selecting the Best TE Materials Properties (ZT vs. T.). Continue Refining n-type $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ for Reproducibility
Dec. 2009–Dec. 2010	Continue Measuring & Categorizing Room Temperature Structural Properties of p-type & n-type TE Materials. Measure E, ν, CTE.
June 2010	Measure High Temperature Structural Properties of n-type TE Materials.
September 2010	Measure High-Temperature Structural Properties of p-type TE Materials
December 2010	Develop and Measure TE Couple Performance Using Selected p-type / n-type TE Materials. Measure I-V Curves at Various Hot-Side / Cold-Side Temperatures.

Technical Approach

- 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

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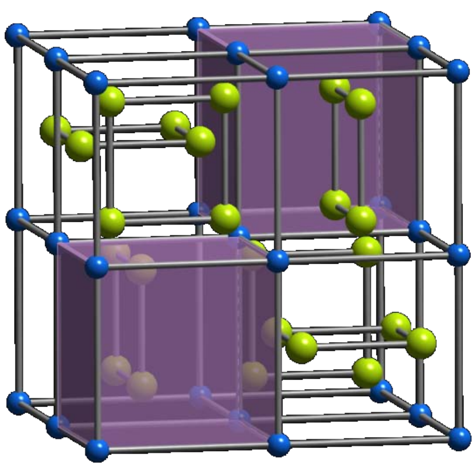
Strategies in Designing *n*-type and *p*-type Skutterudites: $R_xR_y'Co_{4-x}M_xSb_{12}$

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



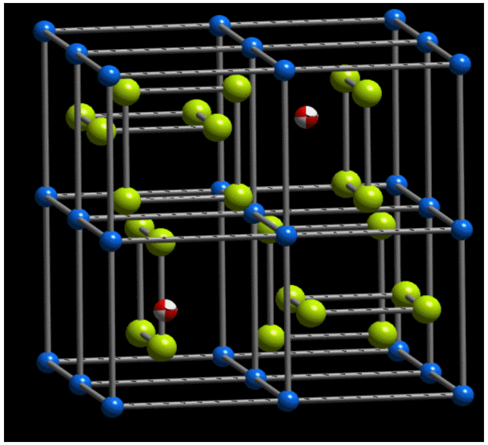
Co_4Sb_{12} (n-type)

Rh_4Sb_{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



$R_xCo_4Sb_{12}$

$R_xR'_yCo_4Sb_{12}$

$R_xCo_{4-z}Rh_zSb_{12}$

$R_xR'_yCo_{4-z}Rh_zSb_{12}$

Technical Approach

- Proactive, Systematic Investigation of Dual- & Tri-Rattler Skutterudites
  - Refine n-type Materials, Characterize at Higher Temperatures & Transition to TE Couple
  - Systematically Develop p-type Materials with Performance Similar to n-type Levels
- TE Property Measurements @ OSU Laboratories
  - Seebeck Coefficient Measurements vs. T
  - Electrical Conductivity Measurements vs. T
  - Thermal Conductivity Measurements vs. T
- Engaging Third-Party Validation
  - ORNL
- Structural / Thermal Property Measurements @ PNNL
  - Resonant Ultra Sound Techniques (E, ν) Up to 300 °C
  - CTE Up to 400 °C
  - Mechanical Strength @ Room Temperature
- 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 Supplemental Slides)
- Demonstrate High-Performance TE Couples for Transition to Waste Energy Recovery Applications

