Synthesis and High Temperature Thermoelectric Characterization of $Y_{1-x}Ca_xCoO_3$ and $YCo_{1-x}Rh_xO_3$

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Outline

• Introduction to Thermoelectrics
• Thermoelectric Oxides
• $Y_{1-x}Ca_xCoO_3$ and $YCo_{1-x}Rh_xO_3$ crystal structure
• $YCo_{1-x}Rh_xO_3$ Thermoelectric characterization
• Conclusions
• Future Projects
Thermoelectrics, who cares?

- Seebeck Effect discovered in 1821

Heat Source $T_H$  
Heat Sink $T_C$  

Direct conversion of heat to electricity!

$Q_H$  
$Q_C$  

$I$  
P-Type  
N-Type
Thermoelectric Applications

• Energy Scavenging
  – Process Heat
  – Automobile Exhaust

• Refrigeration (Peltier Effect)

• Space Exploration, Thermocouples

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>No moving parts, silent</td>
<td>Low Efficiency</td>
</tr>
<tr>
<td>No working fluid required</td>
<td>Unstable at high temperatures</td>
</tr>
<tr>
<td>No maintenance</td>
<td>Some contain toxic heavy metals</td>
</tr>
<tr>
<td>Works on small scale</td>
<td>Materials Challenges</td>
</tr>
</tbody>
</table>
Figure of Merit

\[
ZT = \frac{S^2 T}{\rho \kappa}
\]

Seebeck Coefficient (Thermopower)

Electrical Resistivity

Thermal Conductivity

Thermoelectric Oxides

Perovskite Formula: $\text{RCoO}_3$ ($\text{R} = \text{Rare Earth}$)
Co spin state varies with temperature, low spin is desired (Heikes Formula)

High Spin:
Low Seebeck at High Temp.

Increase temperature, Co-O bond stretches

Ion Labels:
Gray – Rare Earth
Blue – Cobalt
Orange – Oxygen

Y$_{1-x}$Ca$_x$CoO$_3$ and YCo$_{1-x}$Rh$_x$O$_3$

• LaCoO$_3$ most widely studied
• $R_{\text{La}^{3+}} = 1.36$ Å
• $R_{\text{Y}^{3+}} = 1.25$ Å
• Ca$^{2+}$ substitution for Y$^{3+}$: P-Type Doping
• Rh ion stable in low spin state for all temperatures
Solid State Reaction Synthesis

1. Weigh
2. Grind
3. Press Pellet
4. Heat for 12-24 hours at 900-1100 °C in O₂
5. Repeat 3-5 times
6. X-Ray Diffraction

Stoichiometric amounts of Y₂O₃, Co₃O₄, CaCO₃, Rh₂O₃

Mortar and Pestle
Ball Mill

Diameter 10mm
Height 2-3mm

Rigaku Miniflex II
Transport Measurements and SEM

ZEISS SEM/EDS used to determine morphology and confirm composition $Y_{1-x}Ca_xCoO_3$

NETZSCH LaserFlash used to measure thermal diffusivity from 50-500 °C $YCo_{1-x}Rh_xO_3$

ZEM used to measure electrical resistivity and Seebeck coefficient from 200-500 °C $YCo_{1-x}Rh_xO_3$
X Ray Diffraction

\[ YCo_{1-x}Rh_xO_3 \]
\[ Y_{1-x}Ca_xCoO_3 \]

\[ YCoO_3 \rightarrow \text{Pbnm} \]

\[ x=0.70 \]
\[ x=0.50 \]
\[ x=0.30 \]
\[ x=0.15 \]
\[ x=0.10 \]
\[ x=0.05 \]
XRD Fit
$Y_{1-x}Ca_xCoO_3$

