Proactive Strategies for Designing Thermoelectric Materials for Power Generation

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Agenda

- Overview
- Technical Approach & Goals
- Thermoelectric Property Measurements
- Structural Property Measurements
- Vehicle Level Impacts
- Future Plans

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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

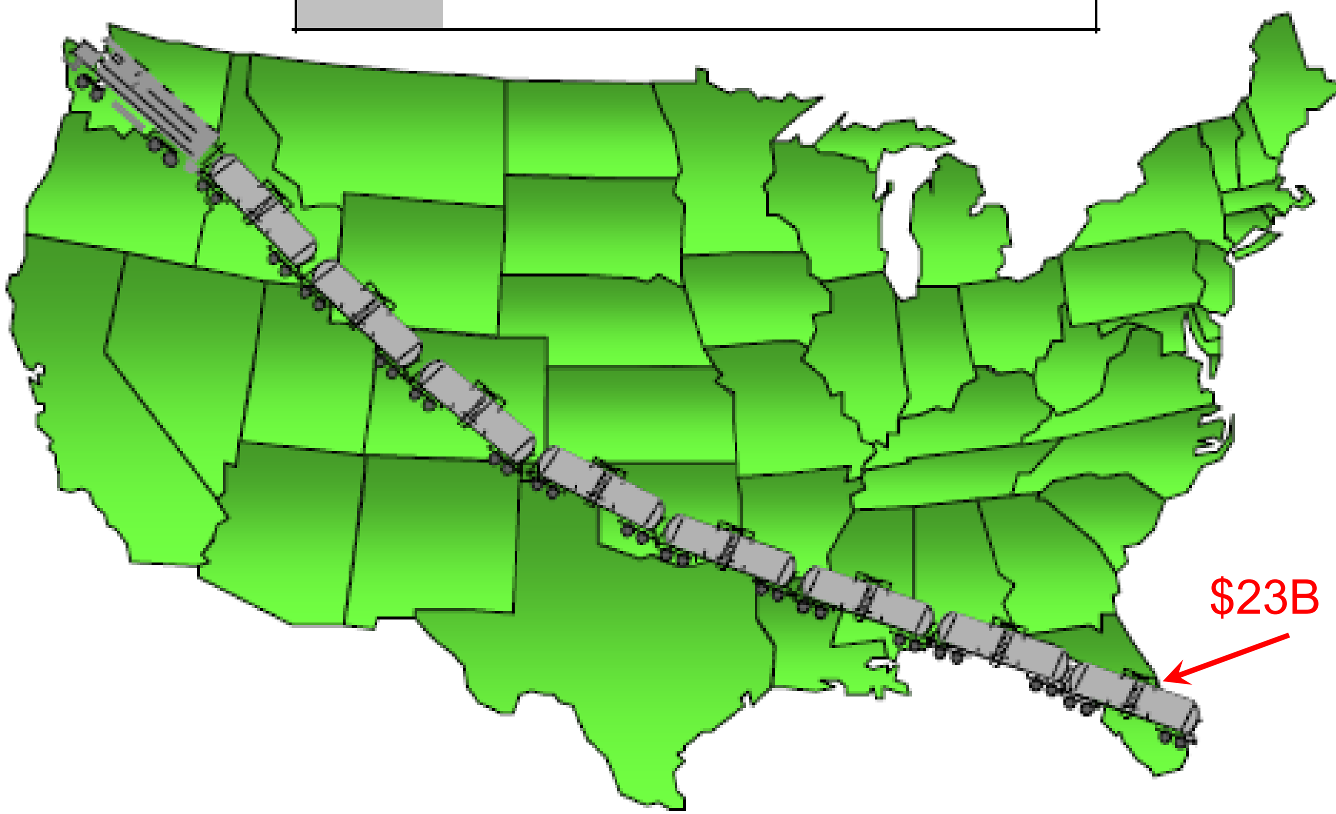
    Needs for Electric-Driven Cooling

- **Industrial Sector**
  - **Another 10 Quads Lost - ~1.8 Quads Recoverable**

The Magnitude of Our Energy Problem

Office of Heavy Vehicle Technologies

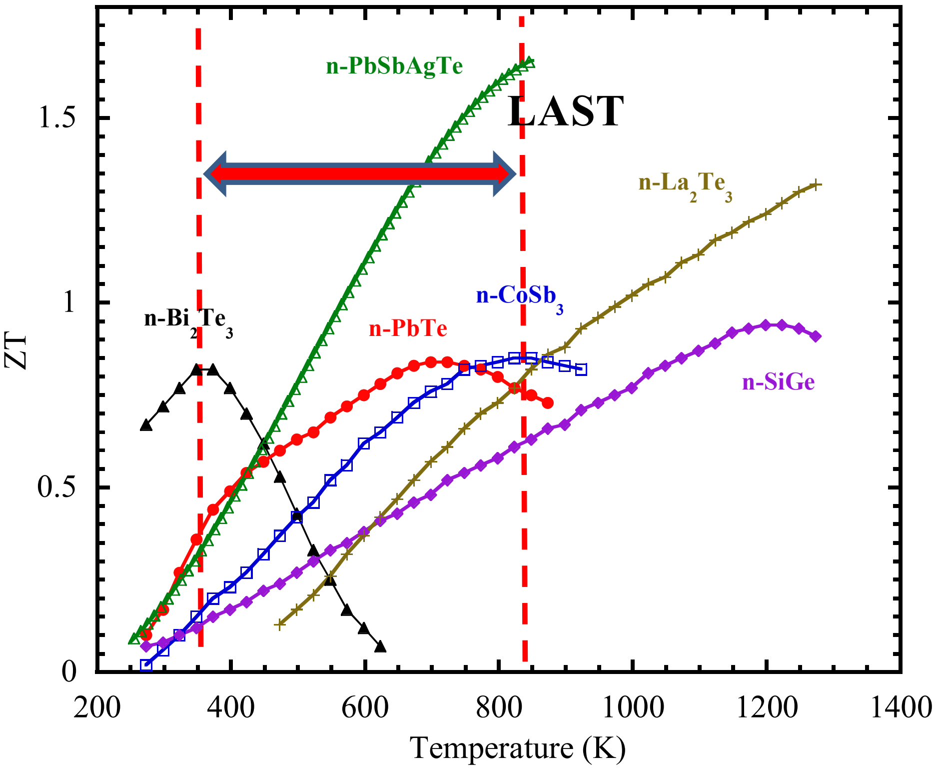
	1973	1997
U.S.	74 Quads	91 Quads
World	225 Quads	365 Quads



