Ceramic High Temperature Thermoelectric Heat Exchanger and Heat Recuperators for Power Generation Systems

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Overview

- **Background**
  - **High grade waste heat & advantages of Thermoelectric (TE) generator**
  - **State-of-the-art TE device and materials**
  - **Obstacles of oxide TE materials and device for high temperature applications**
- **Project objectives and routine lab work flow**
  - **Project objectives**
  - **Materials processing, property measurement & nanostructure characterization**
- **Highlight of current results from PI's group**
  - **Available p-type TE Oxide that over performed SiGe at 800°C.**
  - **Ongoing work of n-type TE oxide with record high electrical performance**
  - **Novel scalable all oxide TE generator with compact design**
- **Summary and future work**

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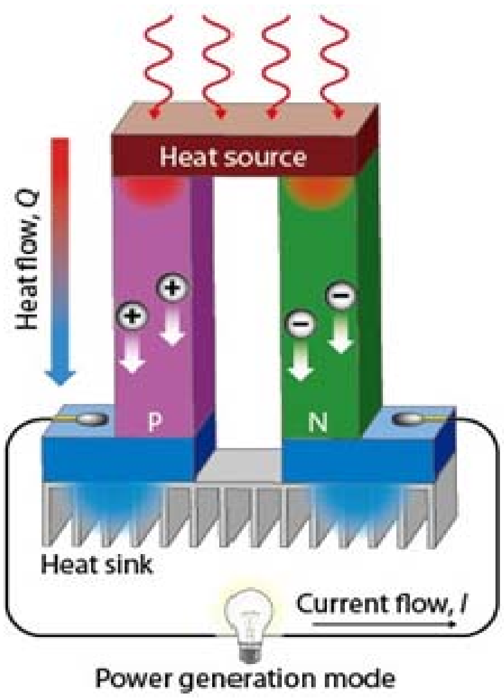
Background: Waste heat & advantages of TE generator

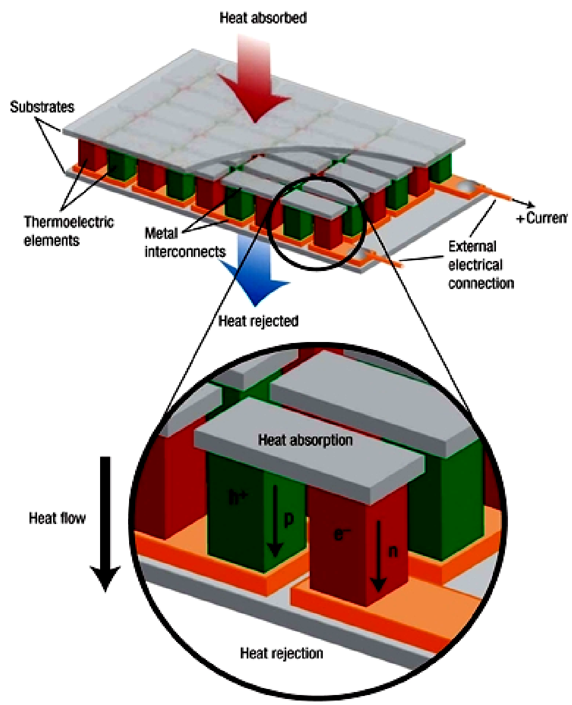
Industry power plants, factories, automobiles, and even portable generators generate enormous amounts of heat that is unproductively released into the environment.

Thermoelectric (TE) materials and devices:
converting temperature differences into electrical power.



Thermoelectric Uni-couple

NPG Asia Mater. 2(4) 152 (2010)



Thermoelectric Module

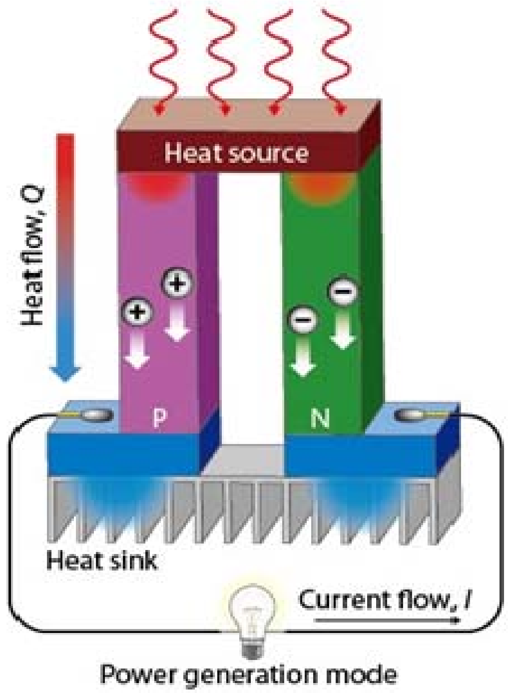
Nature Materials 7, 105 114 (2008)

Advantages of TE generators

- ✓ **No moving parts, silent.**
  (unlike gas turbine engines).
- ✓ **Maintenance-free operation.**
  (without chemical reactions compared to fuel cells).
- ✓ **Long life capability.**
- ✓ **Function over a wide temperature range.**
- ✓ **Position independent.**
- ✓ **Environmental friendliness.**

Background: Waste heat & advantages of TE generator

Thermoelectric materials and devices:
converting temperature differences into electrical power.



Thermoelectric Uni-couple

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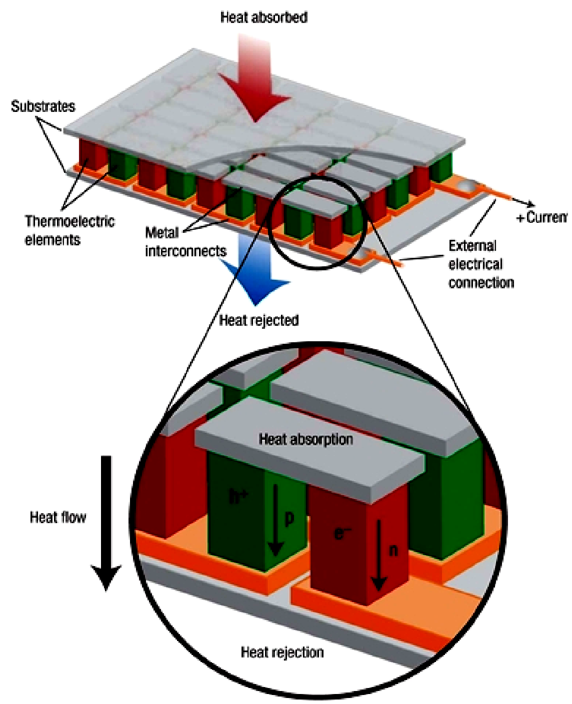

Thermoelectric Module

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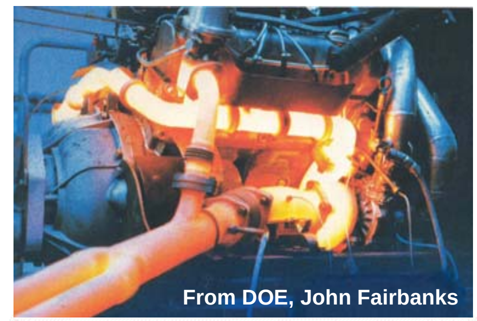
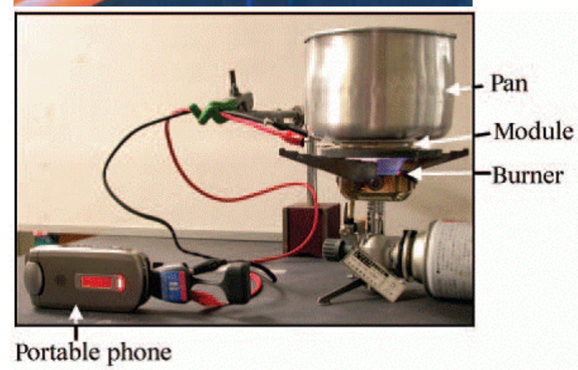




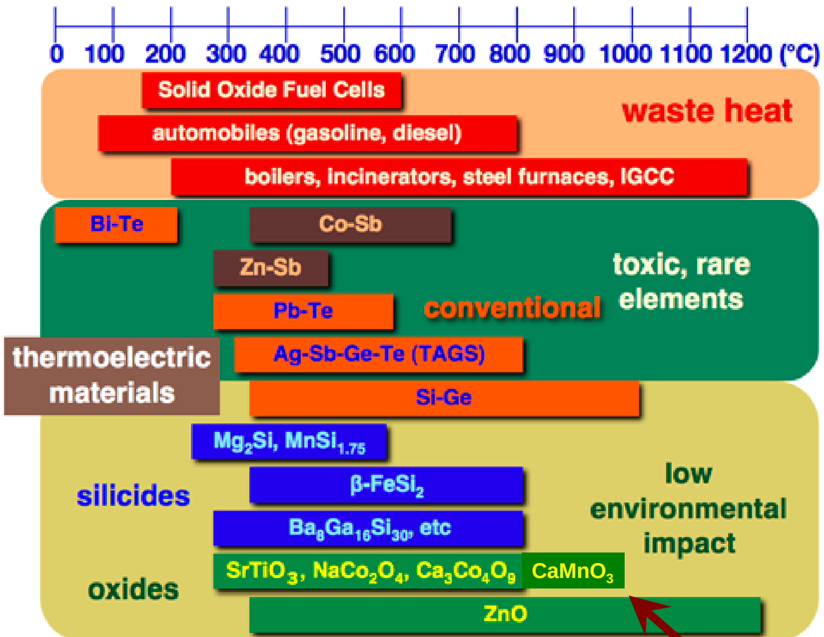
Thermoelectric module charging a phone

MRS Bull. 31 (2006) 188

Background: State-of-the-art TE device and materials & obstacles for high temperature applications

High temperature power generation systems -Solid Oxide Fuel Cells (SOFCs):

- SOFCs operate in the 650-800ºC temperature range and produce a large amount of exhaust heat
- High temperature exhaust gas streams leaving the SOFC stack have a temperature around 600ºC.



Waste heat, operating temperature of thermoelectric materials.

Journal of the Ceramic Society of Japan 119 [11], 770-775, 2011

State-of-the-art thermoelectric materials- heavy-metal-based materials

- Skutterudite $La_{0.9}Fe_3CoSb_{12}$
- Half-Heusler alloys
- Clathrates
- Antimonides Zn_4Sb_3

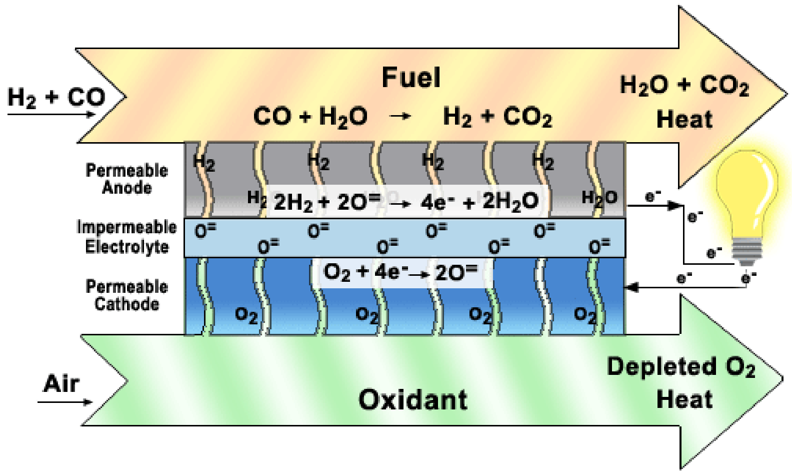
Heavy-metal-based materials: energy conversion efficiency high enough for practical applications. However, they are NOT good for operating at high temperatures range due to:

- decomposition; vaporization and/or melting ; and
- scarce, toxic, environmentally harmful.
- **Require vacuum seal for the devices- high cost.**

$CaMnO_3$, $Ca_3Co_4O_9$

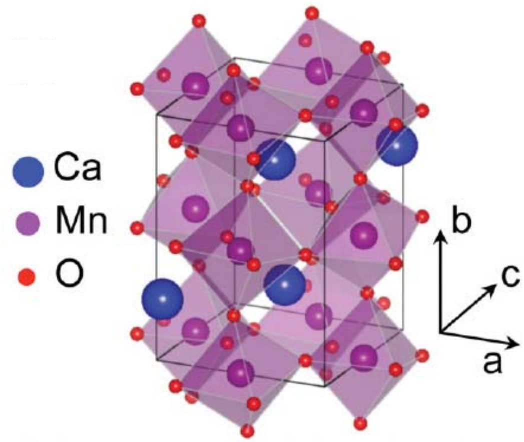
High temperature waste heat recovery

Background: Thermoelectric Oxide & its potential application in SOFCs

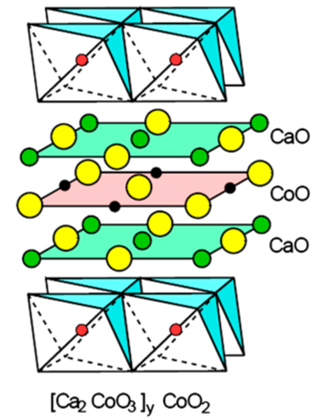


Solid Oxide Fuel Cells (SOFCs)

DOI: 10.1007/978-1-4614-1957-0_2



Phys. Rev. B 85, 214120



Journal of the Ceramic Society of Japan 119, [11], 770-775, 2011

n type
Oxide $CaMnO_3$

p type
Oxide $Ca_3Co_4O_9$

High Temperature Waste Heat in SOFCs:

- SOFCs operate in the 650-800ºC temperature & produce a large amount of exhaust heat.
- High temperature exhaust gas streams leaving the SOFC stack have a temperature ~300-600ºC.

