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

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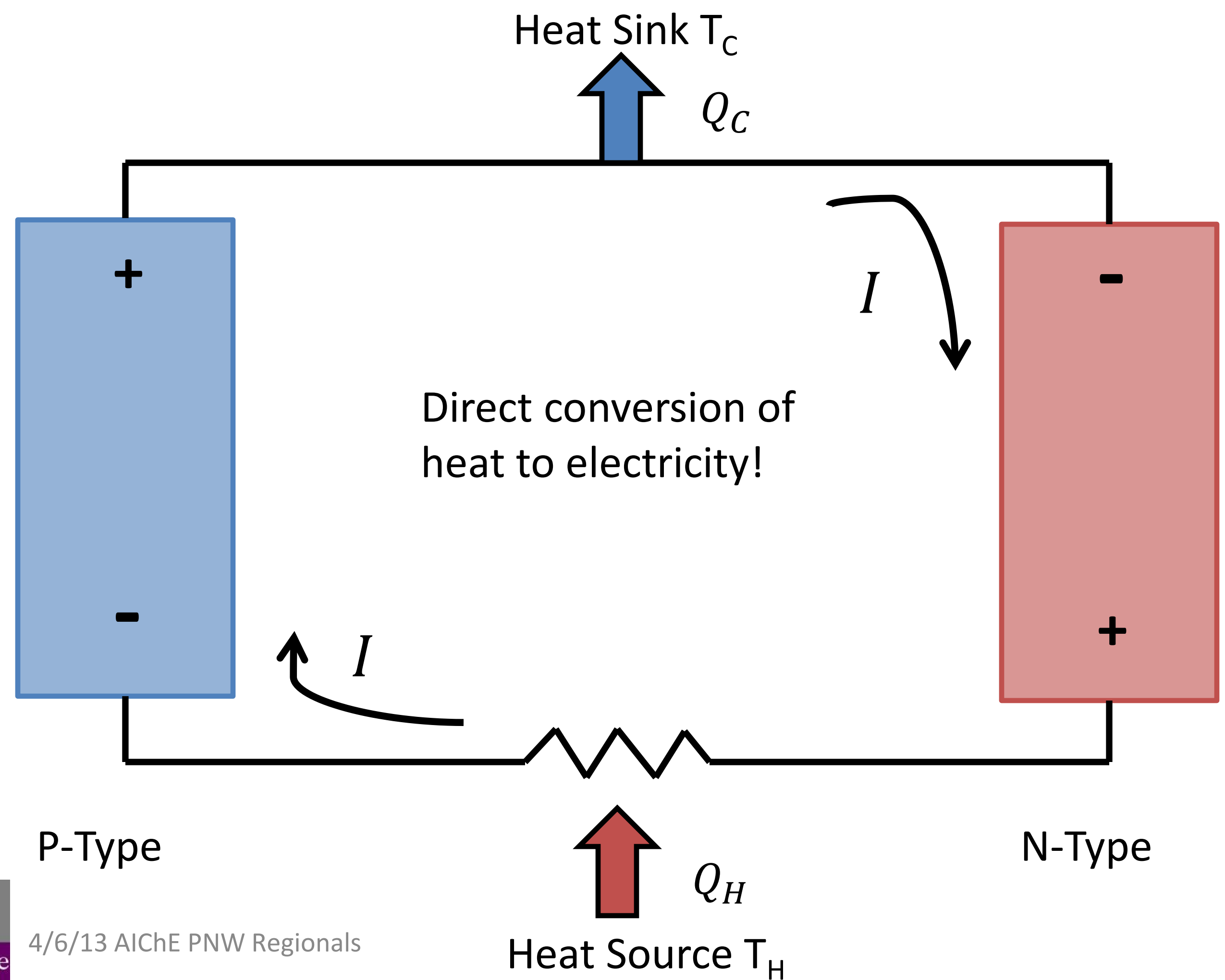
Outline

- 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



Thermoelectric Applications

- Energy Scavenging
  - Process Heat
  - Automobile Exhaust
- Refrigeration (Peltier Effect)
- Space Exploration, Thermocouples

Advantages	Disadvantages
No moving parts, silent No working fluid required No maintenance Works on small scale	Low Efficiency Unstable at high temperatures Some contain toxic heavy metals Materials Challenges