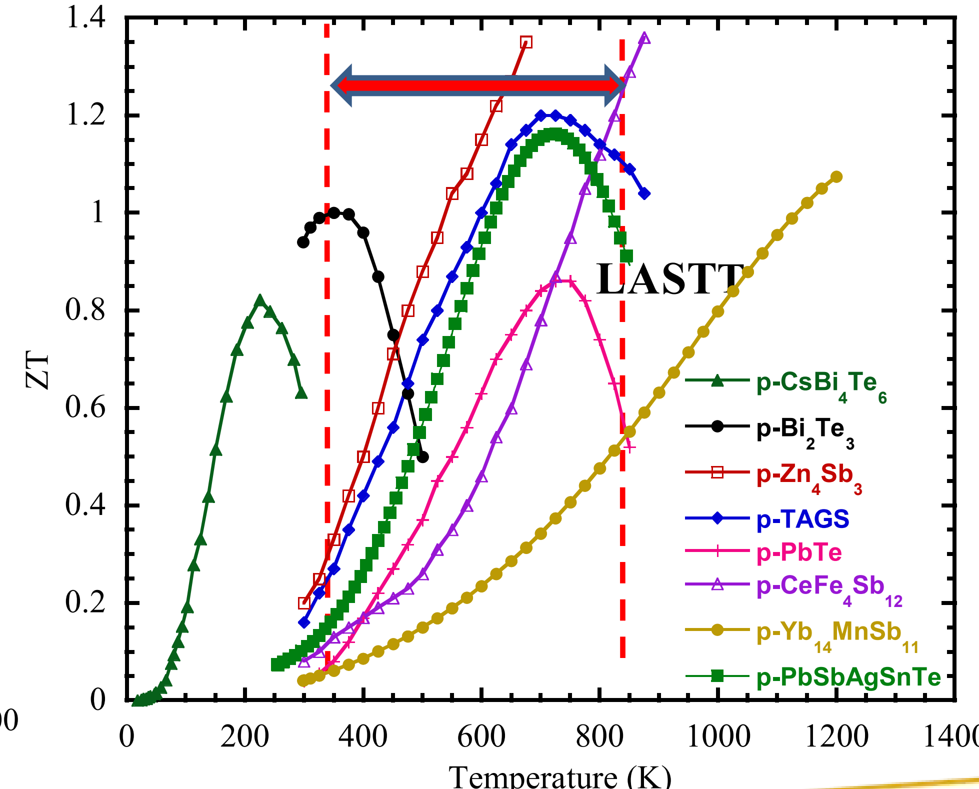
1 Quad of energy is equivalent to 340,000 tank cars of crude oil stretched from Miami to Seattle (3,300 miles).

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

Various Data Here Come from Past TE Materials Programs @ NASA-JPL & Office of Naval Research

Project Objectives

- Continue Design, Synthesis, & Characterization of n-type, Multiple-Rattler In-based Skutterudites Refined in 2008
  - Measure Properties at 300 – 820 K
  - Bulk Materials
  - ZT = 1.6 @ 600 K ($\mathbf{In_xCe_yCo_4Sb_{12}}$)
- Design, Synthesize, & Characterize Corresponding p-type, Multiple-Rattler Skutterudites in Similar Temperature Regimes
- Characterize Thermoelectric & Structural Properties
  - Seebeck Coefficient, Electrical Conductivity, Thermal Conductivity - OSU
  - Elastic modulus, Poisson's ratio, Coefficient of Thermal Expansion – PNNL
  - Transition the Selected n-type & p-type Skutterudite TE Materials into TE Couples
- PNNL to Characterize System-Level Benefits of Material Compositions in Waste Energy Recovery Applications
- Demonstrate High-Performance TE Couples for Transition to Waste Energy Recovery Applications

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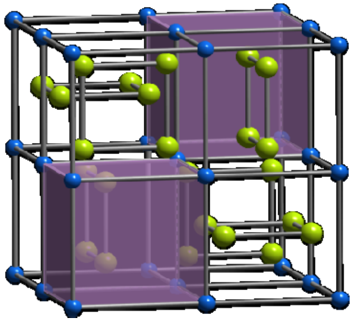
Technical Approach

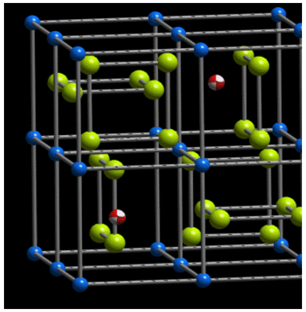
- Proactive, Systematic Investigation of Dual- & Tri-Rattler Skutterudites
  - Refine n-type Materials, Characterize at Higher Temperatures & Transition to TE Couple
  - Systematically Develop p-type Materials with Performance Similar to n-type Levels
- TE Property Measurements @ OSU Laboratories
  - Seebeck Coefficient Measurements vs. T
  - Electrical Conductivity Measurements vs. T
  - Thermal Conductivity Measurements vs. T
- Intend to Engage Third-Party Validation
  - ORNL
- Structural / Thermal Property Measurements @ PNNL
  - Resonant Ultra Sound Techniques (E, ν)
    - Up to ~300 $^\circ$ C
  - CTE
    - Up to ~400 $^\circ$ C
  - Mechanical Strength
    - Room Temperature

