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

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DOE Award – FE0024009

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Overview

➢ Highlight of Current Results

- Significant thermoelectric oxide performance enhancement achieved by this project
- Thermoelectric device power increase by a factor of ~400, due to materials improvement

➢ Background Introduction

- Waste heat & advantages of thermoelectric generator
- State-of-the-art thermoelectric device and materials
- Challenges for the development of oxide thermoelectric materials and device

➢ Project Objectives and Approaches

- Project objectives
- Materials processing, property measurement & nanostructure characterization

➢ p & n Type Thermoelectric Oxide and Generator Developed in PI's Group

- Available p-type thermoelectric oxide
- Ongoing work of n-type thermoelectric oxide with record high energy conversion efficiency
- Novel scalable all oxide thermoelectric generator with compact design

➢ Summary and Future Work

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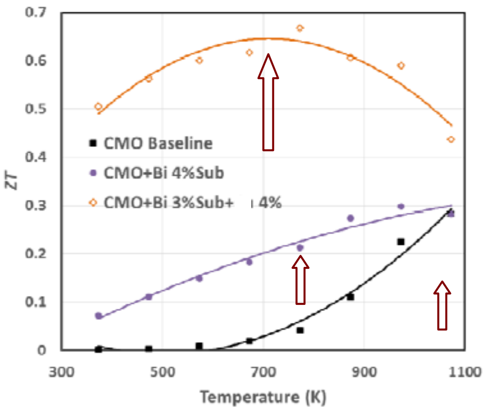
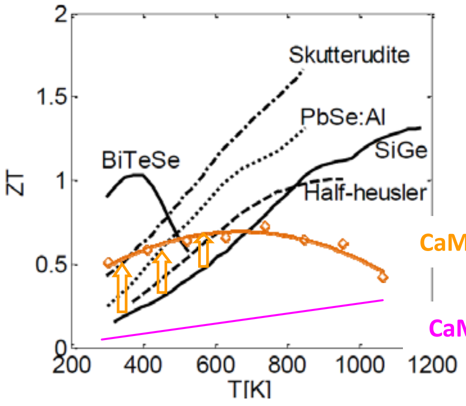


3rd step Improvement

2nd step Improvement

1st step Improvement



$CaMnO_3$ from this project

$CaMnO_3$ in literatures

❖ Thermoelectric device made of bulk scale oxide: p-type based on $Ca_3Co_4O_9$, n-type based on $CaMnO_3$.

- Functioning from room temperature to 980°C, in air directly.
- Resistance to corrosive fluxing agents (e.g, Calcium), oxide particulate, & temperature variation.

❖ n-type bulk ceramics based on $CaMnO_3$ developed through this project.

- Achieved highest (among literatures) energy conversion efficiency ZT value of 0.67 at 773K;
- ZT of 0.67 is factor of 2 of highest reported value in the literatures of ZT~ 0.3.
- High plateau of the ZT, from room temperature to 1073K; Outperform SiGe from RT to 773K.

- Low cost conventional solution based processing, no need of specialized costly micro-fabrication.
- Low cost oxide materials, in comparison with the state-of-the-art thermoelectric SiGe and Bi-Te.

Bulk scale oxide ~ 30$/Kg; Bulk scale SiGe ~ 600$/Kg; Bulk scale Bi-Te ~100$/kg.

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Background: Waste Heat & Its Recovery

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

Temperature Range and Characteristics for Industrial Waste Heat

Waste Heat Source	Temperature Range (° F)	Temperature Range (° C)
Furnace or heating system exhaust gases	600 - 2000	**316 - 1093**
Gas (combustion) turbine exhaust gases	900 - 1100	**482 - 593**
Jacket cooling water	190 - 200	**88 - 93**
Exhaust gases (for gas fuels)	900 - 1100	**482 - 593**
Hot surfaces	150 - 600	**66 - 316**
Compressor after-inter cooler water	100 - 180	**38 - 82**
Hot products	200 - 2500	**93 - 1371**
Steam vents or leaks	250 - 600	**121 - 316**
Condensate	150 - 500	**66 - 260**
Emission control devices - thermal oxidizers, etc.	150 - 1500	**66 - 816**

Waste Heat Recovery Systems by Temperature Range

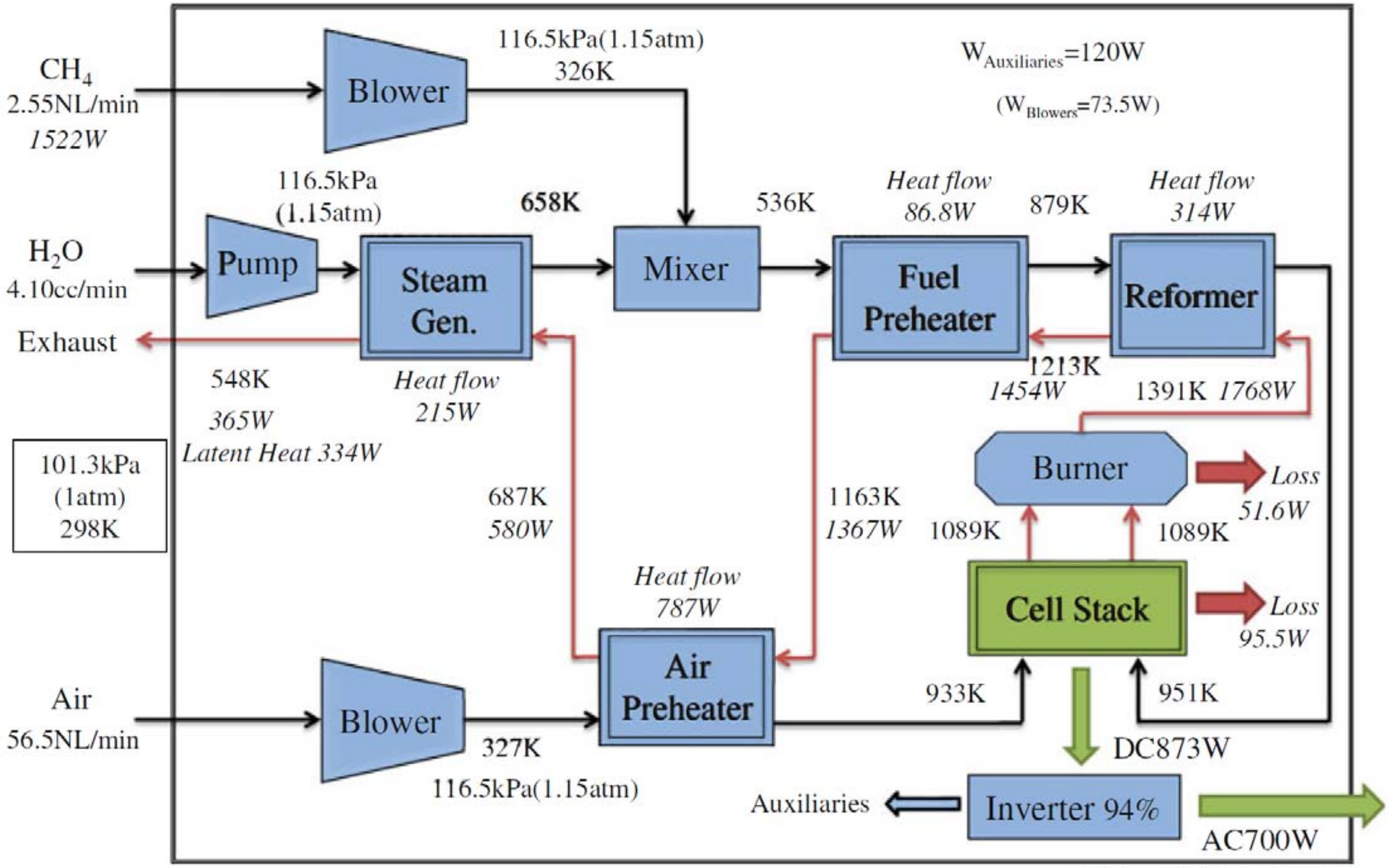
Ultra-High Temperature > 871° C	High Temperature 649° C to 871° C	Medium Temperature 316° C to 649° C	Low Temperature 121° C to 316° C	Ultra-Low Temperature < 121° C

DOE-2015 report on "Waste Heat Recovery Technology Assessment":

Waste heat is NOT recovered in two temperature ranges: Ultra-low (< 121°C) and ultra-high (> 871 °C), due to issues associated with technology, materials, economics.

https://energy.gov/sites/prod/files/2015/02/f19/QTR%20Ch8%20-%20Waste%20Heat%20Recovery%20TA%20Feb-13-2015.pdf

Background: Waste Heat in Solid Oxide Fuel Cell (SOFC) System

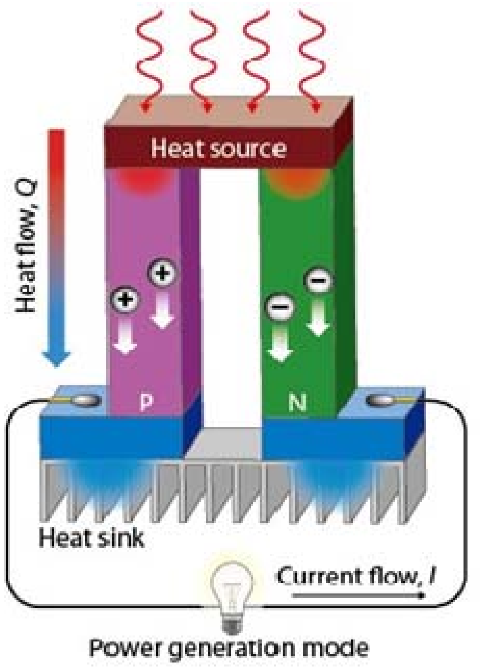


Journal of ELECTRONIC MATERIALS, Vol. 42, No. 7, 2013

- **SOFC technology has been extensively investigated over the past 20 years.**
- **Complete stacks are in place (for example: 700 W AC systems for residence in Japan).**
- **SOFC operates at high temperatures of ~800°C, over extended period of >40,000 hours.**
- **Electricity is the desired product, and heat is surplus.**

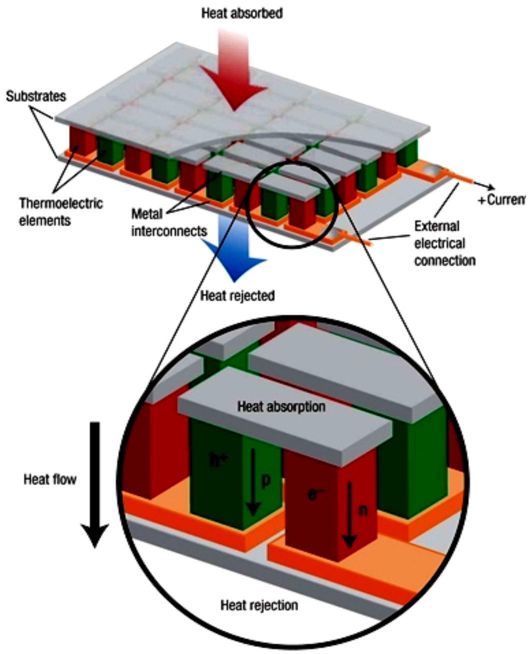
Background: Waste Heat Recovery & Thermoelectric (TE) Generator

Thermoelectric 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)

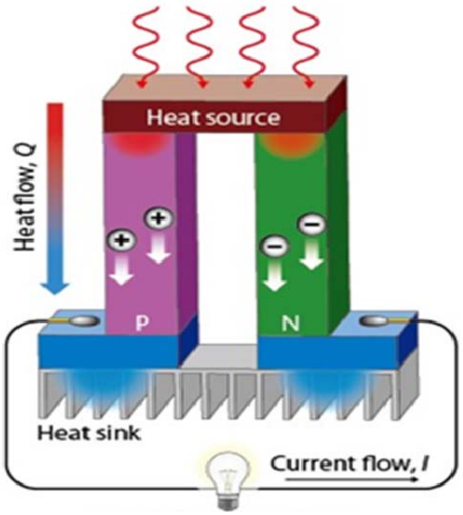
Advantages of TE generators

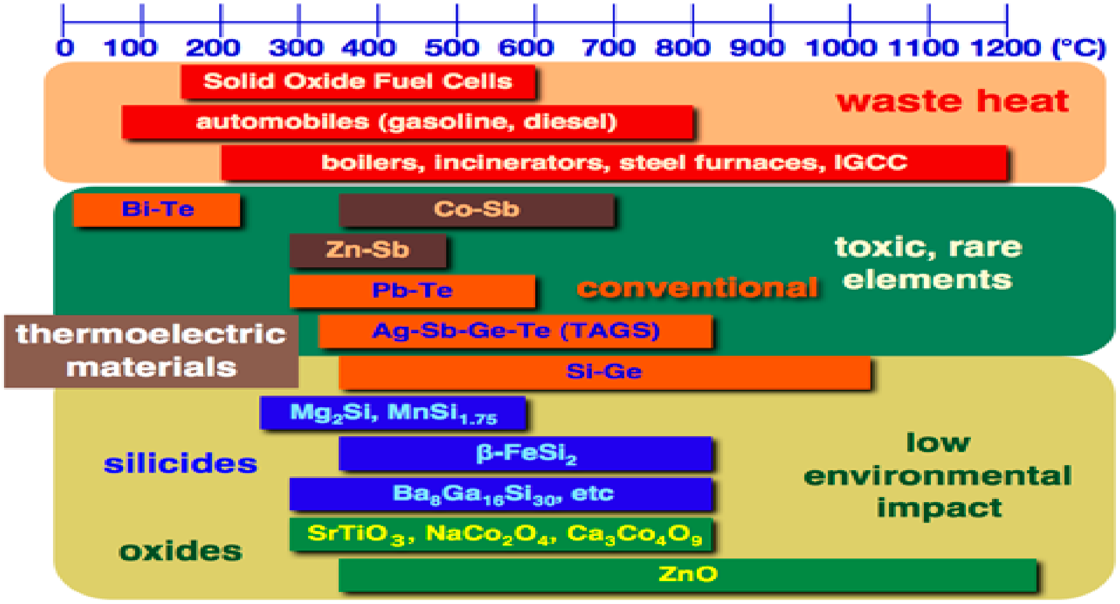
- ✓ **No moving parts, silent.** (unlike gas turbine engines).
- ✓ **Maintenance-free operation.** (without chemical reactions compared to fuel cells).
- ✓ **Long life capability.**
- ✓ **Function over a wide temperature range.**
- ✓ **Position independent**.
- ✓ **Environmental friendliness.**

Importance of TE generators to the DOE Crosscutting programs:

- ✓ **Powering the wireless sensors & devices at high temperatures and harsh environments.**
- ✓ **Development of ceramic heat-exchanger and recuperators with dual function of waste heat recovery and power generation.**

Background: Thermoelectric Materials





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

Thermoelectric Oxides:

- ➢ p-type $Ca_3Co_4O_9$ and n-type $CaMnO_3$.
- ➢ Light weight, non toxic, low cost.
- ➢ High thermal stability in air.