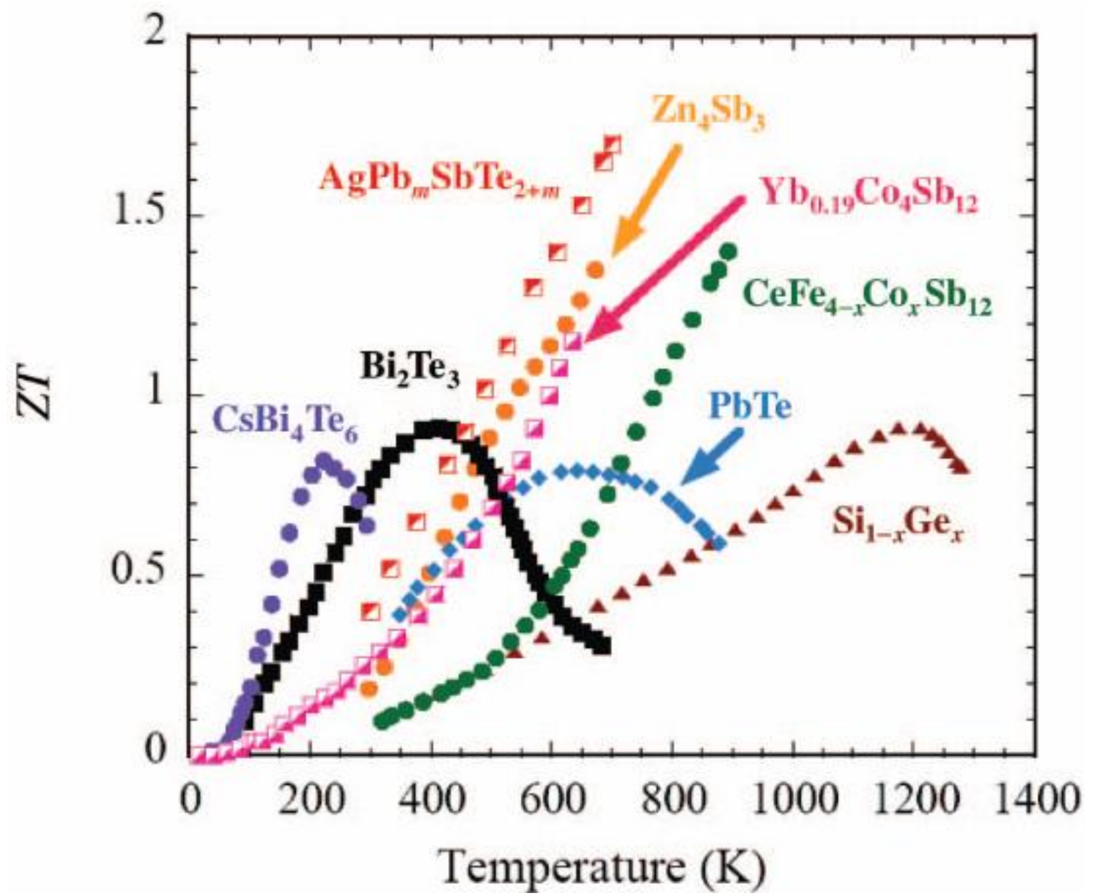
Figure of Merit

Seebeck Coefficient (Thermopower)

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

Electrical Resistivity

Thermal Conductivity



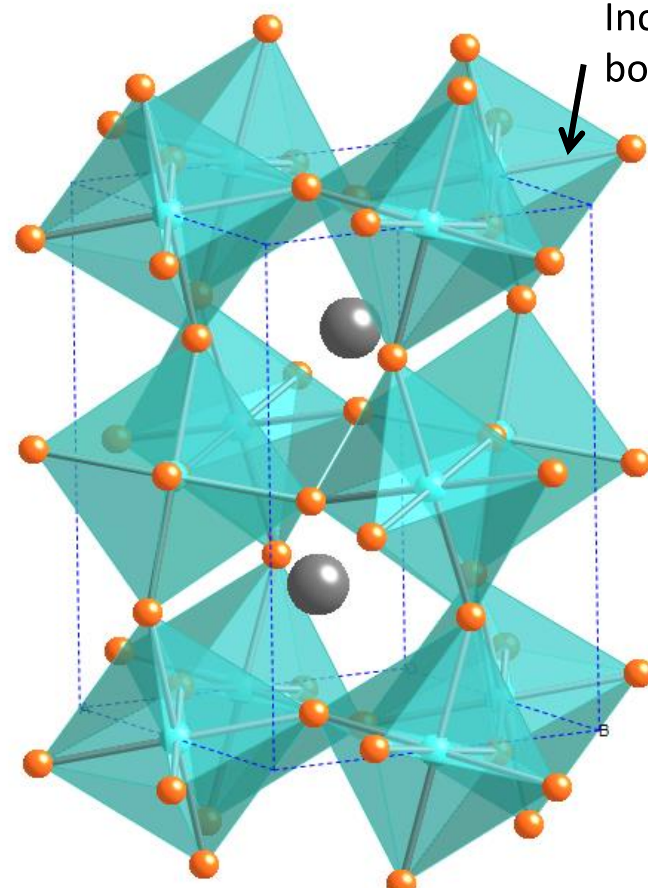
T. Tritt, M. A. Subramanian, MRS Bull. 31, 188 (2006).

Thermoelectric Oxides

Perovskite Formula: $RCoO_3$ (R = 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

