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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Agenda

- Overview – Timeline, Budget, Technical Barriers, & Collaborations
- Objectives
- Relevance
- Technical Approach
- Project Accomplishments
- Collaborations & Coordination
- Future Work
- Summary
## Timeline
- Project Start Date: 15 December 2008
- Project End Date: 15 December 2011
- 75% Complete

## 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 $260K ($130 K To Date)

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

### Proactive Strategies for Designing Thermoelectric Materials for Power Generation - Overview

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### Materials
- \( \text{R}_x \text{Co}_4 \text{Sb}_{12} \)

### Specimen between Transducers

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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: \(\sim 5.7\) quads/yr exhausted down the tail pipe
    - \(\sim 5\) 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
    - \(\sim 1.5\) 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

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


- 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

Assuming p-type TE Materials Show Similar Performance as n-type Materials

**Preferred TE Design Regime**

- $T_{\text{exh}} = 773$ K
- $T_{\text{amb}} = 373$ K
- $m_h = 0.03$ kg/s
- $UA_h = 200$ W/K

**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

\[ Z^*T = \frac{\alpha^2 \cdot T}{\rho \cdot \kappa} \]

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

Z*T vs. Temperature for Various p-type TE Materials
Strategies in Designing \textit{n}-type and \textit{p}-type Skutterudites: $R_xR_y'C_{4-x}M_xSb_{12}$

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

- Single Rattler Systems
- Multiple Rattler Systems

**This Year’s Focus:**

- \textit{n}-type $\text{In}_{0.2}\text{Co}_{4}\text{Sb}_{12}$
- \textit{n}-type $\text{In}_{x}\text{Ce}_{y}\text{Co}_{4}\text{Sb}_{12}$
- \textit{n}-type $\text{In}_{x}\text{Ce}_{y}\text{Yb}_{z}\text{Co}_{4}\text{Sb}_{12}$

$R^{2+}$: Ba, Ce, Sr, Ca, Ag, Pd, R$^{3+}$: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, In, Sc
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
- 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

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestones:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan. 2010 – Oct. 2010</td>
<td>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$<em>{0.2}$Ce$</em>{0.15}$Co$<em>4$Sb$</em>{12}$ and In$_{0.2}$Co$<em>4$Sb$</em>{12}$ for Reproducibility. p-type LASTT Materials Selected in October 2010.</td>
</tr>
<tr>
<td>September 2011</td>
<td>Measure High Temperature Structural Properties of n-type TE Materials.</td>
</tr>
<tr>
<td>December 2011</td>
<td>Develop and Measure TE Couple Performance Using In n-type In$<em>{0.2}$Ce$</em>{0.15}$Co$<em>4$Sb$</em>{12}$ and/or In$_{0.2}$Co$<em>4$Sb$</em>{12}$ materials coupled with p-type LASTT TE materials. Tellurex Corporation As Commercialization Partner</td>
</tr>
</tbody>
</table>
Technical Approach - TE Properties Characterization

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

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

Density measurements

Uncertainties:
S ±5%; ρ ±5%; λ ±10%

Standards:
Constantan n- & p-Bi₂Te₃

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

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

QD - PPMS(5-300K)
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 $\nu$ at Multiple Temperatures Spanning Room Temperature to 300 °C

- RUS Systems
  - Room Temperature Shown Right & Below
  - High-Temperature System in Reviewer Charts
Project Accomplishments

n-Type $\text{In}_x\text{Ce}_y\text{Co}_4\text{Sb}_{12}$ TE Properties

- $\text{In}_{0.2}\text{Co}_4\text{Sb}_{12}$ ZT $\sim 1.2$ @ 600 K (highly reproducible).
- Several $\text{In}_{0.2}\text{Ce}_y\text{Co}_4\text{Sb}_{12}$ showed ZT $= 1.2$-$1.45$ at 625 K.
- There is an enhancement of ZT when Ce is co-filled with In.
- Cerium ($\text{Ce}^{3+}$, $\text{Ce}^{4+}$) mixed valency may play a role. Enhancement of Seebeck values.
- Last year one $\text{In}_{0.2}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$ sample showed ZT $\sim 1.5$ – 1.6 around 500 K. Working on reproducing it. (See reviewer only slides)
## n-type Structural and TE Properties