Thermoelectric Oxides:

Largely neglected until recently, due to low thermoelectric energy conversion efficiency.

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

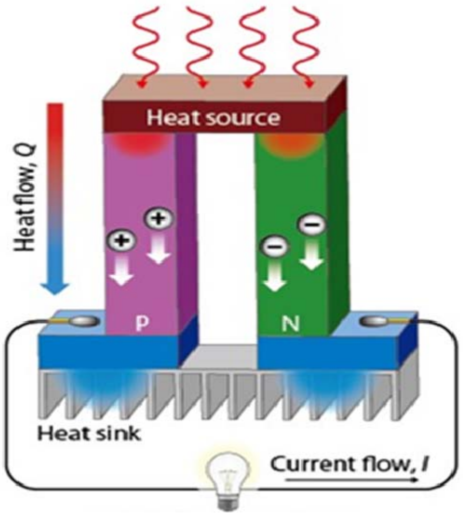
- High energy conversion efficiency
- Skutterudite $La_{0.9}Fe_3CoSb_{12}$; Half-Heusler alloys
- Clathrates; Antimonides Zn_4Sb_3

Heavy-metal-based materials:

NOT good for operating at high temperatures:

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

Background: Energy Conversion Efficiency & ZT for Mateirals



$$\eta = \frac{T_h - T_c}{T_h}\,\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_c/T_h}$$

T_h, T_c: temperatures on hot & cold sides; $T = (T_h+T_c)/2$

***ZT*, Figure of merit:**

- Dimensionless value; material's conversion efficiency.
- ZT~1 (~10% efficiency) for practical use.

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

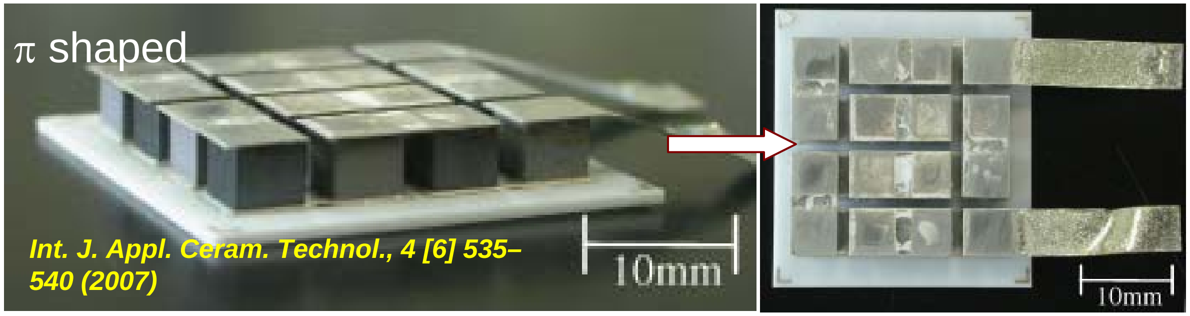
S: absolute Seebeck coefficient $\Delta V/\Delta T$
σ: Electrical conductivity ($1/\rho$)
ρ: Electrical resistivity
σS^2: Power Factor
$(\kappa_e + \kappa_L) = k_{total}$, Total thermal conductivity,
$k_{total} = \lambda C_p \rho$
C_p: specific heat, λ: thermal diffusivity, ρ: density.

Peaking *ZT* value for best heavy metal based TE materials: *ZT* > 1. (~10% efficiency).

Low *ZT* value reported for bulk oxide in literatures: $Ca_3Co_4O_9 < 0.3$; $CaMnO_3 < 0.3$

Oxide TE device: Urgent need to improve the *ZT* for thermoelectric bulk ceramics.

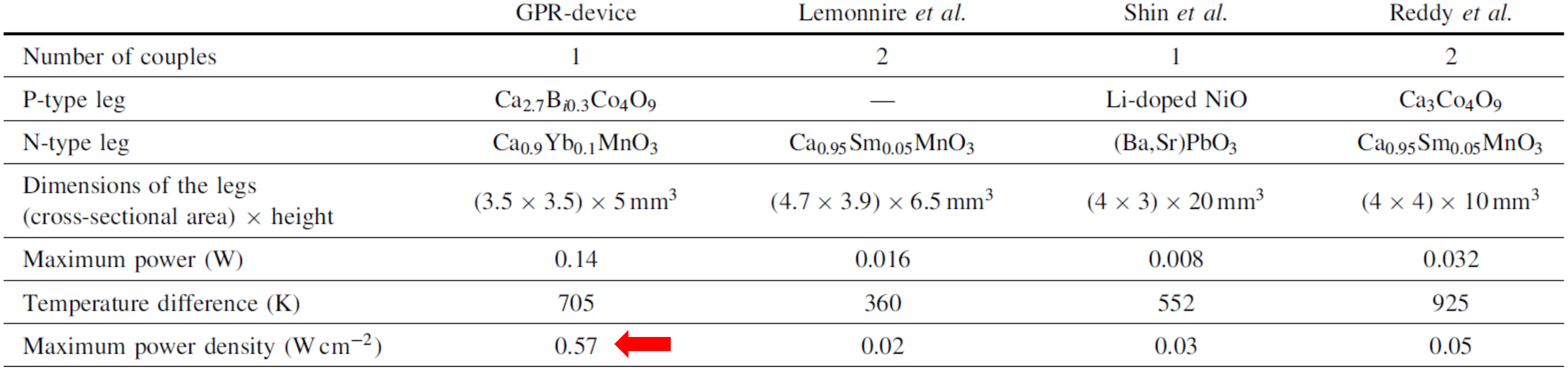
Background: Device Level Challenges for Oxide TE Generators



Int. J. Appl. Ceram. Technol., 4 [6] 535–540 (2007)

Energy Conversion and Management 52 (2011) 335–339

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	$Ca_{2.7}B_{i0.3}Co_4O_9$	—	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 "π shaped" devices: (adapted from conventional metal based devices).

- **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).

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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.

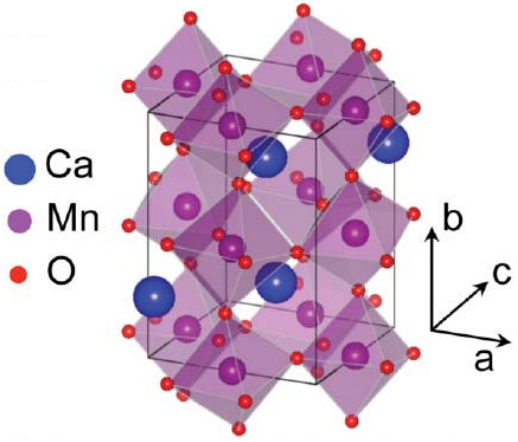
Approaches:

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

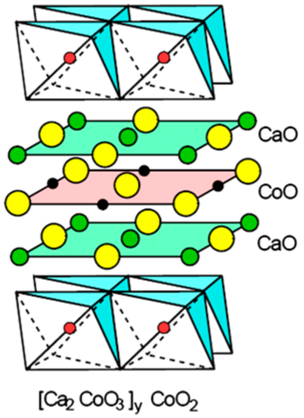
Project Objectives and Target Materials Systems

High Temperature Waste Heat in Solid Oxide Fuel Cells (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.
- TE generator can be placed in **air-preheater**, **steam generator**, and **exhaust outlet**.
- **TE-heat exchanger** is promising, but **lack of cost-effective high performance TE materials**.
- Currently suggested TE materials for **TE-heat exchangers** include **SiGe, Zn_4Sb_3** that are facing problems of **high cost, oxidation in air** and **low thermal stability at over 250ºC**.



n type: $CaMnO_3$



p type $Ca_3Co_4O_9$

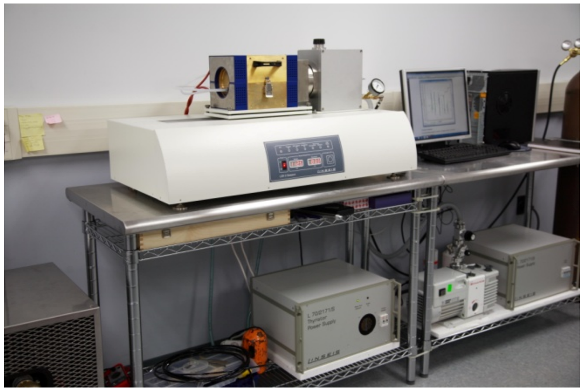
$Ca_3Co_4O_9$ & $CaMnO_3$ for power systems:

- High thermal stability functioning from room temperature to 980°C, in air directly.
- Resistance to corrosive fluxing agents (e.g, Calcium), oxide particulate, & temperature variation.
- Low cost, and light weight, non toxic.

Challenges of oxide application of high temperature TE-heat exchanger:

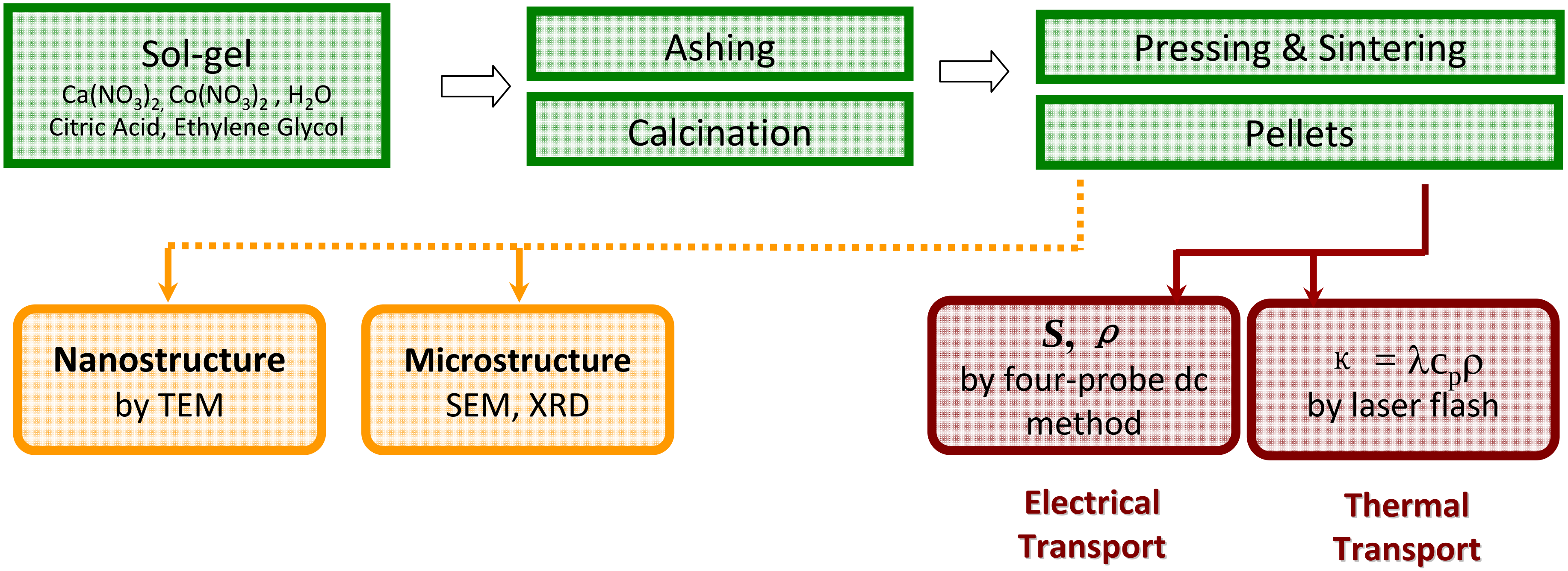
- **Materials Level:** Need to enhance energy conversion efficiency of polycrystalline oxide.
- **Device level:** Need better design of the all oxide TE generators.

Lab and Equipment for Thermoelectric Materials & Device



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

Methodology and Routine Lab Work Flow



Sol-gel

$Ca(NO_3)_2$, $Co(NO_3)_2$, H_2O

Citric Acid, Ethylene Glycol

Ashing

Calcination

Pressing & Sintering

Pellets

Nanostructure

by TEM

Microstructure

SEM, XRD

S, ρ

by four-probe dc method

$\kappa = \lambda c_p \rho$

by laser flash

Electrical Transport

Thermal Transport

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

Even for 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**

Precursor Powder Processing and Sintering of Pellets

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

→

Ashing

Calcination

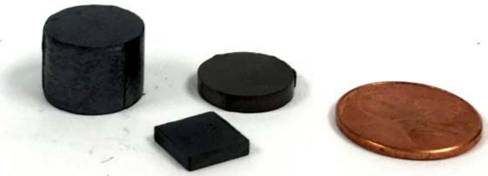
→

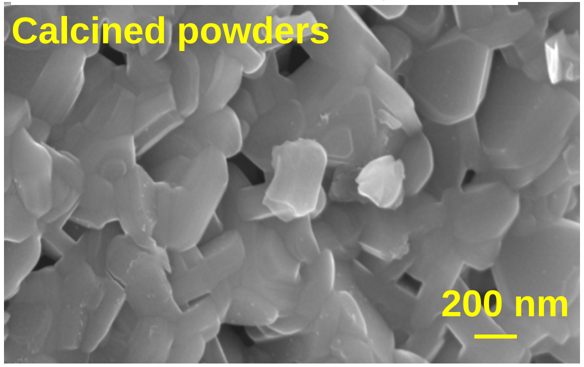
Pressing & Sintering

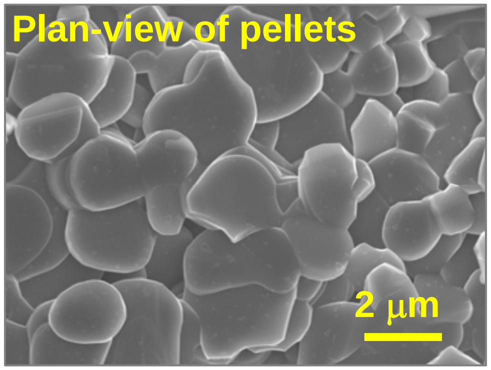
Pellets

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.

Advantages:

- ✓ Chemistry of bulk oxide is uniform, can be controlled accurately.
- ✓ Simple, fast, low cost processing.
- ✓ No need of costly specially micro fabrication.

