Proactive Strategies for Designing Thermoelectric Materials for Power Generation

PNNL / ONAMI Joint Project on Advanced TE Materials & Systems

Project ID #pm_13_hendricks

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Office of Vehicle Technologies 2009 Annual Merit Review

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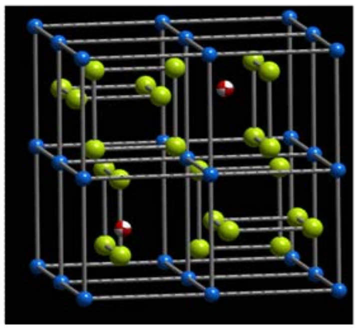
Agenda

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

Proactive Strategies for Designing Thermoelectric Materials for Power Generation - Overview

Timeline

- Project Start Date: 15 December 2008
- Project End Date: 15 December 2009
- 30% Complete



$R_xCo_4Sb_{12}$

OVT Barriers

- Achieve Stretch Thermal Efficiencies of 55% in Heavy-Duty Engines by 2013
  - Fuel Economy Increases of 10% over 2010
  - Improve Cost-Effectiveness & Performance of Exhaust Heat Recovery
- Improve Light-Duty Vehicle Fuel Efficiency up to10%
- High-Performance Waste Energy Recovery Materials to Integrate into Advanced Engines
  - Lower-Quality Exhaust Energy Available in Already-Efficient CIDI or LTC engines
- Methods for Maintaining Fuel Economy at Light-Loads

Budget

- Total FY 2009 Project Funding $260K
- FY 2009 Received To-Date $113K

Partners

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

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ONAMI OREGON NANOSCIENCE AND MICROTECHNOLOGIES INSTITUTE

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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**

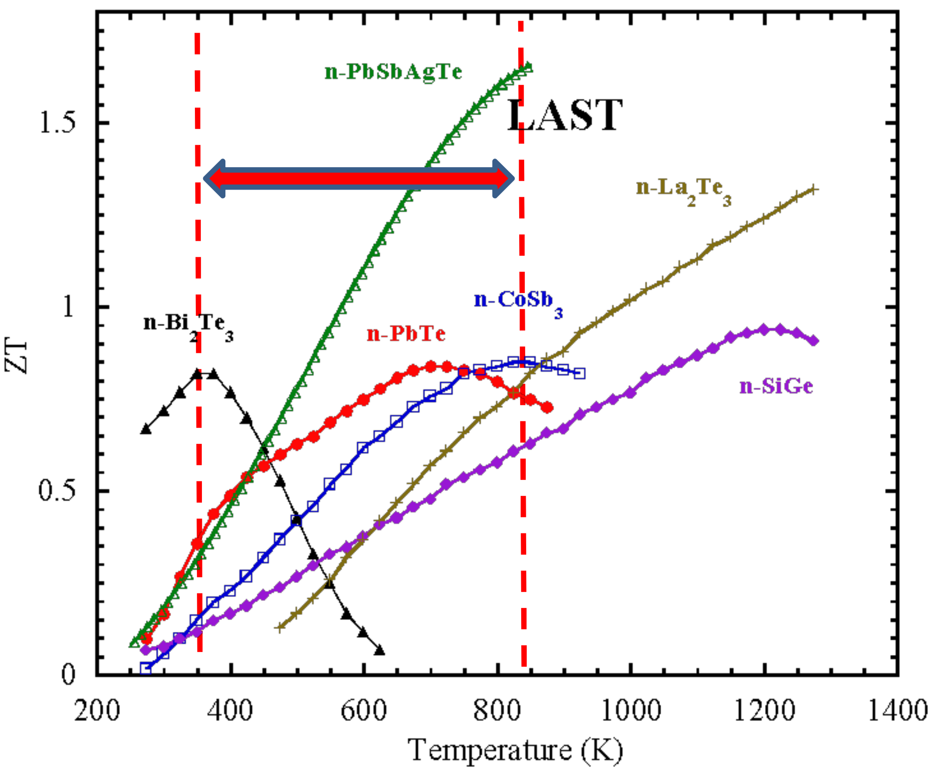
    Move Toward Electrification – Micro, Mild, and Full

