High Temperature Thermoelectric Oxides Engineered at Multiple Length Scales for Energy Harvesting

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Introduction

- Thermoelectric (TE) oxides for waste heat recovery in coal fired power and industrial plants (high-temp/corrosive environments)

- Significant progress in the development of *p*-type TE oxides (e.g., ZT = 1.2 at 800 K for <u>single crystal</u> $NaCo_2O_4$)

- Similar breakthroughs not yet achieved for *n*-type TE oxides. Essential to develop n-type TE oxide materials.

- Recent progress:

  Anomalous S and σ behavior (i.e., parallel rise and fall) near the Curie point (T_c) in reduced $Sr_xBa_{1-x}Nb_2O_{6-\delta}$ (SBN) materials.

  Possibility of high TE performance in niobate-based ferroelectric materials systems in reduced forms.

Overall Goal: Investigate potential materials and processing technology of n-type oxides with high TE performance using combination of the developed material compositions and hierarchical designed microstructures.

Technical Objective: Establish beneficial combination of ferroelectricity (FE) and thermoelectricity (TE) in the vicinity of the Curie temperatures.

Specific Objectives:

- Use of combinatorial materials exploration approach for rapid screening of a broad range of compositions to search for promising n-type TE materials.
- Develop processing routes to make desired crystalline phases and anisotropic porous structures to evaluate the effect of micro- and macro-pores on thermoelectric properties.

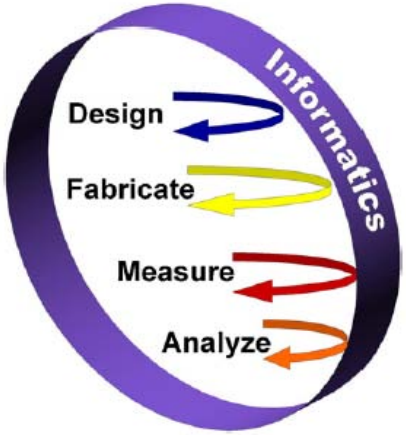
Scope of Work

1) Explore new niobate-based thin-film systems for TE applications
   - Combinatorial materials exploration (CME)

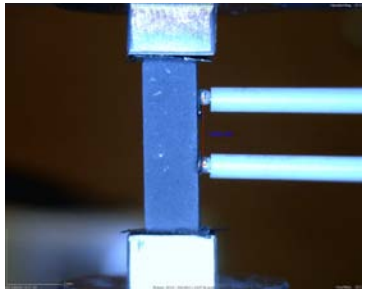
     FY-1 $Sr_xBa_{1-x}Nb_2O_6$ (SBN)

     FY-2 $M:(Sr, Ba)_2Nb_2O_7$ (M:SBN)

     FY-3 $Sr_xBi_{2-x}Nb_2O_9$ (SBiN)



2) Fabricate dense, textured polycrystalline ceramics based on compositions from CME results and evaluate TE properties
   - Solution combustion synthesis
   - Reduction
   - Sinter-forging and templated grain growth



3) Design and process hierarchical porous polycrystalline ceramics
   - Effect of CO_2 on the TE properties

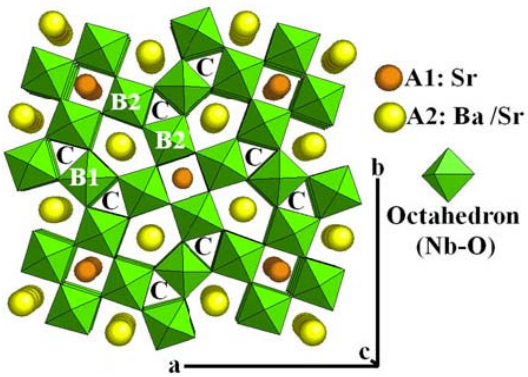
APPLIED PHYSICS LETTERS 96, 031910 (2010)