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Low ZT of Polycrystalline $Ca_3Co_4O_9$ Ceramics Reported in Literatures

Figure of merit ZT of $Ca_3Co_4O_9$: Single crystal ZT ~ 1; Polycrystal low ZT of ~0.3 reported. **Why ?**

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

S: absolute Seebeck coefficient $\Delta V/\Delta T$
σ: Electrical conductivity ($1/\rho$)
ρ: Electrical resistivity
σS^2: Electrical power factor
$(\kappa_e + \kappa_L) = k_{total}$, Total thermal conductivity,
total = $\lambda C_p \rho$
C_p: specific heat, λ: thermal diffusivity, ρ: density.

Strongly inter-correlated Carrier concentration n, Electrical Resistivity ρ, Seebeck Coefficient S.

$$\rho = \frac{1}{\sigma} = \frac{1}{\mu n e}$$

ρ – Electrical Resistivity
μ – Carrier Mobility
n – Carrier Concentration

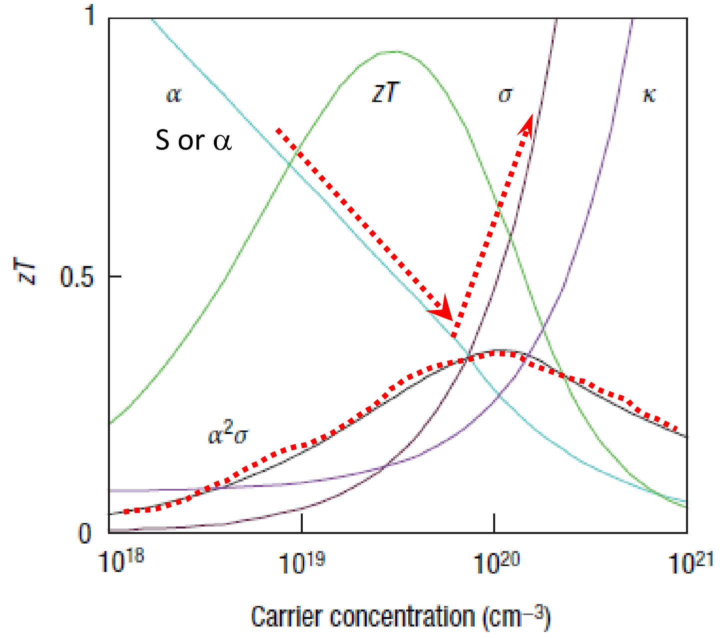
$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

Parameters strongly correlated through "n"

When n ↑ ⇨ σ ↑
⇨ S ↓

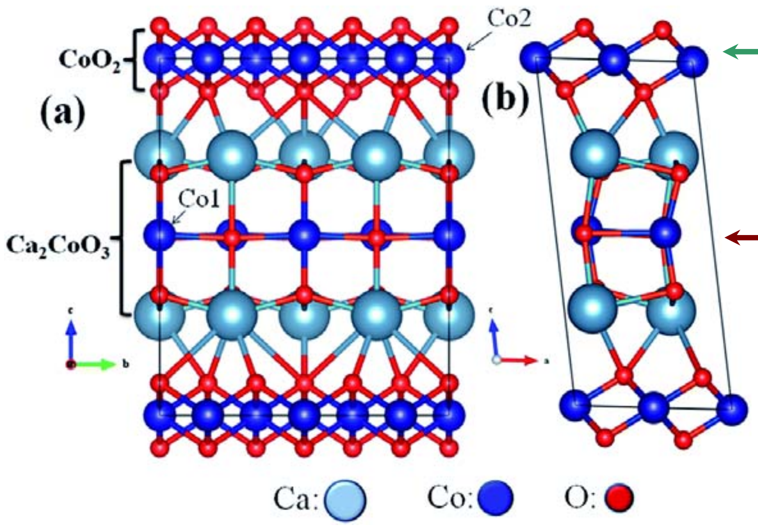
De-coupling parameters to increase S & σ

Goal: n ↓ ⇨ S ↑
μ ↑ ⇨ σ ↑



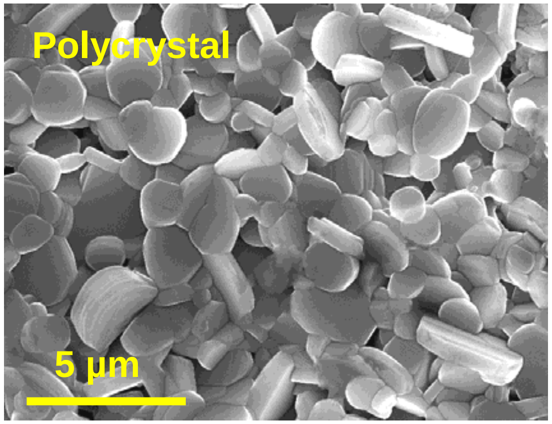
Nature Materials 7, 105 114 (2008)

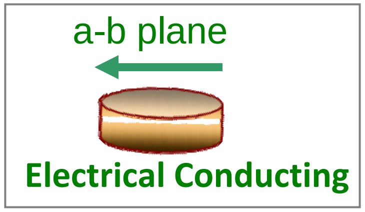
Large Anisotropy of $Ca_3Co_4O_9$ Unit Cell and Crystals



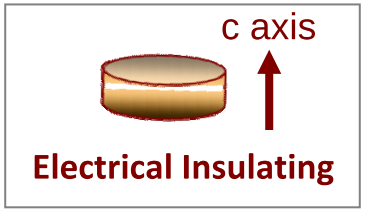
CoO_2 layer (CdI_2): **Electrical Conducting.**

Ca_2CoO_3 distorted rock-salt: **Electrical Insulating.**

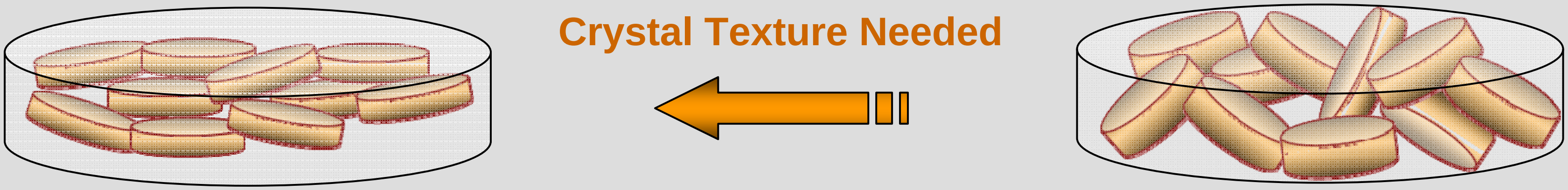




Electrical Conducting



Electrical Insulating



Crystal Texture Needed

Challenges: Improving overall ZT of polycrystal $Ca_3Co_4O_9$ ceramics

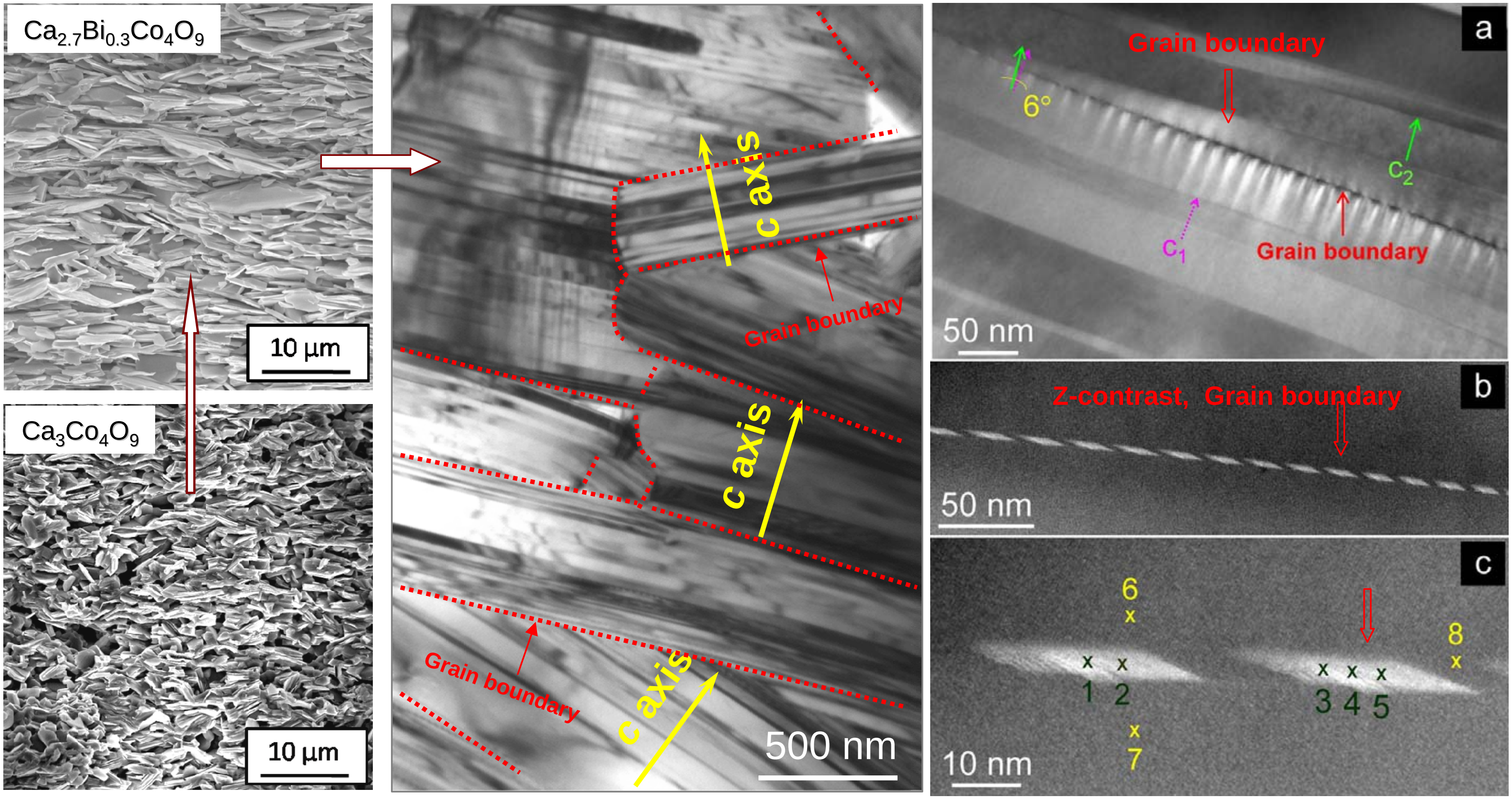
- Improve electrical conductivity through crystal texture development
- Increase Power Factor by increasing S, decrease electrical resistivity
- Reduce thermal conductivity

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

Approaches:

- ✓ **Modifying the chemistry** of polycrstalline $Ca_3Co_4O_9$;
- ✓ Adding dopants and **driving the dopants to segregate at the grain boundaries (GBs).**

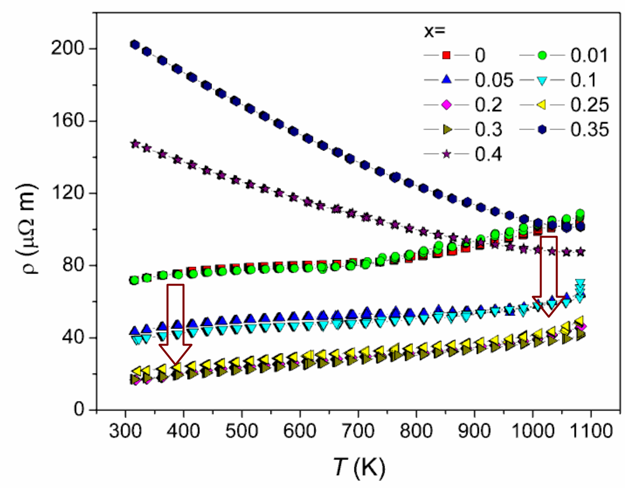
Bi Dopants GB Segregation to Promote Texture in $Ca_3Co_4O_9$

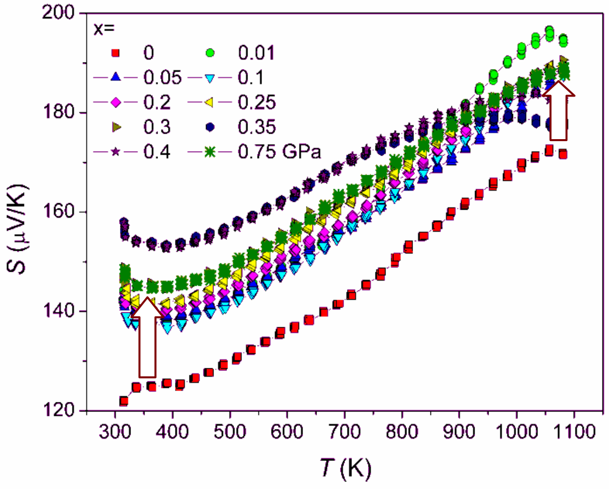


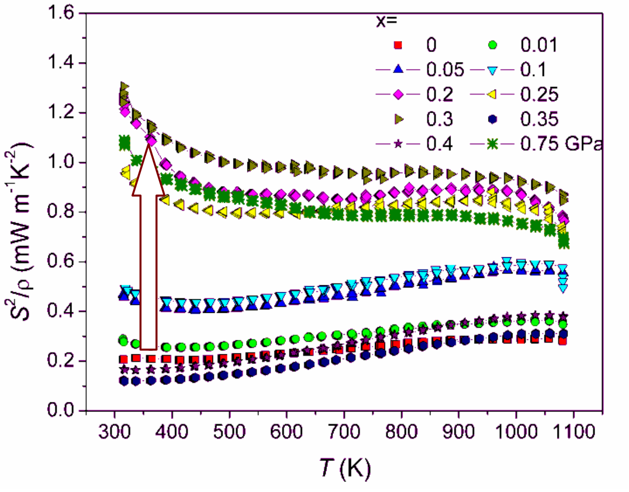
- Significant texture development due to Bi-doping.
- Bismuth deposits at grain & grain boundaries (GBs).
- Significant amount of **Bismuth segregation** to the grain boundaries.