Multiple Rattlers in Skutterudites: $R_xR_y'Co_4Sb_{12}$



Co_4Sb_{12}

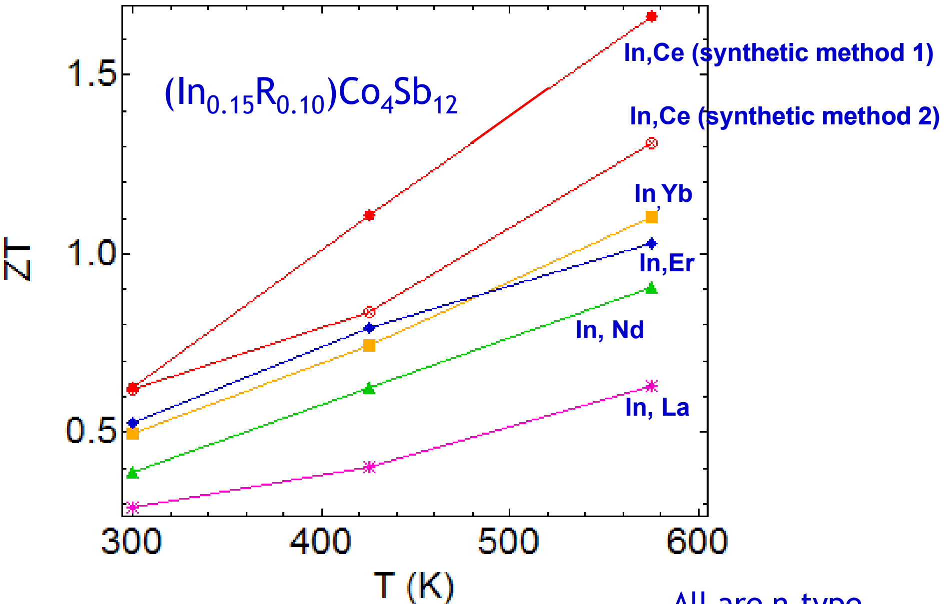
Multiple Rattlers



$R_xCo_4Sb_{12}$

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



All are n-type

- **$In_xCo_4Sb_{12}$ Shows High ZT ~1 at 573 K**
- **$In_xLn_yCo_4Sb_{12}$ Increases the ZT >1.5 at 573K**
- **All are n-types; High Performance <u>p-types are Needed</u>**
- **High Performance TE Materials Expected**
  - Bulk-Type Materials for Easier Device Manufacture & Integration
  - Transition Results to Energy Recovery Projects As Appropriate & Quickly As Possible

Project Accomplishments

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

Resistance temperature detector (RTD) sensor access

Argon gas inlet

Gas preheat

High temperature RUS transducers

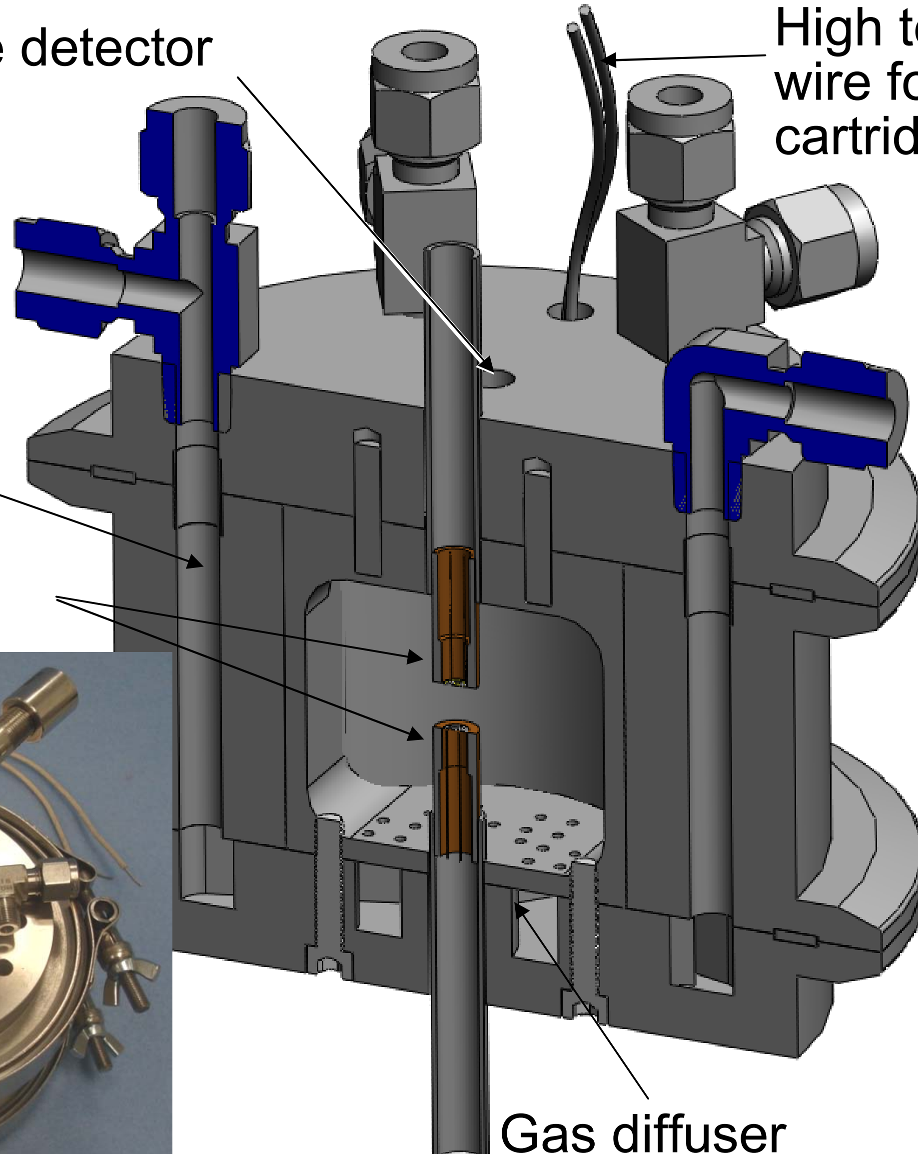
High temperature wire for three resistive cartridge heaters

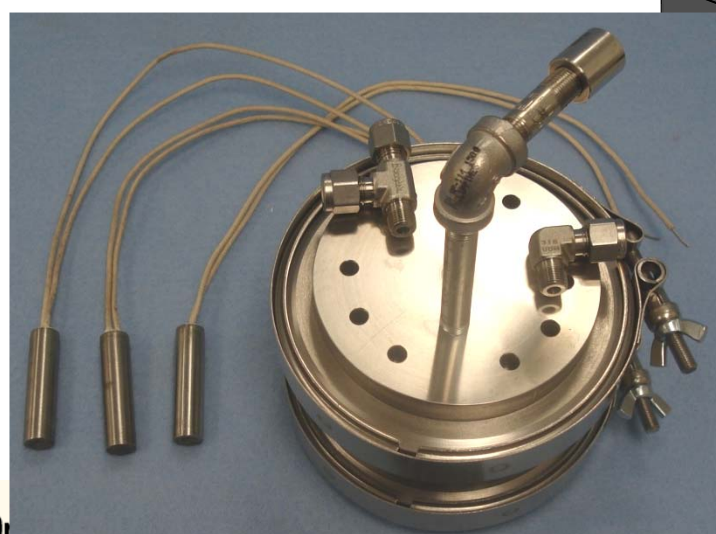
Upper fixture with fixed transducer

Primary components and fittings are stainless steel.