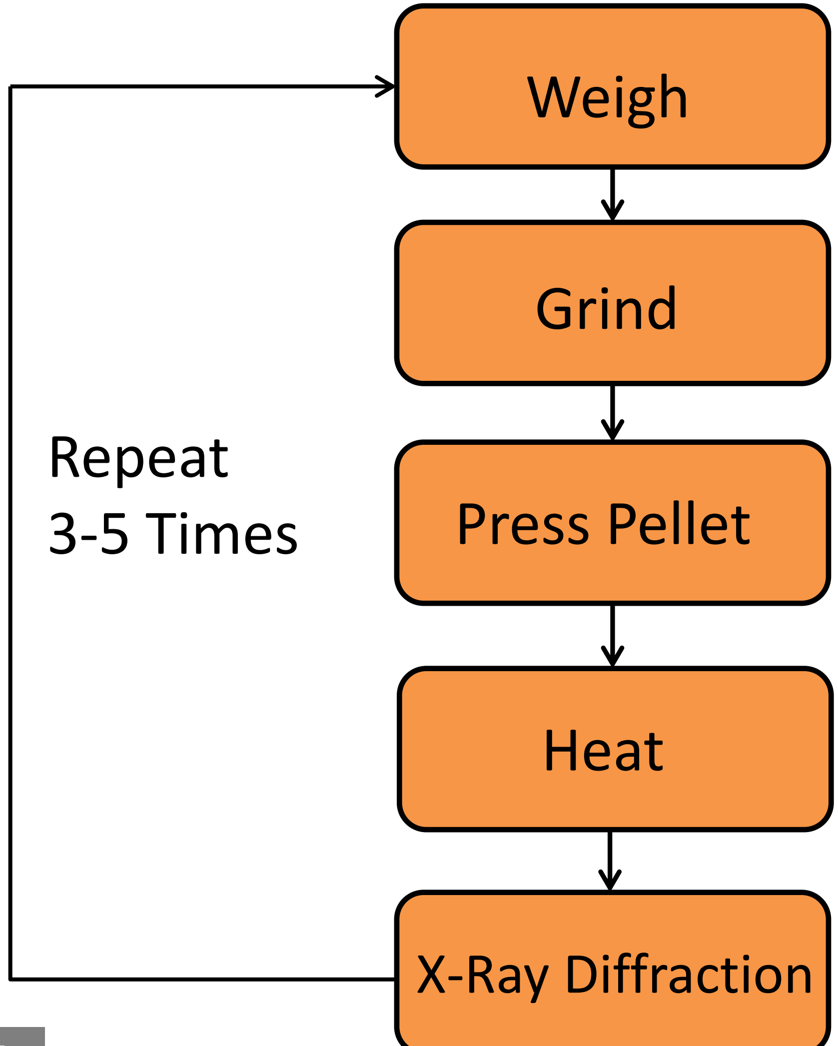
W. Koshibae et. al, Phys. Rev. B 62, 11 (2000)

$Y_{1-x}Ca_xCoO_3$ and $YCo_{1-x}Rh_xO_3$

- $LaCoO_3$ most widely studied
- R_{La3+}= 1.36 Å
- R_{Y3+}= 1.25 Å
- Ca^{2+} substitution for Y^{3+}: P-Type Doping
- Rh ion stable in low spin state for all temperatures

I. Terasaki et. al, Dalton Transactions 39, 4 (2010)

Solid State Reaction Synthesis



Stoichiometric amounts of
Y_2O_3, Co_3O_4, $CaCO_3$, Rh_2O_3

Mortar and Pestle
Ball Mill

Diameter 10mm
Height 2-3mm

12-24 Hours
900-1100 ^{o}C in O_2

Rigaku Miniflex II

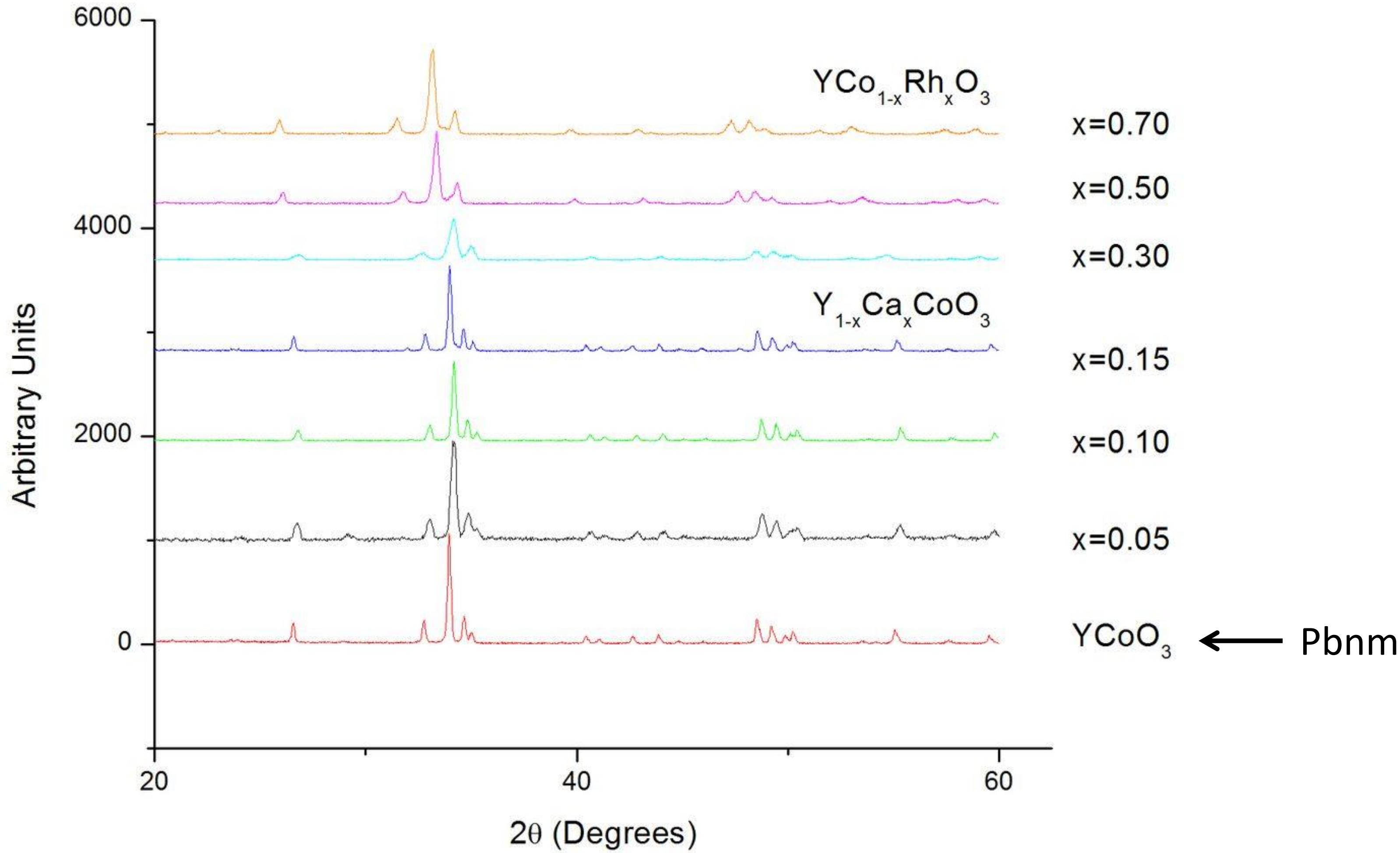
Transport Measurements and SEM

ZEM used to measure electrical resistivity and Seebeck coefficient from 200-500 ^{o}C
$YCo_{1-x}Rh_xO_3$