	GB	GB	GB	GB	GB	Grain	Grain	Grain
at %	1	2	3	4	5	6	7	8
Ca	17.97	19.63	19.15	17.79	18.28	23.00	22.21	21.01
Co	21.42	22.49	23.34	24.30	26.12	22.31	24.26	21.66
O	54.25	53.08	50.94	51.33	50.11	52.54	51.99	56.28
Bi	**6.36**	**4.80**	**6.58**	**6.59**	**5.48**	**2.15**	**1.53**	**1.05**

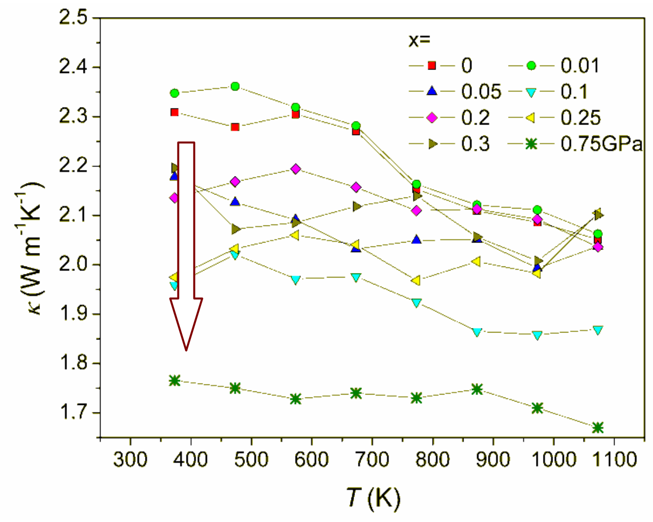
ZT Enhancement Through GB Dopants Segregation in $Ca_3Bi_xCo_4O_9$

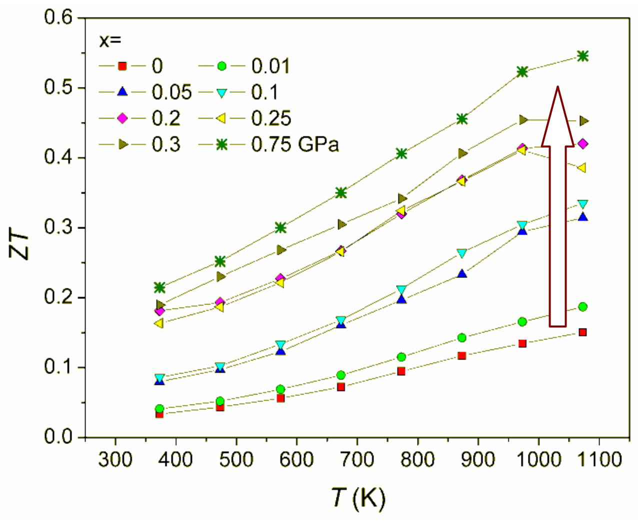






Decrease electrical resistivity, with the increase of the Bi-addition level in $Ca_3Bi_xCo_4O_9$ to x=0.35.
Increase Seebeck coefficient as the Bi concentration level increase;





Highest power factor at from room temperature to 1073K.

Highest of ZT=0.55 at 1073K for $Ca_3Co_4O_9$, processed using conventional methods.

ZT approached that for p-type SiGe at low temperatures.

Available p-type Bulk Scale Oxide $Ca_3Co_4O_9$

Simple Approach: **Driving dopants to segregate at the grain boundaries (GBs) of bulk ceramics.**

Simultaneously Increase Seebeck Coefficient S and Electrical Conductivity σ.

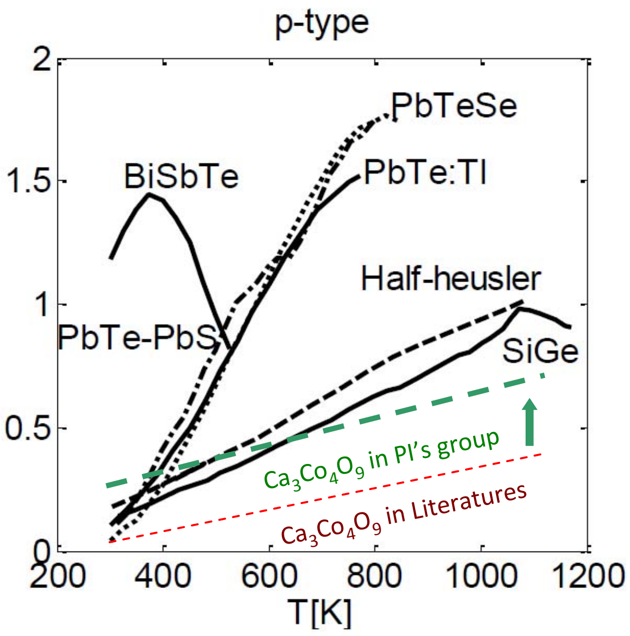
✓ **First group discovered dopants GB segregation to improve TE performance.**

- Identified driving force for GB segregation.
- Have discovered 4 different sets of dopants respectively.
- All 4-sets different dopants resulted in the similar effects & performance enhancement.

✓ **Increase the ZT to 0.55 at 800°C.**

✓ **Highest ZT for $Ca_3Co_4O_9$ synthesized using the conventional solution based synthesis and pelletization.**

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

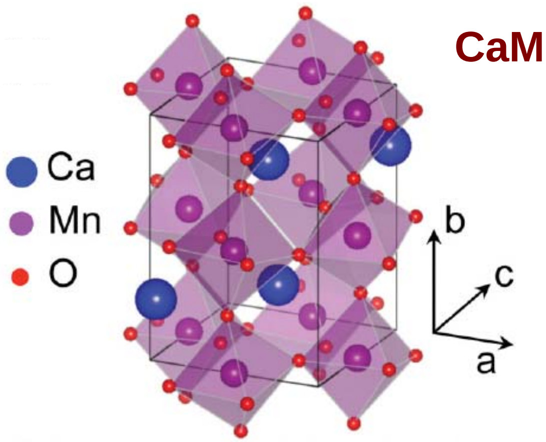


NSF-CAREER, NSF-1254594, DMR Ceramics Program

Overview

- Highlight of Current Results
  - Significant thermoelectric oxide performance enhancement achieved by this project
  - Thermoelectric device power increase by a factor of ~400, due to materials improvement
- Background Introduction
  - Waste heat & advantages of thermoelectric generator
  - State-of-the-art thermoelectric device and materials
  - Challenges for the development of oxide thermoelectric materials and device
- Project Objectives and Approaches
  - Project objectives
  - Materials processing, property measurement & nanostructure characterization
- **p & n Type Thermoelectric Oxide and Generator Developed in PI's Group**
  - Available p-type thermoelectric oxide
  - **Ongoing work of n-type thermoelectric oxide with record high energy conversion efficiency**
  - Novel scalable all oxide thermoelectric generator with compact design
- Summary and Future Work

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, reported in the literatures.

- Thermal conductivity: low k ~ 1-2 $Wm^{-1}K^{-1}$.
- High electrical resistivity ρ, σ = 1/ρ;
- Low Seebeck coefficient S.

Material	ρ (μΩ m)	S (μV/K)	PF (mW/mK²)	κ (W/mK)	ZT	T (K)	Year	Citation
$CaMn_{1-x}Nb_xO_3$	350	-250		0.8	0.32	1060	2008 2009	Acta Mater, 57 (2009), pp. 5667–5680 Inorg Chem, 47 (2008), pp. 8077–8085
$Ca_{1-2x}Dy_xYb_xMnO_3$	80	-180	0.4	1.5	0.27	1073	2015	Ceramics International 41 (2015) 1535–1539
$Ca_{1-x}Bi_xMn_{1-y}V_yO_3$		-180		1.5	0.21	1050	2008	Solid State Comm, 145 (2008), pp. 132–136
$Ca_{1-x}Yb_xMnO_3$	80	-150	0.3	1.6	0.2	1000	2009	Chem Mater, 21 (2009), pp. 4653–4660
$Ca_{0.96}Dy_{0.02}Tm_{0.02}MnO_3$	100	-190	0.27	1.5	0.17	973	2014	Ceram Inter, 40 (2014), pp. 15531–15536
$Ca_{1-x}Ho_xMnO_3$	65	-150	0.32	1.8	0.16	1000	2008	Journal of Applied Physics 104, 093703 (2008)
$Ca_{1-x}Gd_xMn_{1-x}W_xO_3$		-200	0.32	2.6	0.12	973	2017	J Alloys Comp, 699 (2017) 788-795

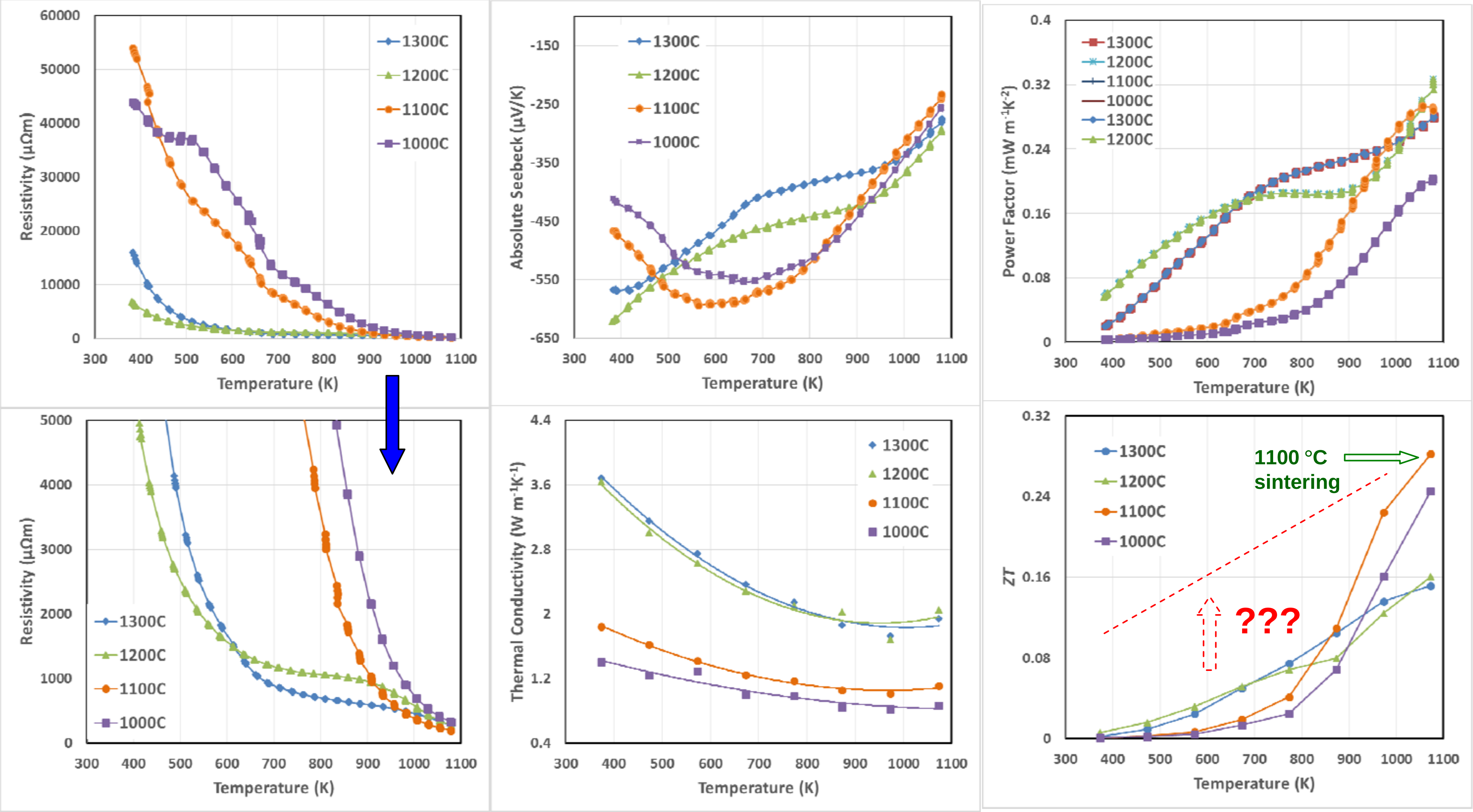
Approaches & progress made by this project to improve the performance of bulk $CaMnO_3$:

1st step: Increase peaking ZT of **pure $CaMnO_3$** to **0.28**; Approaching the best doped ones in literatures.

2nd step: Further increase the **Bi-doped $CaMnO_3$** ZT to **0.3**, dramatic increase the ZT at low temperatures;

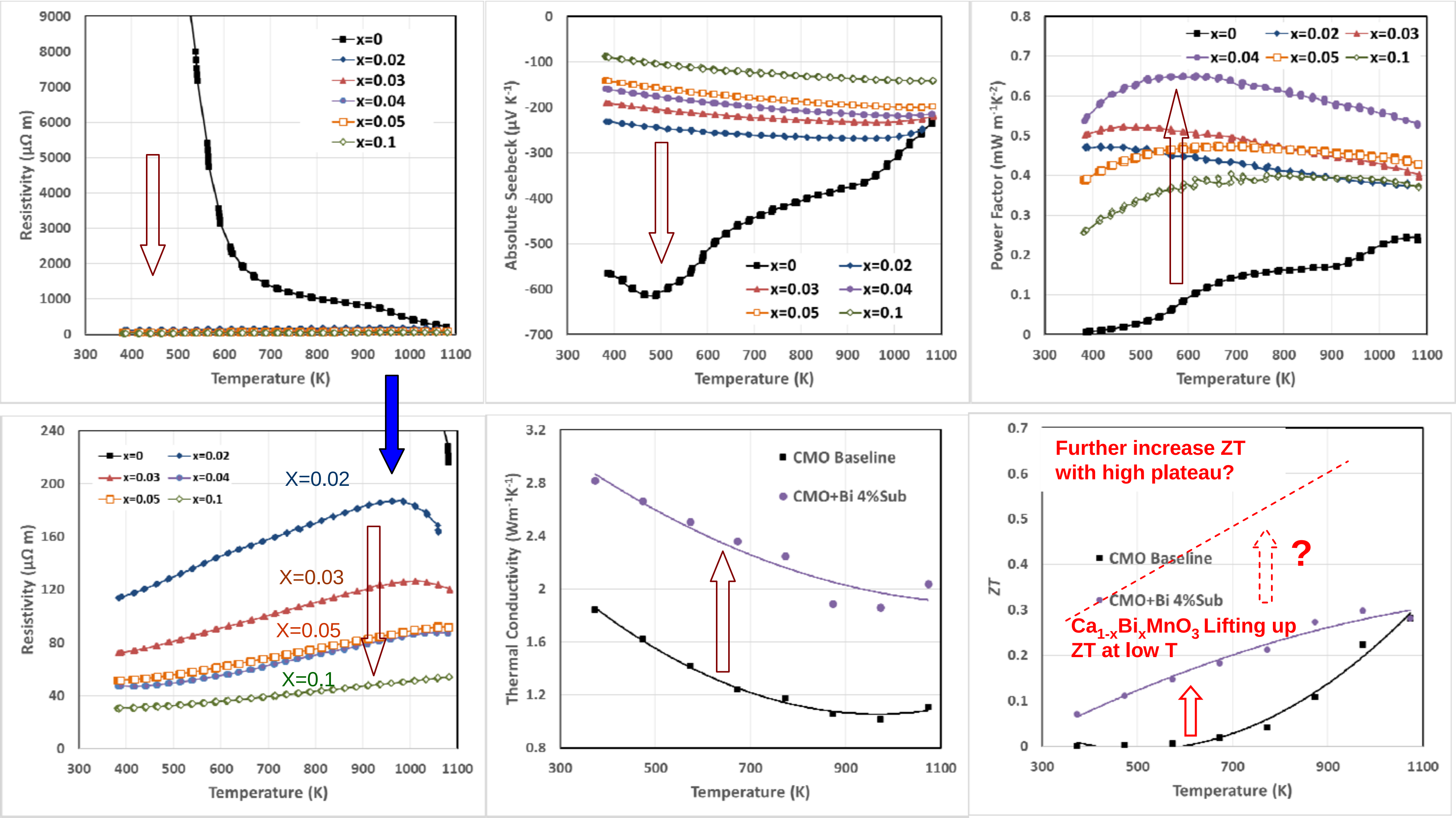
3rd step: Increase the peaking ZT of **Bi-doped $CaMnO_3$** to **0.67** through **liquid phase** sintering.