    Needs for Power Generation

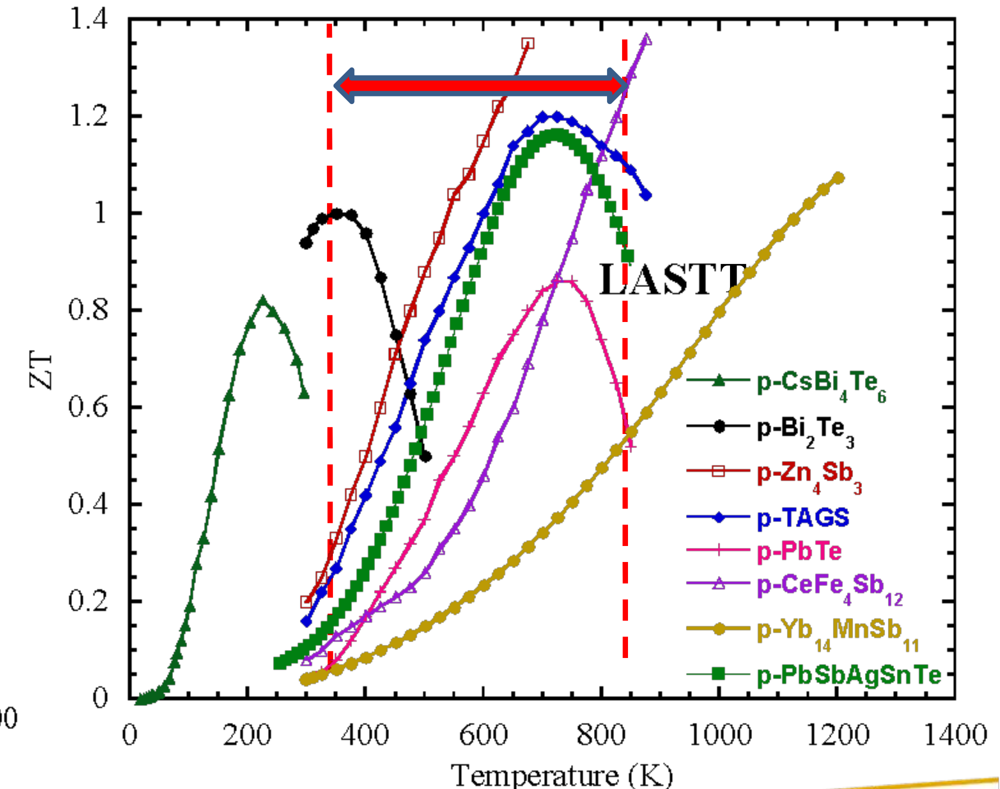
    Needs for Electric-Driven Cooling

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

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, Sythesize, & 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

Schedule / Milestones

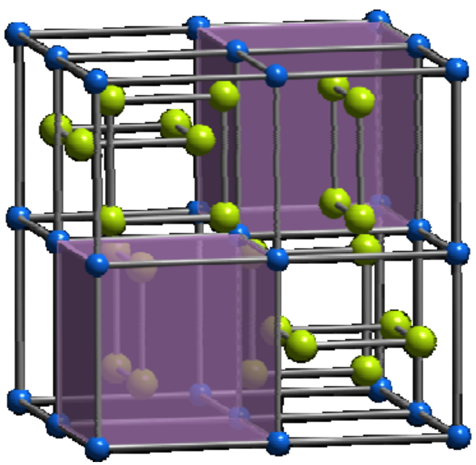
Month/Year	Milestones:
Dec-08 – Dec. 09	P-type and n-type Thermoelectric Development & Testing. Optimize Compositions for TE Performance. Measure TE Properties (Seebeck Coefficient, Electrical Resistivity, & Thermal Conductivity). On-going throughout the year due to third-party validation .
July-09	Select p-type & n-type TE Materials for Structural Testing. Criteria Will Be Selecting the Best TE Materials Properties (ZT vs. T.)
August-09	Measure Room Temperature Structural Properties of p-type & n-type TE Materials. Measure E, ν, Mechanical Strength.
October 09	Measure High Temperature Structural Properties of p-type & n-type TE Materials.
December 09	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

- 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 °C
  - CTE
    - Up to 400 °C
  - Mechanical Strength
    - Room Temperature

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

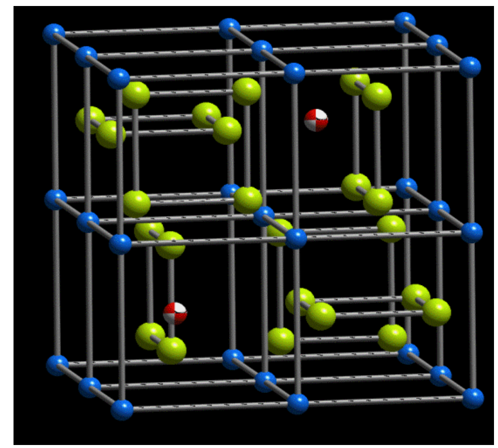
- Multiple Rattler Systems Dramatically Reduce Thermal Conductivity While Maintaining Electrical Conductivity & Seebeck Coefficient
  - Single Rattler Systems
  - Multiple Rattler Systems



Co_4Sb_{12} (n-type)

Rh_4Sb_{12} (p-type)