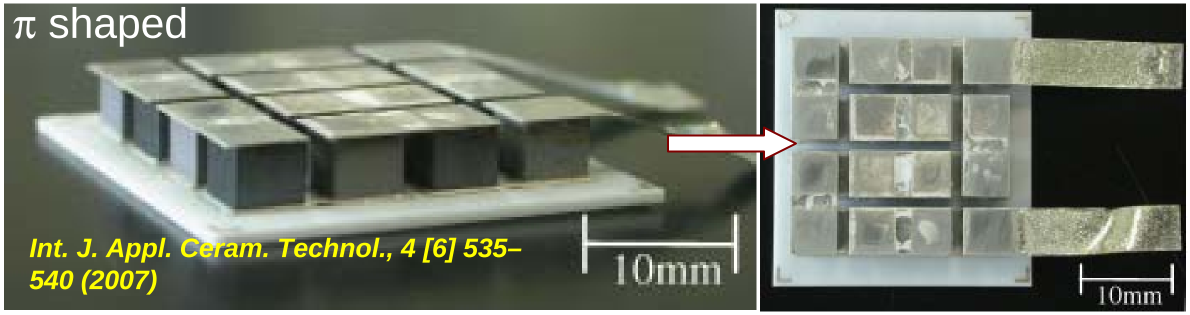
Oxide $Ca_3Co_4O_9$ & $CaMnO_3$, are particularly promising for high temperature applications

- **Low cost, and light weight.**
- **High thermal stability in air up to 980ºC.**
- **Non toxic.**

Challenge for oxide application of high temperature waste heat recovery:

- **Device level:** Need better design of the all oxide TE generators.
- **Materials Level:** Need to enhance energy conversion efficiency of polycrystalline oxide.

Background: Device Level Challenges for Oxide TE Generators



Literatures: TE materials & maximum output power P_{max} for oxide module, *Japanese JAP v.49 (2010) 071101]*

	GPR-device	Lemonnire *et al.*	Shin *et al.*	Reddy *et al.*
Number of couples	1	2	1	2
P-type leg	$Ca_{2.7}Bi_{0.3}Co_4O_9$	—	Li-doped NiO	$Ca_3Co_4O_9$
N-type leg	$Ca_{0.9}Yb_{0.1}MnO_3$	$Ca_{0.95}Sm_{0.05}MnO_3$	$(Ba,Sr)PbO_3$	$Ca_{0.95}Sm_{0.05}MnO_3$
Dimensions of the legs (cross-sectional area) × height	$(3.5 \times 3.5) \times 5\,mm^3$	$(4.7 \times 3.9) \times 6.5\,mm^3$	$(4 \times 3) \times 20\,mm^3$	$(4 \times 4) \times 10\,mm^3$
Maximum power (W)	0.14	0.016	0.008	0.032
Temperature difference (K)	705	360	552	925
Maximum power density ($W\,cm^{-2}$)	0.57	0.02	0.03	0.05

Critical issues for the conventional devices (adapted from modules for metals):

- **Difficulty of selection of interconnect materials.**
- **Interfaces and the contact resistance**: Open circuit voltage from modules ~only 54% of theoretical value, loss from interfaces & contact resistance.
- **Adiabatic blocks** are essential to maintain the temperature difference between hot and the cold sides of the module. Back-filling some blocking materials is needed.
- **Large size** (caused by the π shaped) and **heavy in weight** (large amount interconnect metals).

Background: Materials Level Challenges for Oxide TE Generators

The conversion efficiency: *the dimensionless figure-of-merit ZT.*

For practical application, $ZT \sim 1$; 10% energy conversion efficiency.

$$ZT = \frac{\sigma S^2}{(\kappa_e + \kappa_L)} \cdot T$$

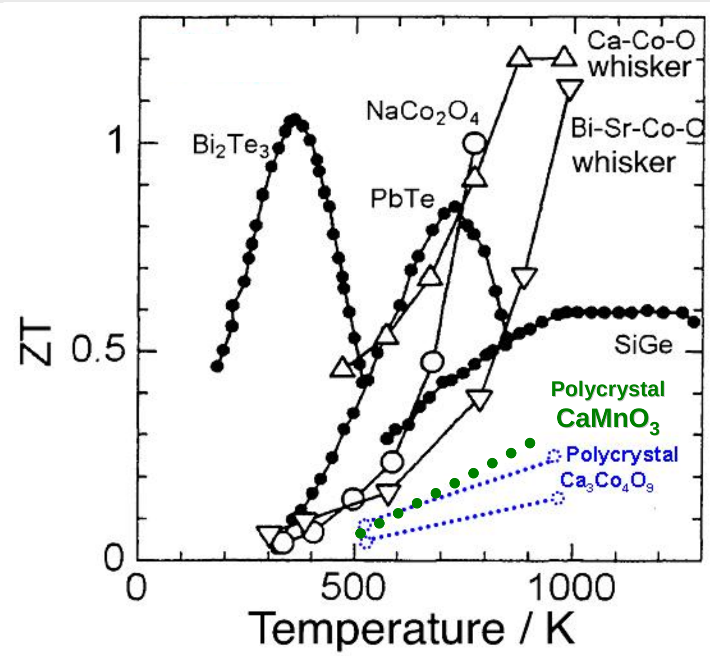
S: absolute Seebeck coefficient $\Delta V/\Delta T$

σ: Electrical conductivity ($1/\rho$)

ρ: Electrical resistivity

σS^2: Power Factor

($\kappa_e + \kappa_L$): Total thermal conductivity



Michitaka Ohtaki, J. Ceramic Society of Japan 119, 770 2011

Challenge for thermoelectric Oxide $CaMnO_3$ and $Ca_3Co_4O_9$

- **Enhance the performance of polycrystalline materials for applications in large scale**

Possible routes of improving the performance:

- **Lower the thermal conductivity of ($\kappa_e + \kappa_L$)**
- **Increase the electrical transport power factor of σS^2, by increasing the S, and decrease ρ**

Background: Materials Level Challenges for Oxide TE Generators

The conversion efficiency: *the dimensionless figure-of-merit ZT.*

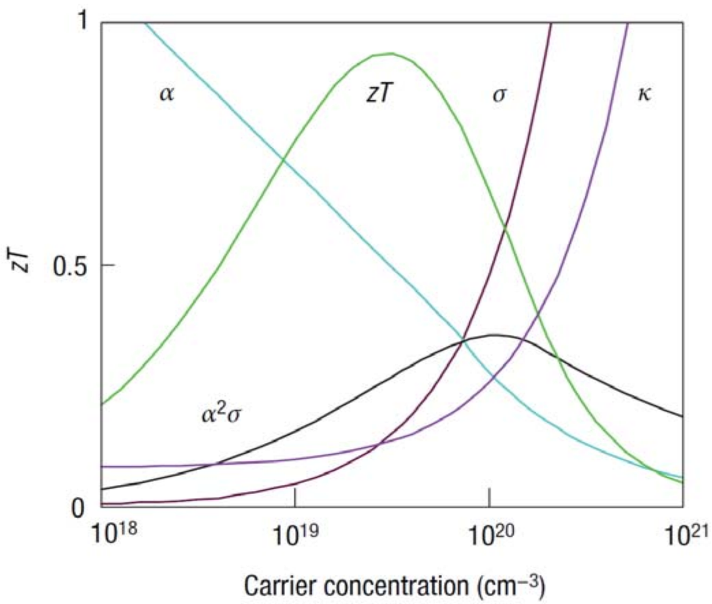
For practical application, $ZT \sim 1$.

$$ZT = \frac{\sigma S^2}{(\kappa_e + \kappa_L)} \cdot T$$

S or α: absolute Seebeck coefficient $\Delta V/\Delta T$

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

n: carrier concentration; m: effective mass*



Nature Materials 7, 105 114 (2008)

Carrier concentration *n* increase will **increase the electrical conductivity σ** & **decrease the Seebeck coefficient**.
Ideal for increasing the power factor: **Decrease the carrier concentration** (increase S) & **increase the carrier mobility** (increase σ).

σ: Electrical conductivity (1/ρ)

$$1/\rho = \sigma = ne\mu$$

n: carrier concentration
μ: *carrier mobility*

Difficulty in Increase the electrical transport power factor of σS^2.

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- Highlight of current results from PI's group
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Project Objectives

Objective: develop *all-oxide TE generators*, which will be *highly efficient, cheaply produced, compact/small, lightweight, non-toxic, and highly stable in air at high temperatures*, for recovering the waste heat from power systems including SOFCs at temperatures of up to 980ºC in air.

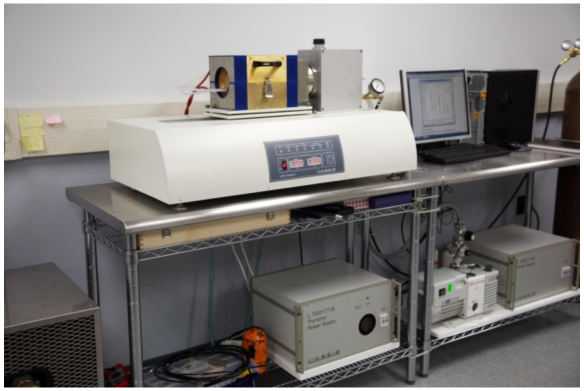
Novel device configurations will be developed using mature, inexpensive, easily scalable manufacturing techniques.

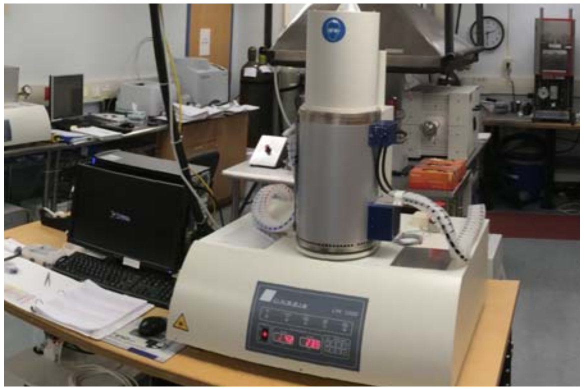
In comparison with *commercially* available TE generators (TEGs) that are mostly working in the low temperature regime of *up to 300ºC* or so, the proposed generators are targeted for *medium to high temperature up to 980ºC in air*, at which the commercially conventional TE device will not perform. In addition, since the generators are ceramic, they can be integrated into ceramic heat exchangers without needing sealing between the TEG and the heat exchanger.

Approaches:

- **Materials level:** Improve oxides performance through nanostructure engineering.
- **Device level:** Novel device with compact design, low cost, and scale up ready.

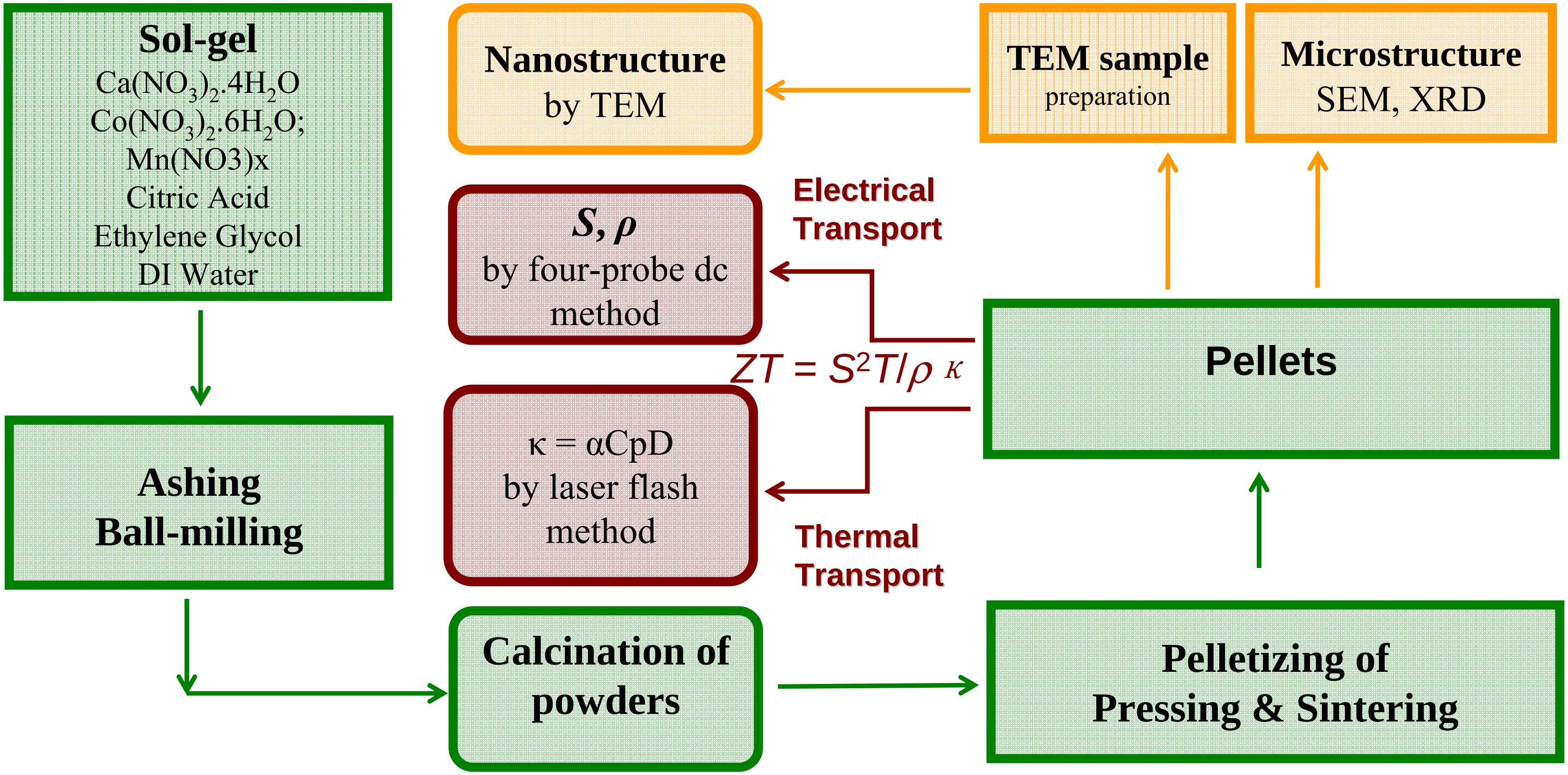
Lab for Thermoelectric Materials & Device