1st step: Optimization of Baseline Pure $CaMnO_3$: Peaking *ZT* of 0.28



- **Electrical resistivity decrease dramatically with the increase of the sintering temperature;**
- **Thermal conductivity also increase with the increase of the sintering temperature.**
- **Pure $CaMnO_3$ reaches the maximum ZT of 0.28 at 1073K,** approaching the best doped ones in literatures.
- **ZT is low at the low temperature region due to the low power factor, due to high electrical resistivity.**

2nd step: Performance Increase by Bi-substitution of Ca, $Ca_{1-x}Bi_xMnO_3$



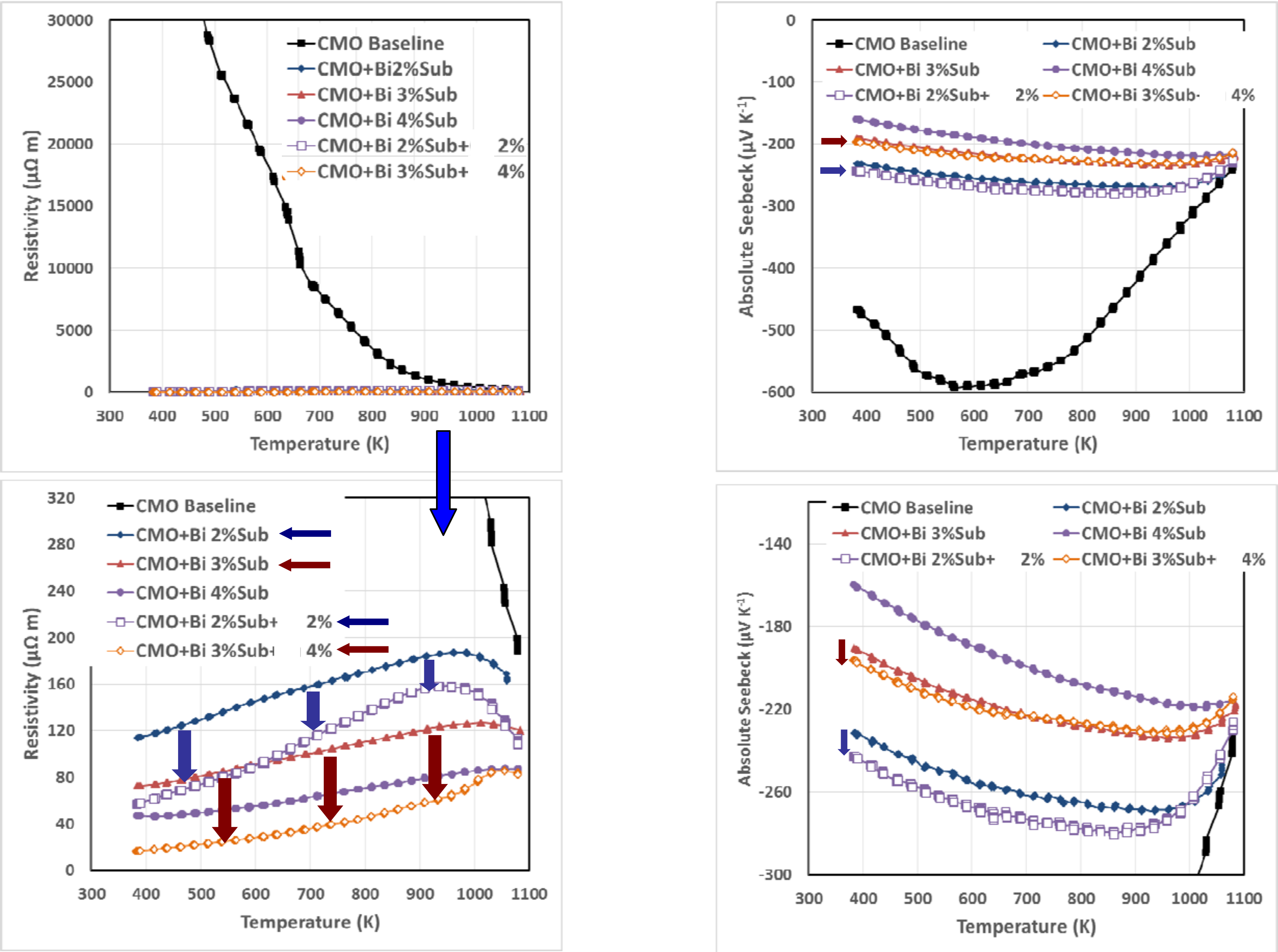
Further increase ZT with high plateau?

$Ca_{1-x}Bi_xMnO_3$ Lifting up ZT at low T

$Ca_{1-x}Bi_xMnO_3$ Pellets sintered at 1100°C:

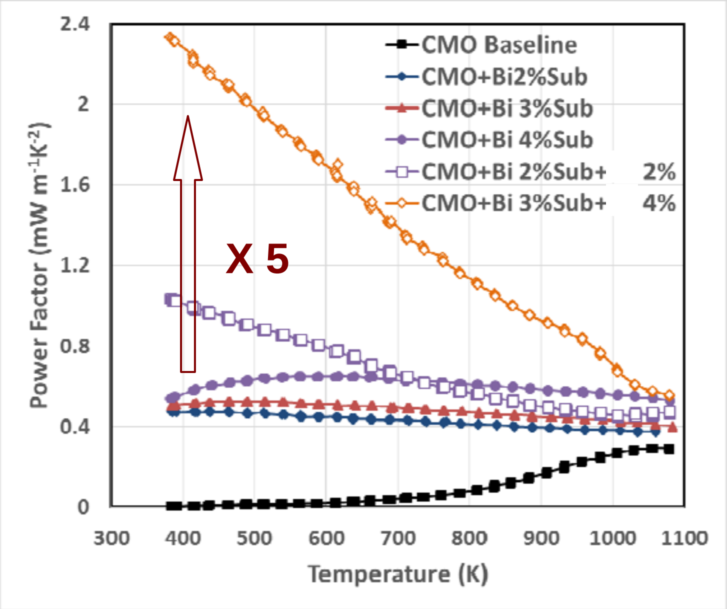
- Electrical resistivity decrease dramatically with the increase of Bi; Seebeck coefficient decreases too.
- Power factor increase, (due to decrease in resistivity), in comparison with that baseline sample.
- Thermal conductivity increases, and ZT at low temperature regime is significantly increased.

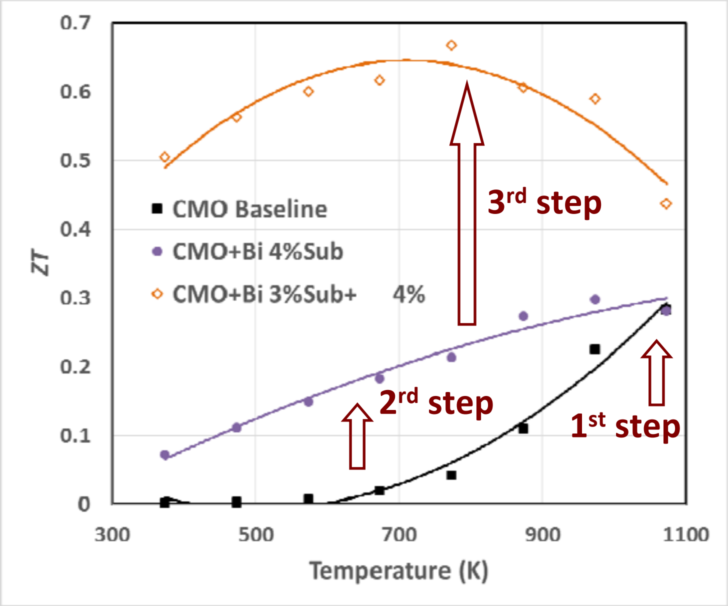
3rd step: Synergetic Bi Substitution & M addition, $Ca_{1-x}Bi_xMnM_yO_3$

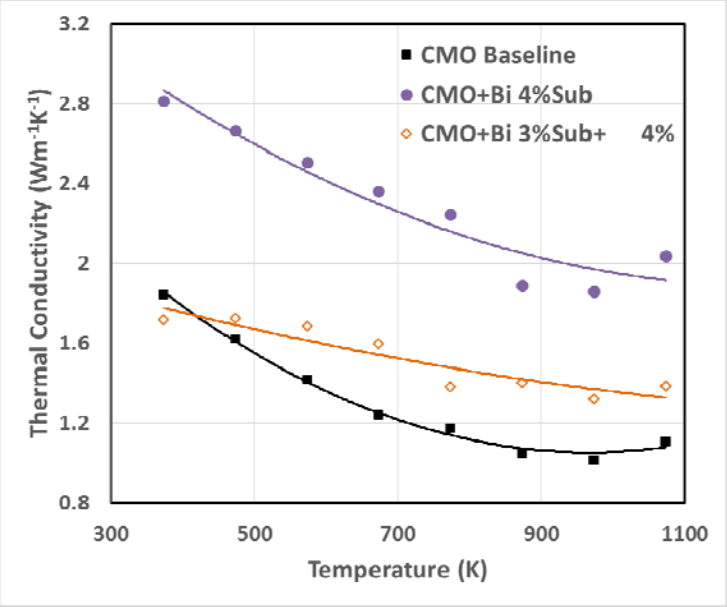


- M addition in the $Ca_{1-x}Bi_xMnM_yO_3$ further decrease the resistivity.
- Seebeck coefficient follows the same trend of that without M addition, value slightly increased.

3rd step: Synergetic Bi Substitution & M addition, $Ca_{1-x}Bi_xMnM_yO_3$





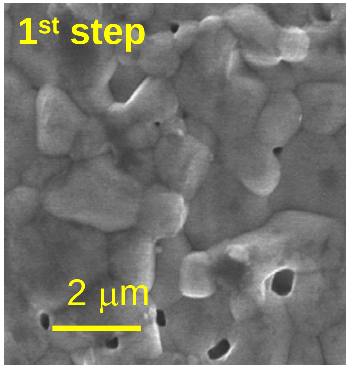


$Ca_{1-x}Bi_xMnM_yO_3$:

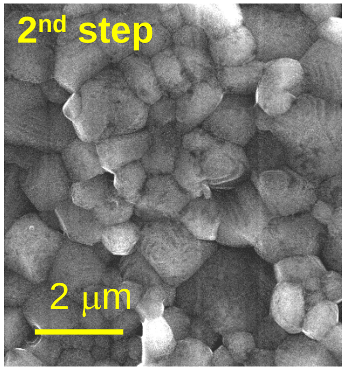
n-type bulk scale oxide based on $CaMnO_3$ developed through this project.

- Achieved the highest power factor at low temperature regime.
- Achieved **highest** (among literatures) energy conversion efficiency **ZT** value of **0.67** at 773K;
- **Factor of 2** higher than that of reported ZT value in the literature of 0.3.
- **High plateau of the ZT**, from room temperature to 1073K.

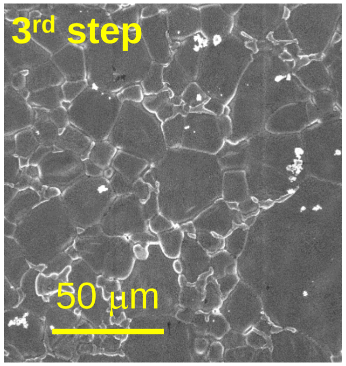
Microstructure of $CaMnMO_{3,}$ Induced by Bi Substitution & M Addition