<table>
<thead>
<tr>
<th>Specimen Label and Comments</th>
<th>$\rho$, density (g/cm$^3$)</th>
<th>$\nu$, Poisson's ratio</th>
<th>CTE ($10^{-6}$/C) (298 – 673 K)</th>
<th>$E$, Elastic Modulus ($10^{11}$ N/m$^2$)</th>
<th>$ZT$ (@ 625 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Te$_3$ Alloys</td>
<td>0.21-0.37</td>
<td>0.21-0.37</td>
<td>14 (21 (Anisotropic))</td>
<td>0.40-0.47</td>
<td>0.0-0.1</td>
</tr>
<tr>
<td>PbTe</td>
<td>0.26</td>
<td>0.26</td>
<td>0.58</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>CoSb$_3$ (literature)</td>
<td>0.222</td>
<td>0.222</td>
<td>1.396</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>CoSb$_3$ (PNNL)</td>
<td>0.225-0.226</td>
<td>0.225-0.226</td>
<td>1.391-1.398</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In$_{0.1}$Co$<em>4$Sb$</em>{12}$ (PNNL)</td>
<td>0.227</td>
<td>0.227</td>
<td>1.396</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In$<em>{0.1}$Y$</em>{0.1}$Co$<em>4$Sb$</em>{12}$ (PNNL)</td>
<td>0.247</td>
<td>0.247</td>
<td>1.413</td>
<td>~0.5</td>
<td></td>
</tr>
<tr>
<td>In$<em>{0.15}$Ce$</em>{0.1}$Co$<em>4$Sb$</em>{12}$ – PNNL3</td>
<td>0.185</td>
<td>0.185</td>
<td>1.339</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>2-5-2010 --- REPEAT of 1-21-2010</td>
<td>~7.314</td>
<td>~7.314</td>
<td>8.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In$<em>{0.15}$Ce$</em>{0.1}$Co$<em>4$Sb$</em>{12}$ – LB1</td>
<td>0.215</td>
<td>0.215</td>
<td>1.348</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>2-5-2010</td>
<td>7.304</td>
<td>7.304</td>
<td>8.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In$<em>{0.15}$Ce$</em>{0.1}$Co$<em>4$Sb$</em>{12}$ – LB2</td>
<td>0.204</td>
<td>0.204</td>
<td>1.326</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>2-9-2010</td>
<td>7.264</td>
<td>7.264</td>
<td>8.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In$<em>{0.2}$Ce$</em>{0.15}$Co$<em>4$Sb$</em>{12}$ _03161035_3-17-10</td>
<td>0.210-0.214</td>
<td>0.210-0.214</td>
<td>1.182-1.185 (2 samples)</td>
<td>1.3-1.4 (1.5-1.6 @ 500K)</td>
<td></td>
</tr>
<tr>
<td>6-08-2010 - BNW-60608 – 88(M1-M31)</td>
<td>7.019</td>
<td>7.019</td>
<td>8.11-8.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In$_{0.2}$Co$<em>4$Sb$</em>{12}$ – A05061030-A</td>
<td>0.208-0.218</td>
<td>0.208-0.218</td>
<td>1.178-1.238 (2 samples)</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>2010-06-09- BNW-60608 – (M1-M29 &amp; M31 – No M30)</td>
<td>7.06-7.10</td>
<td>7.06-7.10</td>
<td>8.27-8.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In$<em>{0.2}$Yb$</em>{0.1}$Ce$_{0.05}$Co$<em>4$Sb$</em>{12}$- KB0627100_7-23-10 2010-08-16-BNW-60608-123 (M1-M27)</td>
<td>0.207</td>
<td>0.207</td>
<td>0.895</td>
<td>1.2</td>
<td></td>
</tr>
</tbody>
</table>
Thermal Cycling Results