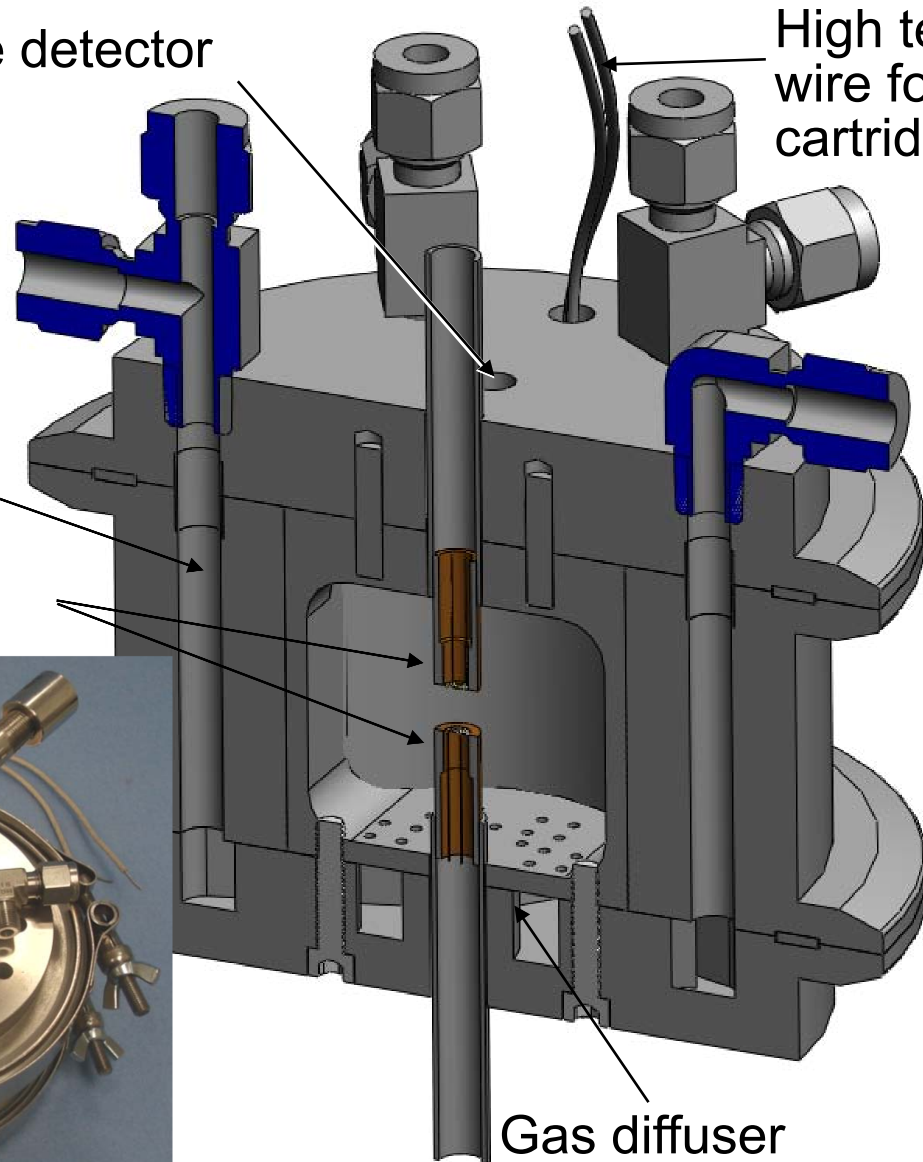
Project Accomplishments

Structural Property Measurements

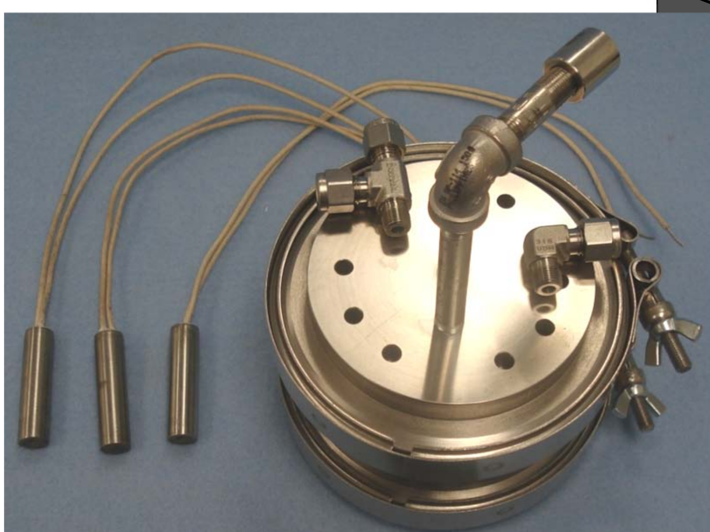
- Measured Coefficient of Thermal Expansion & Determined Elastic Material Properties Over Elevated Temperatures
    - Measured Coefficient of Thermal Expansion
    - Modified Existing RUS System for Material Property Measurement at Elevated Temperatures
    - Currently Measuring E and *v* at Multiple Temperatures Spanning Room Temperature to 300 ºC
- RUS Systems
    - Room Temperature Shown Right
    - High-Temperature System in Next Charts

Specimen between Transceivers

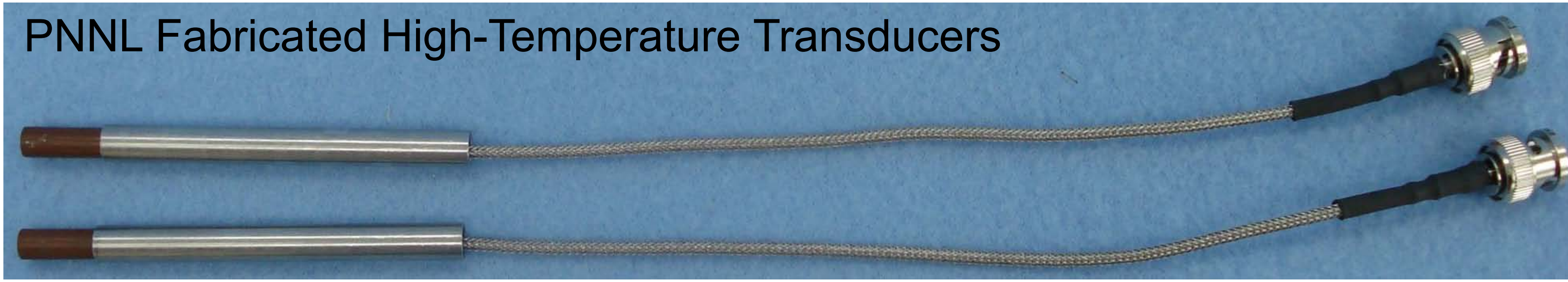
Elastic Moduli Estimate by Resonant Ultrasound Spectroscopy: High Temperature Test Chamber

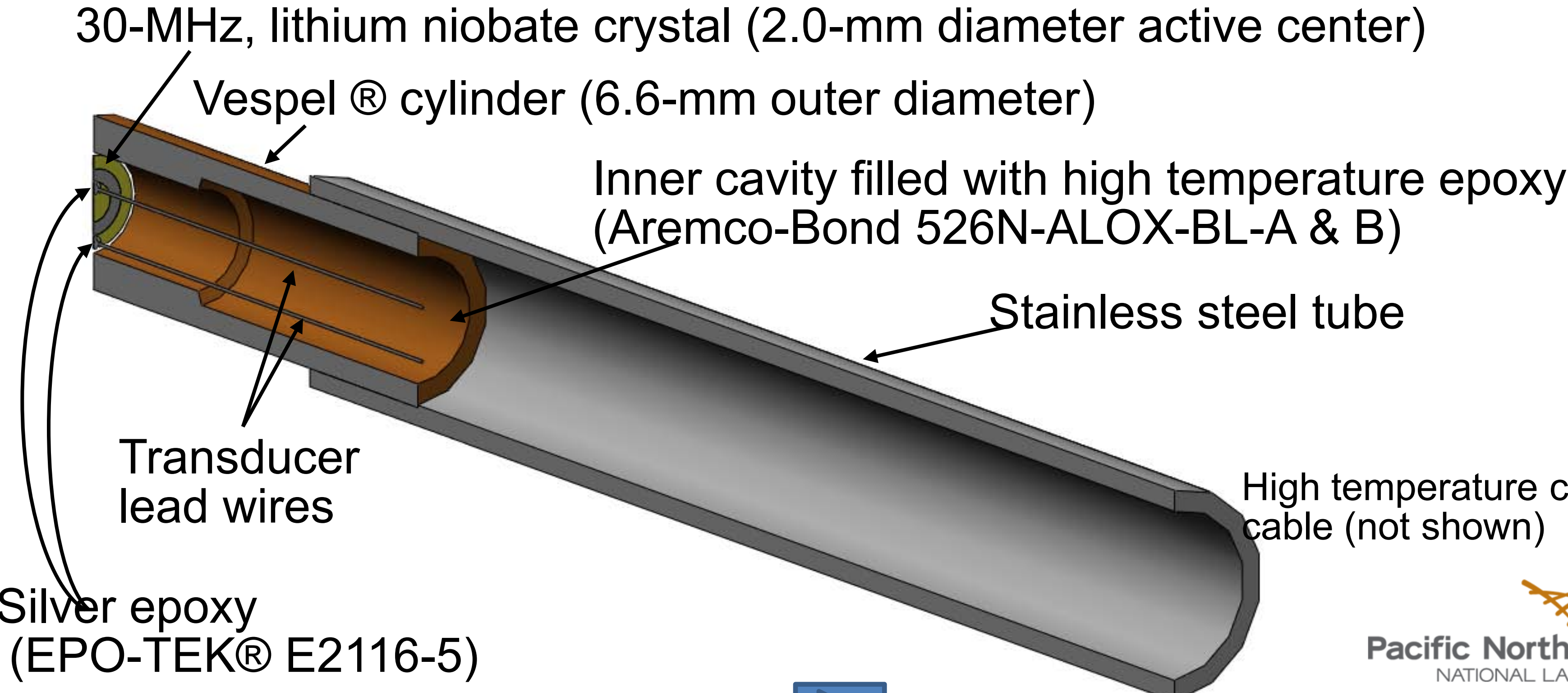


Primary components and fittings are stainless steel.