Single and Multiple Rattlers



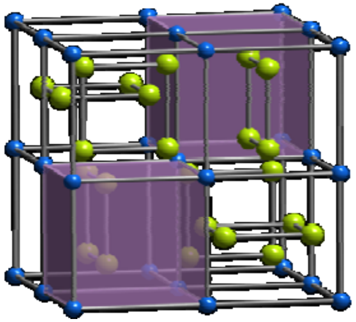
$R_xCo_4Sb_{12}$

$R_xR'_yCo_4Sb_{12}$

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

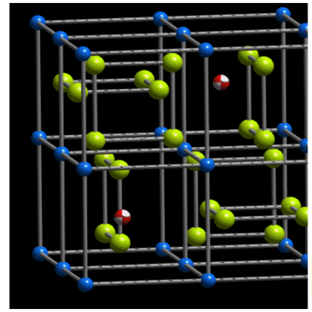
$R_xR'_yCo_{4-z}Rh_zSb_{12}$

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



Co_4Sb_{12}

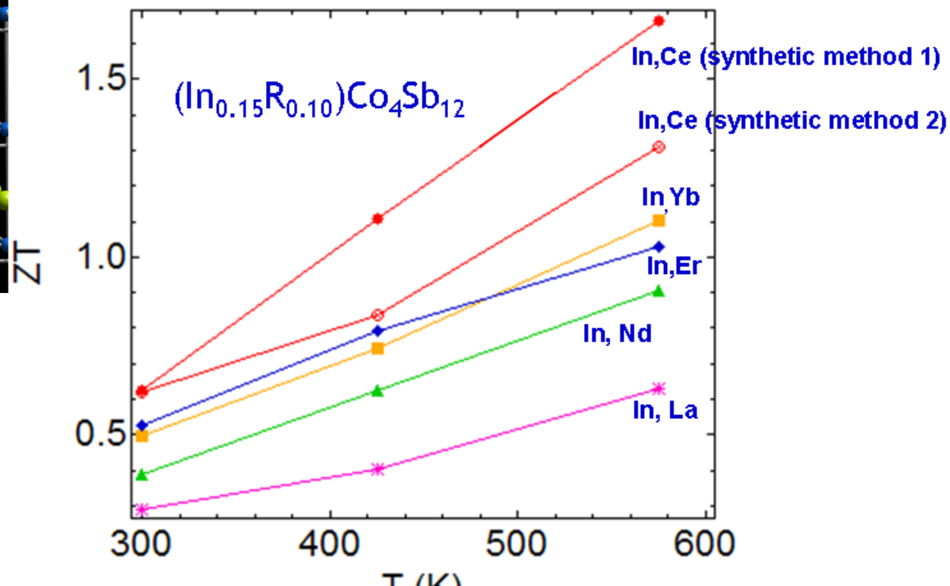
Multiple Rattlers



$R_xCo_4Sb_{12}$

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

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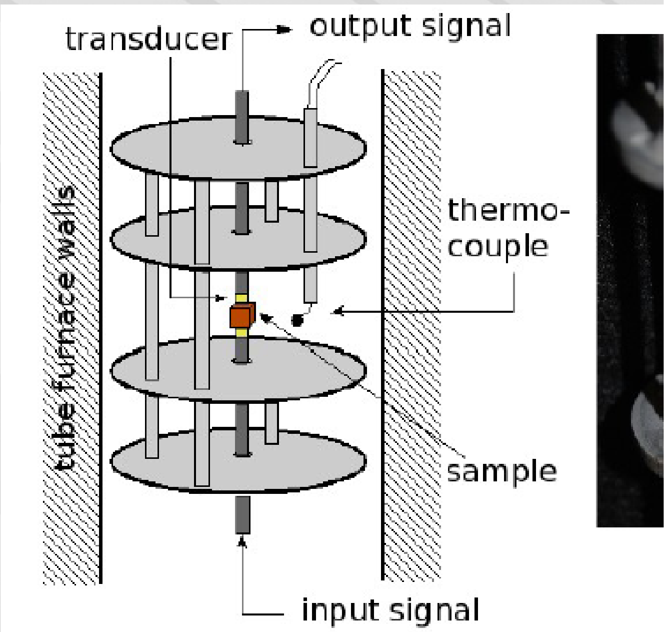
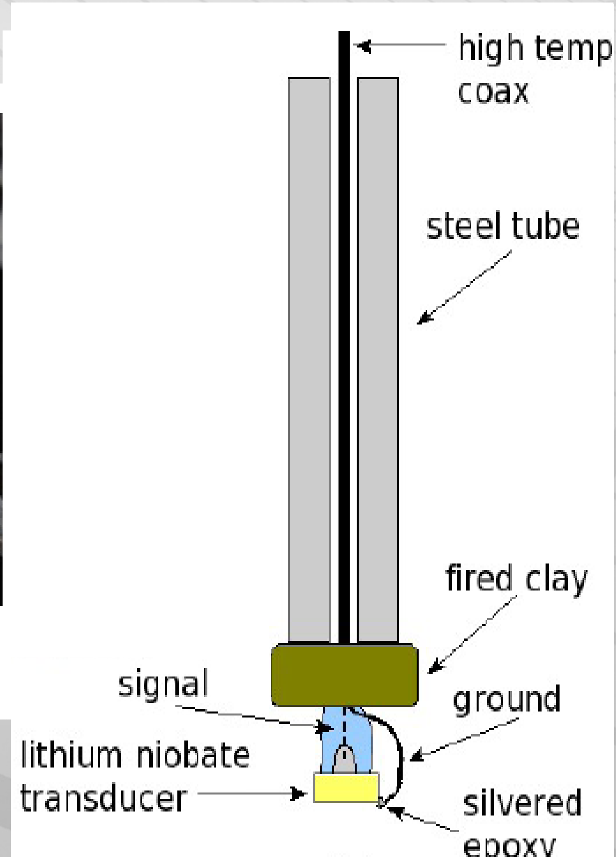
Structural Property Measurement Task Plan