- Linseis LSR-1100, Seebeck and Electrical Resistivity, from 25^{o}C to 1100^{o}C.
- Linseis LFA-1200, Laser Flash Analyzer, Thermal conductivity, from 25^{o}C to 1250^{o}C.

Routine work flow: Synthesis, Measurement and Characterization



Polycrystalline $Ca_3Co_4O_9$ or $CaMnO_3$ Pellets

- Sol-gel chemical route, calcinations, pressing and sintering.

Thermoelectric properties measurement

- Seebeck coefficient, electrical resistivity: Linseis LSR-1100.
- Thermal-conductivity: Linseis LFA-1200.

Nanostructure & chemistry characterization

- Transmission Electron Microscopy.

Every step in the processing matters

Pure baseline pellets, keys:

- Chemistry & mixing of sol-gel
- Ashing and ball-milling time
- Calcination gas and temperature
- Pressing pressure and temperature
- Sintering gas and temperature

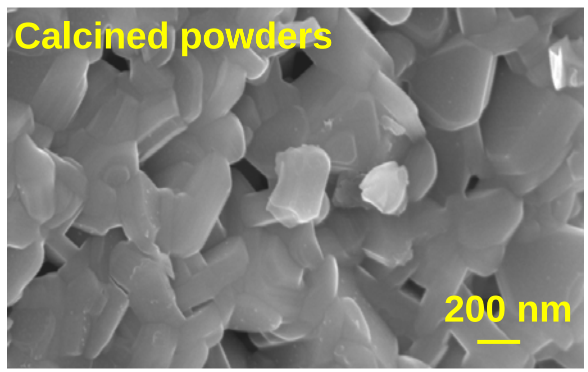
Powder Processing and Sintering of Pellets

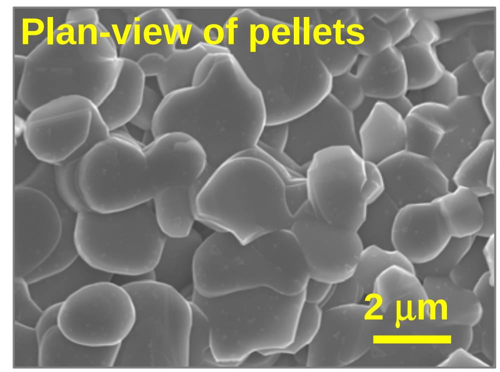
Sol-gel
$Ca(NO_3)_2$, $Co(NO_3)_2$, H_2O
Citric Acid, Ethylene Glycol

⇒ **Ashing** / **Calcination** ⇒ **Pressing & Sintering** / **Pellets with texture**

p-type $Ca_3Co_4O_9$

n-type $CaMnO_3$





- ❖ **Sol-gel chemical routes making gels.**
- ❖ **Ashes from gel, and calcined powders with nano crystals.**
- ❖ **Pressing into pellets.**
- ❖ **Significant grain growth & densification during sintering.**

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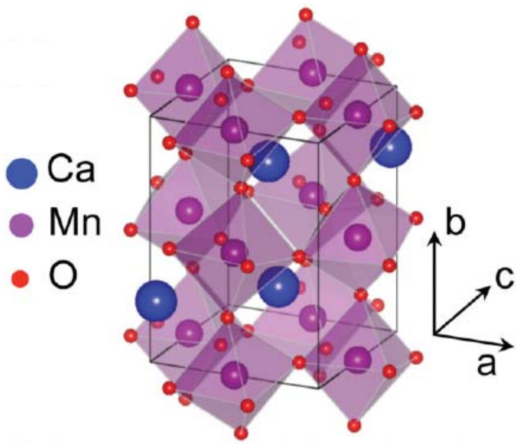
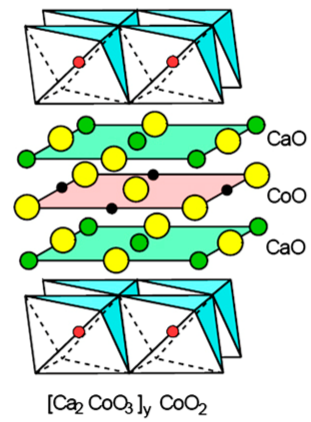
Current Work: All Oxide TE Generators

n type
Oxide $CaMnO_3$



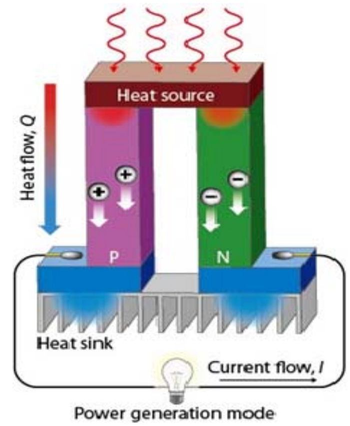
Phys. Rev. B 85, 214120

p type
Oxide $Ca_3Co_4O_9$



Journal of the Ceramic Society of Japan 119, [11], 770-775, 2011

High temperature < 980ºC in air.



NPG Asia Mater. 2(4) 152 (2010)

High Temperature Waste Heat in the Power Generation Systems such as SOFCs:

- SOFCs operate in the 650-800°C temperature & produce a large amount of exhaust heat.
- High temperature exhaust gas streams leaving the SOFC stack have a temperature ~ 300-600°C.

Approaches of improving the materials performance:

- **p-type:** Available polycrystal bulk scale $Ca_3Co_4O_9$ that outperform SiGe at 800°C.
- **n-type:** Improve the performance of polycrystal bulk scale $CaMnO_3$.

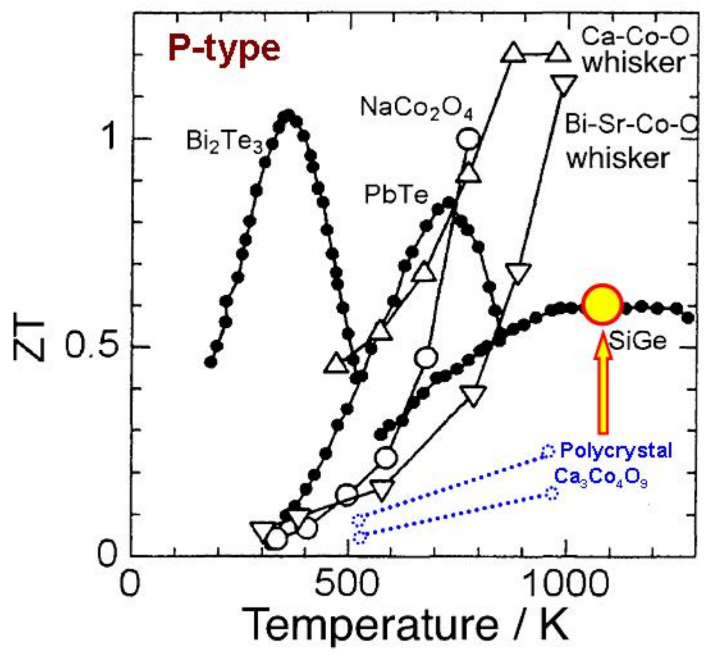
Available p-type oxide:

Bulk scale polycrystal $Ca_3Co_4O_9$

✓ Simultaneously Increase Seebeck Coefficient S and Electrical Conductivity **σ**.

✓ Increase the ZT to 0.52 at 800ºC

By dopants Ba grain boundary segregation.



$$ZT = \frac{\sigma S^2}{(\kappa_e + \kappa_L)} \cdot T$$

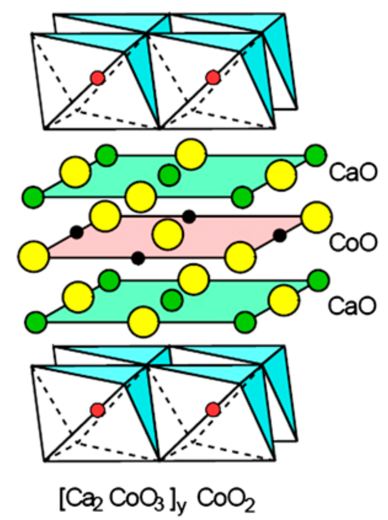
S: absolute Seebeck coefficient $\Delta V/\Delta T$

σ: Electrical conductivity (1/ρ)