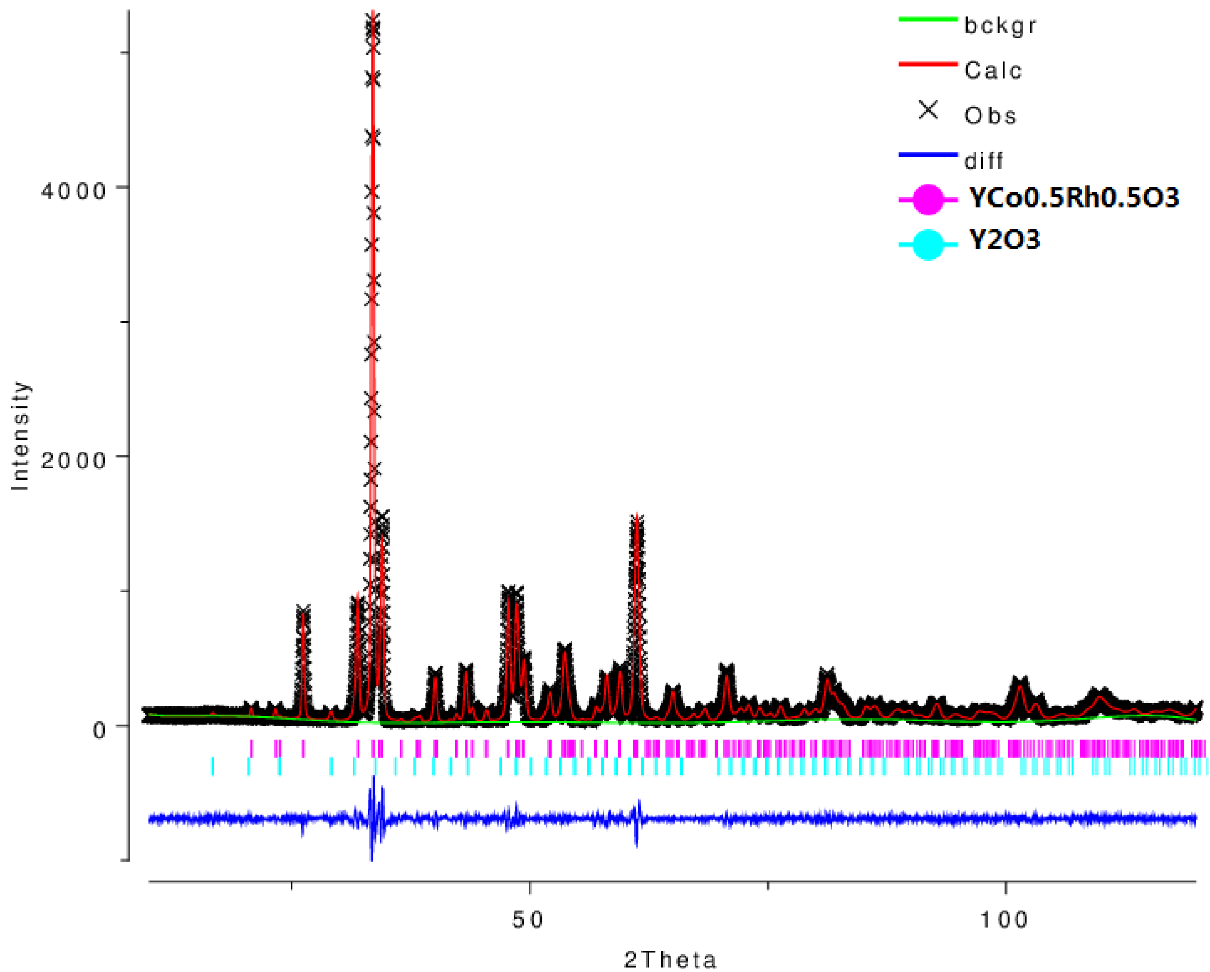
ZEISS SEM/EDS used to determine morphology and confirm composition
$Y_{1-x}Ca_xCoO_3$