- Measure Material Strengths at Room Temperature & Determine Elastic Material Properties Over Elevated Temperatures
  - Measure Material Strength by Means of ASTM Standard C 1499-05 (Ring on Ring Biaxial Flexure Test)
  - Modify Existing RUS System for Material Property Measurement at Elevated Temperatures
  - Measure E and *v* at Multiple Temperatures Spanning Room Temperature to 300 ºC
- Modify existing Quasar RI-2000 Resonant Ultra-Sound system
  - Purge Gas to Prevent Specimen Oxidation: Nitrogen or Argon
  - Design to Hold Stable Temperature (± 2º C target at 300º C)
  - Fabricate High Temperature Transceivers
  - Validate RUS Measurement at 300º C
  - Estimate ρ and then E and *v* by Fitting RUS Spectra With Predicted Values

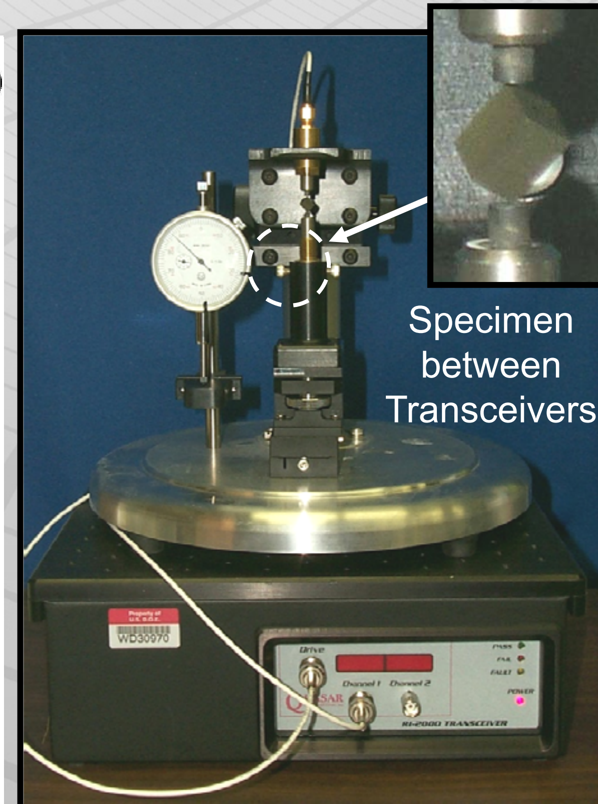
Structural Property Measurement Systems



Source: Li, Adebisi, and Gladden