Scanning Electron Microscopy
Further Evidence of Substitution

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Actual Composition*</th>
</tr>
</thead>
<tbody>
<tr>
<td>YCoO\textsubscript{3}</td>
<td>Y\textsubscript{1.16}CoO\textsubscript{3-δ}</td>
</tr>
<tr>
<td>Y\textsubscript{0.98}Ca\textsubscript{0.02}CoO\textsubscript{3}</td>
<td>Y\textsubscript{1.08}Ca\textsubscript{0.01}CoO\textsubscript{3-δ}</td>
</tr>
<tr>
<td>Y\textsubscript{0.95}Ca\textsubscript{0.05}CoO\textsubscript{3}</td>
<td>Y\textsubscript{1.05}Ca\textsubscript{0.07}CoO\textsubscript{3-δ}</td>
</tr>
<tr>
<td>Y\textsubscript{0.90}Ca\textsubscript{0.10}CoO\textsubscript{3}</td>
<td>Y\textsubscript{1.15}Ca\textsubscript{0.11}CoO\textsubscript{3-δ}</td>
</tr>
<tr>
<td>Y\textsubscript{0.80}Ca\textsubscript{0.20}CoO\textsubscript{3}</td>
<td>Y\textsubscript{1.06}Ca\textsubscript{0.19}CoO\textsubscript{3-δ}</td>
</tr>
<tr>
<td>Y\textsubscript{0.70}Ca\textsubscript{0.30}CoO\textsubscript{3}</td>
<td>Y\textsubscript{0.81}Ca\textsubscript{0.22}CoO\textsubscript{3-δ}</td>
</tr>
</tbody>
</table>

Energy Dispersive Spectroscopy

*The instrument overcompensated for Sr in an SrTiO\textsubscript{3} standard, so actual Y compositions are lower than they appear.
YCo$_{1-x}$Rh$_x$O$_3$ Seebeck/Resistivity

Theoretical value for LS Co: 154 $\mu$V/K

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J. Li et. al, JSSC 183, 6 (2010)

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YCo$_{1-x}$Rh$_x$O$_3$ Thermal Conductivity

Sample relative density: 50-55%

Could high porosity be causing low thermal conductivity?

$k$ calculated from collected thermal diffusivity data, experimental density, specific heat of LaCoO$_3$


Li et. al, JSSC 183, 6 (2010)

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$YCo_{1-x}Rh_xO_3$ Lattice Thermal Conductivity

$$K = K_{ch} + K_{lattice}$$

Wiedemann-Franz Law:

$$K_{ch} = \frac{LT}{\rho}$$

Lorenz Number = $2.44 \times 10^{-3}$ WΩK$^{-2}$

If lattice vibrations are suppressed by porosity:
Not effect of composition, but of macrostructure.
$YCo_{1-x}Rh_xO_3$ Figure of Merit

![Graph showing the figure of merit for $YCo_{1-x}Rh_xO_3$ and $LaCo_{1-x}Rh_xO_3$](image)

- $YCo_{1-x}Rh_xO_3$
  - $YCoO_3$
  - $x=0.3$
  - $x=0.5$
  - $x=0.7$

- $LaCo_{1-x}Rh_xO_3$
  - $LaCoO_3$
  - $x=0.1$
  - $x=0.2$
  - $x=0.3$
  - $x=0.4$
  - $x=0.5$

$J. Li et. al, JSSC 183, 6 (2010)$
Conclusions

• Thermoelectric oxides are desirable because of non-toxicity and high-temperature stability.
• \( Y_{1-x}Ca_xCoO_3 \) \((0 \leq x \leq 0.20)\) and \( YCo_{1-x}Rh_xO_3 \) \((0 \leq x \leq 1.0)\) synthesized by solid state reaction.
• All compositions had Pbnm space group identical to \( YCoO_3 \).
• \( YCo_{1-x}Rh_xO_3 \) high temperature Seebeck coefficient converged near the theoretical value of 154 \( \mu \)V/K for LS Co ions.
• \( YCo_{1-x}Rh_xO_3 \) low thermal conductivity was almost due solely to lattice vibrations, possibly suppressed by large porosity.
• \( YCoO_3 \) ZT improved with substitution of Rh for Co.
• \( YCo_{1-x}Rh_xO_3 \) ZT \( \approx 0.09 \) at 750K, increasing with temperature.
Acknowledgements

• Jorge Morales (CCNY) for assistance with SEM
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References

T. Tritt, M. A. Subramanian, MRS Bull. 31, 188 (2006)
J. Li et. al, JSSC 183, 6 (2010)
Thank you!

Questions?