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

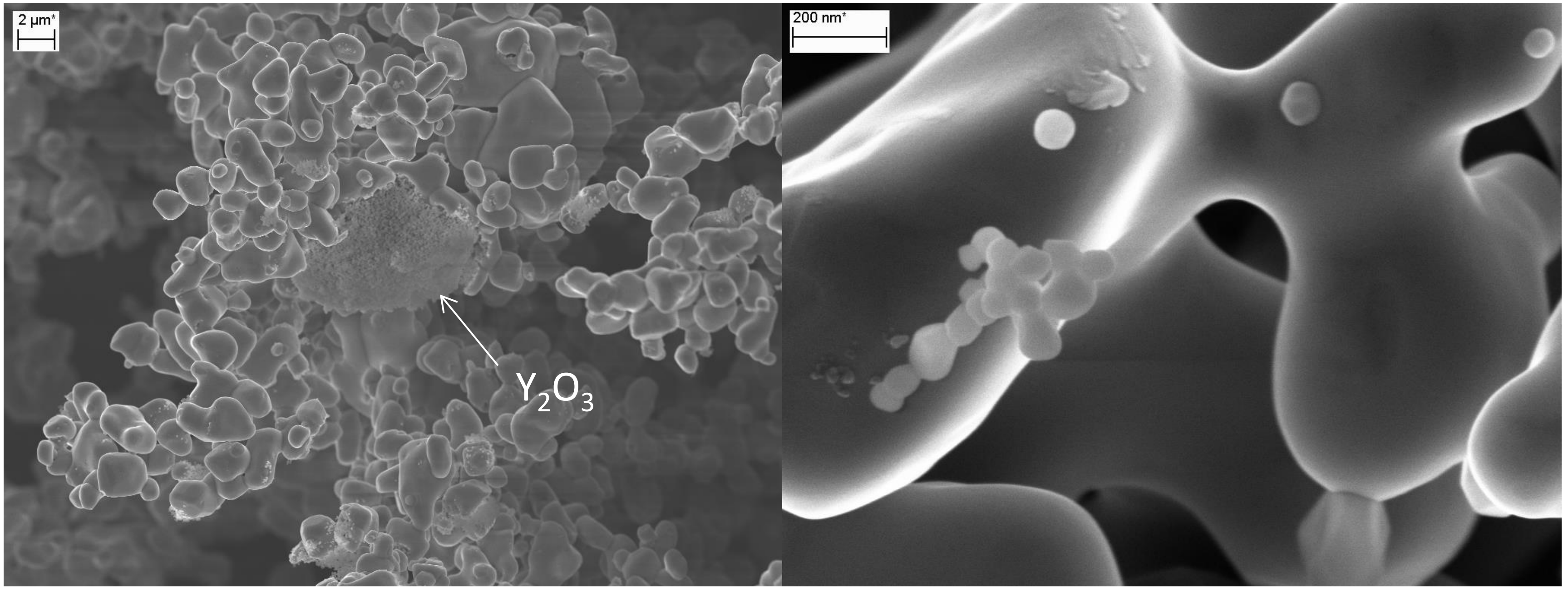
X Ray Diffraction



XRD Fit


bckgr
Calc
Obs
diff
YCo0.5Rh0.5O3
Y2O3
Intensity
4000
2000
0
50
100
2Theta

$Y_{1-x}Ca_xCoO_3$
Scanning Electron Microscopy

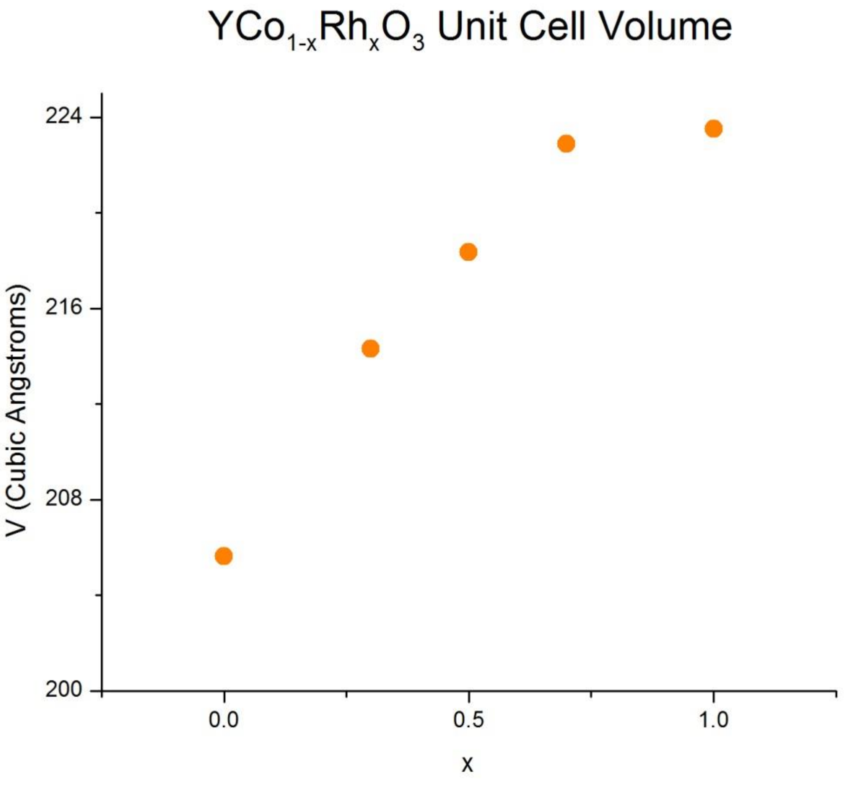


Further Evidence of Substitution

Nominal Composition	Actual Composition*
$YCoO_3$	$Y_{1.16}CoO_{3-\delta}$
$Y_{0.98}Ca_{0.02}CoO_3$	$Y_{1.08}Ca_{0.01}CoO_{3-\delta}$
$Y_{0.95}Ca_{0.05}CoO_3$	$Y_{1.05}Ca_{0.07}CoO_{3-\delta}$
$Y_{0.90}Ca_{0.10}CoO_3$	$Y_{1.15}Ca_{0.11}CoO_{3-\delta}$
$Y_{0.80}Ca_{0.20}CoO_3$	$Y_{1.06}Ca_{0.19}CoO_{3-\delta}$
$Y_{0.70}Ca_{0.30}CoO_3$	$Y_{0.81}Ca_{0.22}CoO_{3-\delta}$