- Materials showing 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

<table>
<thead>
<tr>
<th>Material Description</th>
<th>Temperature [°C]</th>
<th>Before Thermal Cycling</th>
<th>After Thermal Cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Young’s Modulus, $E_{10^9}$ [N/m²]</td>
<td>Poisson’s Ratio, $\nu$</td>
</tr>
<tr>
<td>$\text{In}<em>{0.15}\text{Ce}</em>{0.1}\text{Co}<em>4\text{Sb}</em>{12}$ (LBL1) – n-type</td>
<td>20-22</td>
<td>134.8</td>
<td>0.215</td>
</tr>
<tr>
<td>$\text{In}<em>{0.15}\text{Ce}</em>{0.1}\text{Co}<em>4\text{Sb}</em>{12}$ (LBL2) – n-type</td>
<td>20-22</td>
<td>132.6</td>
<td>0.204</td>
</tr>
<tr>
<td>$\text{In}<em>{0.15}\text{Ce}</em>{0.1}\text{Co}<em>4\text{Sb}</em>{12}$ (PNNL3-G1B) n-type</td>
<td>20-22</td>
<td>133.9</td>
<td>0.185</td>
</tr>
<tr>
<td>$\text{In}<em>{0.2}\text{Ce}</em>{0.15}\text{Co}<em>4\text{Sb}</em>{12}$ n-type</td>
<td>20.6</td>
<td>124.5</td>
<td>0.213</td>
</tr>
<tr>
<td>$\text{In}<em>{0.2}\text{Ce}</em>{0.05}\text{Yb}_{0.1}\text{Co}<em>4\text{Sb}</em>{12}$ n-type</td>
<td>20-22</td>
<td>109.5</td>
<td>0.213</td>
</tr>
<tr>
<td>$\text{In}<em>{0.2}\text{Ce}</em>{0.17}\text{Co}<em>4\text{Sb}</em>{12}$ – n-type</td>
<td>19.9</td>
<td>89.5</td>
<td>0.208</td>
</tr>
</tbody>
</table>
In\textsubscript{0.15}Ce\textsubscript{0.1}Co\textsubscript{4}Sb\textsubscript{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

<table>
<thead>
<tr>
<th>Specimen Label and Composition</th>
<th>Seebeck Coefficient [µV/K]</th>
<th>Electrical Resistivity [mΩ-cm]</th>
<th>Power Factor [µW/cm-K²]</th>
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<th>Electrical Resistivity [mΩ-cm]</th>
<th>Power Factor [µW/cm-K²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>In\textsubscript{0.15}Ce\textsubscript{0.1}Co\textsubscript{4}Sb\textsubscript{12} (LB1 sample)</td>
<td>-259</td>
<td>2.33</td>
<td>28.7</td>
<td>-315</td>
<td>2.55</td>
<td>38.9 (+35.5%)</td>
</tr>
<tr>
<td>In\textsubscript{0.15}Ce\textsubscript{0.1}Co\textsubscript{4}Sb\textsubscript{12} (LB2 sample)</td>
<td>-259</td>
<td>2.33</td>
<td>28.7</td>
<td>-329</td>
<td>3.32</td>
<td>32.6 (+13.6%)</td>
</tr>
</tbody>
</table>
Thermal Cycling Impacts on Power Factor

- $\text{In}_{0.2}\text{Ce}_{0.17}\text{Co}_{4}\text{Sb}_{12}$ showed 36% increase in PF @ 525 K
- $\text{In}_{0.2}\text{Ce}_{0.15}\text{Co}_{4}\text{Sb}_{12}$ showed similar increases in Seebeck coefficient
- HOWEVER, $\text{In}_{0.2}\text{Ce}_{0.05}\text{Yb}_{0.1}\text{Co}_{4}\text{Sb}_{12}$ showed 36% decrease in PF @ 525 K
- Materials that behave this way after thermal cycling can’t be used in WER

Thermal cycling a real differentiator - Tri-Rattler compounds showing meta-stable states

![Graphs showing changes in Seebeck coefficient and resistivity before and after thermal cycling for different compounds.](Image)
Thermal Cycling Impacts on Thermal Conductivity

- Major Discovery – Thermal Conductivity Decreases After Thermal Cycling in These Materials
  - $\text{In}_{0.2}\text{Co}_{4}\text{Sb}_{12}$ - $\lambda$ Decreases By ~ 3% or Stays Approximately the Same
  - $\text{In}_{0.2}\text{Ce}_{0.15}\text{Co}_{4}\text{Sb}_{12}$ – $\lambda$ Decreases By ~8%
- Coupled with Increases in Power Factor ($\alpha^2/\rho$) Increases ZT by 1.4X
$p$-Type Skutterudites To Date

- ZT of $\sim 0.48$ is obtained for $\text{In}_{0.2}\text{Yb}_{0.1}\text{Ce}_{0.05}\text{Co}_3\text{FeSb}_{12}$ & $\text{In}_{0.2}\text{Yb}_{0.05}\text{Ce}_{0.1}\text{Co}_3\text{FeSb}_{12}$ 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
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
Future Work & Path Forward