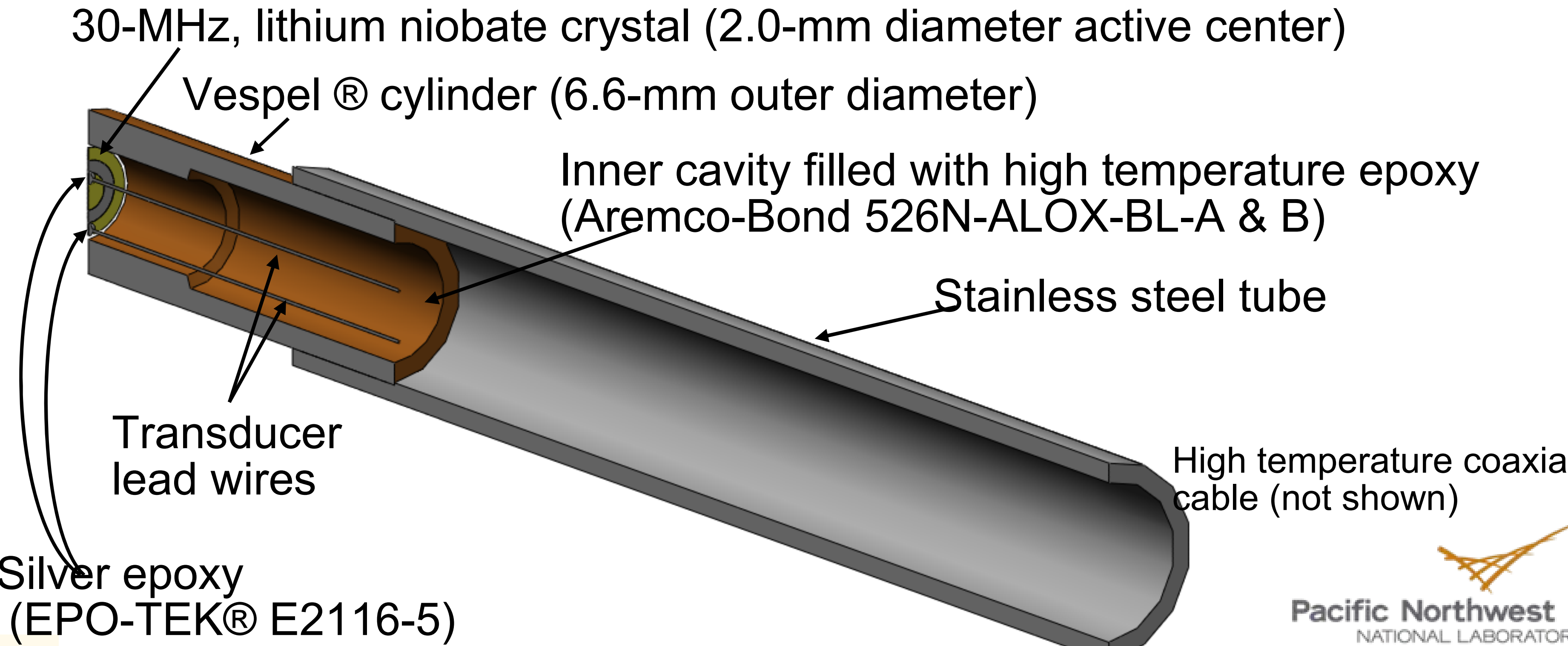
Lower fixture

Gas diffuser

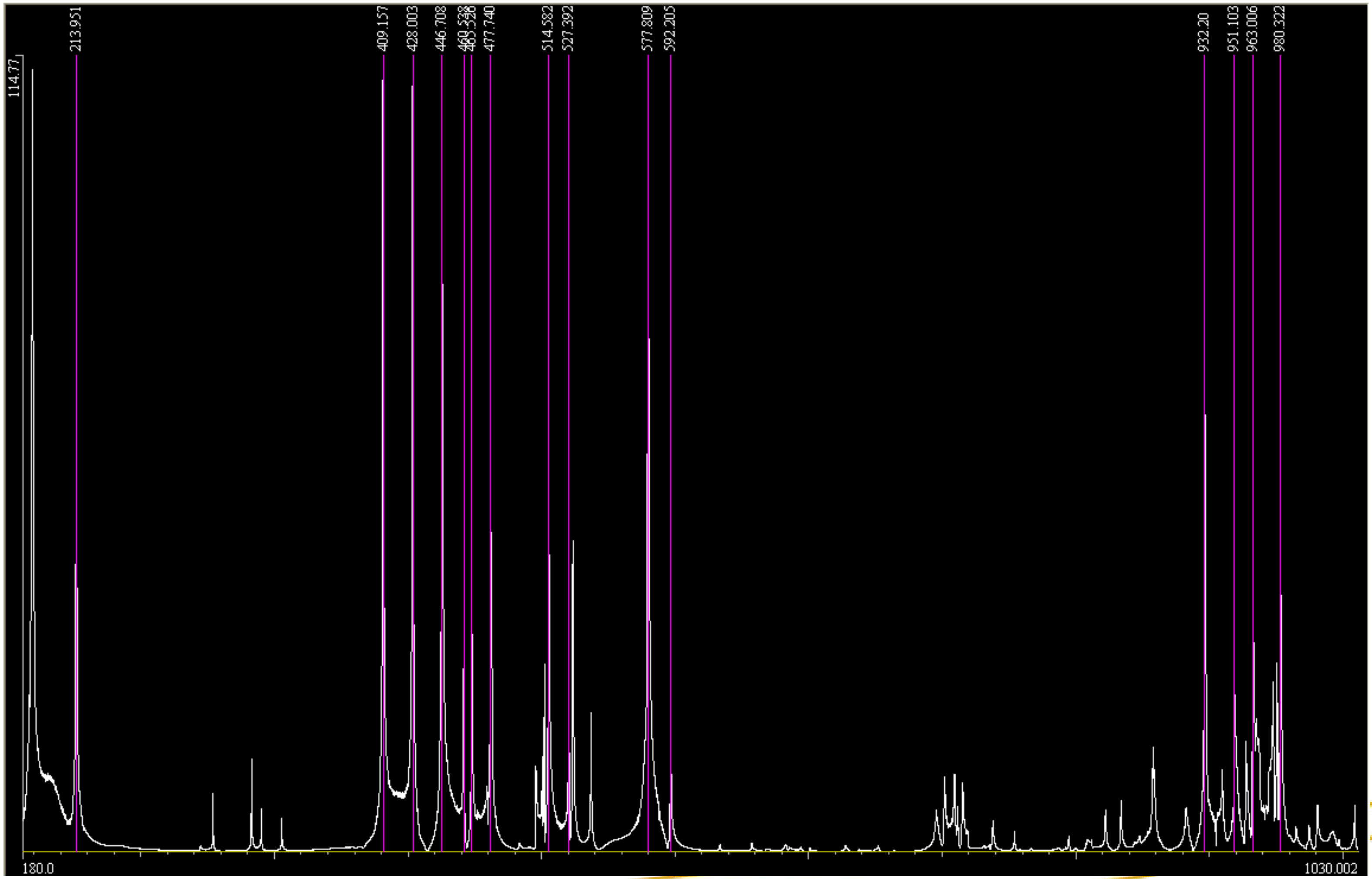




Elastic Moduli Estimate by Resonant Ultrasound Spectroscopy: High Temperature Transducers