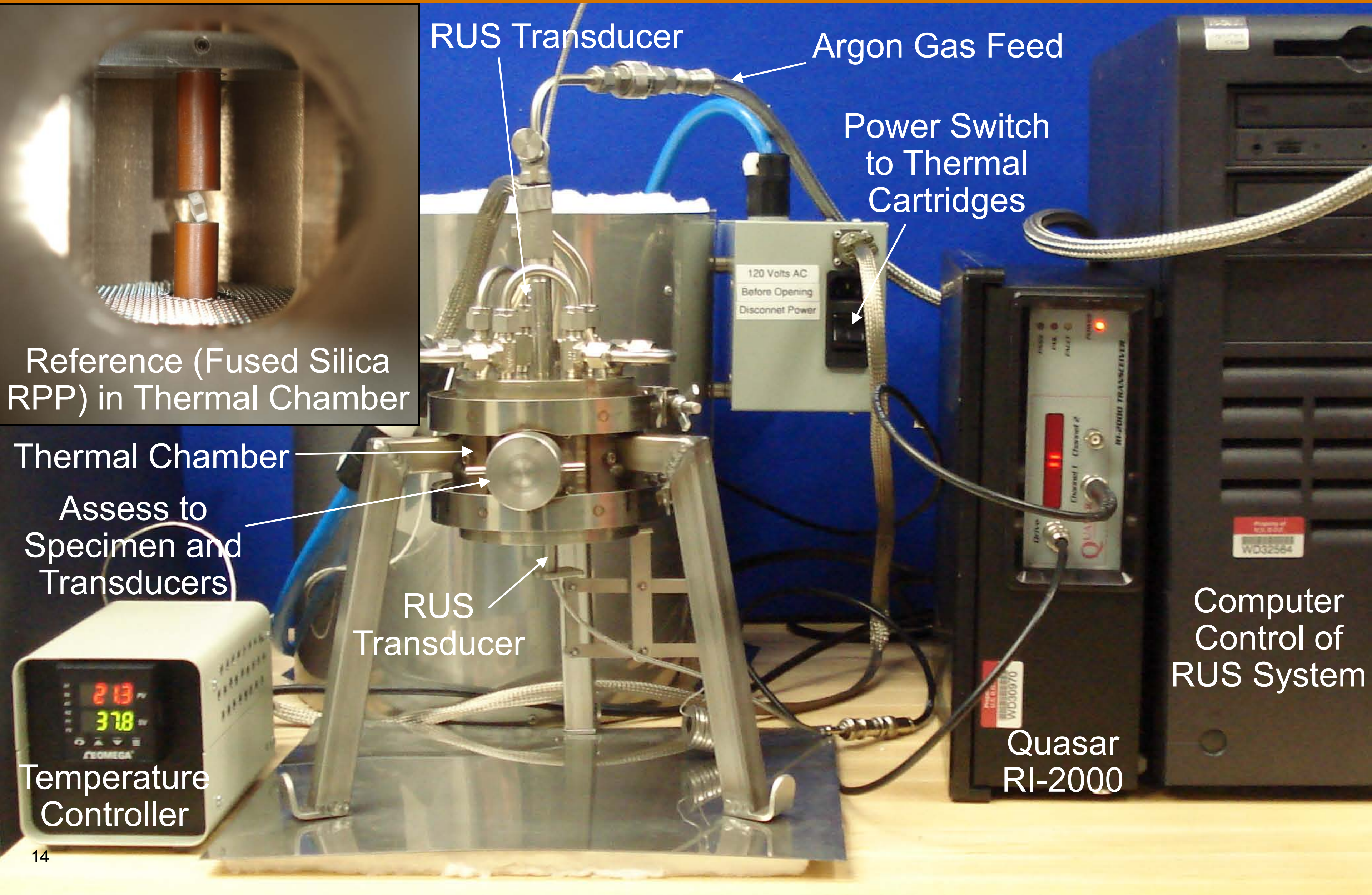


Elastic Moduli Estimate by Resonant Ultrasound Spectroscopy: High Temperature Transducers