ρ: Electrical resistivity

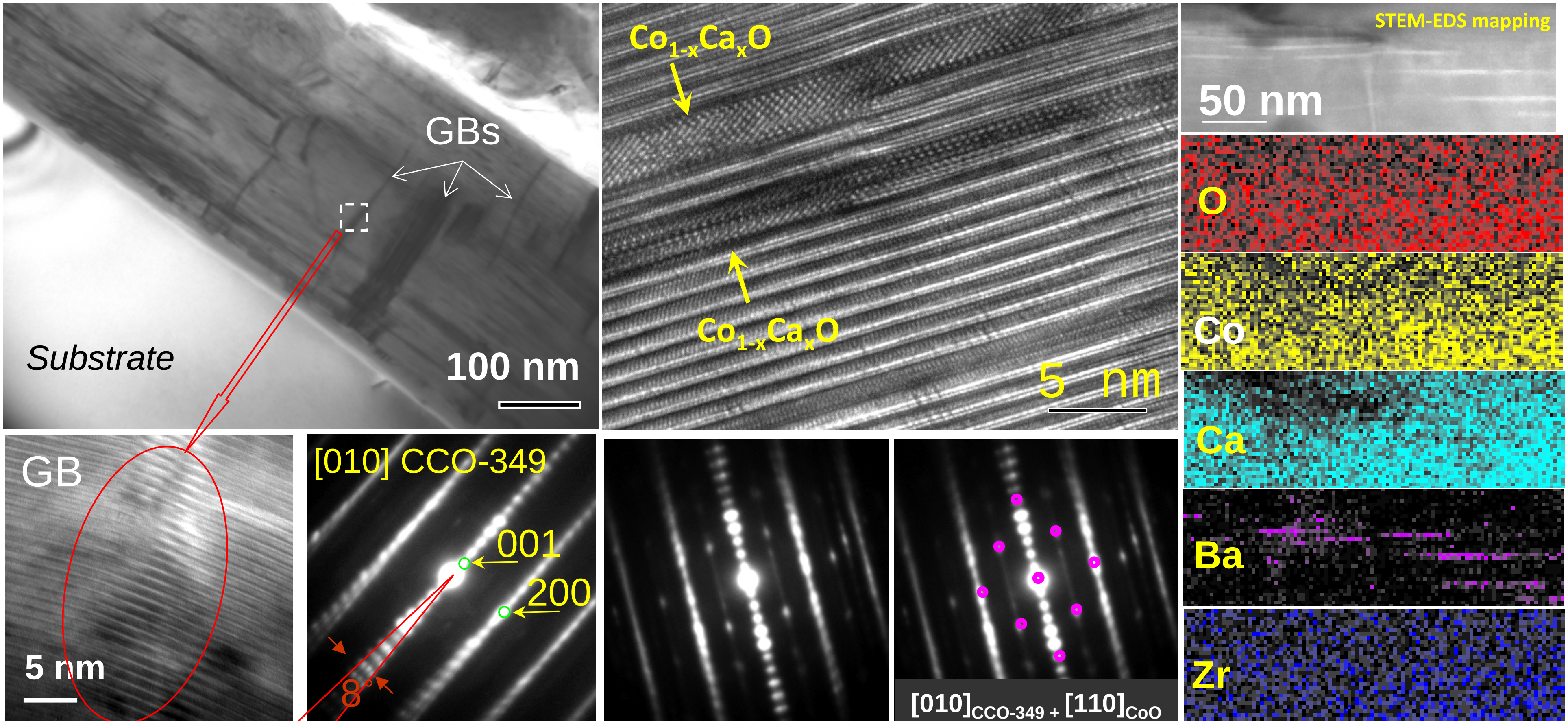
σS^2: Power Factor

$(\kappa_e + \kappa_L)$: Total thermal conductivity



p-type $Ca_3Co_4O_9$

Ba segregation to the Grain Boundaries of $Ca_3Co_4O_9$

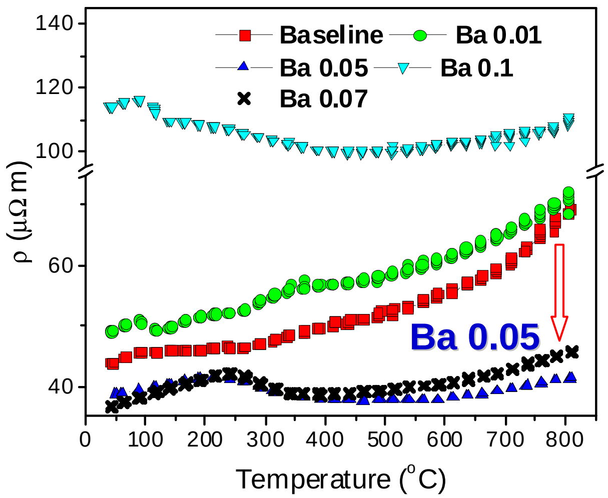


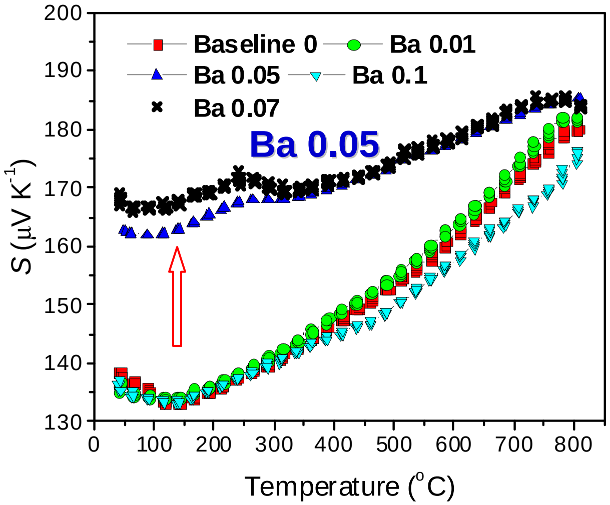
Previous results from pulsed laser deposition (PLD) film $Ca_3Co_4O_9$ with addition of $BaZrO_3$

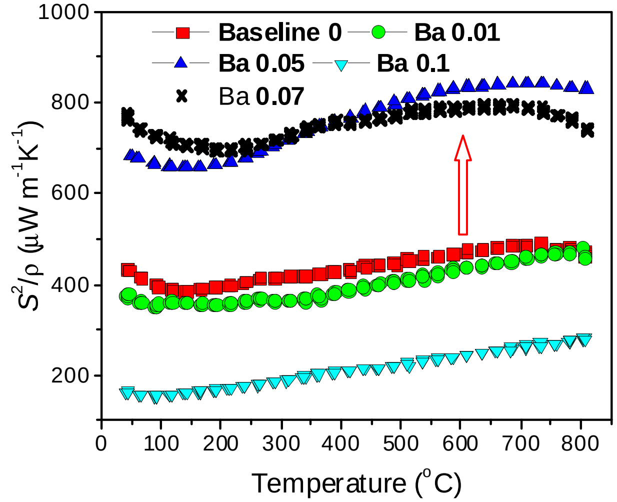
- Thin film (200 nm) is with vertical grain boundaries, and lamella secondary phase.
- Secondary phase is lamella, coherent with $Ca_3Co_4O_9$ with the thickness of 1-4 nm.
- The secondary phase is indexed as $Co_{1-x}Ca_xO$. Zr is uniformly distributed over both phases.
- Ba segregated into the grain boundaries and the secondary phases.

p-type $Ca_3Co_4O_9$

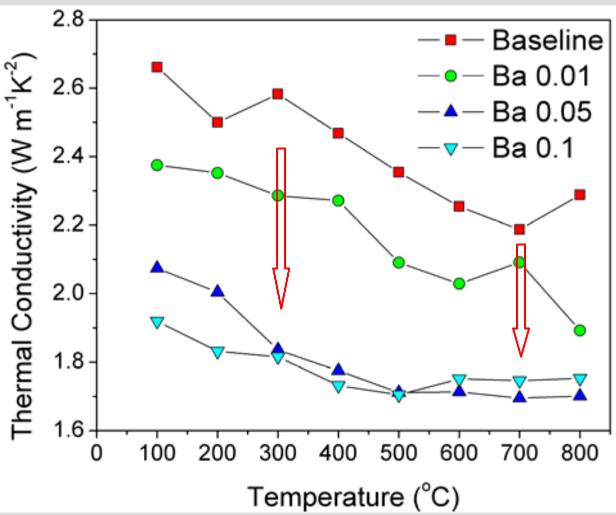
Non- stoichiometric addition: $Ca_3Co_4Ba_xO_9$ (x: 0, 0.01, 0.05, 0.07, 0.1)

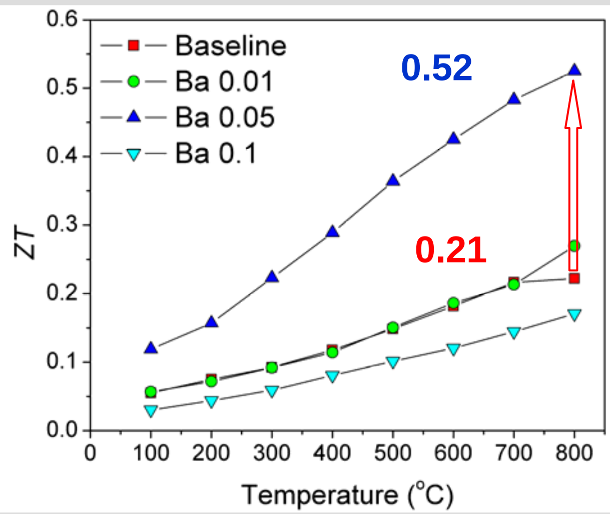






Seebeck coefficient largely increase, large decrease in carrier concentration; at Ba of X=0.05; Resistivity decrease, Metal-semiconductor transition ~200°C; increase in carrier mobility.





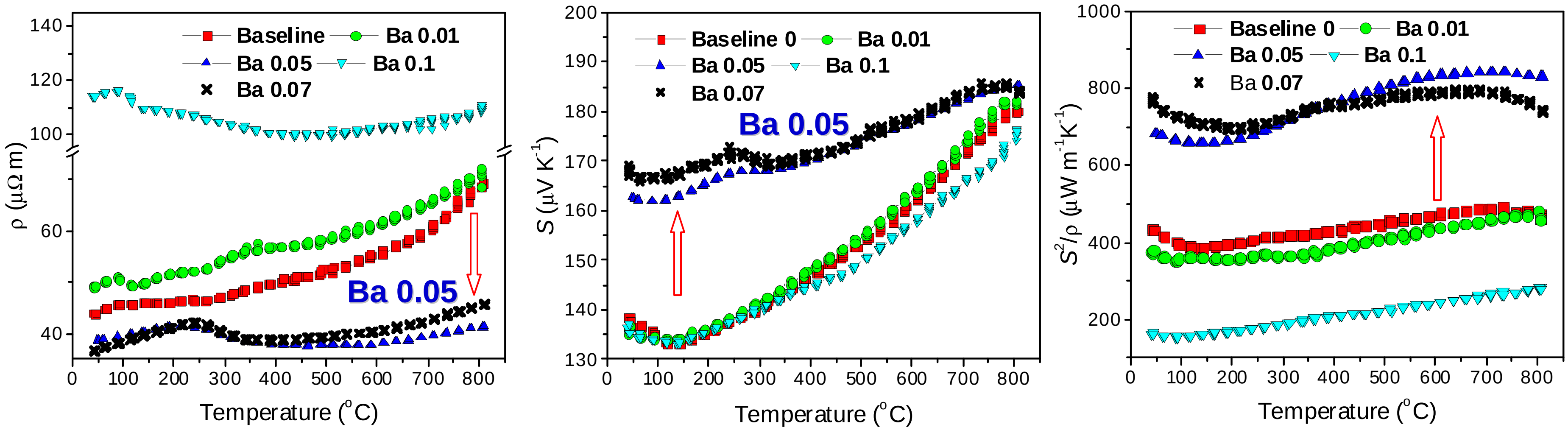
- **Highest Seebeck at RT.**
- **Highest power factor at 800°C.**

- **One of the highest ZT at 800°C for $Ca_3Co_4O_9$.**
- **ZT approached that for p-type SiGe.**

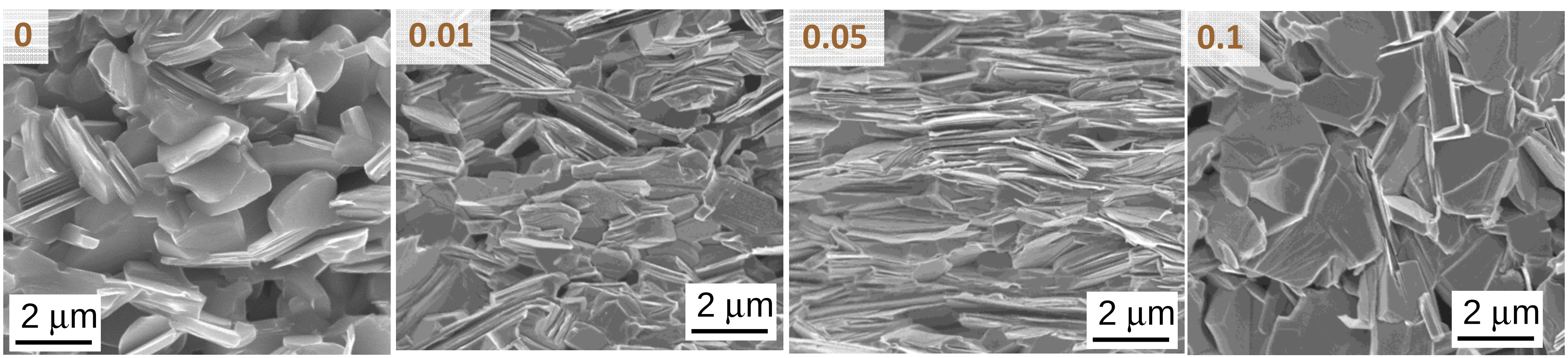
Thermal conductivity decrease as the Ba level increase.
At optimum Ba addition, the peaking ZT of $Ca_3Ba_{0.05}Co_4O_9$ is 0.52.

p-type $Ca_3Co_4O_9$

Non- stoichiometric addition: $Ca_3Co_4Ba_xO_9$ (x: 0, 0.01, 0.05, 0.07, 0.1)



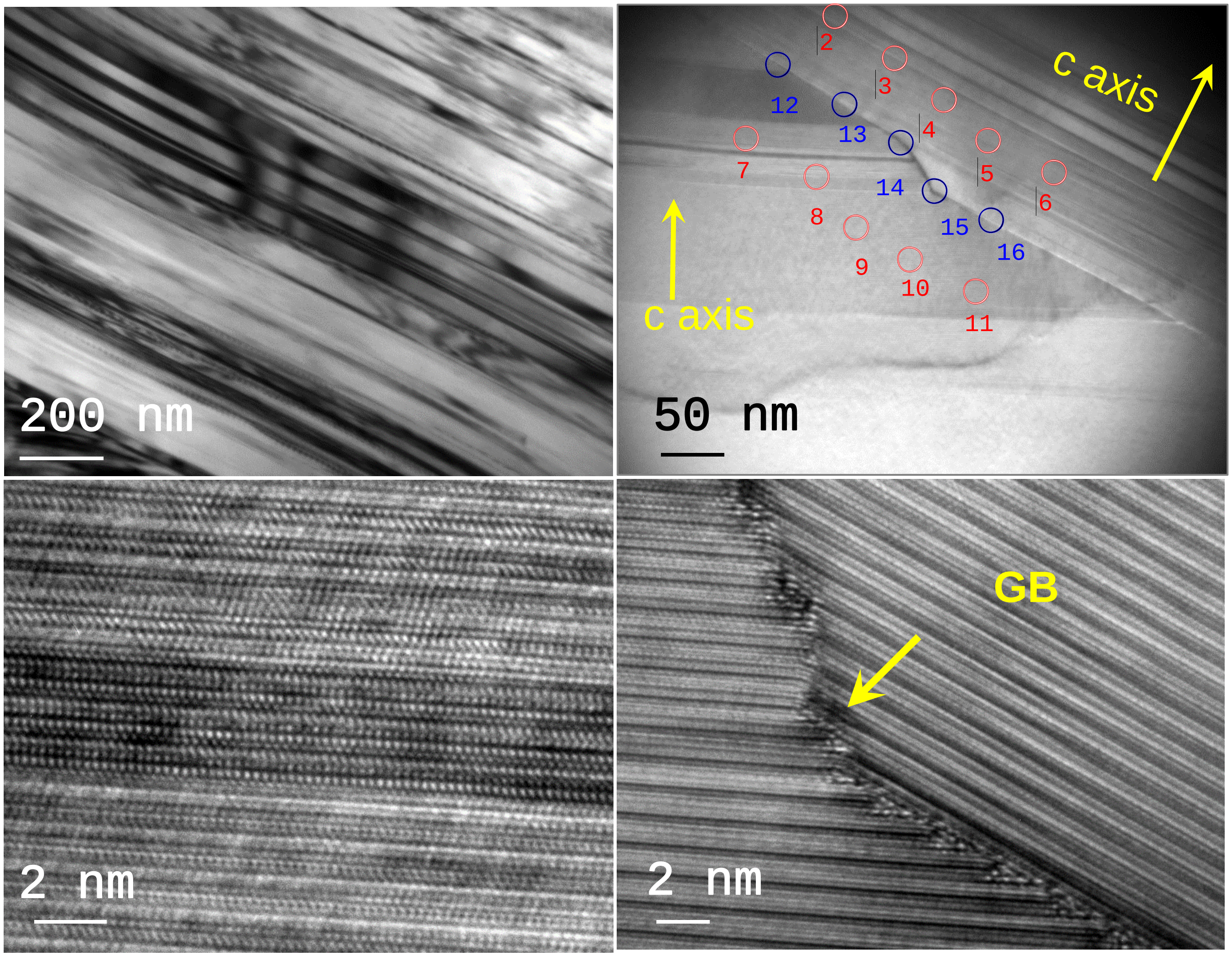
Seebeck coefficient largely increase, large decrease in carrier concentration; at Ba of X=0.05; Resistivity decrease, Metal-semiconductor transition ~200°C; increase in carrier mobility.