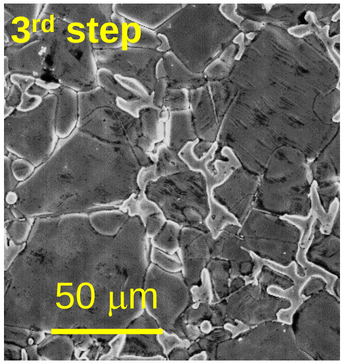
$CaMnO_3$



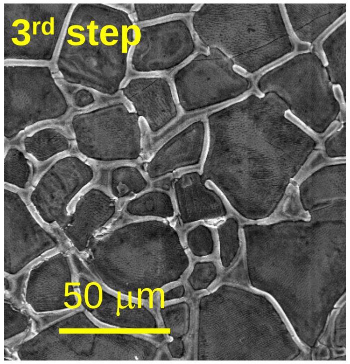
$Ca_{0.97}Bi_{0.03}MnO_3$



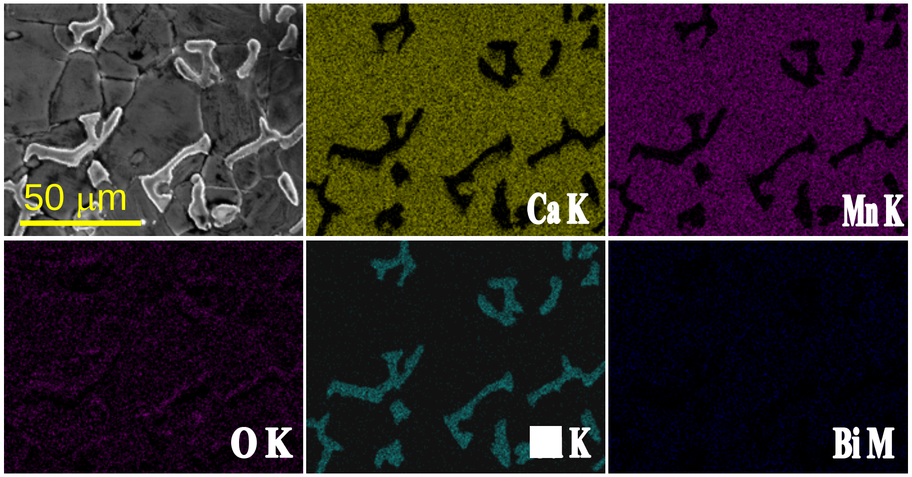
$Ca_{0.97}Bi_{0.03}M_{0.02}MnO_3$



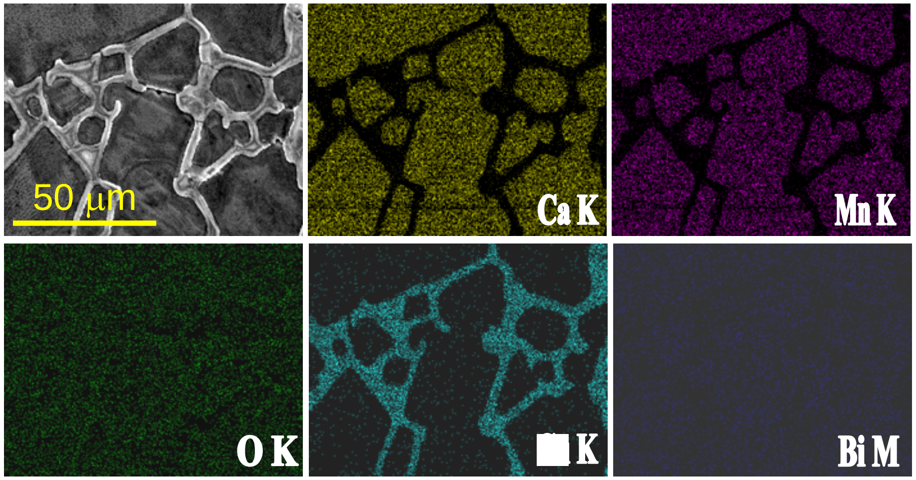
$Ca_{0.97}Bi_{0.03}M_{0.04}MnO_3$



$Ca_{0.97}Bi_{0.03}M_{0.15}MnO_3$



M sparsely distributed in $Ca_{1-x}Bi_xM_{0.04}MnO_3$



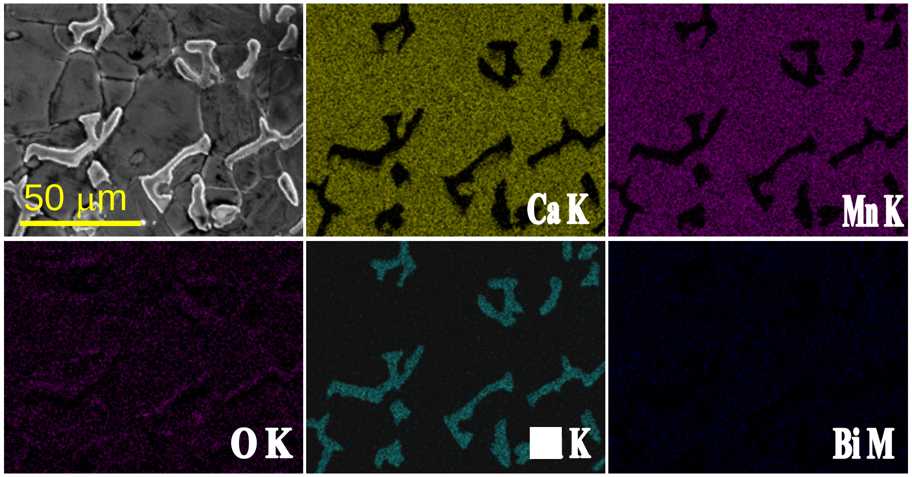
M liquid phase percolated in $Ca_{1-x}Bi_xM_{0.15}MnO_3$

Bi doping: No morphology & grain size (~ 1 μm) changes for $Ca_{1-x}Bi_xMnO_3$.

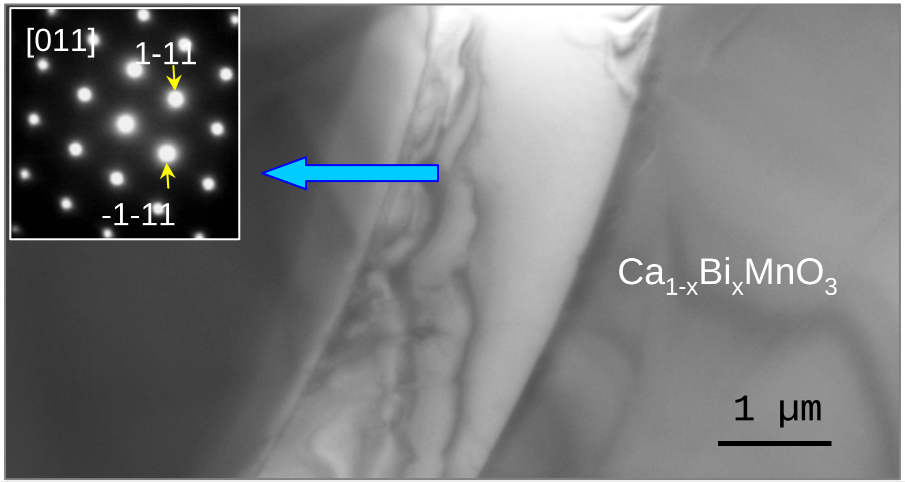
M- addition: Increased grain size (to ~ 20 μm), formation of grain boundary M oxide secondary phases.

M- addition: liquid phase (discrete phase) become percolated network with the increase M addition.

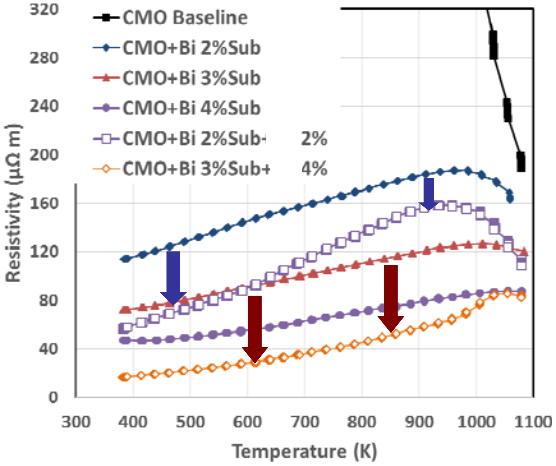
Microstructure Changes Induced by Bi and M Doping

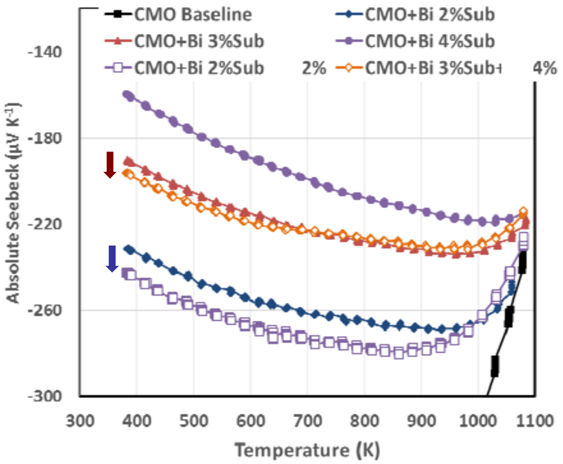


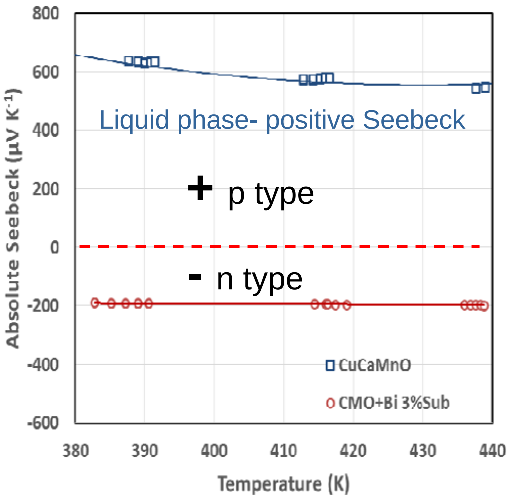
M sparsely distributed in $Ca_{1-x}Bi_xM_{0.04}MnO_3$



M having solid-bonded interface with $Ca_{1-x}Bi_xMnO_3$

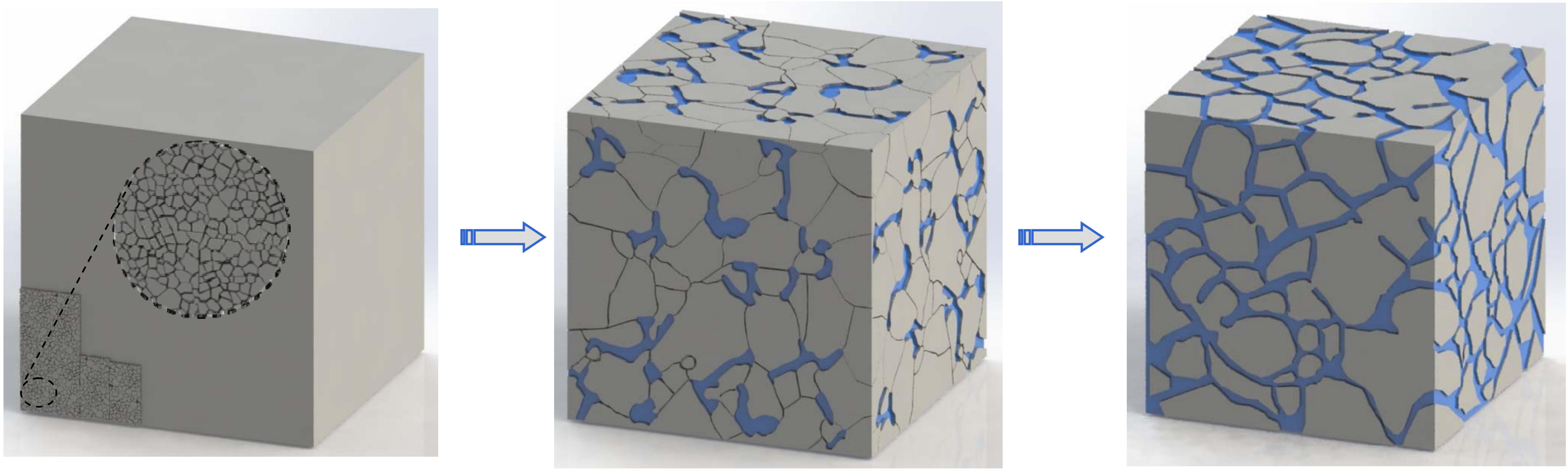






- M oxide is a p-type, while $Ca_{1-x}Bi_xMnO_3$ is a n-type conductor.
- M GB phase, slightly increase Seebeck coefficient & decrease electrical resistivity, indicating **significantly increased carrier mobility, induced by M at GB.**
- **M oxide** is melted as **liquid** at 1100°C, under the same conditions $Ca_{1-x}Bi_xMnM_yO_3$ is sintered.

Evolution of liquid phase at $Ca_{1-x}Bi_xMnO_3$ grain boundaries



$Ca_{1-x}Bi_xMnO_3$ $Ca_{1-x}Bi_xMnM_{0.04}O_3$ $Ca_{1-x}Bi_xMnM_{0.15}O_3$

Advantages of liquid phase sintering of $Ca_{1-x}Bi_xMnO_3$.

(1). Enhance mechanical toughness, eliminate the ceramic pellets cracking during the sintering process.

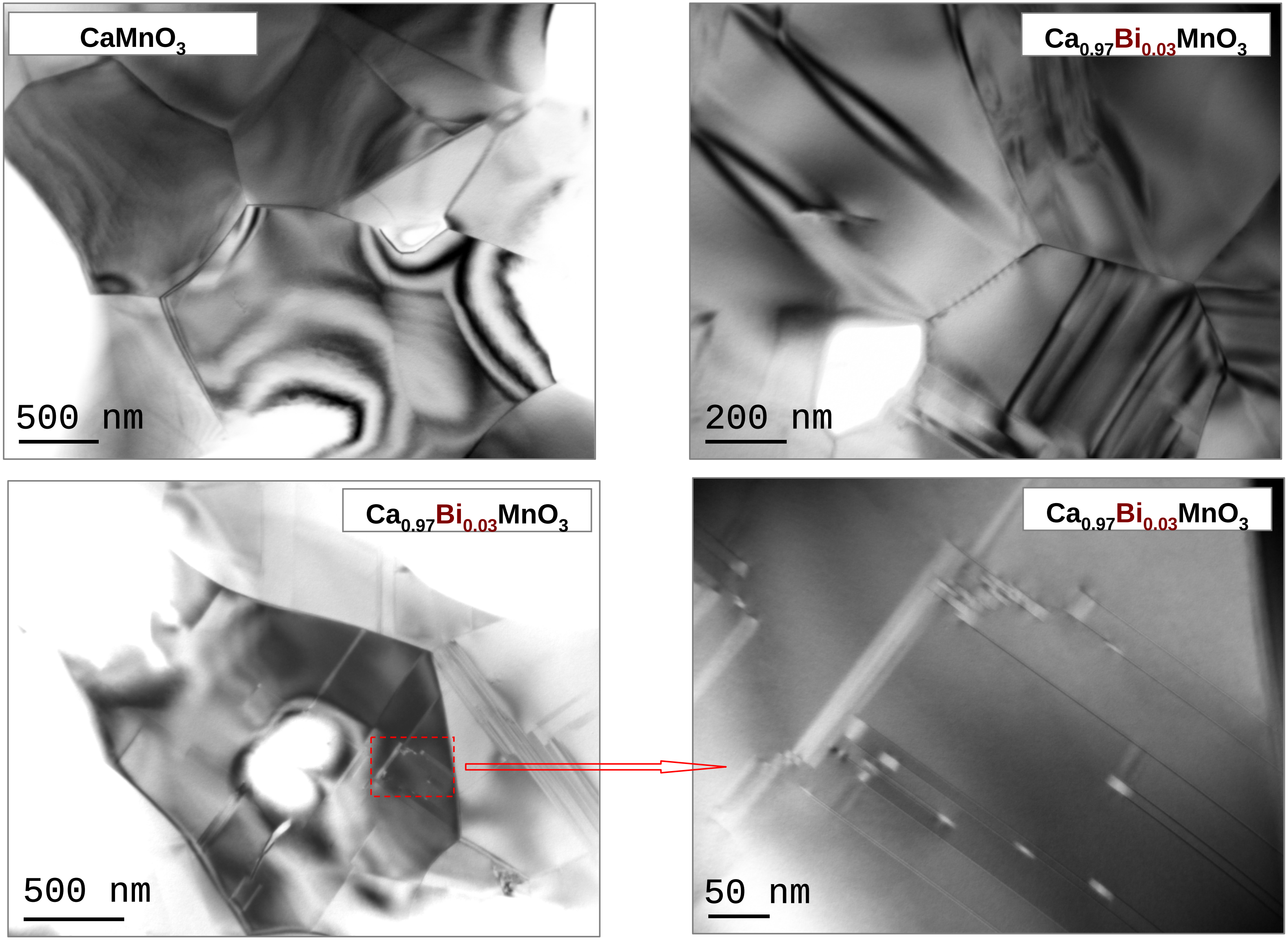
(2). Improve the carrier mobility, and increase electrical power factor.