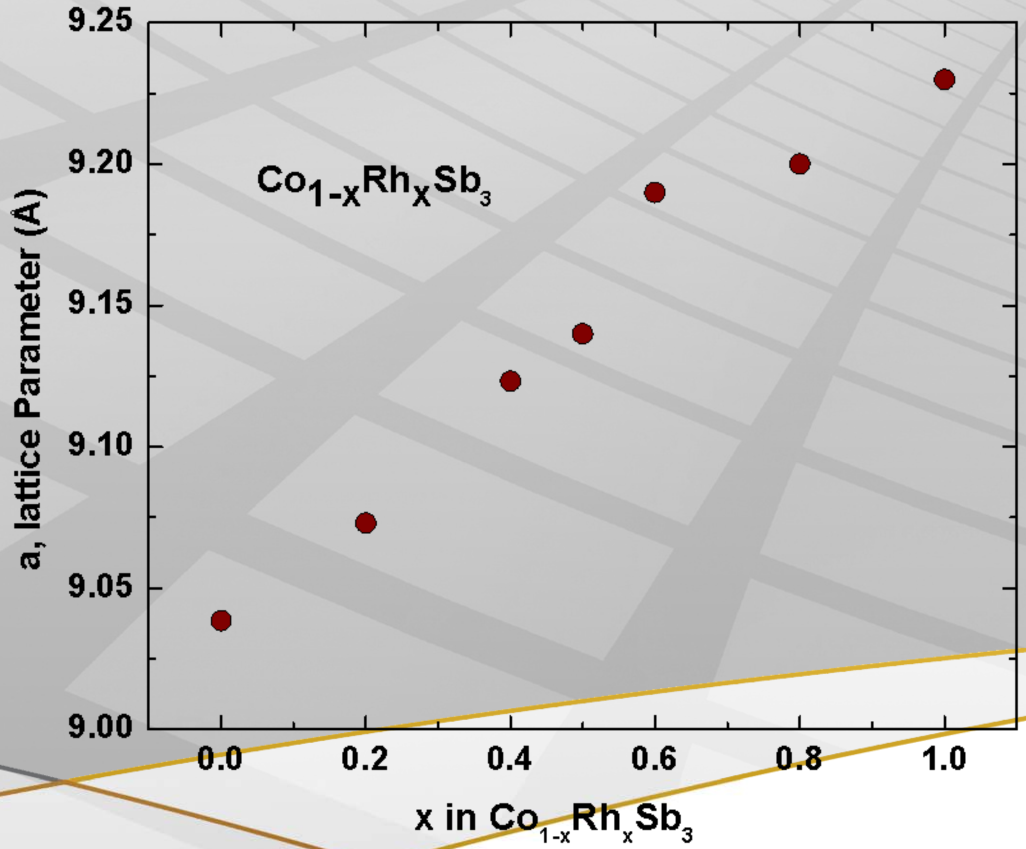
High-Temperature Transceivers



Quasar RI-2000 at PNNL

$Co_{1-x}Rh_xSb_3$ (without Rattlers): *p*-type skutterudites

- Entire Cubic Solid Solution Range is Possible
- All Are Single-Phase Compounds



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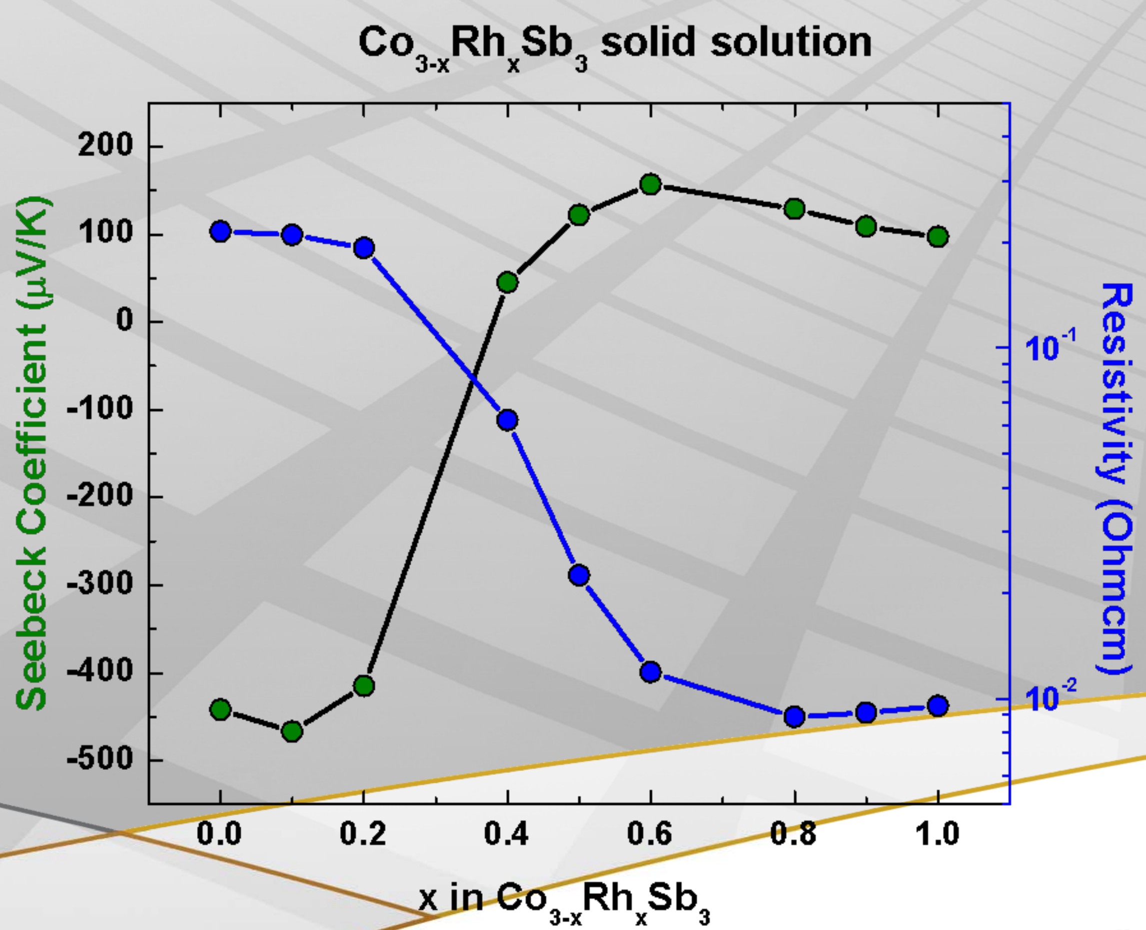
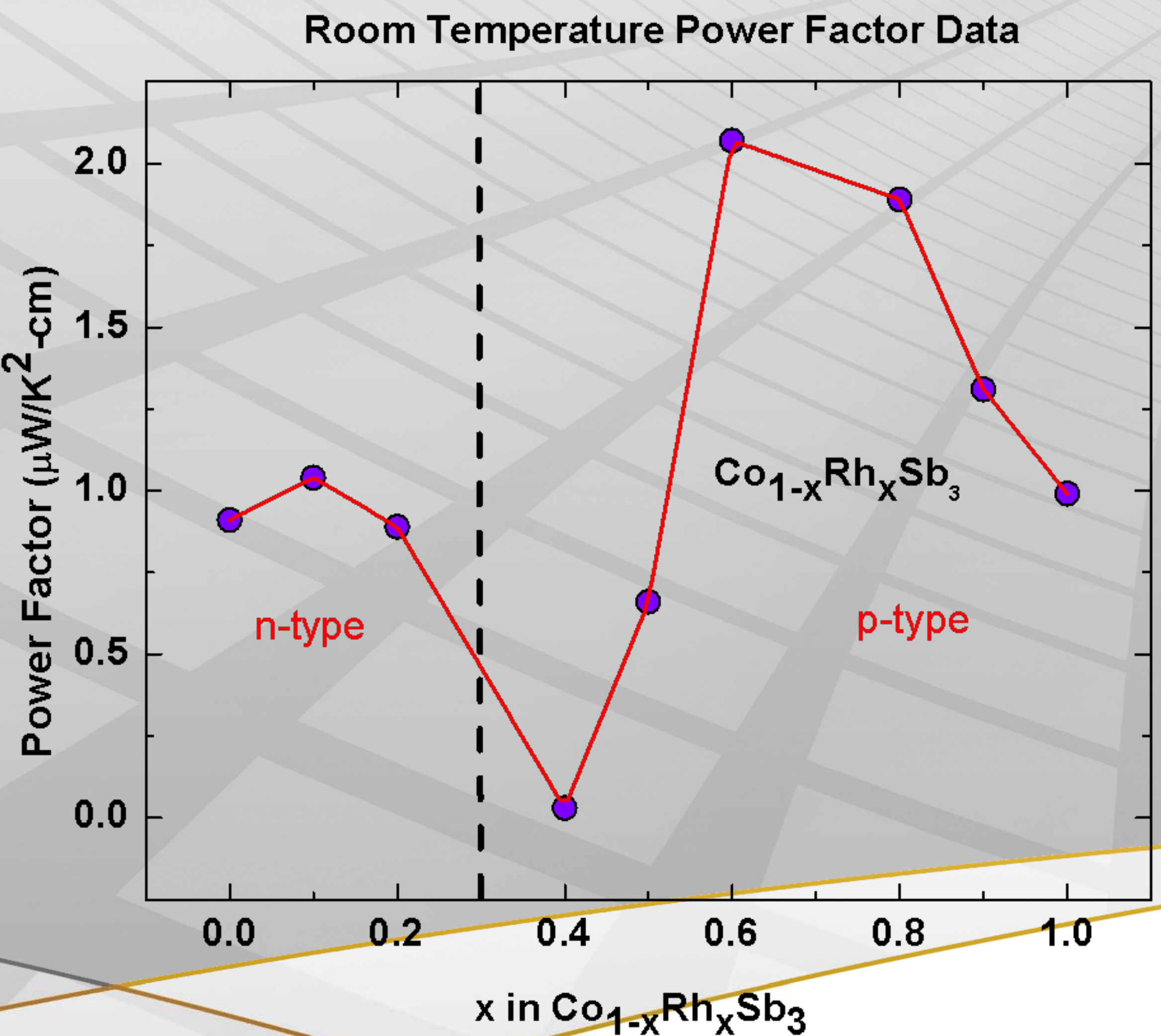
$Co_{1-x}Rh_xSb_3$ (without Rattlers): Electrical Data