- Optimize Synthesis Procedures for \( n \)-type (In,R)Co\(_4\)Sb\(_{12}\) Compositions
  - Focus on In\(_{0.2}\)Co\(_4\)Sb\(_{12}\) and In\(_{0.2}\)Ce\(_{0.15}\)Co\(_4\)Sb\(_{12}\) \( n \)-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, \( \nu(T) \)
  - 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-Temperature CTE Testing Completed
- Good Structural Stability Upon Thermal Cycling
- Thermal Cycling Has Quite Positive Impacts on TE Properties: \( \frac{\alpha^2}{\rho} \uparrow \kappa \downarrow \)
- 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
(InCe)-based Compounds - Seebeck Coefficient, Electrical Resistivity, Thermal Conductivity vs. Temperature

In\textsubscript{0.2}Ce\textsubscript{0.1}Co\textsubscript{4}Sb\textsubscript{12} SEM 1 um Resolution

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965
RUS High Temperature Measurement System

Reference (Fused Silica RPP) in Thermal Chamber

Thermal Chamber

Assess to Specimen and Transducers

RUS Transducer

Argon Gas Feed

Power Switch to Thermal Cartridges

RUS Transducer

Computer Control of RUS System

Quasar RI-2000

Temperature Controller

26
ORNL Test Data Comparisons
XRD Analysis Results Show Pure, Single-Phase Crystal Structures

- $\text{In}_{0.2}\text{Ce}_{0.17}\text{Co}_{4}\text{Sb}_{12}$; $a = 9.0862$ Å
- $\text{In}_{0.2}\text{Yb}_{0.05}\text{Ce}_{0.1}\text{Co}_{4}\text{Sb}_{12}$; $a = 9.0656$ Å
- $\text{In}_{0.2}\text{Yb}_{0.1}\text{Ce}_{0.05}\text{Co}_{4}\text{Sb}_{12}$; $a = 9.0557$ Å
- $\text{In}_{0.2}\text{Ce}_{0.15}\text{Co}_{4}\text{Sb}_{12}$; $a = 9.0452$ Å
- $\text{In}_{0.15}\text{Ce}_{0.15}\text{Co}_{4}\text{Sb}_{12}$; $a = 9.0582$ Å
- $\text{In}_{0.15}\text{Ce}_{0.1}\text{Co}_{4}\text{Sb}_{12}$; $a = 9.0647$ Å
- $\text{In}_{0.2}\text{Ce}_{0.15}\text{Co}_{4}\text{Sb}_{12}$; $a = 9.0849$ Å

- $\text{In}_{0.2}\text{Co}_{4}\text{Sb}_{12}$; $a = 9.0543$ Å
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 - $\text{In}_{0.2} \text{Ce}_{0.15} \text{Co}_{4} \text{Sb}_{12}$ and $\text{In}_{0.2} \text{Co}_{4} \text{Sb}_{12}$. 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 $(\text{InCe})$-based skutterudites
Publications and Presentations


- **Invited Presentation**, European Materials Research Society, Nice, France


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
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

Assuming p-type TE Materials Show the Similar Performance as n-type Materials

- $T_{exh} = 873 \text{ K}$
- $T_{amb} = 373 \text{ K}$
- $m_h = 0.03 \text{ kg/s}$
- $U_{Ah} = 200 \text{ W/K}$

Preferred TE Design Regime

Maximum Efficiency

Power [W]
n-Type $\text{In}_x\text{Ce}_y\text{Co}_4\text{Sb}_{12}$ TE Properties

- Ultimately Led to $\text{ZT} \sim 1.5 - 1.6$ at 425 – 525 K for $\text{In}_{0.2}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$ Compounds
- Once Again – Bulk Materials Easily Integrated into TE Device
- Must Monitoring MicroCracking
ZT vs. Temperature Presented at FY 2010 AMR

Ultimately Led to $ZT \sim 1.5 - 1.6$ at $425 - 525$ K for $\text{In}_{0.2}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$ Compounds
ZT Dependence on Microstructure
\[(\text{In}_{0.15}\text{Ce}_{0.10}\text{Co}_4\text{Sb}_{12})\]