- **SEM images of the fractured surface of the pellets.**
- **Significant crystal texture improves with the Ba addition up to Ba 0.05.**

p-type $Ca_3Co_4O_9$

Grain Boundary Ba Segregation in $Ca_3Co_4Ba_xO_9$



	2	3	4	5	6
O K	63.34	63.03	64.02	63.67	64.72
Ca K	16.32	16.44	15.87	16.22	15.68
Co K	20.34	20.53	20.11	20.11	19.6
Ba L	0	0	0	0	0
GB	12	13	14	15	16
O K	67.76	67.1	67.63	67.21	68.69
Ca K	13.35	13.21	13.89	13.51	13.33
Co K	18.48	19.13	18.21	18.68	17.62
Ba L	0.41	0.55	0.27	0.6	0.37
	7	8	9	10	11
O K	67.55	68.7	68.58	67.1	68.88
Ca K	14.09	13.76	13.69	14.34	13.16
Co K	18.36	17.54	17.73	18.56	17.96
Ba L	0	0	0	0	0

Nanostructure of pellets with Ba substitution $Ca_3Ba_xCo_4O_9$ (X=0.05).

- **Nano-lamella is with the thickness of 5-50 nm.**
- **Grain boundaries are free of secondary crystal phases.**
- **Ba segregated to the grain boundary and no solution in the crystal grains.**

Inorganic Chemistry, 54 (18), 9027–9032, 2015

Highlights of results on p-type bulk scale $Ca_3Co_4O_9$:

In the polycrystal $Ca_3Co_4O_9$ that is with strong anisotropy and requires crystal texture to achieve high performance, first time demonstration showing that Ba segregation at the GBs:

- ✓ **Conventional chemical sol-gel route, pressing and sintering.**
- ✓ **Enhance electrical conductivity; Increase the Seebeck coefficients.**
- ✓ **Highest Seebck coefficient (165μv/k) at room temperature and high ZT (0.52) at 800 C, approached that of p type of Si-Ge, was achieved for sample with minute amount of doping Ba.**

Publications in engineering the grain boundaries of thermoelectric $Ca_3Co_4O_9$:

- ➢ **Thermoelectric Performance of Calcium Cobaltite through Barium Grain Boundary Segregation,** *Inorganic Chemistry, 2015, DOI: 10.1021/acs.inorgchem.5b01296*
- ➢ **Phase Evolution and Thermoelectric Performance of Calcium Cobaltite upon High Temperature Aging,** *Ceramics International 2015. DOI information: 10.1016/j.ceramint.2015.05.052*
- ➢ **Grain Boundary Segregation and Thermoelectric Performance Enhancement of Bismuth Doped Calcium Cobaltite,** *Journal of European Ceramic Society, 2015.*
- ➢ **Selective Doping the Lattice and Grain Boundaries and Synergetic Tuning the Seebeck Coefficient and Electrical Conductivity of Calcium Cobaltite Ceramics**, *(to be submitted).*
- ➢ **Nanostructure Origin of Thermoelectric Performance Enhancement of Calcium Cobaltite with Bi non-stoichiometric addition,** *(to be submitted).*
- ➢ **Evidence of High Thermal Stability of Ca3Co4O9 Ceramics At the Temperatures Up to 980°C,** *(to be submitted)*.
- ➢ **Significant Enhancement of Electrical Transport Properties of Thermoelectric Ca3Co4O9+d through Yb Doping,** *Solid State Communications 152 (2012) 1509–1512.*
- ➢ **Effect of precursor calcination temperature on the microstructure and thermoelectric properties of Ca3Co4O9 ceramics,** *J Sol-Gel Sci Technol, DOI 10.1007/s10971-012-2894-4, 64:627–636, 2012.*

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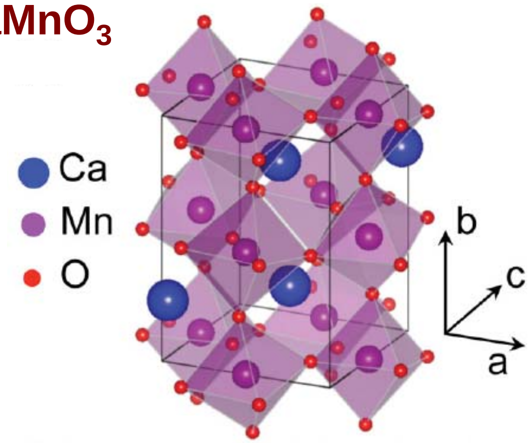
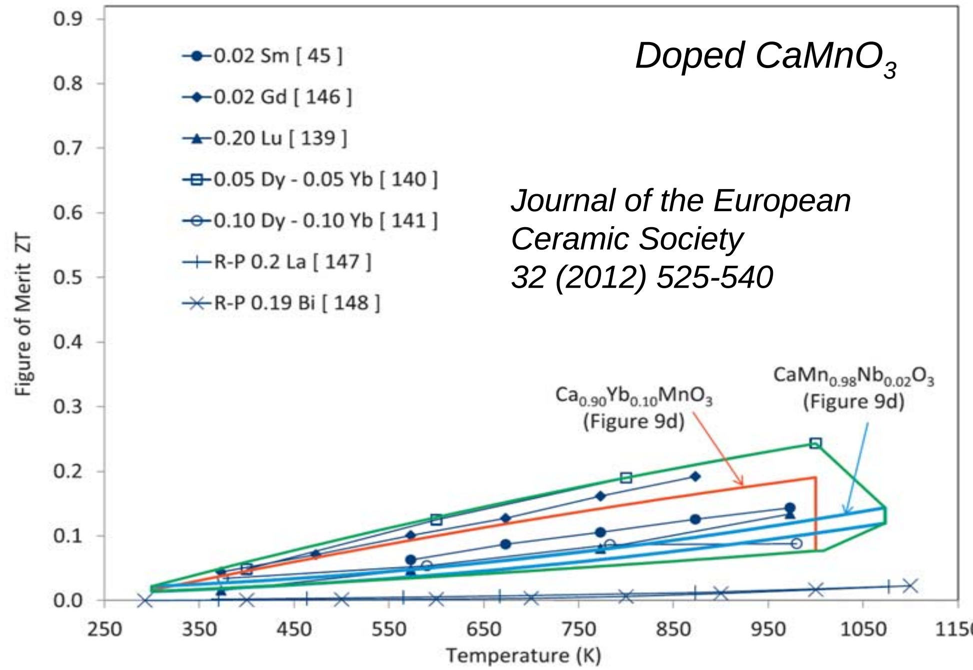
Main issues for the performance of n-type $CaMnO_3$

$CaMnO_3$



$$ZT = \frac{\sigma S^2}{(\kappa_e + \kappa_L)} \cdot T$$

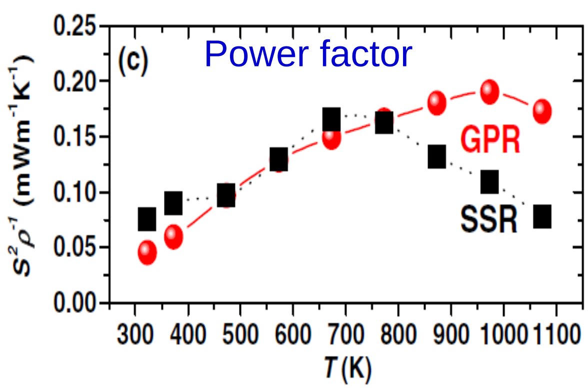


- **ZT < 0.3.**
- **Thermal conductivity:**
  low k ~ 1-2 $Wm^{-1}K^{-1}$.

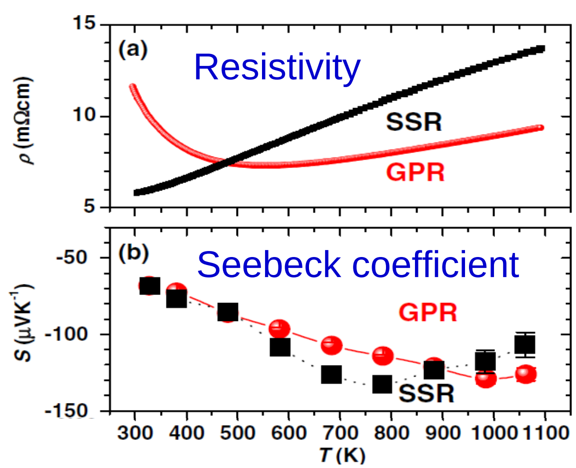
Main issues:

- **High electrical resistivity**
- **Low Seebeck coefficient**
  < 150 - 50 μVK^{-1} .
- **Low power factor**
  < 0.4 $mWm^{-1}K^{-2}$.

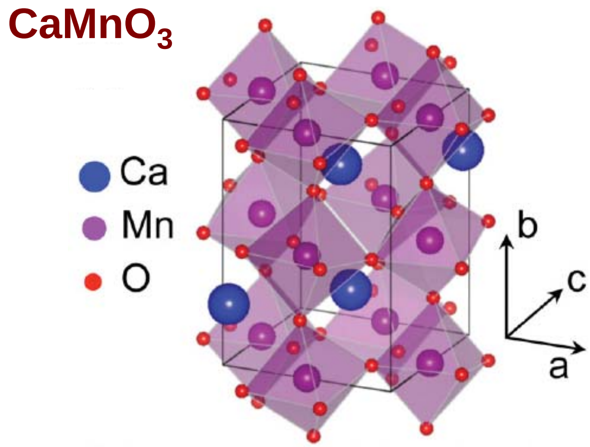
ZT of < 0.3 in literatures for pure & doped $CaMnO_3$.



Japanese JAP v.49 (2010) 071101]



Improving thermoelectric performance of n type $CaMnO_3$



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Main issues:

- High electrical resistivity
- Low Seebeck coefficient
  < 150 - 50 μVK^{-1} .
- Low power factor
  < 0.4 $mWm^{-1}K^{-2}$.