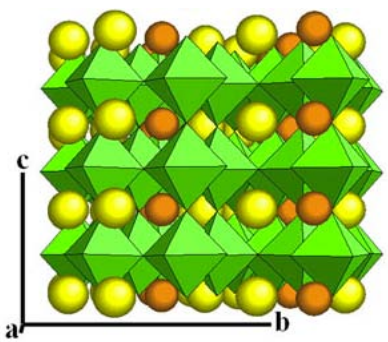
$Sr_xBa_{1-x}Nb_2O_{6-\delta}$ Ferroelectric-thermoelectrics: Crystal anisotropy, conduction mechanism, and power factor

Soonil Lee,[a] Rudeger H. T. Wilke, Susan Trolier-McKinstry, Shujun Zhang, and Clive A. Randall
Center for Dielectric Studies, Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

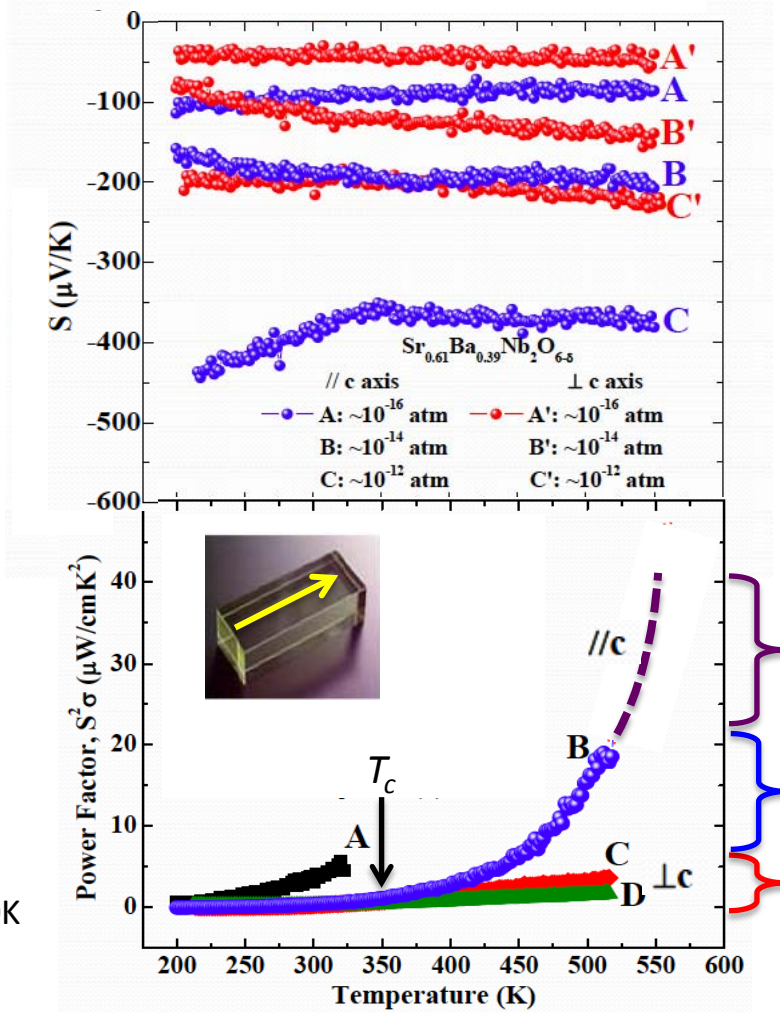
$Sr_{0.61}Ba_{0.39}Nb_2O_{6-\delta}$ single crystal

(Tetragonal Tungsten Bronze)





- 4/mmm-4/mm phase transition at ~350K
- Thermal conductivity ~0.6W/mK



Possible----
Then sensational!

Wow!
Very competitive!