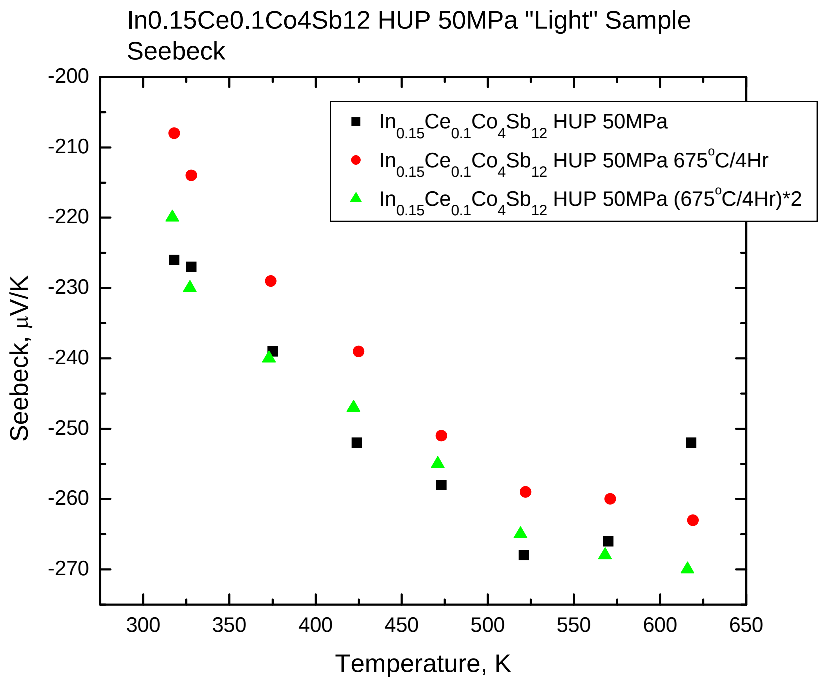


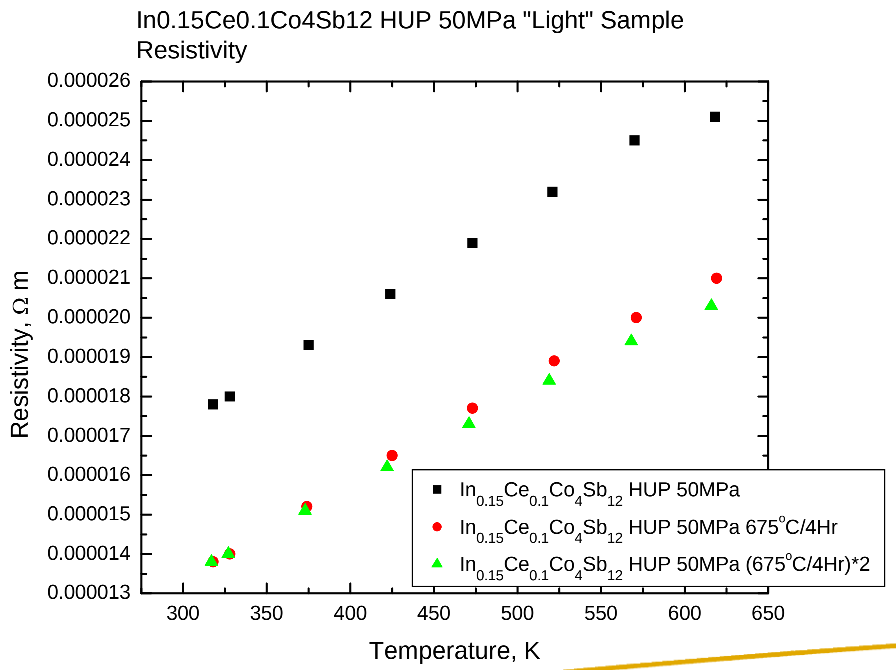
RUS High Temperature Measurement System



n-Type $In_xCe_yCo_4Sb_{12}$ TE Properties

- $In_xCe_yCo_4Sb_{12}$ Created Using Sintering & Hot-Pressing Processes
  - Moderate Hot-Pressing Pressures (50 MPa)





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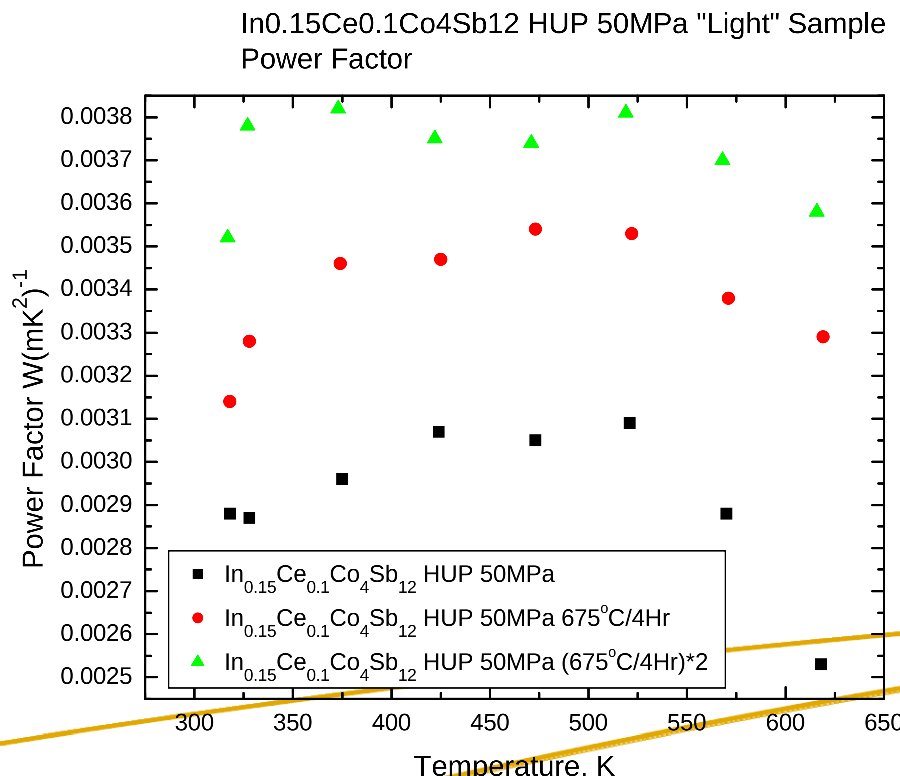
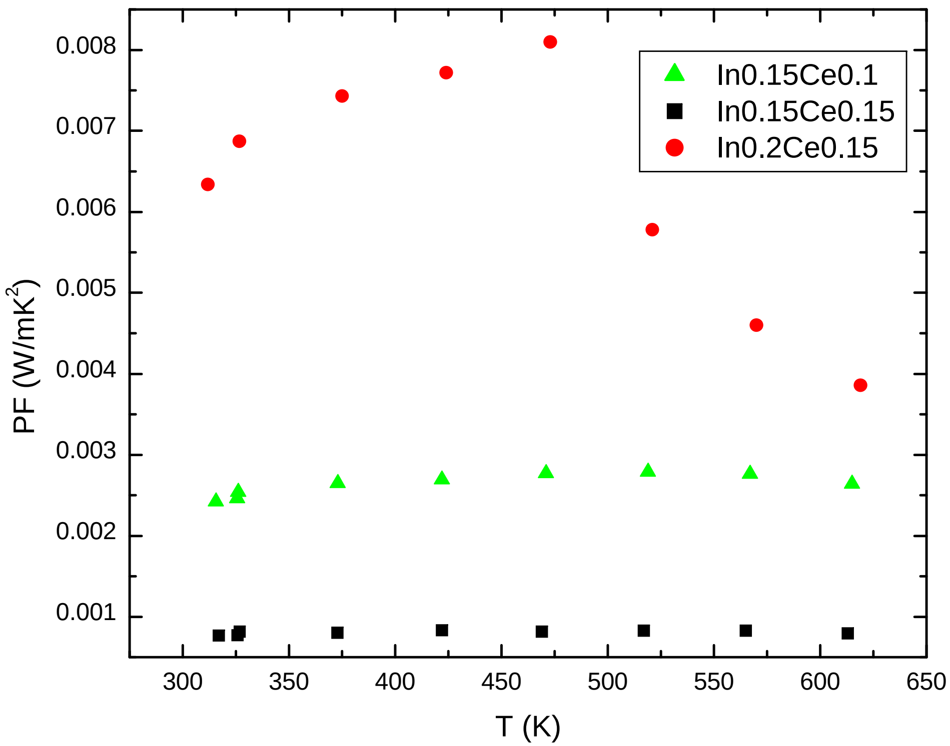
n-Type $In_xCe_yCo_4Sb_{12}$ TE Properties