Current work of nanostructure engineering:

Increase the electrical power factor Polycrystal $CaMnO_3$

✓ **Cation doping within the lattice**

- **Bi substitution and addition:**
- Ce substitution
- La substitution
- Sr substitution

✓ **Grain boundary 2nd phase of MO_x:**

- Bi substitution and dopant M addition
- M secondary phase formation at the GBs

Outcome of nanostructure engineering $CaMnO_3$ Of $Ca_{0.97}Bi_{0.03}MnM_{0.04}O_3$: (M-dopant used in this project)

✓ **Low resistivity**

✓ **High Seebeck coefficient**

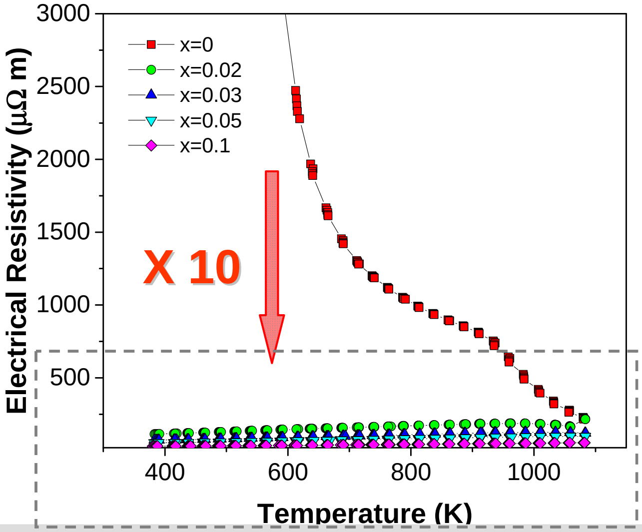
✓ **High electrical power factor**

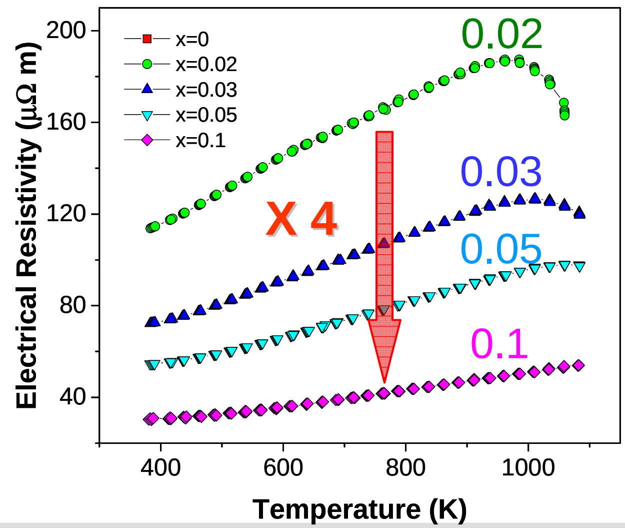
✓ **Record high power factor 0.87 $mWm^{-1}K^{-2}$:**

(factor of ~2 of that highest value currently reported in the literatures).

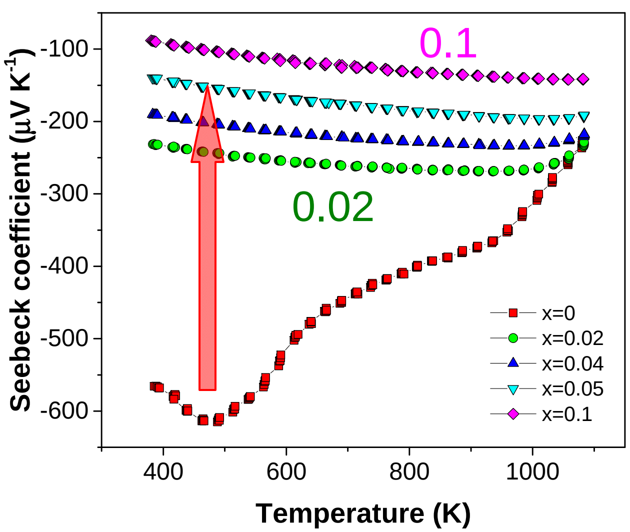
n type $CaMnO_3$

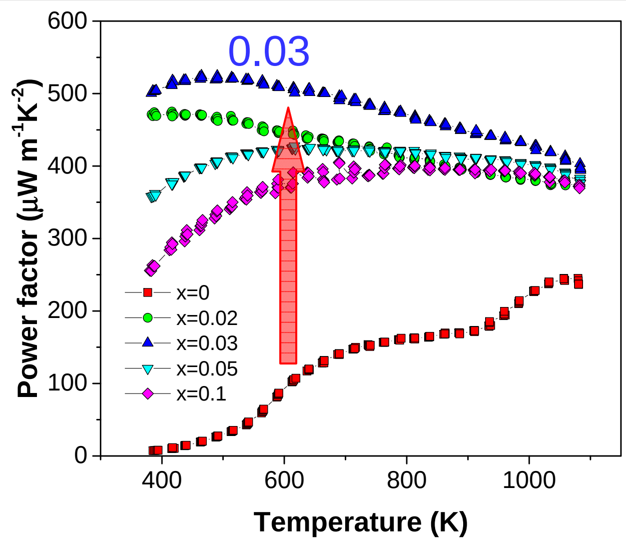
Bi Substitution of Ca: $Ca_{1-x}Bi_xMnO_3$ (x: 0, 0.02, 0.03, 0.05, 0.1)





Significantly reduced electric resistivity with the increase of the Bi doping level.



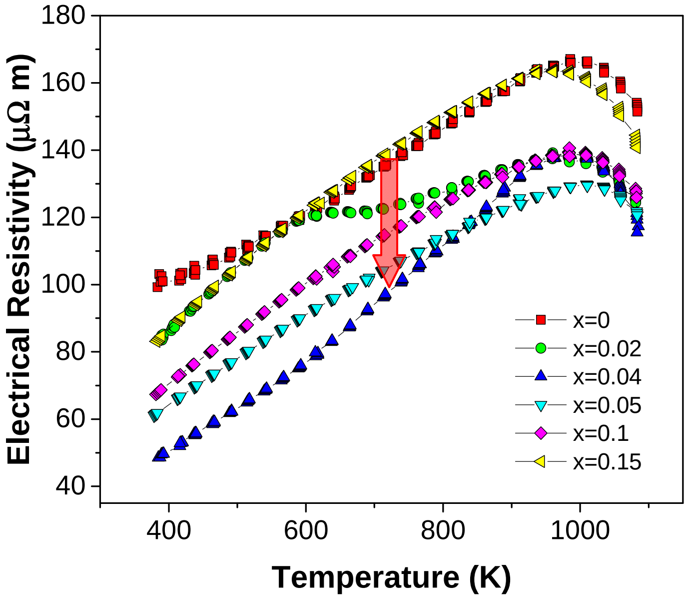


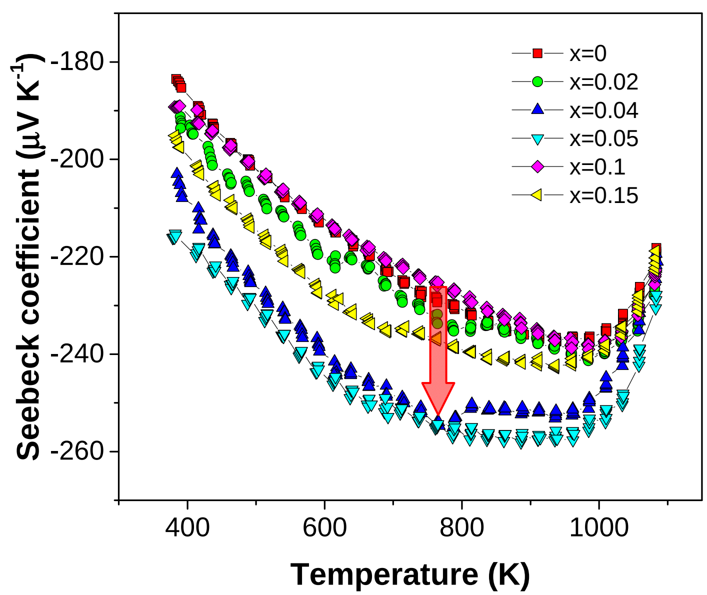
Seebeck coefficient decreases with the increase of the Bi-doping level.

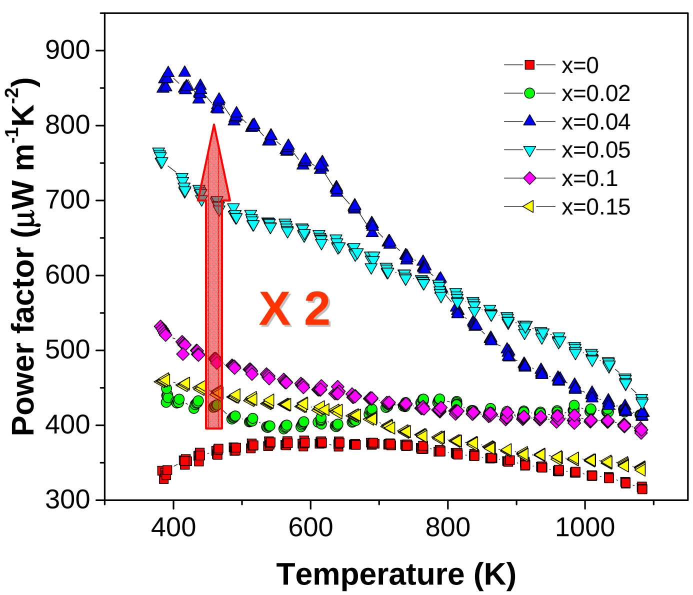
Significant increase of the power factor, as the Bi doping increase to 0.03, in $Ca_{0.97}Bi_{0.03}MnO_3$.

n type $CaMnO_3$

Bi Substitution & M non-stoichiometric addition:







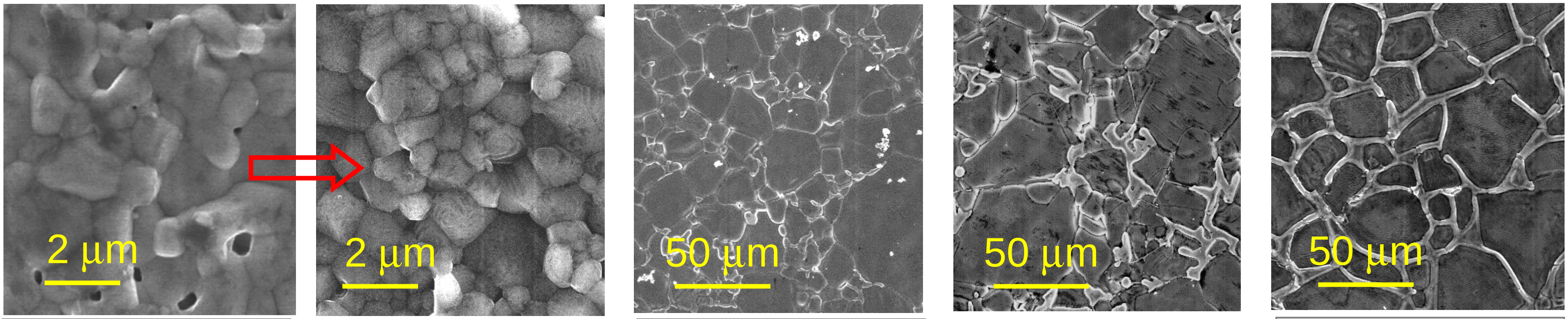
Based on $Ca_{0.97}Bi_{0.03}MnO_3$,

Further enhancement using $Ca_{0.97}Bi_{0.03}MnM_xO_3$.

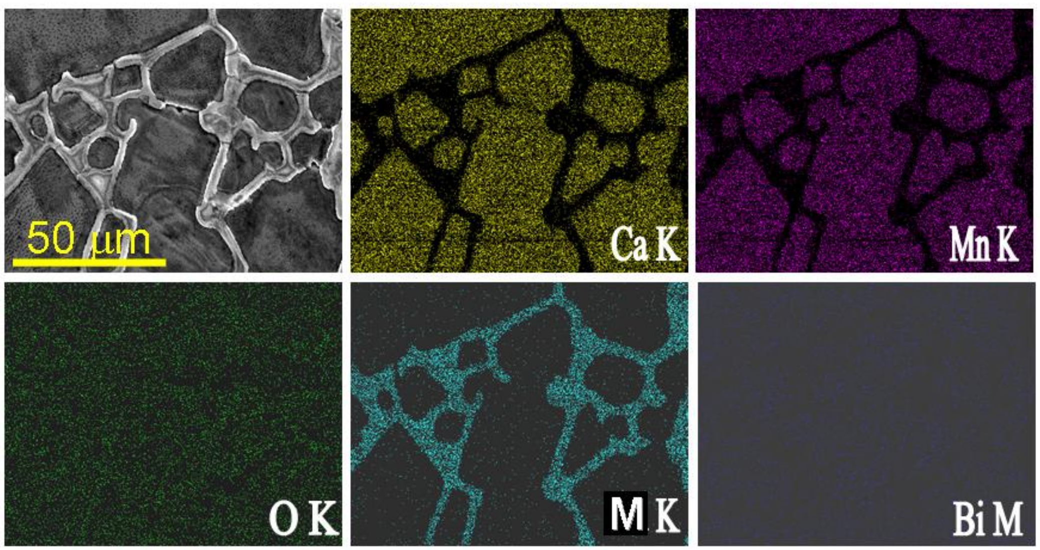
- Further reduced resistivity as dopant M increased to x=0.04.
- Further increased Seebeck coefficient as the dopant M increased to x=0.04.
- Significantly higher power factor of 0.87 $mWm^{-1}K^{-2}$.
- Record high power factor currently. **(factor of ~2 of that currently reported in the literatures).**

n type $CaMnO_3$

Microstructure Changes induced by Bi and M doping



$CaMnO_3$ | $Ca_{0.97}Bi_{0.03}MnO_3$ | $Ca_{0.97}Bi_{0.03}M_{0.02}MnO_3$ | $Ca_{0.97}Bi_{0.03}M_{0.05}MnO_3$ | $Ca_{0.97}Bi_{0.03}M_{0.15}MnO_3$



Bi doping:

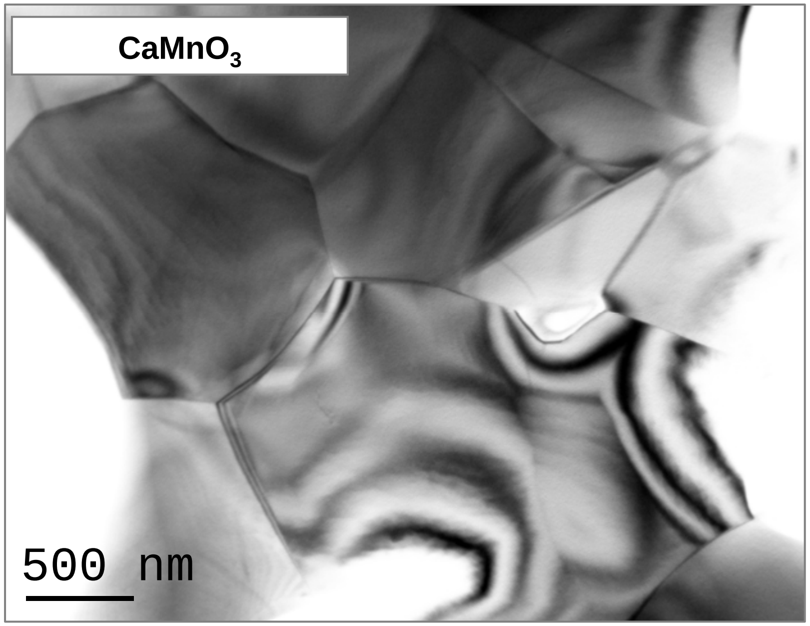
- No morphology & size changes.
- Nano defects changes.