Resonant Ultrasound Spectroscopy
PNNL



Spectrum spanning 180 – 1,030 Hz

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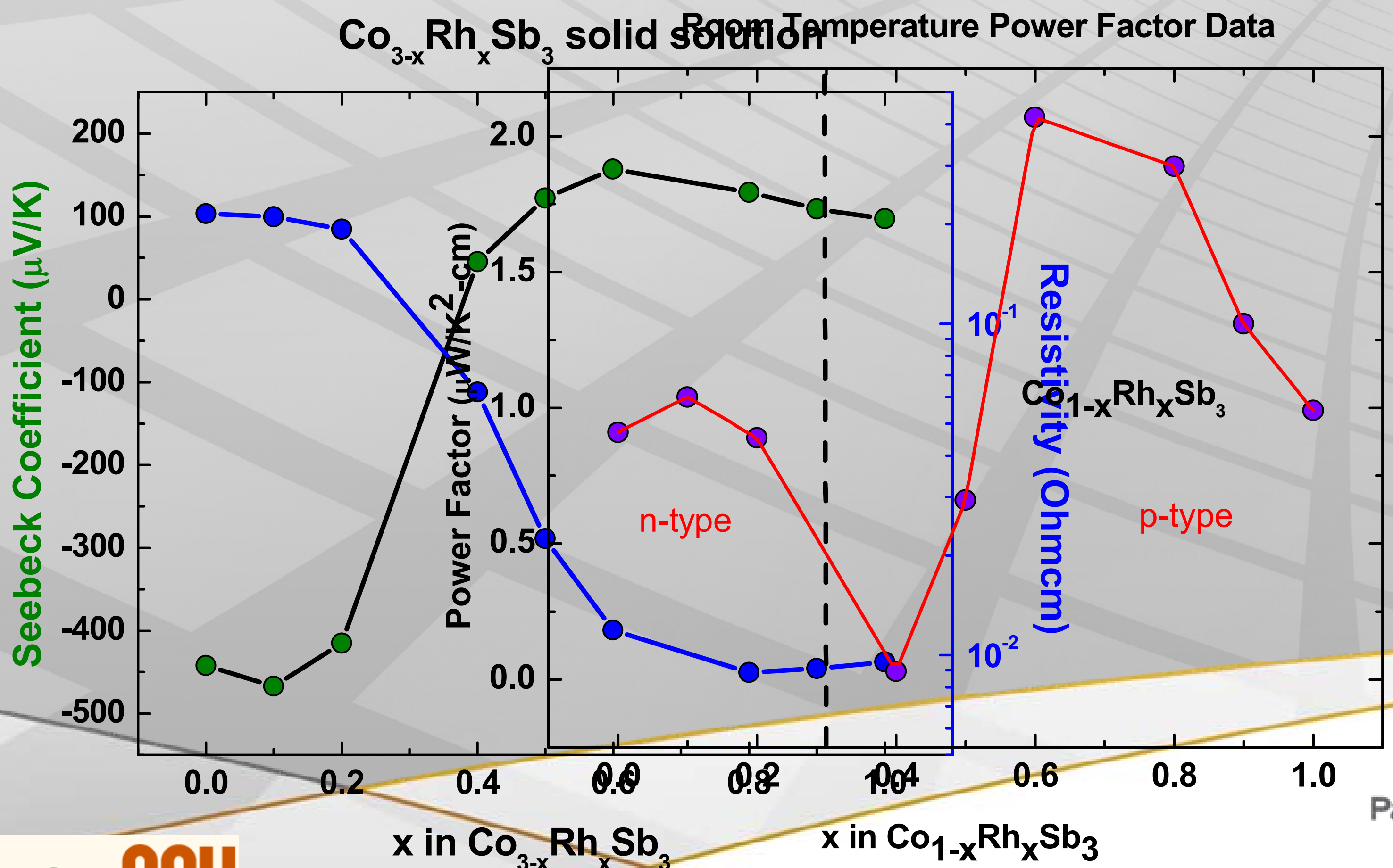
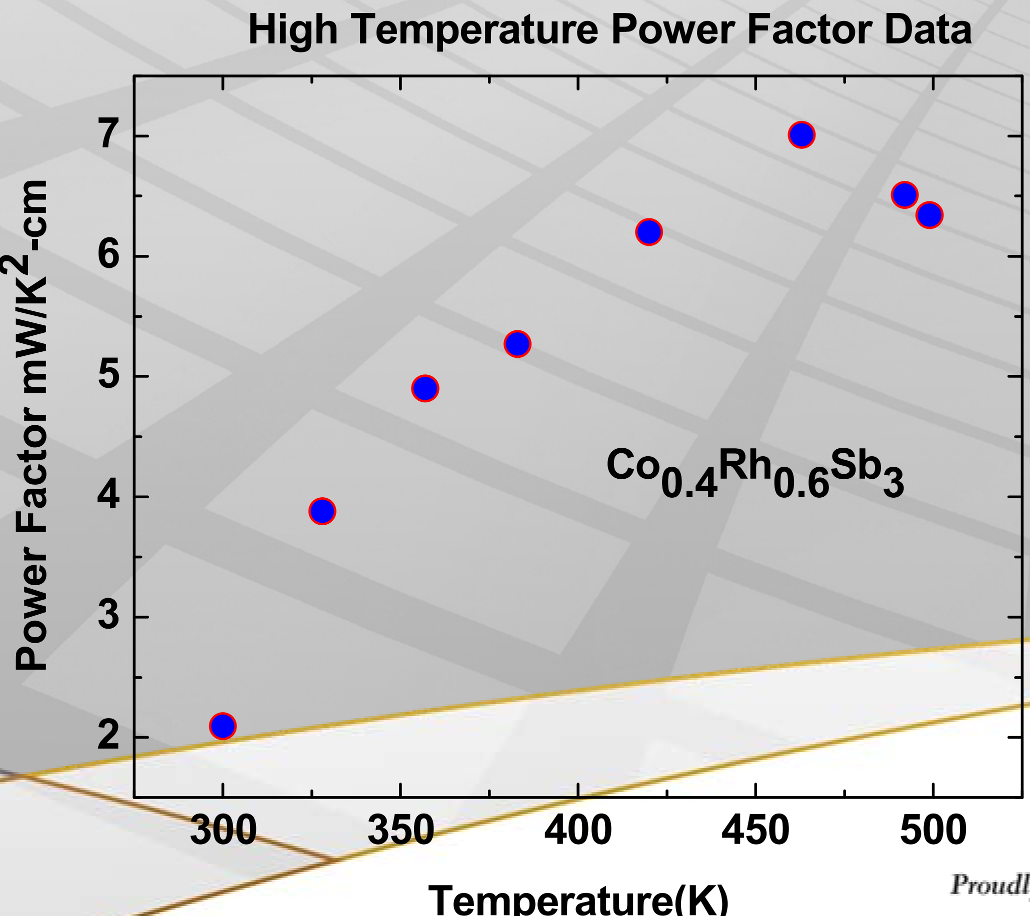
$Co_{1-x}Rh_xSb_3$ (without Rattlers): Electrical Data