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

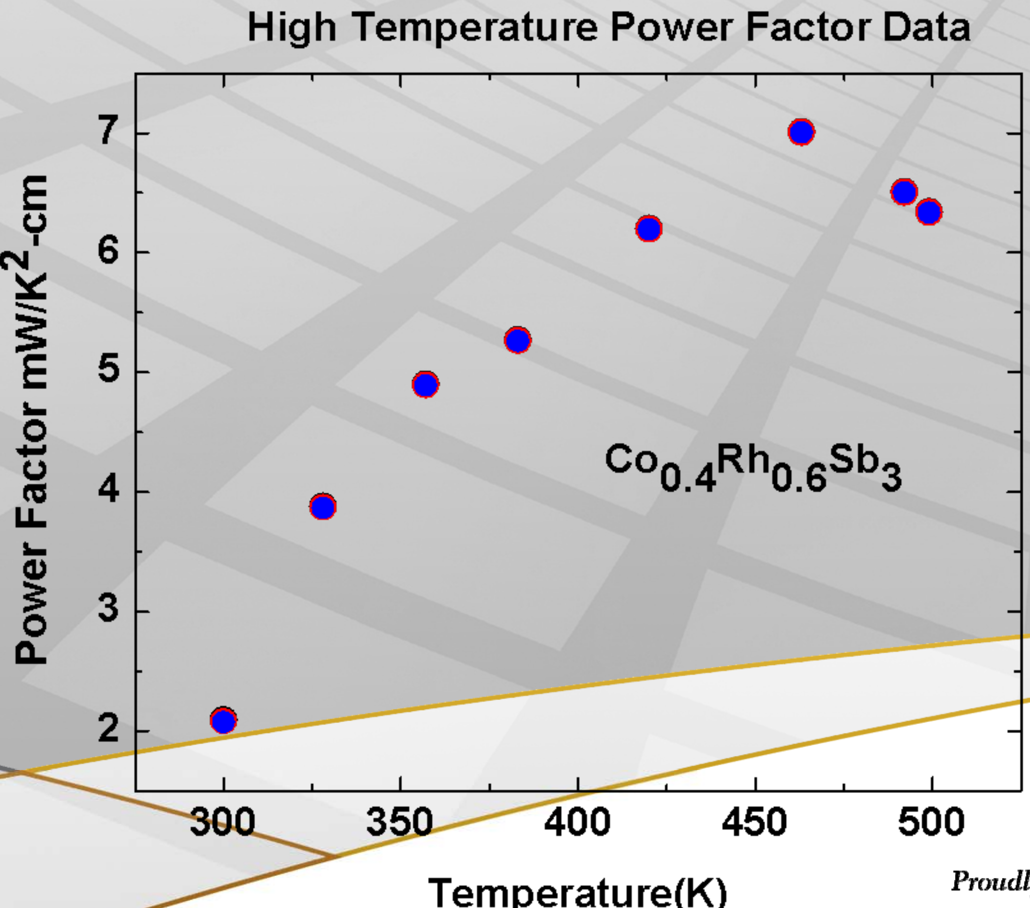


$Co_{1-x}Rh_xSb_3$ (without Rattlers): RT Power Factor data



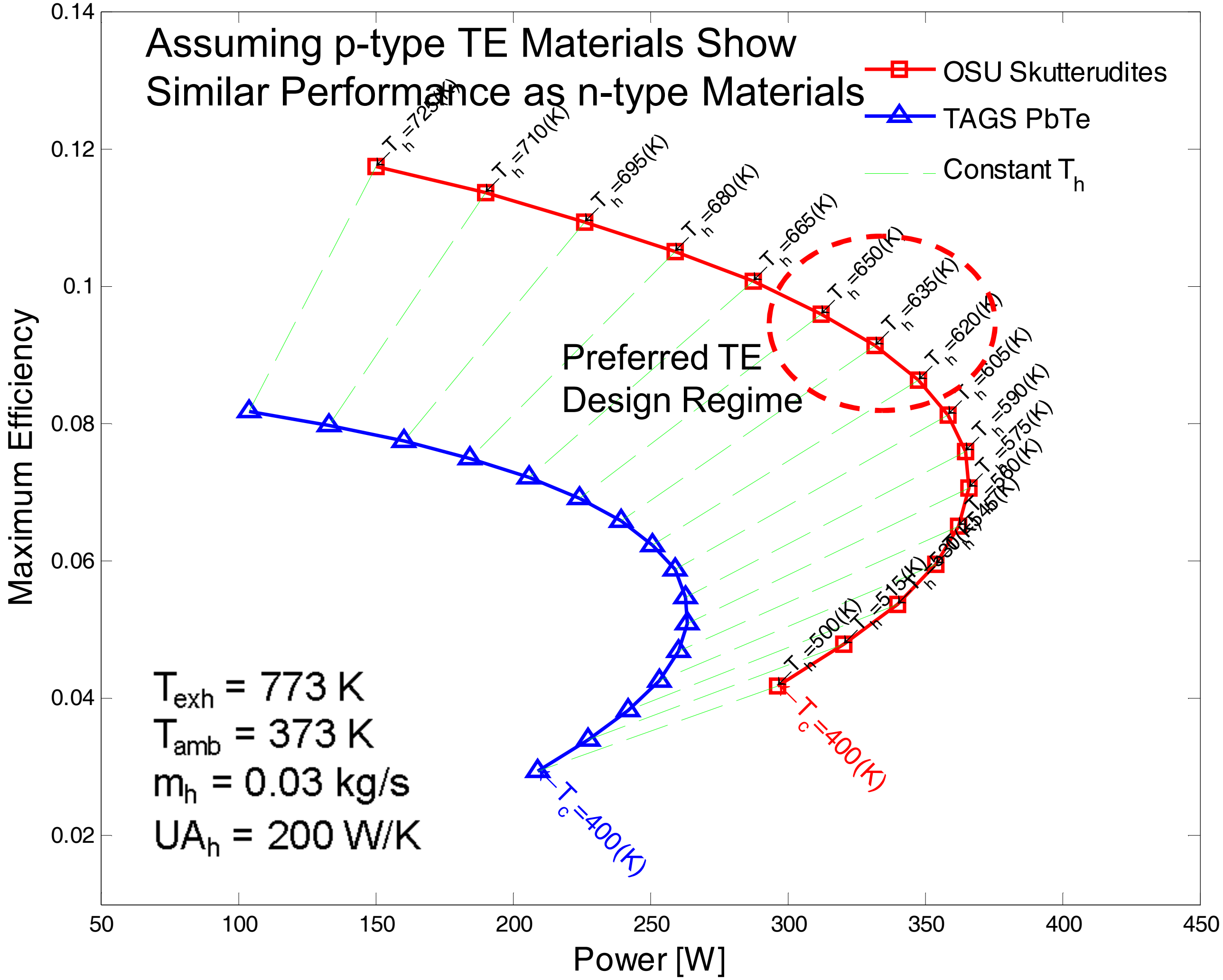
$Co_{1-x}Rh_xSb_3$ (without Rattlers): High temperature power factor