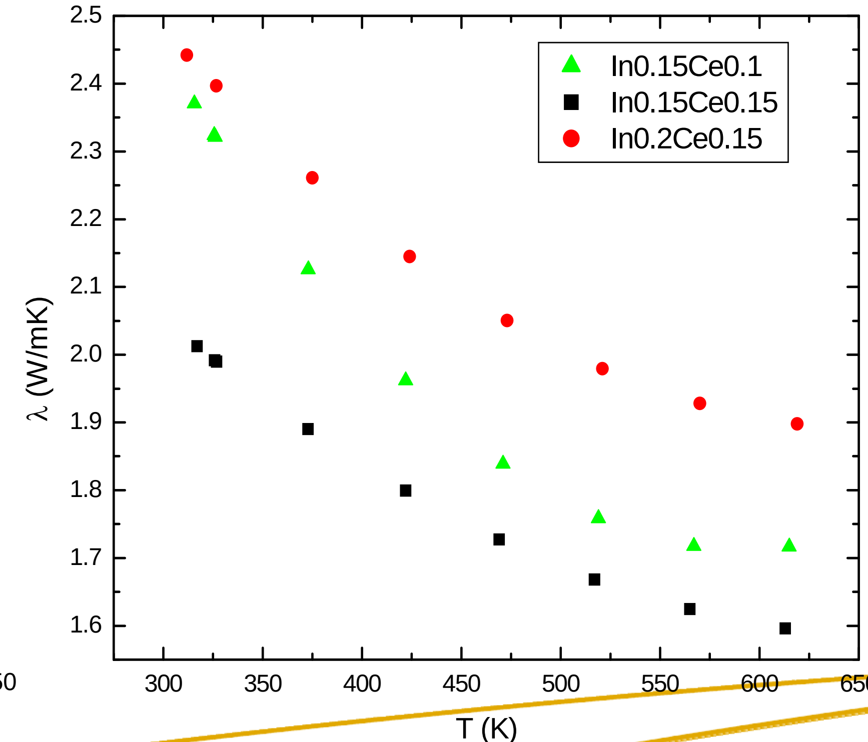
- $In_xCe_yCo_4Sb_{12}$ Created Using Sintering & Hot-Pressing Processes
  - Moderate Hot-Pressing Pressures (50 MPa)
- High Power Factors Exhibited in $In_{0.15}Ce_{0.1}Co_4Sb_{12}$ Compounds
  - Fairly Insensitive to Temperature From 350 – 550 K



n-Type $In_xCe_yCo_4Sb_{12}$ TE Properties

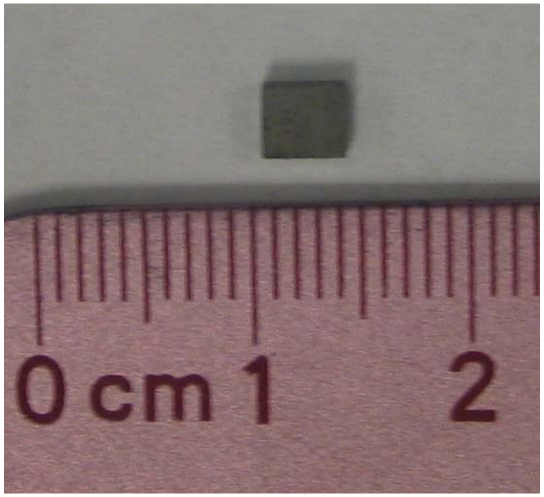
- Ultimately Led to ZT ~ 1.5 – 1.6 at 425 – 525 K for $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ Compounds
- Once Again – Bulk Materials Easily Integrated into TE Device

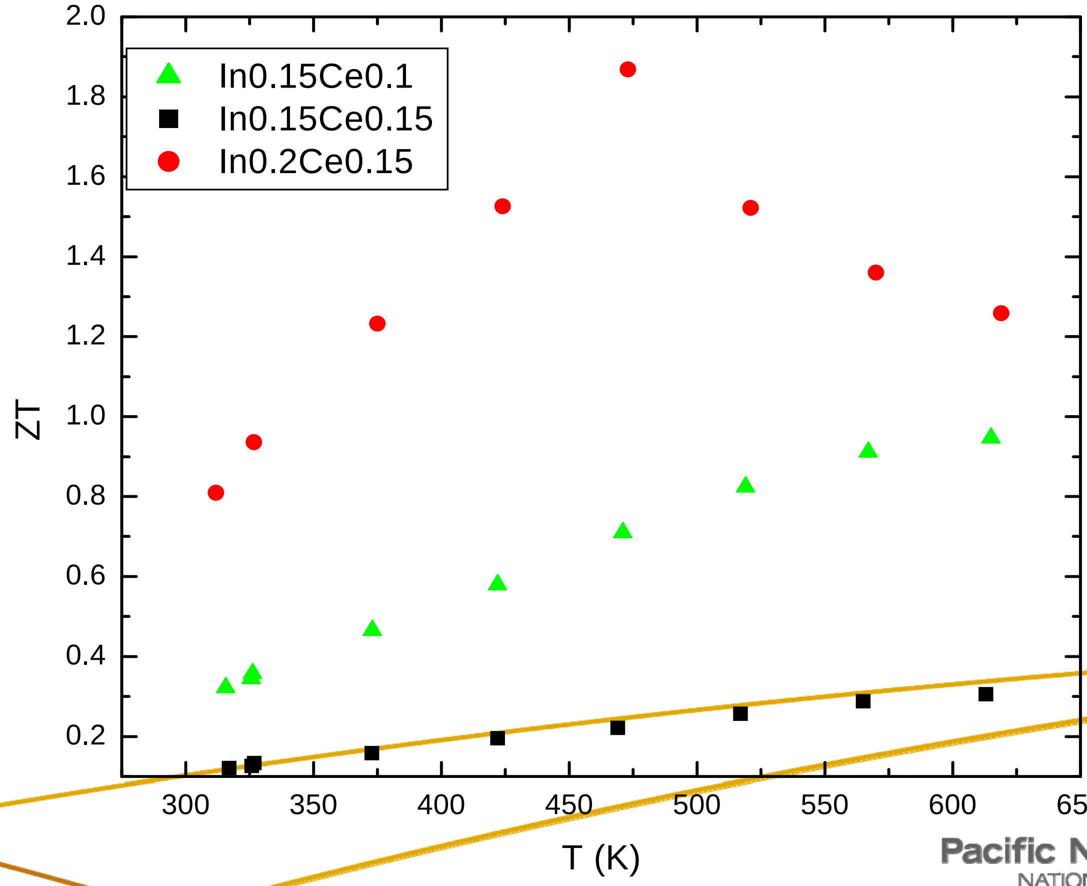




n-Type $In_xCe_yCo_4Sb_{12}$ TE Properties

- 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





n-Type Thermoelectric & Structural Properties

Specimen Label and Comments	Temperature (ºC)	ρ, density (g/cm³)	υ, Poisson's ratio	*E*, Modulus of Elasticity (10^{11} N/m²)	rms error (%)
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ - LBL1 2-5-2010	---	7.303	0.215	1.348	0.12
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ - LBL1 3-9-2010	20.6	7.303	0.204	1.344	0.33
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ – LBL2 2-9-2010	---	7.264	0.204	1.326	0.49
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ – LBL2 3-10-2010	21.5	7.264	0.200	1.319	0.40
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ – PNNL3-G1B 1-21-2010	---	7.315	0.181	1.339	---
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ – PNNL3-G1B 2-05-2010 Repeat 1-21-2010	---	7.315	0.185	1.339	---
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ – PNNL3-G1B 3-25-2010	20.8	7.315	0.194	1.358	0.78
$In_{0.2}Co_4Sb_{12}$ – NM211_3-5-10 3-30-2010 - BNW-60608 – 15	---	5.694	0.185	0.666	0.34