- High Electrical Conductivity
- Both n- and p-type Compositions Can Be Made

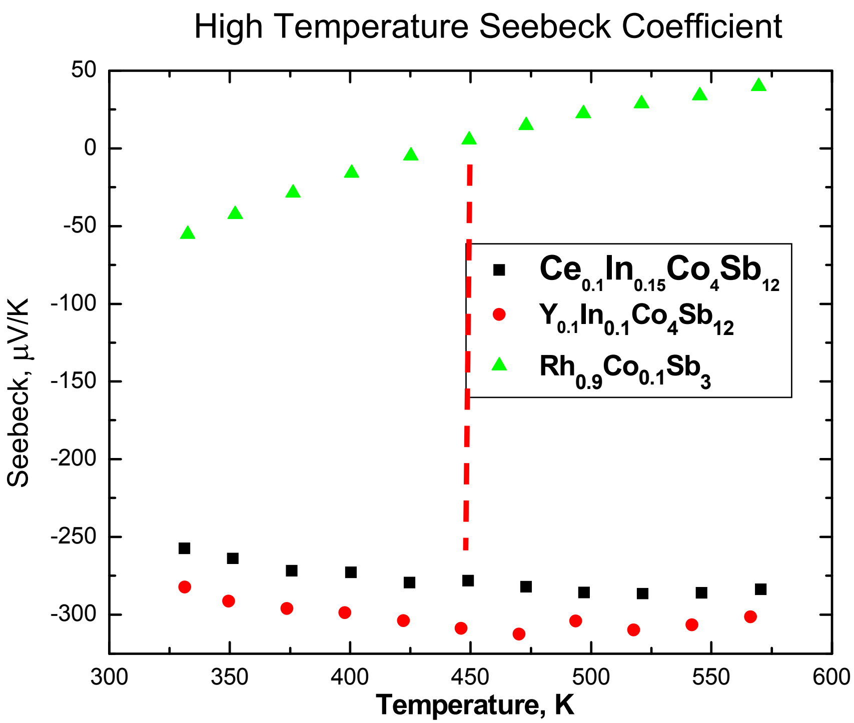


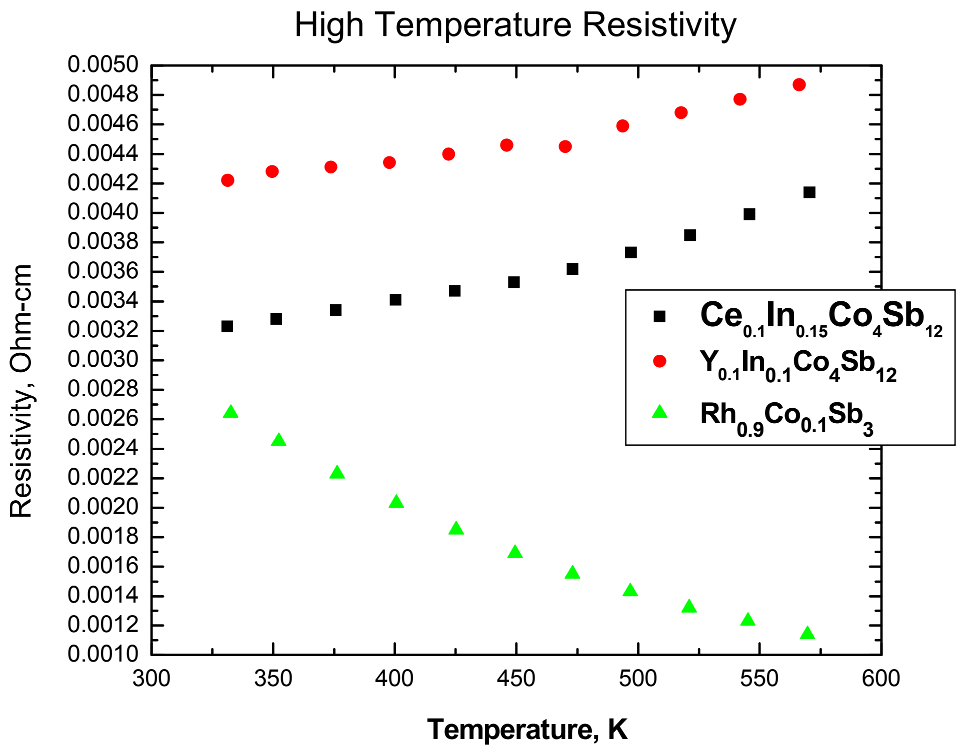
$Co_{1-x}Rh_xSb_3$ (without Rattlers): High temperature power factor

- Power Factor Temperature Dependency for p-type x= 0.6 sample
- Further Characterizations Such as Thermal Conductivity Are In Progress
- Higher Power Factor Combinations Being Pursued & Developed
  - Seeking to Match n-type Performance