- 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



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

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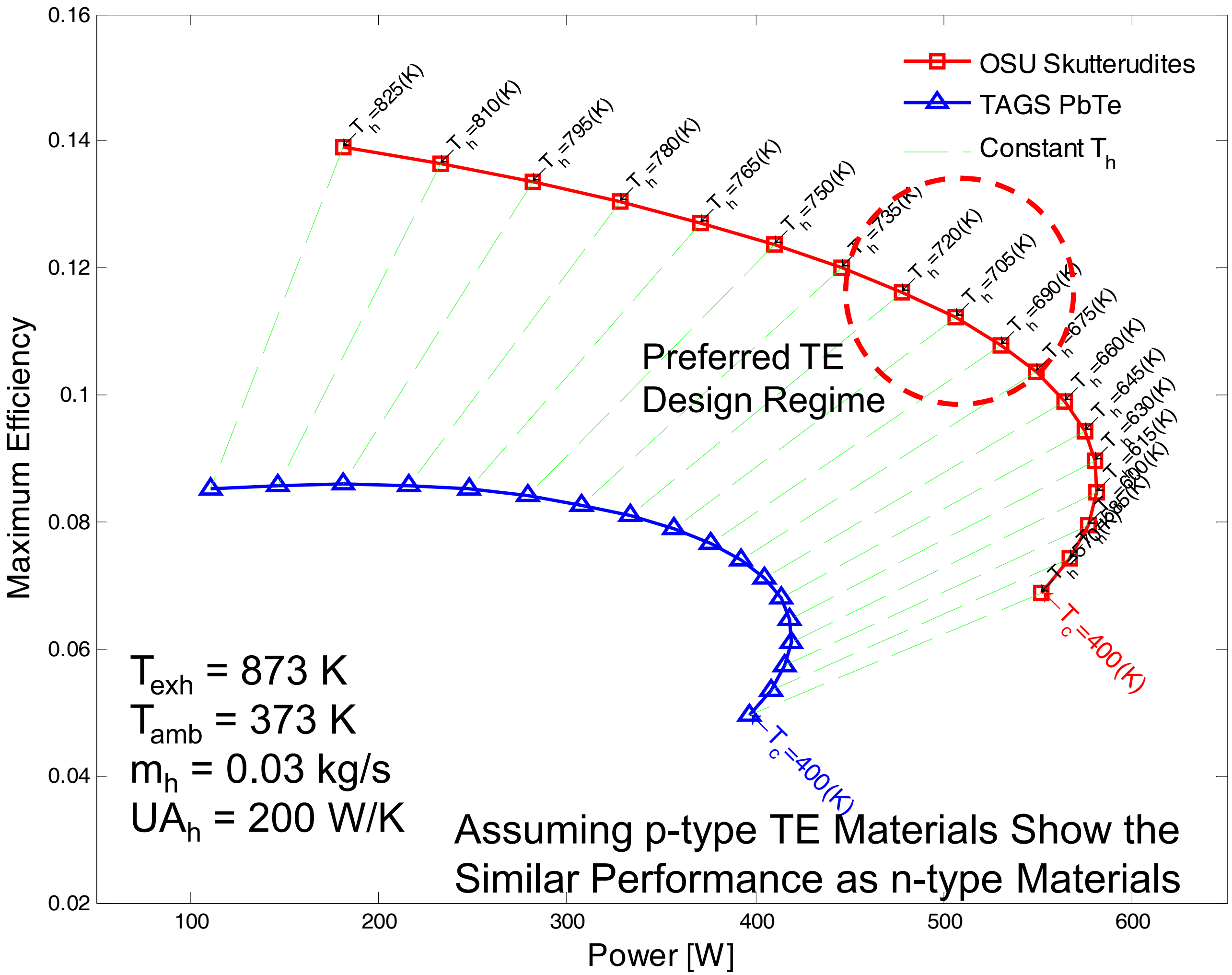

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  - More Power (for Given Heat Input)
  - Smaller Systems
  - Lighter Systems

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
- 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
  - Structural Test Equipment Identified
- 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

Acknowledgement

We sincerely thank Jerry Gibbs and John Fairbanks, Office of Vehicle Technologies Propulsion Materials, for their support of this project.

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

Aristotle

Questions & Discussion