n-Type Thermoelectric & Structural Properties

Specimen Label and Comments	ρ, density (g/cm³)	υ, Poisson's ratio	*CTE (/°C)*	*E,* Elastic Modulus (10^{11} N/m²)	*ZT (@ 600 K)*
$CoSb_3$ (literature)		0.222		1.396	0.6
$La_{0.75}CoFe_3Sb_{12}$ (literature)		0.228		1.365	
$CoSb_3$ (PNNL)		0.226	12.8×10^{-6}	1.398	
$CoSb_3$ (PNNL)		0.225		1.391	
$In_{0.1}Co_4Sb_{12}$ (PNNL)		0.227	8.37×10^{-6}	1.396	
$Y_{0.1}In_{0.1}Co_4Sb_{12}$ (PNNL)		0.247	9.26×10^{-6}	1.413	0.82
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ – PNNL3 1-21-2010 --- chip off corner	~7.314	0.181		1.339	
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ – PNNL3 2-5-2010 --- REPEAT of 1-21-2010	~7.314	0.185	8.61×10^{-6}	1.339	0.95
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ - LB1 2-5-2010	7.304	0.215	8.56×10^{-6}	1.348	0.95
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ - LB2 2-9-2010	7.264	0.204	8.26×10^{-6}	1.326	0.95
$In_{0.2}Ce_{0.15}Co_4Sb_{12}$ - 03161035 4-13-2010 (Preliminary Data)	7.019	0.105	$8.11\text{-}8.34 \times 10^{-6}$	1.066	1.4 (1.5-1.6 @ 475K)

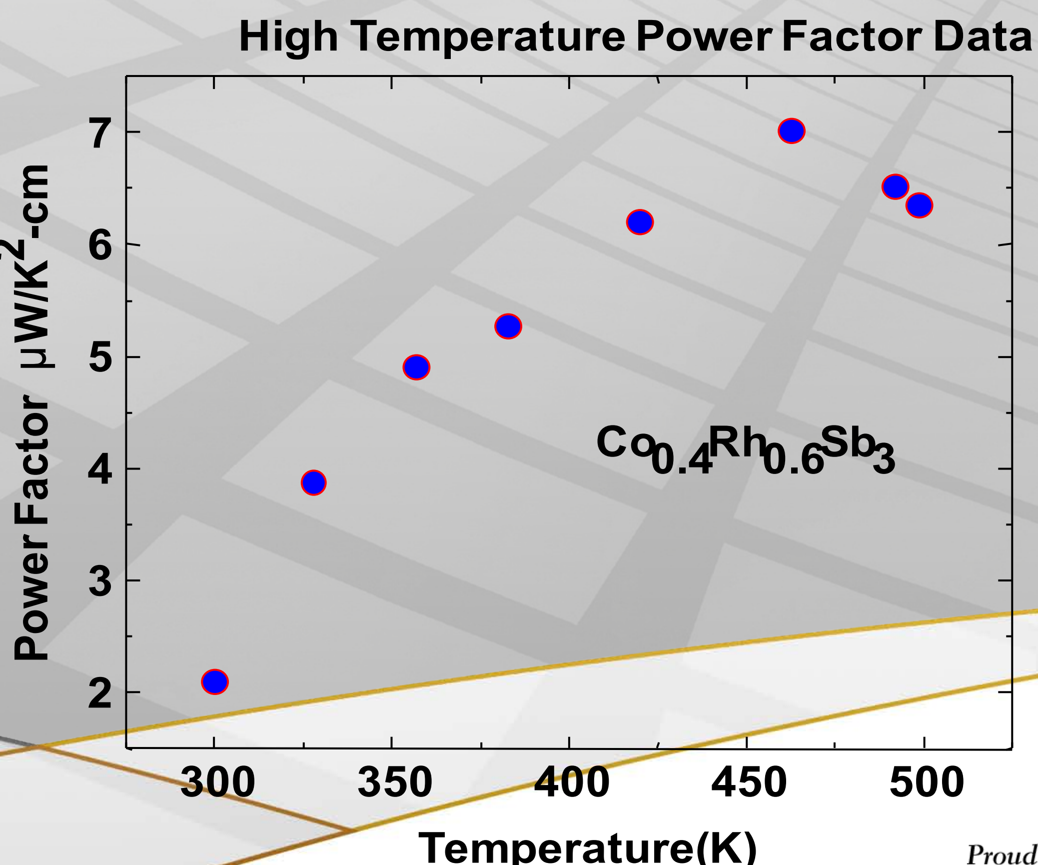
Resonant Ultrasound Spectroscopy (E, ν) Measurements
Thermal Cycling Effects

- Thermal Fatigue Cycling Showing Good Stability
  - 200 Cycles
  - 40 °C to 400 °C
- Good Indicator of Reliability in Future TE Modules

	Temperature [°C]	Before Thermal Cycling		After Thermal Cycling	
		Young's Modulus, E X 10^9 [N/m^2]	Poisson's Ratio, ν	Young's Modulus, E X 10^9 [N/m^2]	Poisson's Ratio, ν
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (LBL1)	20-22	134.8	0.215	134.4	0.204
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (LBL2)	20-22	132.6	0.204	131.9	0.200
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (PNNL3-G1B)	20-22	133.9	0.185	135.8	0.194

p-Type $Co_{1-x}Rh_xSb_3$ (without Rattlers): High Temperature Power Factor

- Power Factor Temperature Dependency for p-type x= 0.6 sample
  - x = 0.6 was optimum composition
- Higher Power Factor, But Costs Too High as Pointed Out @ 2009 OVT Merit Review
- Reported Last Year, But Work Discontinued Due to Cost & κ