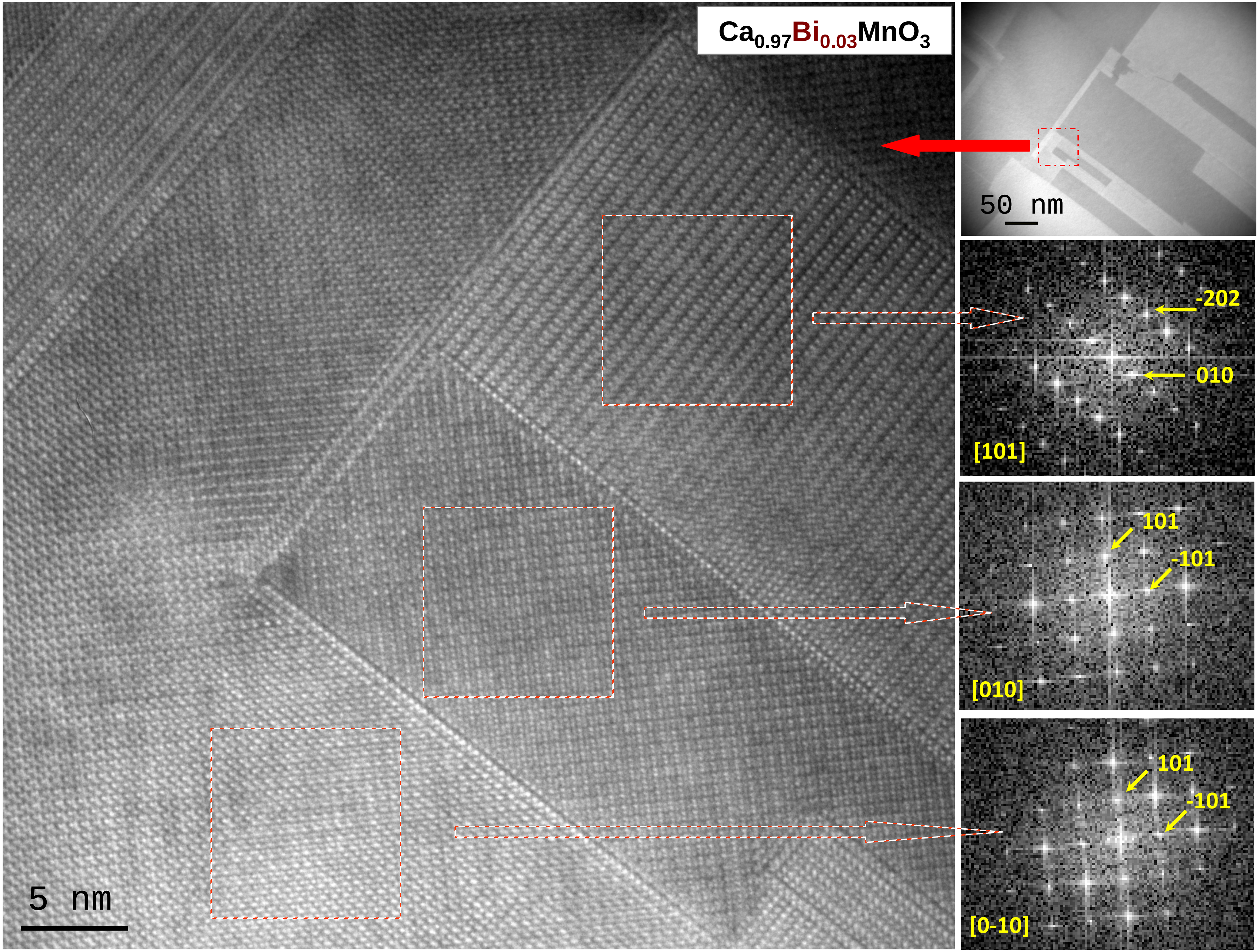
(3). Lower the thermal conductivity by adding the interface for phonon scatting.

(4). There is optimum level of liquid phase to be added to enhance the properties, and over addition of M cause the properties deterioration.

(5). Liquid phase increase the grain size of $Ca_{1-x}Bi_xMnO_3$, but **does not cause additional nano-defects** within the $Ca_{1-x}Bi_xMnO_3$ grains.

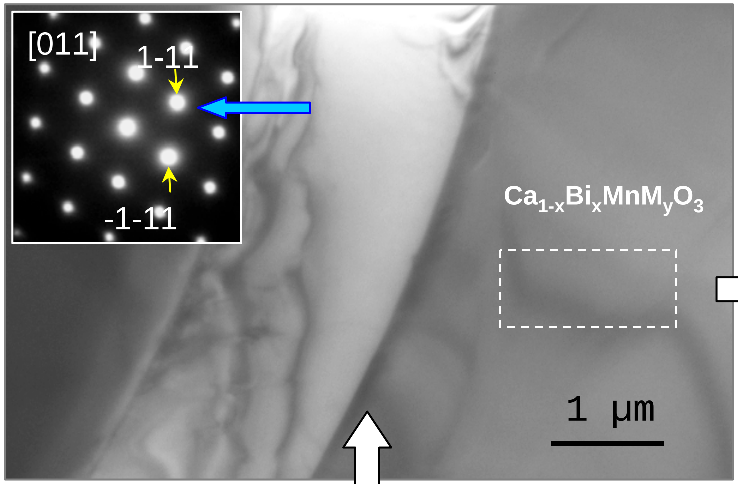
Formation of Nano Twinning Defects Induced by Bi doping

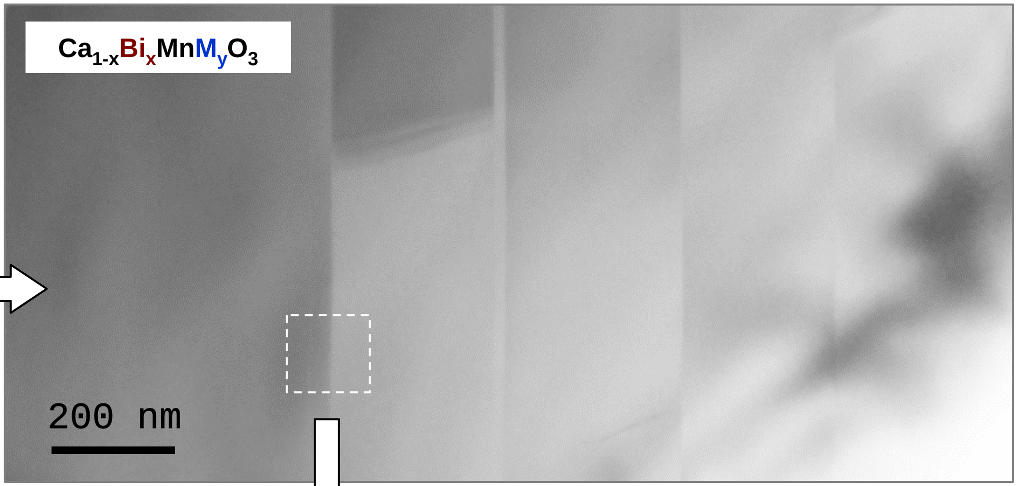


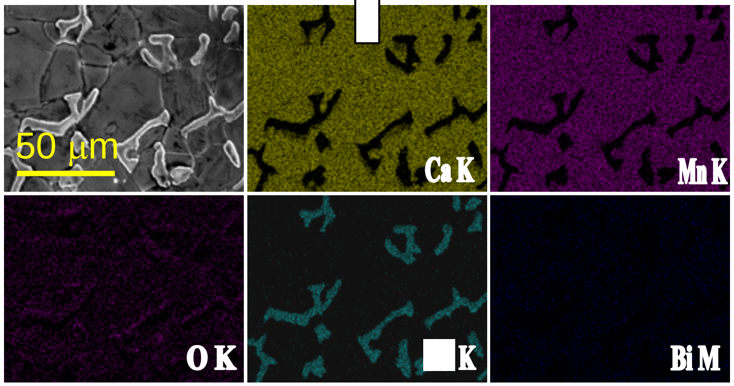


$Ca_{0.97}Bi_{0.03}MnO_3$
50 nm
-202
010
[101]
101
-101
[010]
101
-101
[0-10]
5 nm

No Further Crystal Defects in CaBi$_x$MnO$_3$ Induced by M Addition

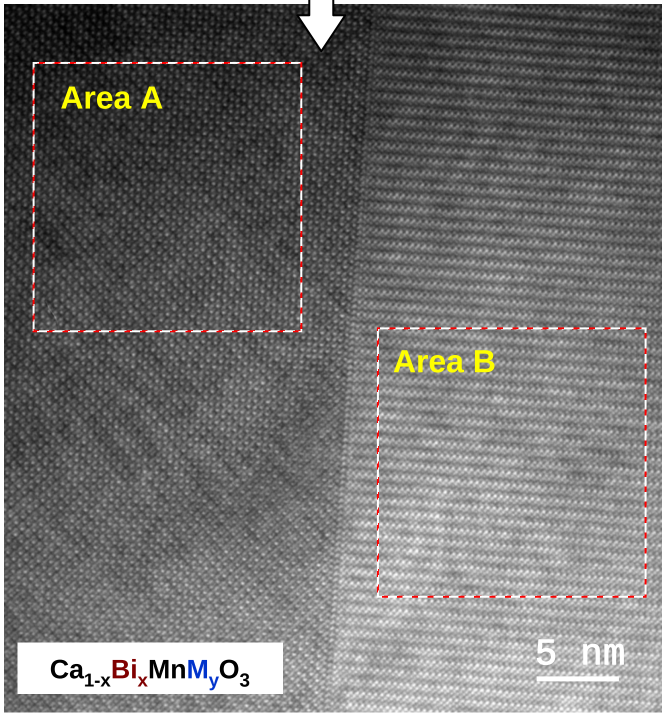


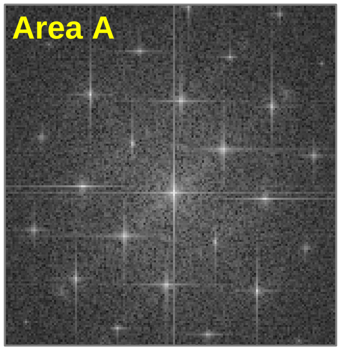


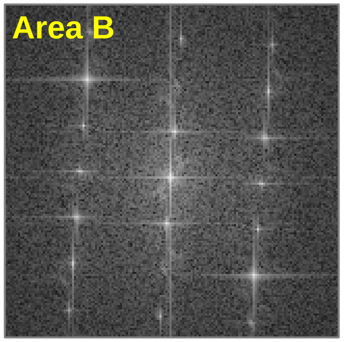


Ca$_{1-x}$Bi$_x$MnM$_y$O$_3$

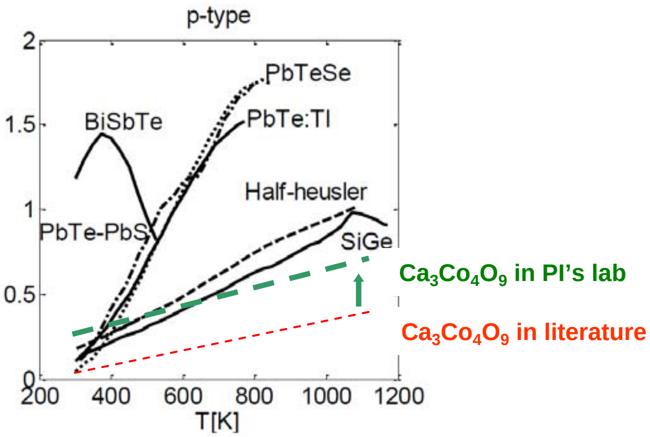
- liquid phase increase the grain size of Ca$_{1-x}$Bi$_x$MnO$_3$ at micron scales.
- **M does not cause additional nano-defects within Ca$_{1-x}$Bi$_x$MnO$_3$ grains.**

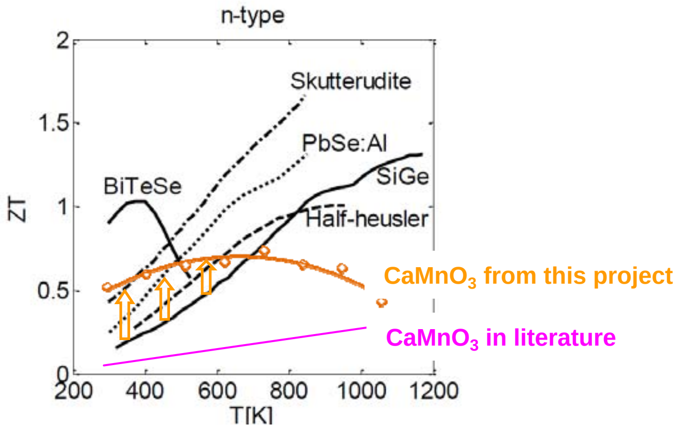






Cost and Performance Comparison Between Oxide, SiGe, Bi-Te





Material	Manufacturing type	Material cost ($/kg)	ZT
Bi_2Te_3	Bulk	110	0.74
$Bi_{0.52}Sb_{1.48}Te_3$	Bulk	125	1.05
SiGe	Bulk	679	0.30
$Ca_{2.4}Bi_{0.3}Na_{0.3}CoO_9$	Bulk	30	0.13
$Na_{0.7}CoO_{2-\delta}$	Bulk	36	0.52

Renewable and Sustainable Energy Reviews 32 (2014) 313 – 327; Renewable and Sustainable Energy Reviews 32 (2014) 486–503

n-type bulk scale oxide based on $CaMnO_3$ developed through this project.

- ➢ Achieved highest (among literatures) energy conversion efficiency ZT value of 0.67 at 773K;
- ➢ **ZT of 0.67 is factor of 2 of that highest value reported in the literatures of ZT~ 0.3.**
- ➢ High plateau of the ZT, from room temperature to 1073K. **Outperform SiGe from RT to 773K.**
- ➢ Low cost conventional solution based processing, without need of specialized costly micro-fabrication.
- ➢ Low cost oxide materials, in comparison with the state-of-the-art thermoelectric SiGe and Bi-Te.

Bulk scale oxide ~ 30$/Kg; Bulk scale SiGe ~ 600$/Kg; Bulk scale Bi-Te ~100$/kg.