ZT $\sim 1.4$ @ 600 K

ZT $\sim 1.1$ @ 600 K

Synthetic Method - 1
ZT Dependence on Microstructure

- 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

<table>
<thead>
<tr>
<th>Specimen Label and Comments</th>
<th>Temperature (ºC)</th>
<th>( \rho ), density (g/cm³)</th>
<th>( \nu ), Poisson's ratio</th>
<th>( E ), Modulus of Elasticity (10¹¹ N/m²)</th>
<th>rms error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused Quartz Reference (Manufacturer’s Data)</td>
<td>---</td>
<td>2.203</td>
<td>0.17</td>
<td>0.725</td>
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</tr>
<tr>
<td>Fused Quartz Reference #1 (RUS Estimated)</td>
<td>---</td>
<td>2.122</td>
<td>0.156</td>
<td>0.7216</td>
<td>0.32</td>
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<tr>
<td>Fused Quartz Reference #1 (RUS Estimated)</td>
<td>20.8 - 21.0</td>
<td>2.122</td>
<td>0.155</td>
<td>0.7242</td>
<td>0.42</td>
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<tr>
<td>Fused Quartz Reference #1 (RUS Estimated)</td>
<td>89.2 - 90.8</td>
<td>2.122</td>
<td>0.156</td>
<td>0.7343</td>
<td>0.45</td>
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</tbody>
</table>
p-Type $\text{In}_{0.2}\text{Yb}_x\text{Ce}_y\text{FeCo}_3\text{Sb}_{12}$ Materials – TE Properties

Seebeck Coefficients are Low
p-Type $\text{In}_{0.2}\text{Yb}_x\text{Ce}_y\text{FeCo}_3\text{Sb}_{12}$ Materials – TE Properties

- Relatively Low Thermal Conductivity
- However, Seebeck Coefficient Limiting $ZT \sim 0.48 \ @ \ 710 \ K$
# p-Type In$_{0.2}$Yb$_x$Ce$_y$FeCo$_3$Sb$_{12}$ Materials – Structural Properties

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

<table>
<thead>
<tr>
<th></th>
<th>Temperature [°C]</th>
<th>No Thermal Cycling</th>
<th></th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Young’s Modulus, E $10^9$ [N/m$^2$]</td>
<td>Poisson’s Ratio, $\nu$</td>
<td></td>
</tr>
<tr>
<td>In$<em>{0.2}$Ce$</em>{0.15}$Fe$<em>{0.5}$Co$</em>{3.5}$Sb$_{12}$ p-type</td>
<td>20.3</td>
<td>46.4</td>
<td>0.18</td>
<td>~0.2-0.25 (@673 K)</td>
</tr>
<tr>
<td>In$<em>{0.2}$Yb$</em>{0.05}$Ce$_{0.1}$FeCo$<em>3$Sb$</em>{12}$ p-type</td>
<td>20.4</td>
<td>99.26</td>
<td>0.210</td>
<td>0.48 (@ 710 K)</td>
</tr>
<tr>
<td>In$<em>{0.2}$Yb$</em>{0.1}$Ce$_{0.05}$FeCo$<em>3$Sb$</em>{12}$ p-type</td>
<td>20.8</td>
<td>92.38</td>
<td>0.205</td>
<td>0.48 (@ 710 K)</td>
</tr>
</tbody>
</table>
Next Generation of High Temperature Transducer

- Assembled Transducer

- Vespel Base Material
- Thin Copper Wire as Positive Electrode
- Stainless Steel Shim Washer
- Underlying Lithium Niobate Wafer (RUS Sensor) is sandwiched between two gold foils; positive and ground electrodes, respectively, and is not restricted to allow thermal expansion.
- Gold Foil as Ground Electrode
- Pacific Northwest
  NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965
Next Generation of High Temperature Transducer

- Assembled Transducer

Vespel Base Material

Stainless Steel Shim Washer

Thin Copper Wire as Positive Electrode

Thin Copper Wire as Positive Electrode [Copper wire will have “S” bend (not shown) as stress relief]

High Temperature Silver Epoxy Plug attaches Gold Foil and Copper Wire to Function as Positive Electrode
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
- Upper fixture with fixed transducer
- Primary components and fittings are stainless steel
- Lower fixture
- Gas diffuser
- High temperature wire for three resistive cartridge heaters

Pacific Northwest NATIONAL LABORATORY
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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