Thermoelectric Characterization at OSU
Electronic Properties





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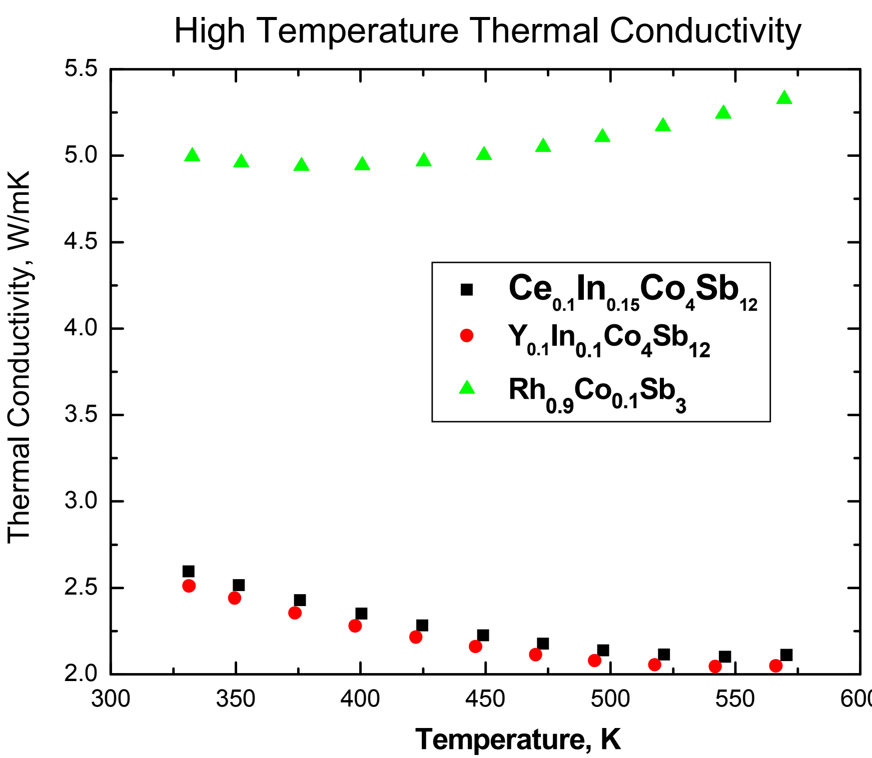
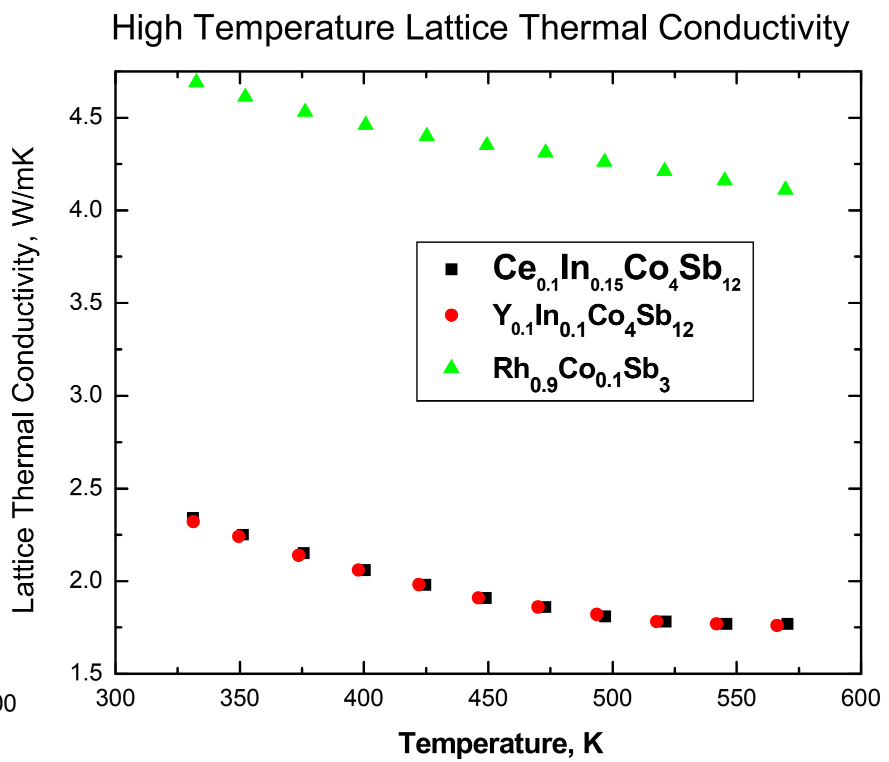
Thermoelectric Characterization at OSU
Thermal Conductivity





$$K_T = K_L + K_e$$

$$K_e = L_o \sigma T$$

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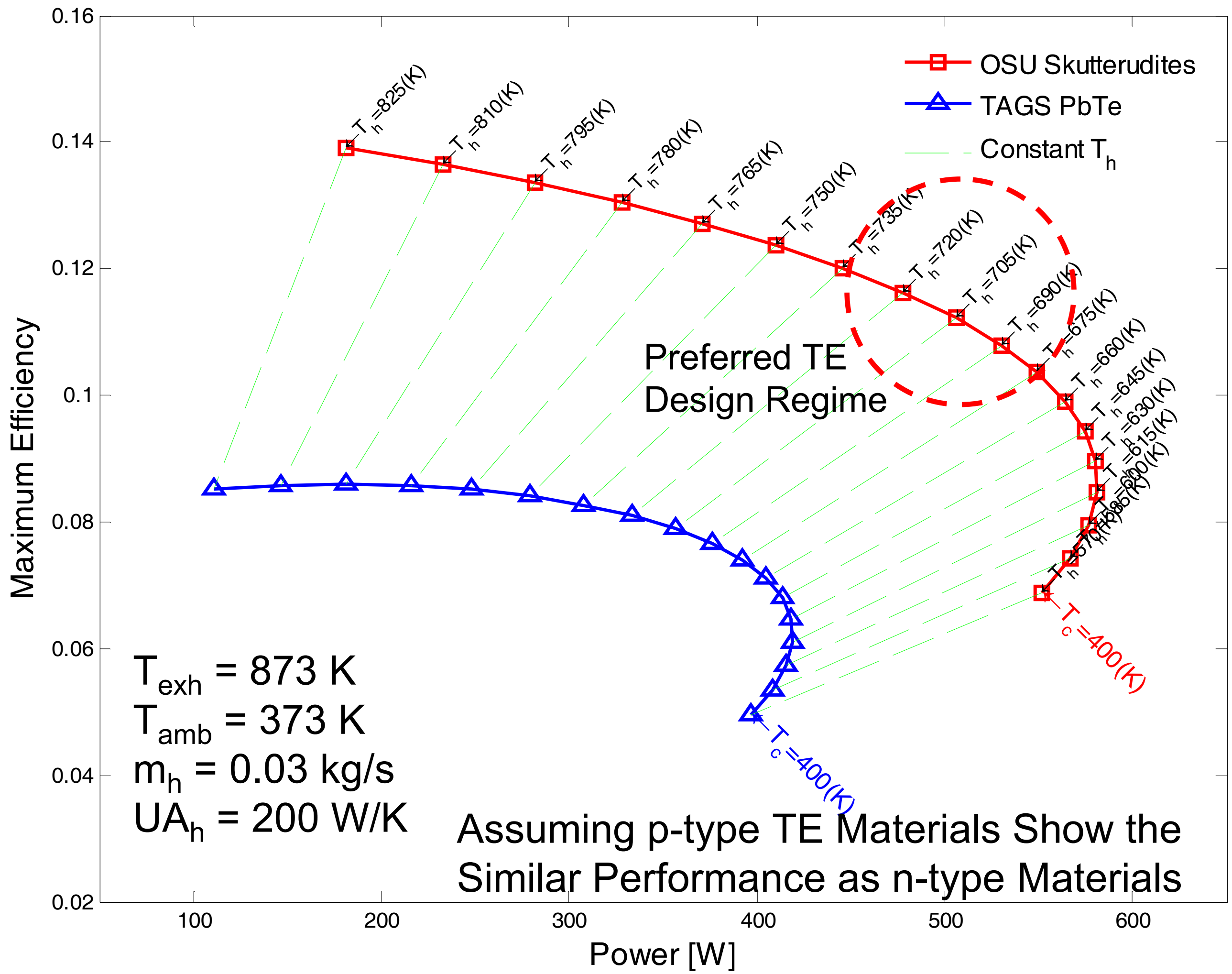
Resonant Ultrasound Spectroscopy & TE Properties
Preliminary Data