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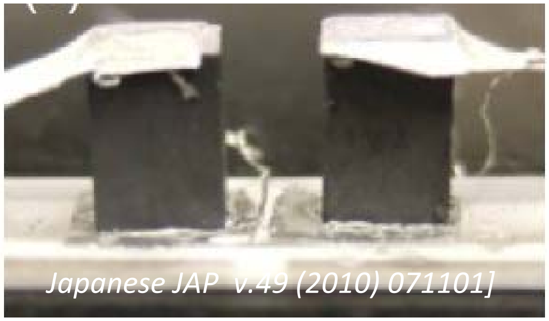
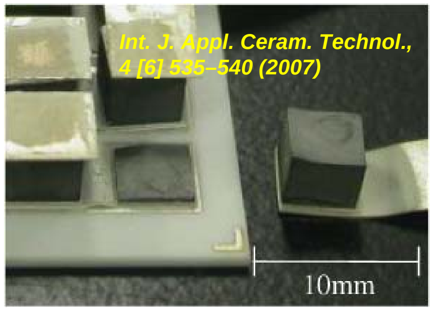
Novel All Oxide Thermoelectric Generator by This Project

Energy Conversion and Management 52 (2011) 335–339



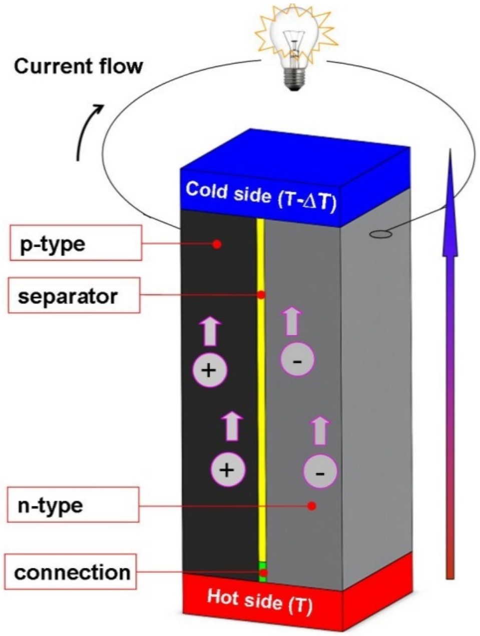
Japanese JAP v.49 (2010) 071101]



Int. J. Appl. Ceram. Technol., 4 [6] 535–540 (2007)

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

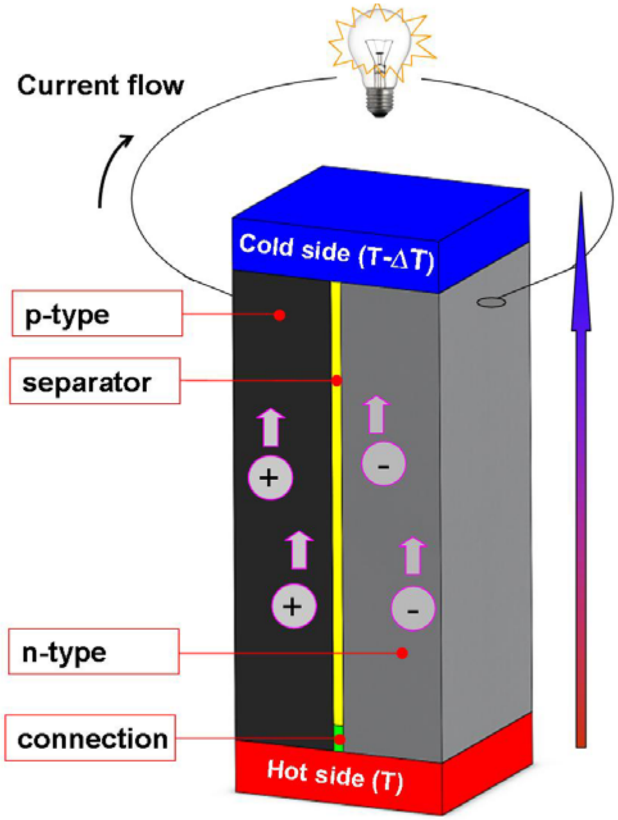
Current work: All oxide thermoelectric generators with increased power density:

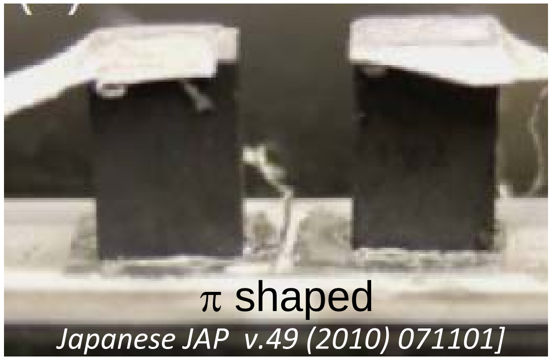


Newly designed TE device for oxide by PIs.

- 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 air.

Novel All Oxide Thermoelectric Generator by This Project




π shaped

Japanese JAP v.49 (2010) 071101]

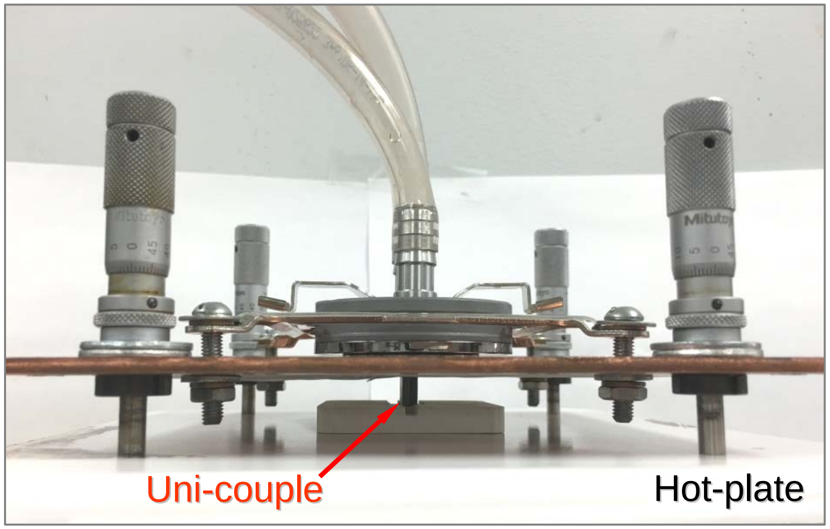
Newly designed devices for oxides features:

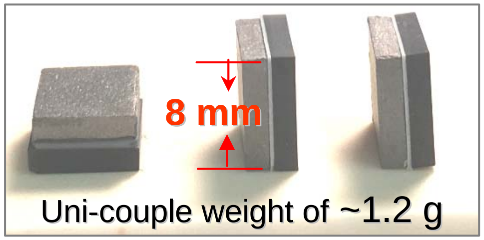
- **Compact integrated design:** strongly textured *p*-type $Ca_3Co_4O_9$ fabricated directly onto an oxide insulating layer, buffered onto *n*-type $CaMnO_3$.
- **Micron-sized, closely-packed eletrical insulating separator** for better thermal management and reduction of the overall-size and weight of the device.
- **Minimal sized electrical interconnection.**

Comparison with conventional π shaped design:

- **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.

Effect of Materials Optimization on the Performance of Device





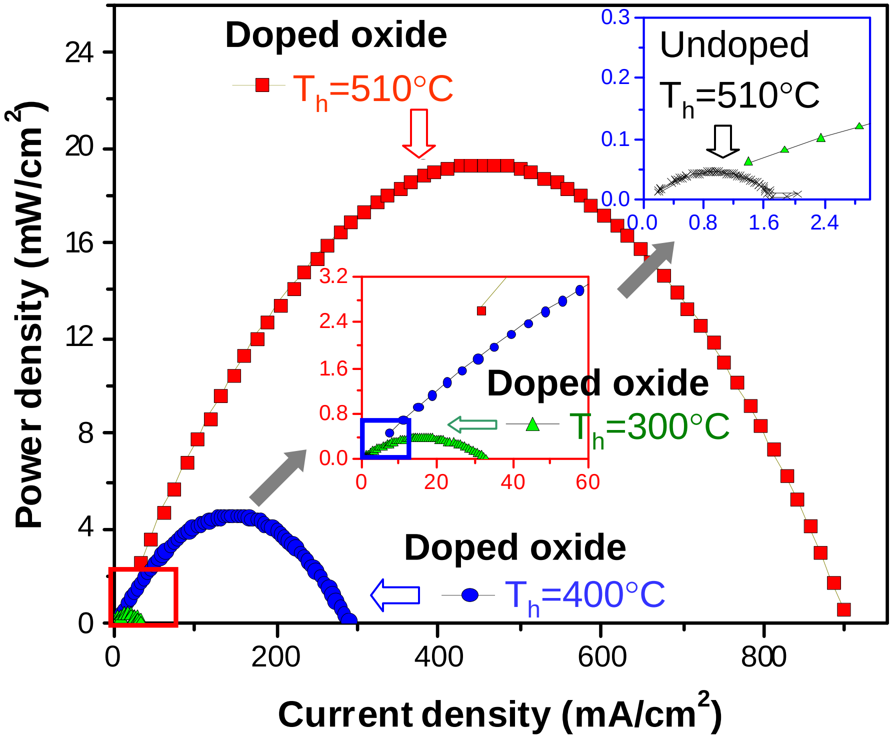
Hot plate	T_h	T_c	ΔT
510 °C	498°C	127°C	371°C
400°C	400°C	92°C	308°C
300°C	310°C	53°C	257°C

Uni-couple: Effect of Materials Optimization

Uni-couples are with the same geometry, but different chemistry of materials for the p & n legs:

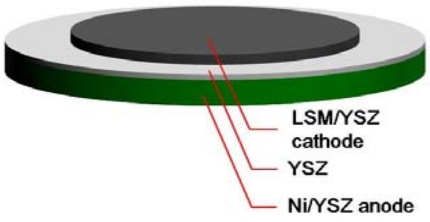
Uni-couple with un-doped materials:
$CaMnO_3$ & $Ca_3Co_4O_9$

Uni-couple with doped & optimized materials:
$Ca_{0.97}Bi_{0.03}MnM_{0.04}O_3$ & $Ca_3Co_4Ba_{0.05}O_9$

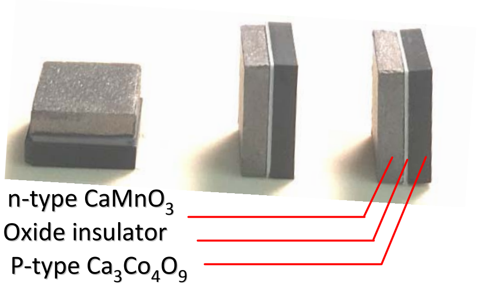


- Power density of the **unicouple** (at T_h of 500°C) with **un-doped materials**: $P=0.05x10^{-3}$ w/cm²
- Power density of the **unicouple** (at T_h of 500°C) with **optimized materials**: P=0.02 w/cm²
- Optimization of materials results in **> 400 times performance enhancement** for the uni-couples.
- ***Without device level optimization***, TE uni-couple configuration in the Figure, using the materials with best performance, at T_h=510°C, uni-couple power density P is ~0.02 w/cm².

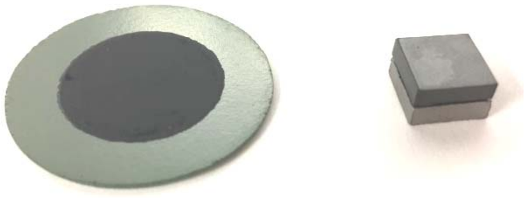
Direct Comparison of TE with SOFC in Power Generation



SOFC Button cell



All oxide TE Uni-couple



SOFC button cell & TE uni-couple

Device	Dimension	weight	Operation environment	Operation temperature	Power density mW/cm^2	Cost	Difficulty of Fabrication
SOFC	Round: d=24 mm; t= ~1.2 mm	~2.3 g (button cell)	**Anode: H_2;** Cathode: air	**750°C**	~252 mW/cm^2	~100$/cell (commercial price)	Complicated & lengthy
TE	Square: 8 x8 mm t=~4 mm	~1.2 g unicouple	**Air** Directly for entire device	**500°C**	~20 mW/cm^2	~0.036$/uni-couple (materials, $30/Kg) ~0.36$ (Materials + Fabrication)	Easy and fast processing
Percentage: TE to SOFC	~50%	~ 50%	H_2 to Air	66%	**~10%**	~0.36%	SOFC: seals. TE: in air.

- Un-optimized unicouple **(~50% of weight** of SOFC button cell) performance at **500°C in air** is **~10% of SOFC** operated at **750°C,** (I = 0.315A/cm^2 at 0.8V), fueled with **H_2**.
- Uni-couple cost is just ~0.4% of the cost of the SOFC button cell.
- TE oxide device is easy, fast and low cost processing. TE device does not need seal, functioning in air.

Overview

- Highlight of Current Results
  - Significant thermoelectric oxide performance enhancement achieved by this project
  - Thermoelectric device power increase by a factor of ~400, due to materials improvement
- Background Introduction
  - Waste heat & advantages of thermoelectric generator
  - State-of-the-art thermoelectric device and materials
  - Challenges for the development of oxide thermoelectric materials and device
- Project Objectives and Approaches
  - Project objectives
  - Materials processing, property measurement & nanostructure characterization
- p & n Type Thermoelectric Oxide and Generator Developed in PI's Group
  - Available p-type thermoelectric oxide
  - Ongoing work of n-type thermoelectric oxide with record high energy conversion efficiency
  - Novel scalable all oxide thermoelectric generator with compact design
- **Summary and Future Work**

Summary and Future Plans

Materials development of n-type $CaMnO_3$ using low cost processing.

Bulk $CaMnO_3$ that is stable up to 1300°C and stable in air, TE performance improved:

- ✓ **Through dopants stoichiometric substitution in the lattice & grain boundary phase formation.**
- ✓ **In the case of Bi and M co-doping in $Ca_{1-x}Bi_xMnM_yO_3$:**
    - **Liquid phase sintering approaches.**
    - **Synergetic approach: Bi in $CaMnO_3$ lattice; liquid phase at the grain boundaries.**
    - **Dramatic electrical performance enhancement induced by liquid phase sintering.**
    - **Highest ZT= 0.67 in the $Ca_{1-x}Bi_xMnM_yO_3$ bulk ceramics.**
    - **ZT of 0.67 achieved through this project, is a factor of 2, of the ZT values reported in the literatures.**

Patent Pending on related materials development by this project.

Novel device of 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 (at the device level) unicouple (with the ~50% weight of SOFC button cell) operated at 500°C is with 10% power density of SOFC button cell operated at 750°C with H_2.**
- ✓ **Unicouple performance could be much further improved- Ongoing work.**

Acknowledgement

National Energy Technology Laboratory

DOE Award – FE0024009

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