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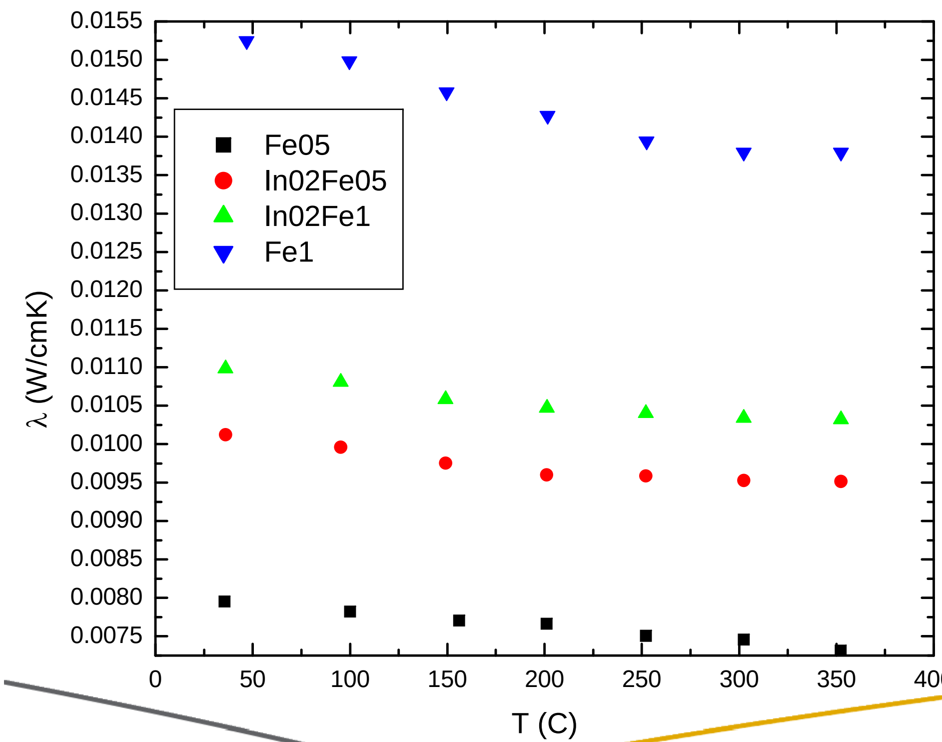
p-Type Skutterudites with High ZT

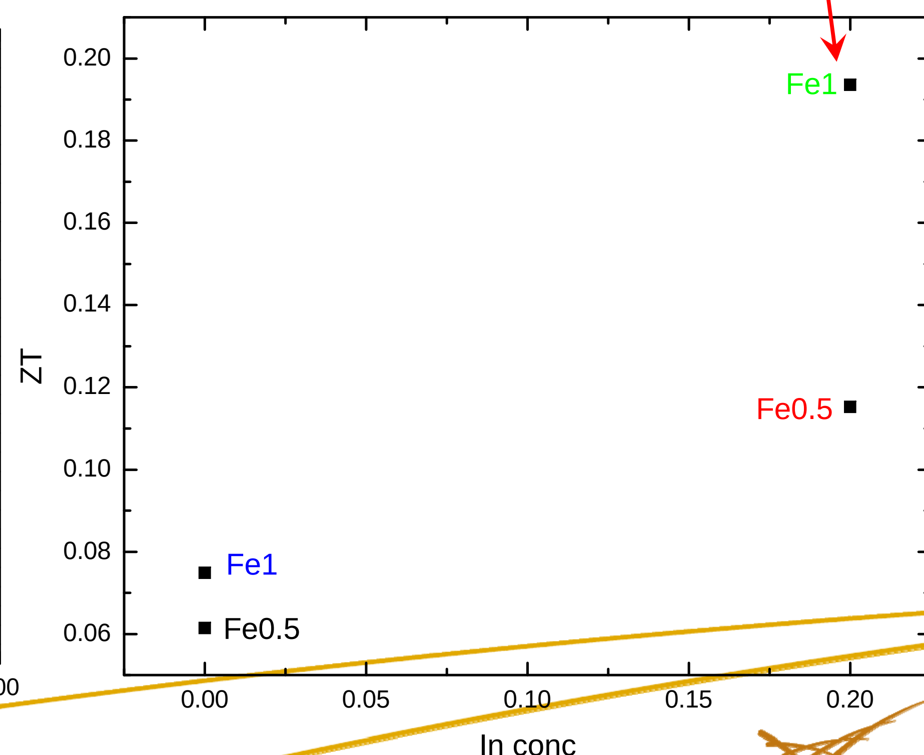
- p-Type Skutterudites Quite Difficult to Produce
- Very Few Dopents Act as Electron Acceptor from the Co-Sb Conduction Band
- Following Compounds are Guiding Our p-Type Investigations
- Reproducibility of Compounds Below Has Not Been Confirmed

S.No	Compound	ZT	Ref
1	$LaFe_{4-x}Co_xSb_{12}$	0.9 at 800 K	B. C. Sales, D. Mandrus, and R. K. Williams, Science 272, 1325 (1996)
2	$CeFe_{4-x}Co_xSb_{12}$ x < 3 p-type x > 3 n-type	0.7 at 800 K; 1.2-1.4 at 900 K	J.-P. Fleurial, T. Caillat, A. Borshchevsky, D. T. Morelli, and G. P. Meisner, in Proceedings of the 15th International Conference on Thermoelectrics (1996) 91
3	$Ce_{0.28}Fe_{1.5}Co_{2.5}Sb_{12}$	1.1 at 750 K	Tang, Xinfeng; Zhang, Qingjie; Chen, Lidong; Goto, Takashi; Hirai, Toshio., Journal of Applied Physics (2005), 97(9) 093712/1-093712/10
4	$Ba_{0.27}Fe_{0.98}Co_{3.02}Sb_{12}$	0.9 at 750 K	Tang, X. F.; Chen, L. D.; Goto, T.; Hirai, T.; Yuan, R. Z., Journal of Materials Research (2002), 17(11), 2953-2959
5	$Ca_{0.18}Ce_{0.12}Fe_{1.45}Co_{2.55}Sb_{12}$	1.2 at 750 K	Tang, Xinfeng; Li, Han; Zhang, Qingjie; Niino, Masayuki; Goto, Takashi.Journal of Applied Physics (2006), 100(12), 123702/1-123702/8