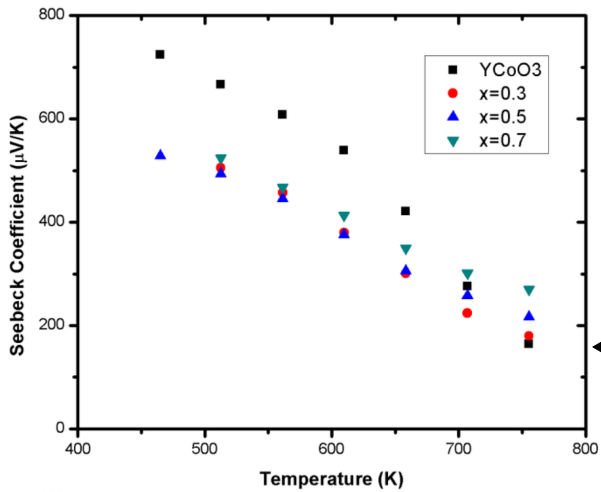
Energy Dispersive Spectroscopy

*The instrument overcompensated for Sr in an $SrTiO_3$ standard, so actual Y compositions are lower than they appear.

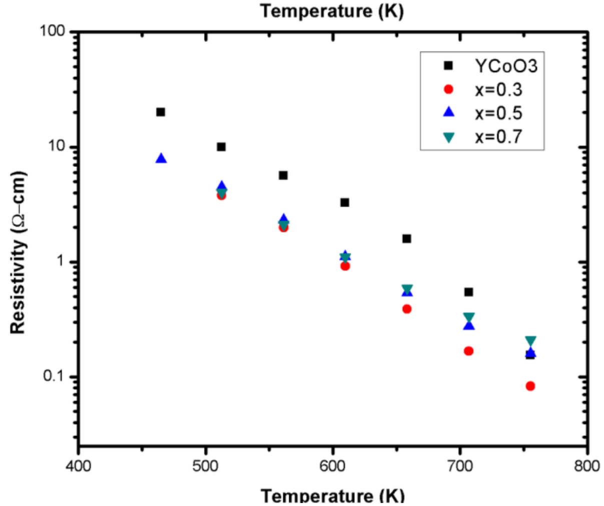


$YCo_{1-x}Rh_xO_3$ Seebeck/Resistivity

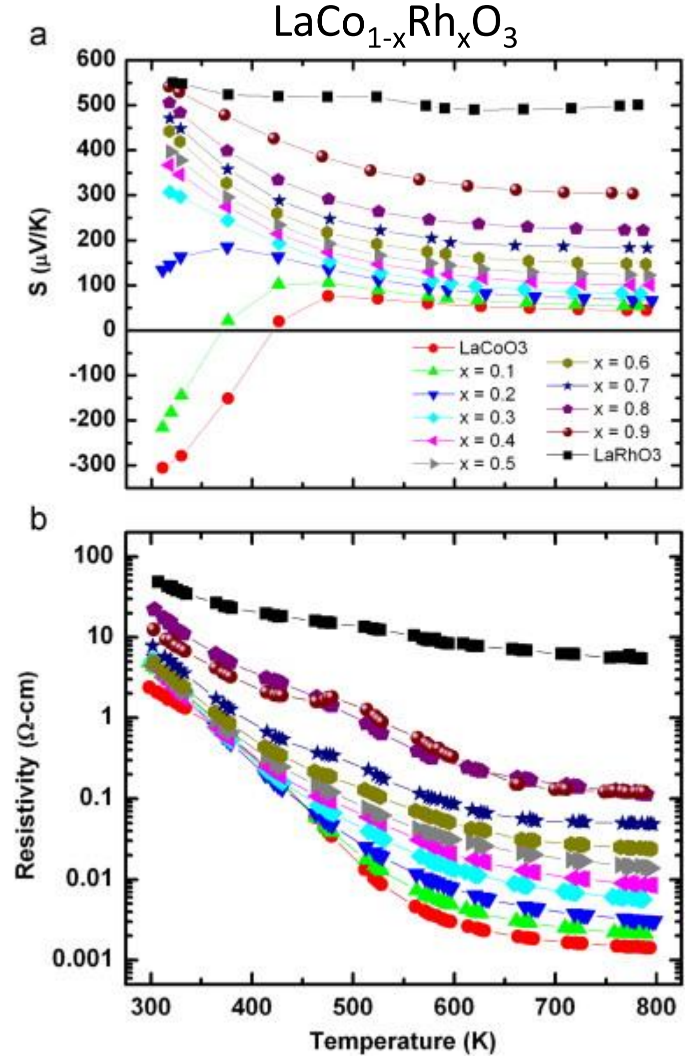
$YCo_{1-x}Rh_xO_3$



Theoretical value for LS Co: 154 μV/K



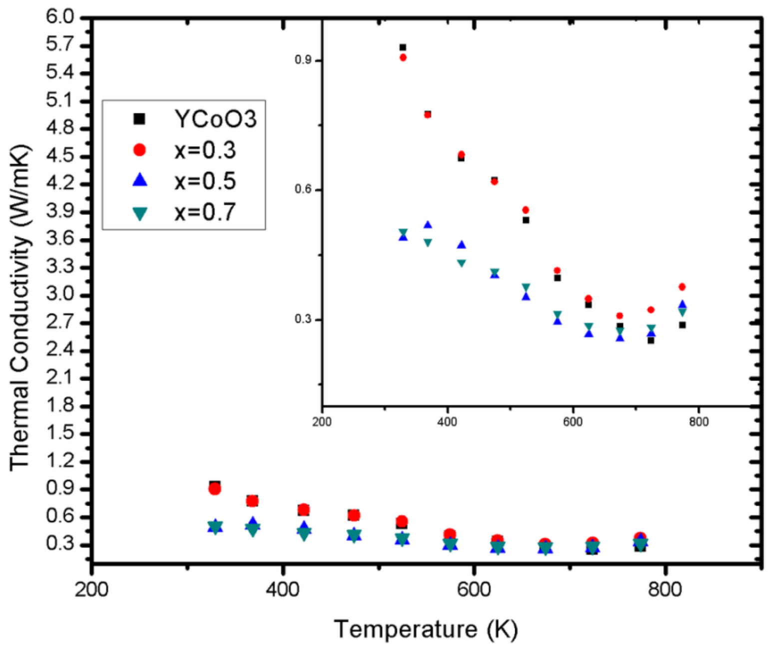
$LaCo_{1-x}Rh_xO_3$



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

$YCo_{1-x}Rh_xO_3$ Thermal Conductivity