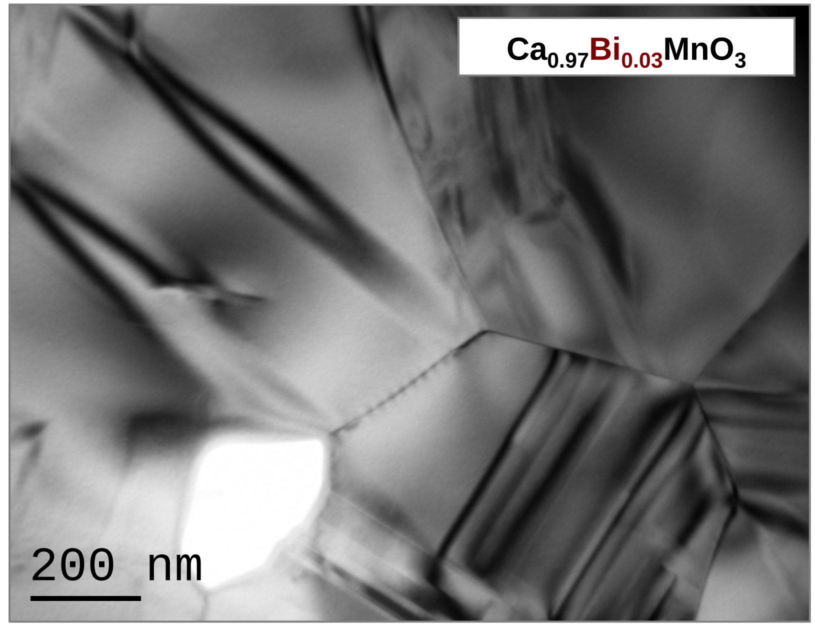
M- addition:

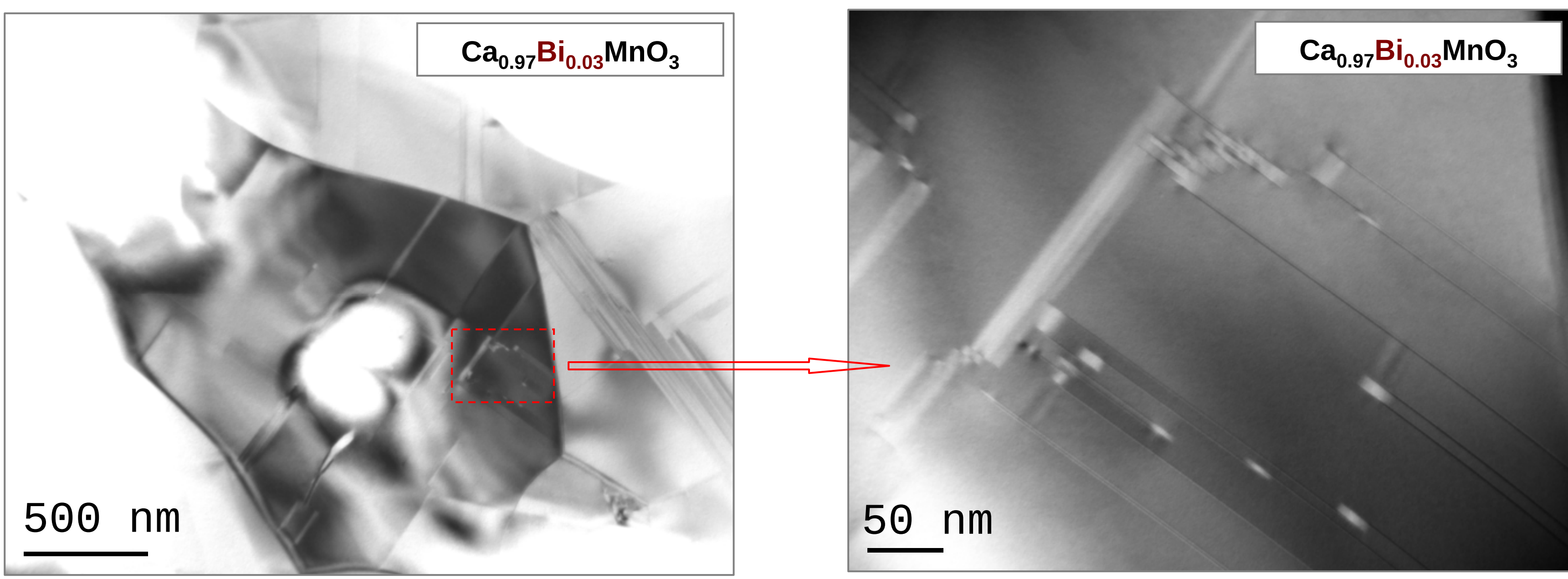
- Increased grain size.
- Formation of grain boundary secondary phases.
- Grain boundary secondary phase is M oxide.

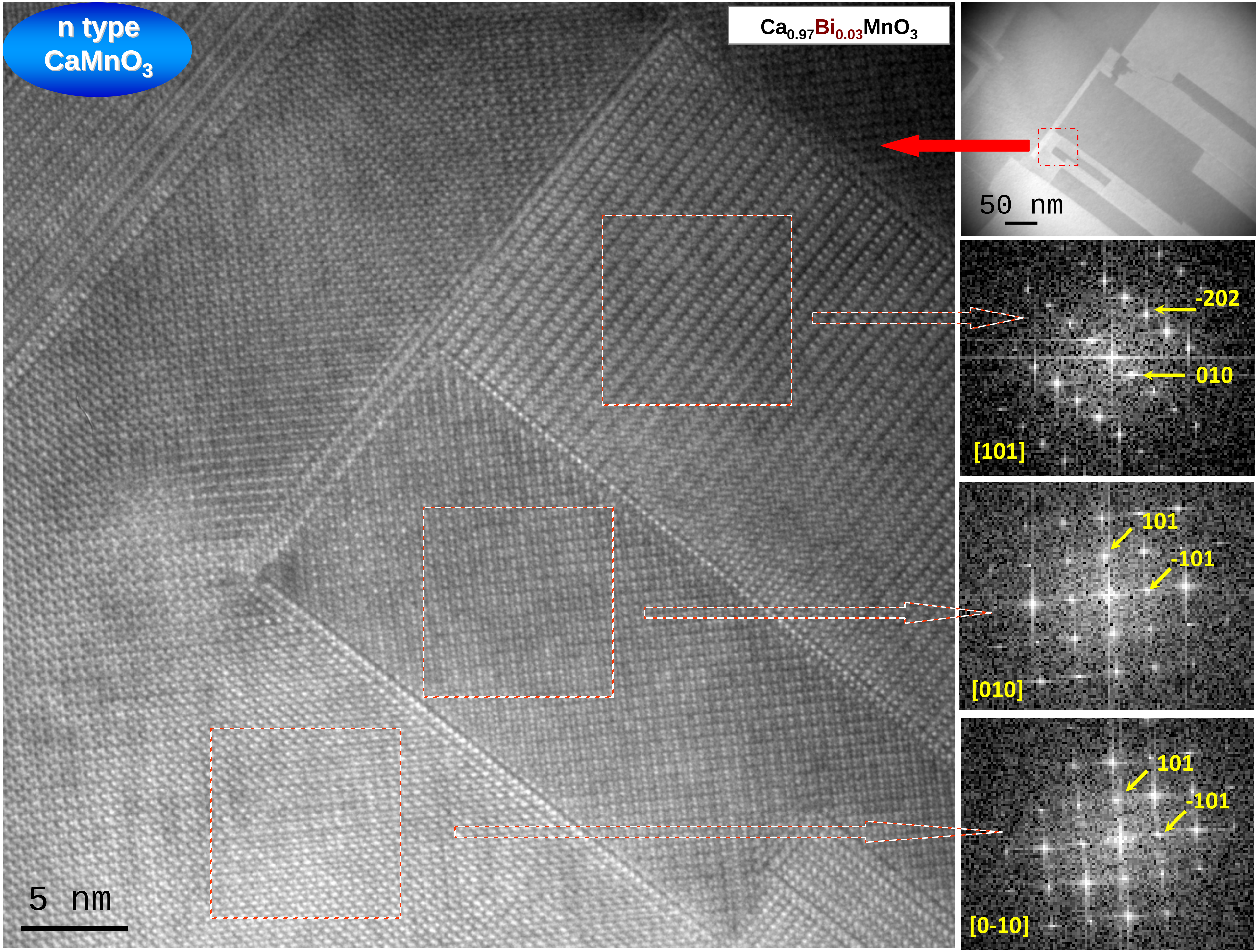
n type $CaMnO_3$

Crystal Defects Changes induced by Bi doping









n type
CaMnO3
Ca0.97Bi0.03MnO3
50 nm
-202
010
[101]
101
-101
[010]
101
-101
[0-10]
5 nm

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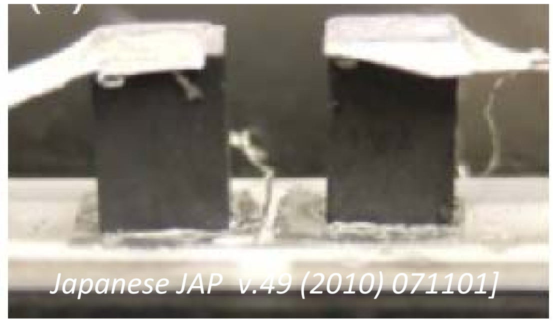
Device

Current work on TE devices



Conventional design (π shaped adopted from that for metals) **of the TE unit couple and modules.**

Current work: All oxide thermoelectric generators with increased power density:

Newly designed TE device for oxide by PIs.

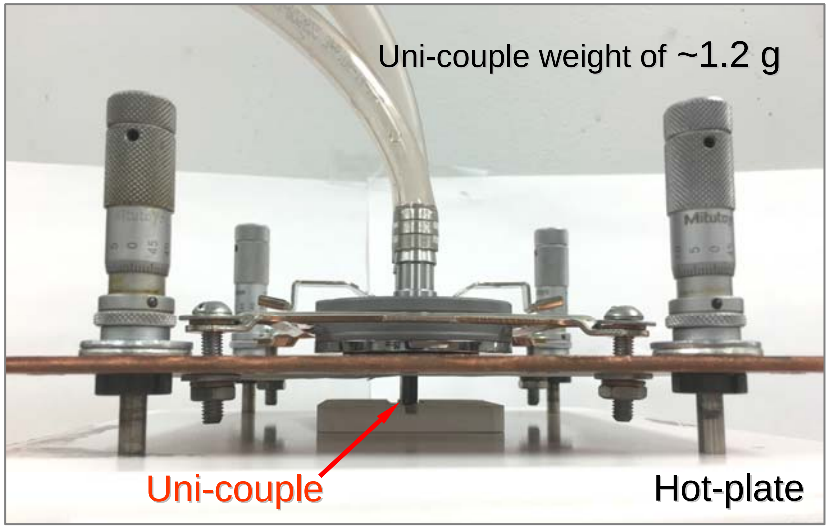
- All oxide ceramic.
- Incorporation of high performance p-type oxide.
- Incorporation of high performance n-type oxide.
- Operation in the high temperature up to 980°C
- Operation directly in the air.

Newly designed devices for oxides features:

- Compact integrated design.
- Minimal-sized, closely-packed insulating for better thermal management and reduction of the overall-size and weight of the device.
- Minimal sized electrical interconnection.
- Significantly reduced size and weight of the entire device.
- Easy to fabricate in anticipation of mass production, with a high potential for use in large-scale applications.