p-Type Skutterudites To Date

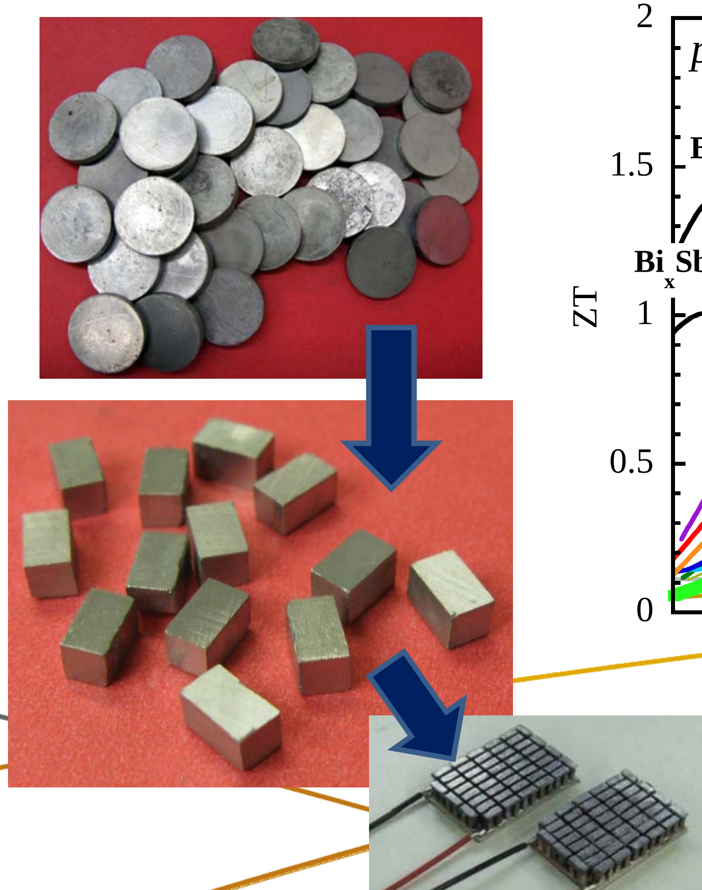
- ZT of ~0.2 is obtained for $In_{0.2}Co_3FeSb_{12}$ at 623 K

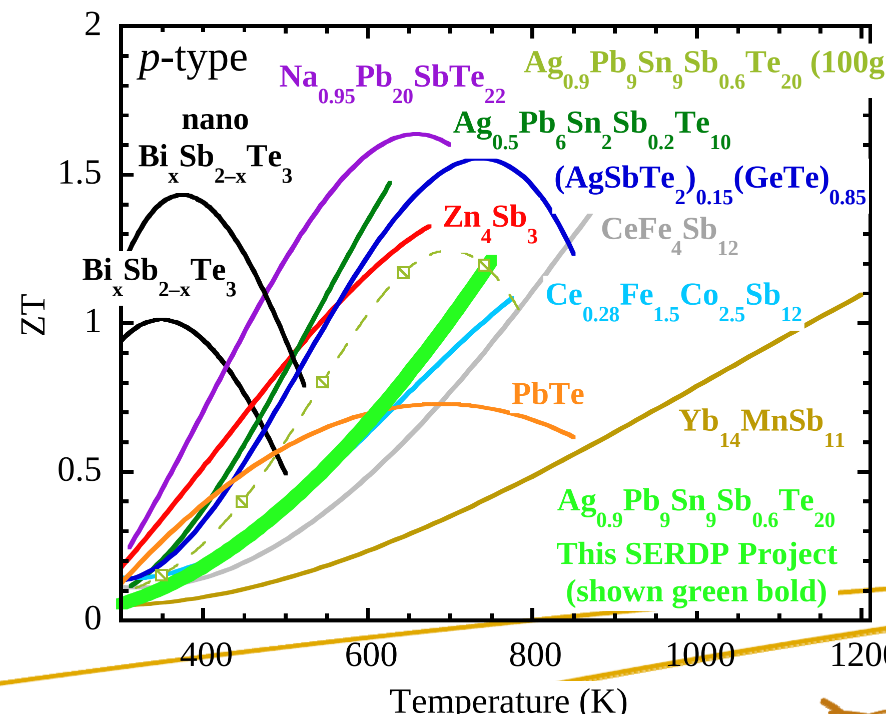




p-Type Skutterudites To Date

- **ZT of ~0.2 is obtained for $In_{0.2}Co_3FeSb_{12}$ at 623 K**
- **p-Type LAST Materials Could be Combined with n-Type In-Ce Based Skutterudites to Demo TE Couple**
  - **Well-Developed Thermoelectrically & Structurally (Tellurex Corp., 2009)**
  - **Demonstrated in TE Modules (Tellurex Corp., 2009)**
  - **ZT = 1.2 @ 750 K**





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
  - BSST LLC
  - ZT Plus
- Coordination with OVT Waste Heat Recovery & Utilization Project

Microproducts Breakthrough Institute

ONAMI
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TELLUREX CORPORATION

Future Work & Path Forward

- Optimize Synthesis Procedures for *n*-type (In,R)Co_4Sb_{12} Compositions
  - Good Reproducibility
  - Fabricating Highly Dense Samples
- Introduce Single & Multiple "Rattlers" (In, Rare Earth) in $Fe_xCo_{4-x}Sb_{12}$, (i.e., $In_y Fe_xCo_{4-x}Sb_{12}$; $Ce_y Fe_xCo_{4-x}Sb_{12}$) For Better *p*-Type Materials
- Characterize TE Properties & Validate with Third Party Testing (ORNL)
- Structural Property Measurements
  - Young's Modulus, E(T)
  - Poisson's Ratio, ν(T)
  - CTE(T)
  - Mechanical Strength
- Transition to TE Couples & Measure Performance

Summary

- Results
  - n-type Skutterudite TE Materials Showing Excellent TE Properties (See Publication)
  - p-type Skutterudite TE Materials Are More Challenging
  - Structural & CTE Testing On-Going; Good Structural Stability Upon Thermal Cycling
  - High Temperature Structural Test Equipment Operational & Calibrated
- Challenges
  - Batch to Batch ZT Reproducibility and Consistent Properties
  - Sintering to High Dense Samples
  - Continue Evaluating Stability Issues During Thermal Cycling
- Benefits
  - System-Level Analyses Show OSU/PNNL Skutterudites Superiority (See Supplements)
    - Higher Performance Than TAGS / PbTe Combinations & Other Skutterudite Combinations
  - 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

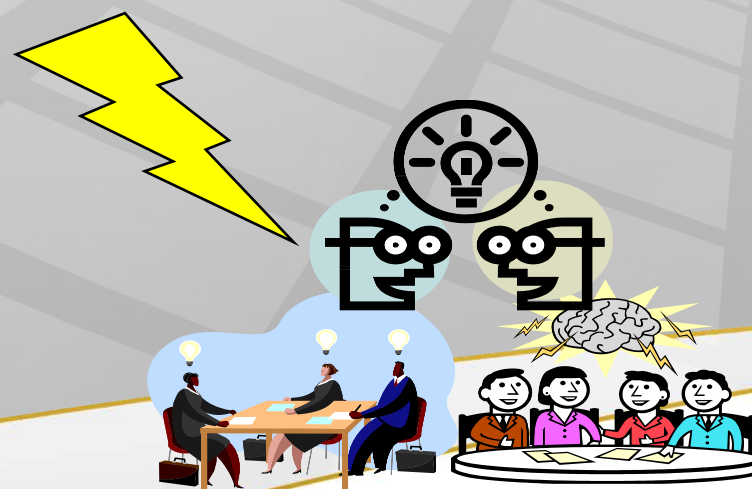
We are What We Repeatedly do. Excellence, Then, is not an Act, But a Habit.

Aristotle

Acknowledgement

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

Questions & Discussion



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