Isotropic	υ, Poisson's	*CTE [/° C]*	*E*, Young's [10^{11}] N/m²	*ZT (@ 600 K)*
$CoSb_3$ (literature)	0.222005842		1.39553067	0.6
$La_{0.75}CoFe_3Sb_{12}$ (literature)	0.227717924		1.36522233	
$CoSb_3$ (PNNL)	0.225592919	12.8×10^{-6}	1.39818091	
$CoSb_3$ (PNNL)	0.224591022		1.39118439	
$In_{0.1}Co_4Sb_{12}$ (PNNL)	0.227384707	8.37×10^{-6}	1.39624829	
$Y_{0.1}In_{0.1}Co_4Sb_{12}$ (PNNL)	0.247137106	9.26×10^{-6}	1.41325577	0.82

- Next TE Materials for Structural Testing (In Process)
  - $In_{0.15}\ Ce_{0.10}\ Co_4\ Sb_{12}$
  - $In_{0.1}\ Y_{0.10}\ Co_4\ Sb_{12}$
  - $Rh_{0.9}\ Co_{0.1}\ Sb_3$

TE Material Impacts on System Design

- System-Level Analyses Show OSU/PNNL Skutterudites Potential Superiority Compared to Common High-Performance Materials
  - Automotive Exhaust Heat Recovery Applications
  - Direct-Fired APU Applications



- Higher System Efficiencies Create:
  - More Power (for Given Heat Input)
  - Smaller Systems
  - Lighter Systems

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 $Co_{0.6}Rh_{0.4}SbO_3$ For Better *p*-type High ZT Materials
- Investigate Other p-type Combinations
- Characterize TE Properties & Validate with Third Party Testing
- Structural Property Measurements
  - Young's Modulus, E(T)
  - Poisson's Ratio, ν(T)
  - CTE(T)
  - Mechanical Strength
- Transition to TE Couples & Measure Performance

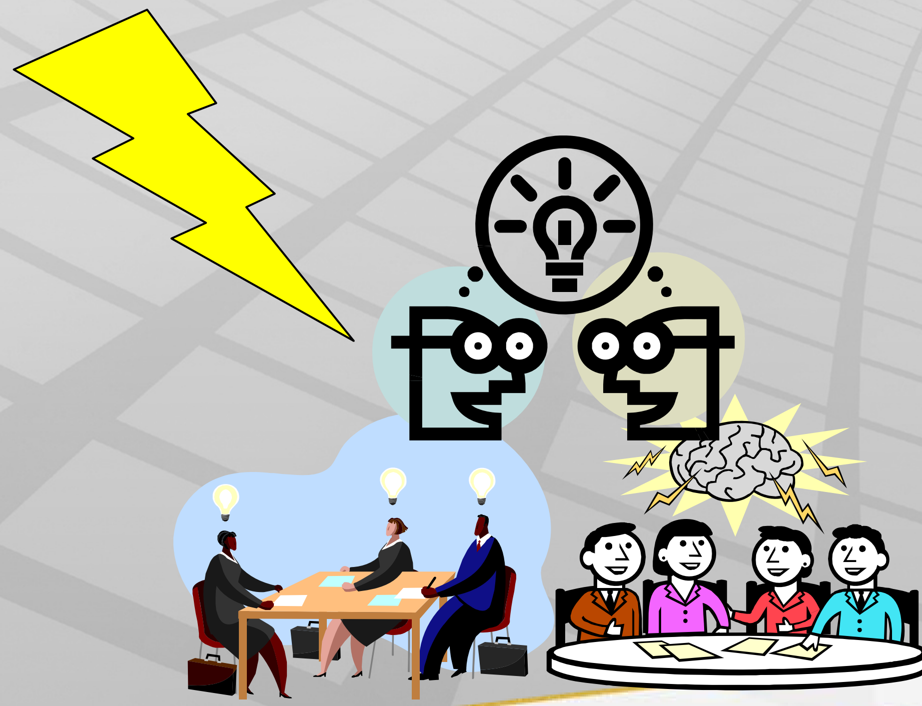
Summary

- Results
  - n-type TE Materials Showing Excellent TE Properties (See Publication)
  - p-type $Co_{1-x}Rh_xSb_3$ TE Materials Showing Promise at This Early Date (March 2009)
  - Structural Testing Plans Developed
  - Preliminary Room Temperature Structural Data Available
  - High-Temperature Structural Test Equipment Fabricated
- Challenges
  - Batch to Batch ZT Reproducibility
  - Sintering to High Dense Samples
  - Stability Issues During Thermal Cycling
- Benefits
  - System-Level Analyses Show OSU/PNNL Skutterudites Superiority
    - 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

Questions & Discussion



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