Device

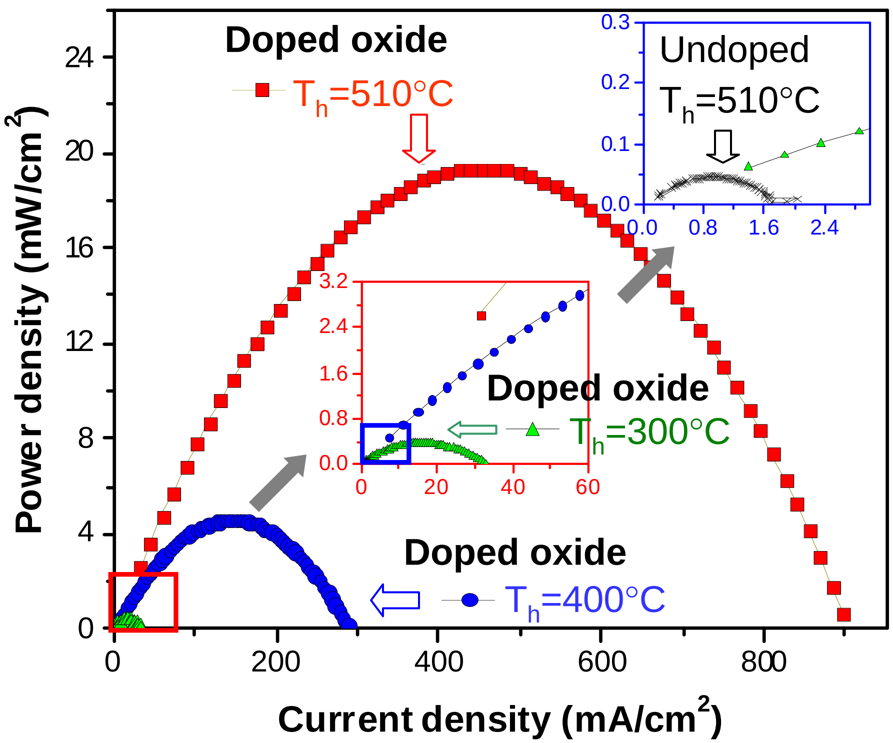
Oxide Thermoelectric Generator with Compact Design



Hot plate	T_h	T_c	ΔT
510 °C	498°C	127°C	371°C
400°C	400°C	92°C	308°C
300°C	310°C	53°C	257°C

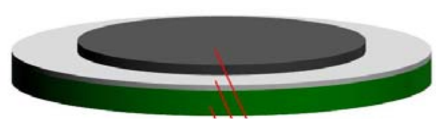
Undoped: $CaMnO_3$ & $Ca_3Co_4O_9$

Doped: $Ca_{0.97}Bi_{0.03}MnM_{0.04}O_3$ & $Ca_3Co_4Ba_{0.05}O_9$



Unicouple: Effect of Materials Optimization

- Optimization of materials results in **> 400 times performance enhancement** for the unicouple.
- Without device level optimization, at T_h=510°C, unicouple power density P is ~0.02 w/cm^2.
- Un-optimized unicouple **(~50% of weight** of SOFC button) performance at **500°C in air** is **~10% of SOFC** operated at **750°C** fuel with **H_2**.

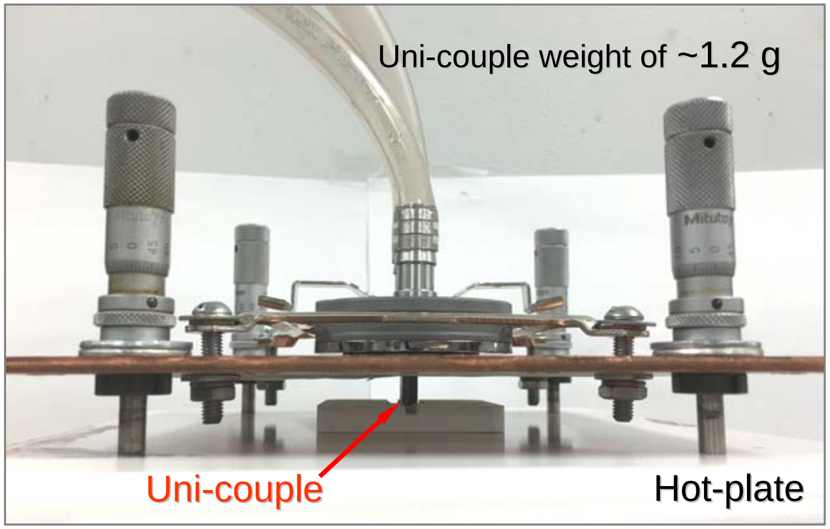


Solid Oxide Fuel Cell

Button cell weight of **~2.3 g**

750°C /48 h	i (A/cm^2)	P (W/cm^2)
at 0.8 V	0.315	0.252

Oxide Thermoelectric Generator with Compact Design



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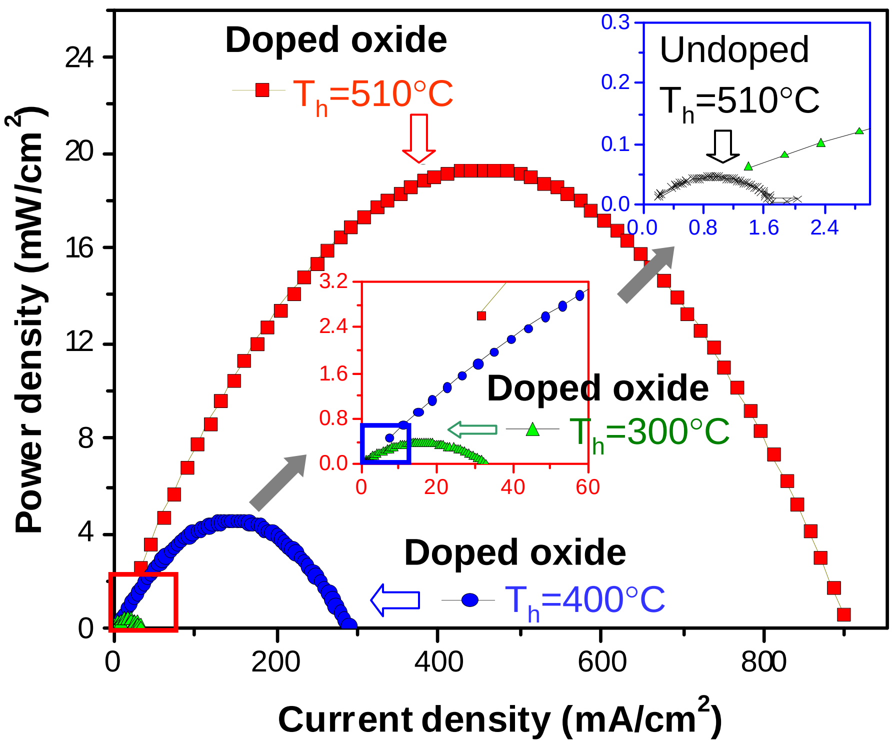
❖ Power density increased ~4 times as T_h raises from 400°C to 510°C. Higher T_h, better performance.

❖ **Performance could be much improved.**



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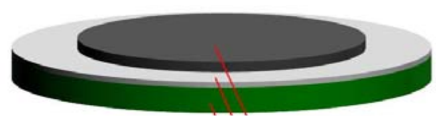

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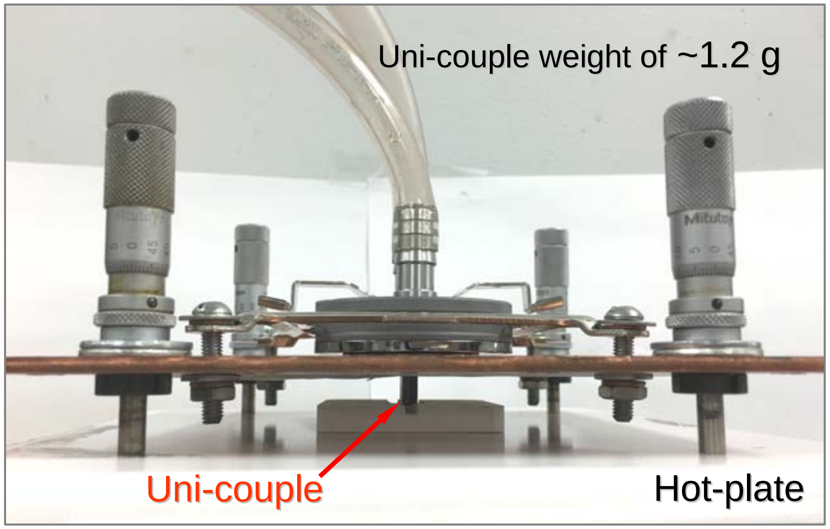

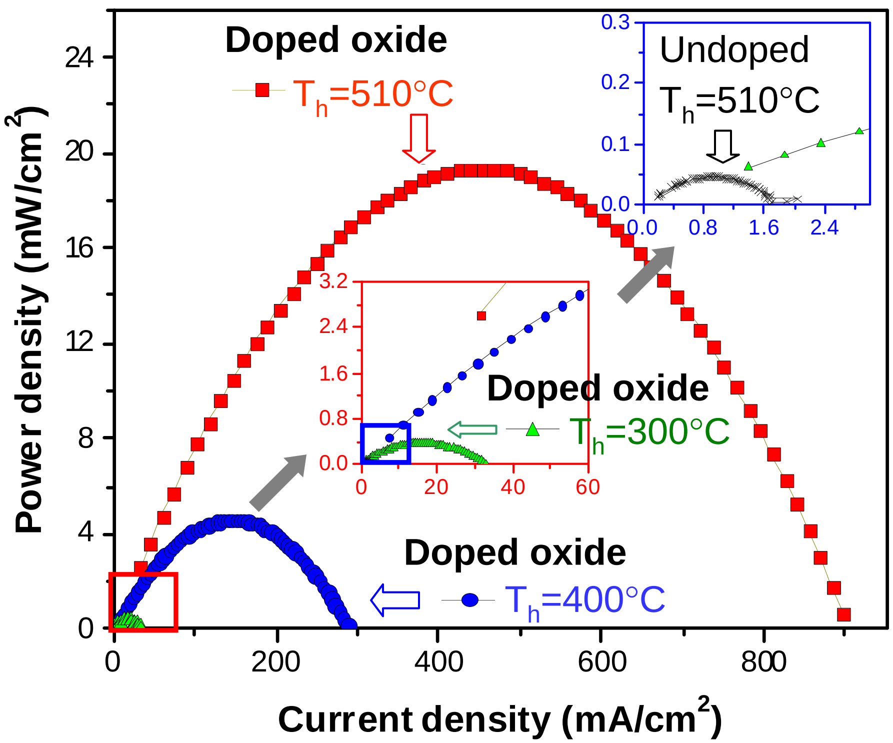

Further optimization of Generator:

- Further improved the materials performance.
- Change Leg dimensions.
- Optimize electrical connection.
- Control temperature difference.
- Fabricate Module (small scale ~10 unicouples).

Unicouple: Effect of Materials Optimization

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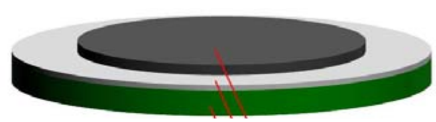

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Summary and Future Plans

Materials development of n-type $CaMnO_3$:

For polycrystal $CaMnO_3$ that is stable at temperature of 1300°C and stable in air, electrical performance could be significantly improved:

- ✓ Through the nanostructure engineering of dopants stoichiometric substitution and grain boundary secondary phase formation.
- ✓ In the case of Bi and M co-doping:
  - Bi in the lattices; dopant M mostly segregated at the grain boundaries.
  - Systematic nanostructure changes induced by Bi doping
  - Dramatic electrical performance enhancement.
  - Record high (factor of ~2 of that highest value currently reported in the literatures) electrical power factor for polycrystal $CaMnO_3$

Novel device of all oxide thermoelectric generator:

- ✓ All oxide thermoelectric generator.
  - Compact design, significantly reduced size, weight, easy scale-up.
  - Operation in the high temperature up to 980°C in air directly.
  - Unicouple performance increased by a factor of 400 by materials performance enhancement.
  - Non-optimized unicouple (with the ~50% weight of SOFC button cell) operated at 500°C is with the 10% power density of SOFC button cell operated at 750°C with H_2.
  - Unicouple performance could be much further improved.

Summary and Future Plans

Future work:

- **Continuing working on the performance improvement of n-type $CaMnO_3$ ceramics.**
- **Optimization of the uni-couple geometry and controlling temperature difference.**
- **Fabrication of thermoelectric module.**
- **Integration of the thermoelectric modules into the power generation systems.**

Publications on n-type $CaMnO_3$ thermoelectric materials & device:

- **Significant Electrical Performance Enhancement of Thermoeletric $CaMnO_3$ Ceramics Induced by Synergetic Cation Substitution and Cation Addition.** *(Ready for submission).*
- **Effect of Grain Boundary Secondary Phase on the Thermoelectric Performance of $CaMnO_3$ Ceramics.** *(Ready for submission).*
- **Systematic Thermoelectric Performance Improvements of $CaMnO_3$ Through Bi doping.** *(In preparation).*
- **Operation dependence of Performance and Nanostructure of $CaMnO_3$ ceramics***.* *(In preparation).*
- **Compact all oxide thermoelectric devices for high temperature power generation.** *(In preparation).*

Acknowledgement

National Energy Technology Laboratory

DOE Award – FE0024009

Program Manager: Richard J. Dunst