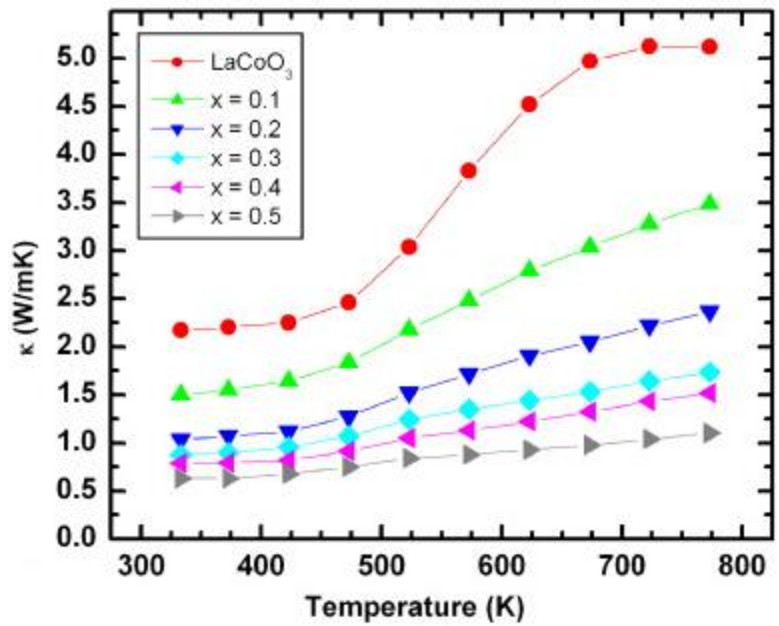
$YCo_{1-x}Rh_xO_3$



Sample relative density: 50-55%

Could high porosity be causing low thermal conductivity?

$LaCo_{1-x}Rh_xO_3$



k calculated from collected thermal diffusivity data, experimental density, specific heat of $LaCoO_3$[1]

[1]*Stolen et. al, Phys. Rev. B 55, 21 (1997)*
Li et. al, JSSC 183, 6 (2010)

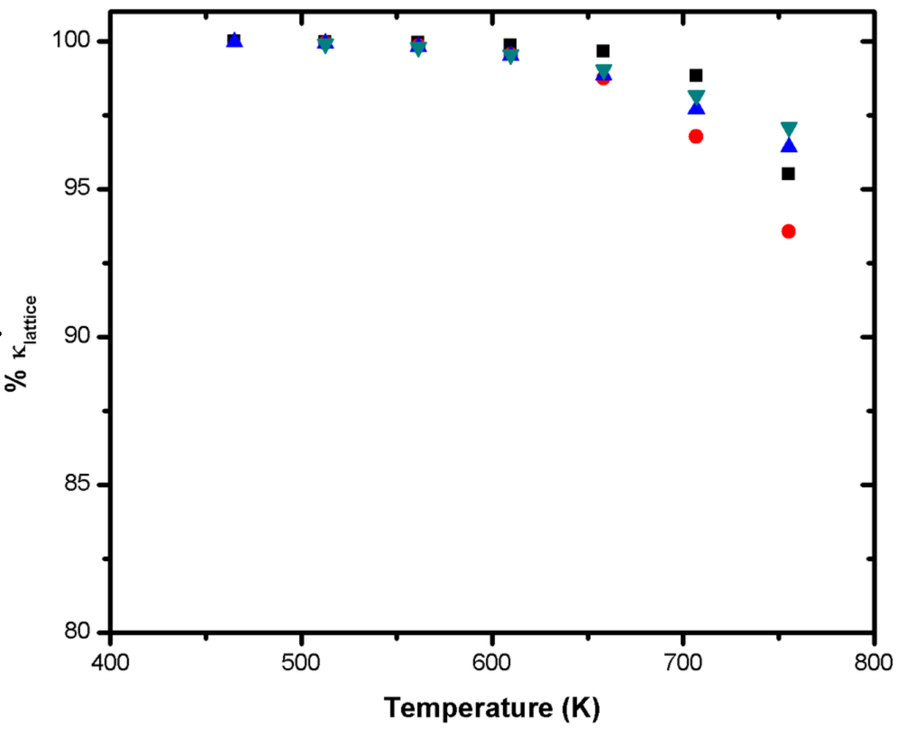
$YCo_{1-x}Rh_xO_3$ Lattice Thermal Conductivity

$$\kappa = \kappa_{ch} + \kappa_{lattice}$$

Wiedemann-Franz Law:

$$\kappa_{ch} = LT / \rho$$

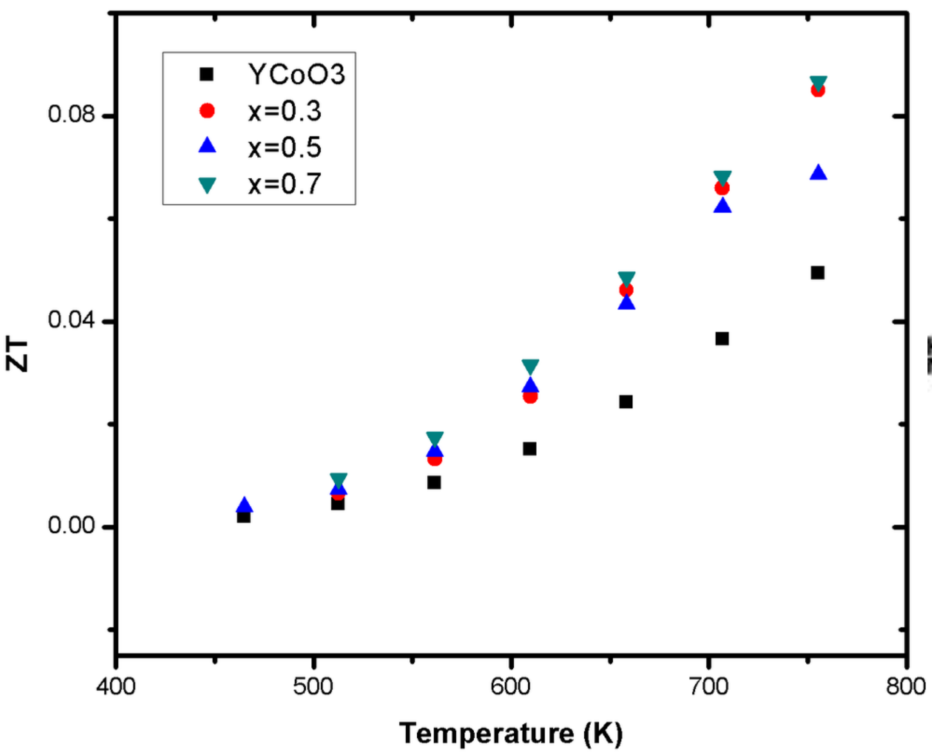
Lorenz Number = 2.44×10^{-8} $W\Omega K^{-2}$



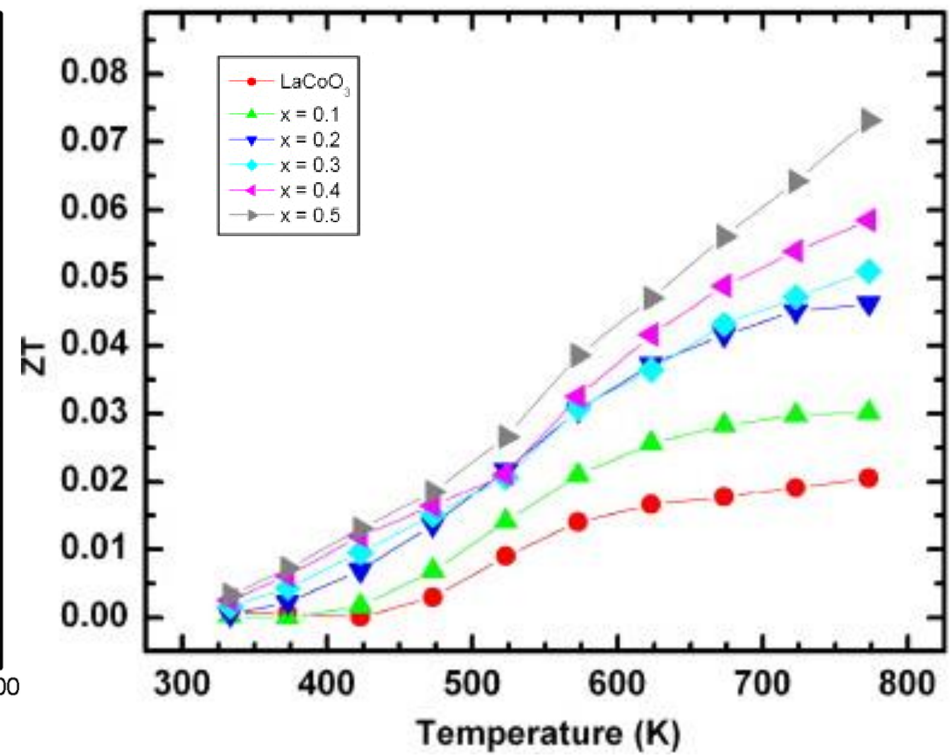
If lattice vibrations are suppressed by porosity:
Not effect of composition, but of macrostructure.

$YCo_{1-x}Rh_xO_3$ Figure of Merit

$YCo_{1-x}Rh_xO_3$



$LaCo_{1-x}Rh_xO_3$



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

Conclusions

- Thermoelectric oxides are desirable because of non-toxicity and high-temperature stability.
- $Y_{1-x}Ca_xCoO_3$ ($0 \le x \le 0.20$) and $YCo_{1-x}Rh_xO_3$ ($0 \le x \le 1.0$) 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 μV/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 ≈ 0.09 at 750K, increasing with temperature.

Acknowledgements

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References

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T. Tritt, M. A. Subramanian, MRS Bull. 31, 188 (2006)

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

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Thank you!

Questions?