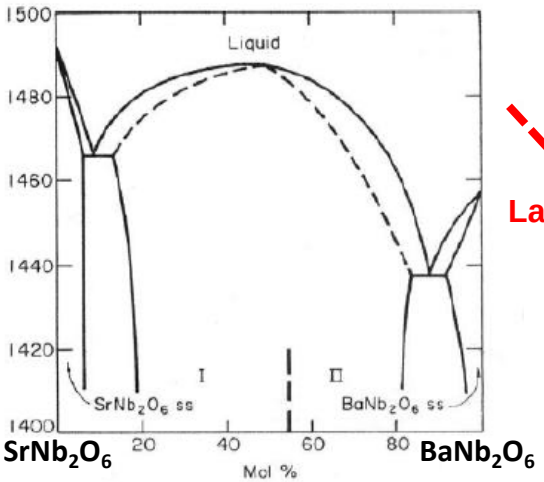
Still competitive value

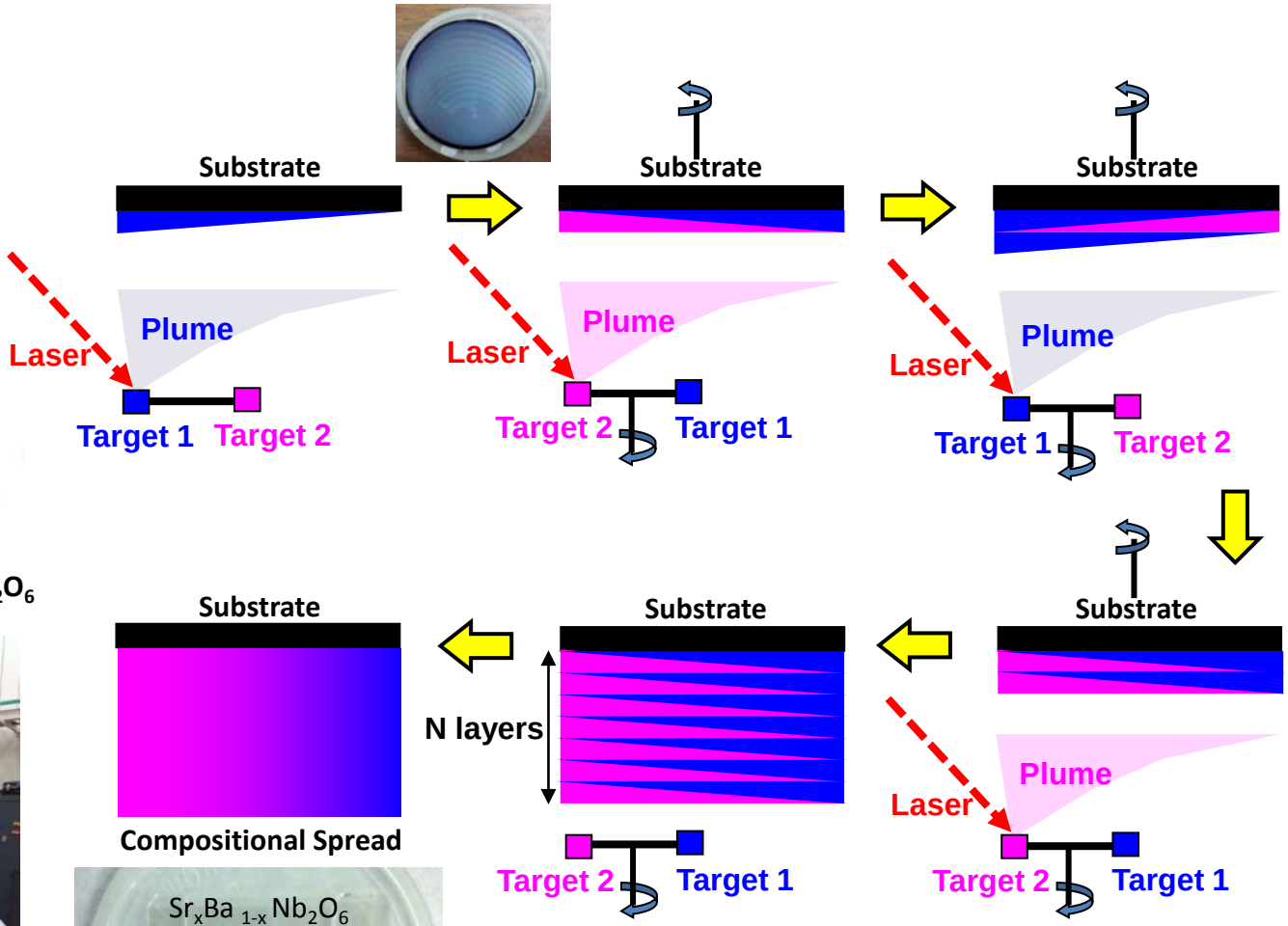
- Can we get similar or even better performance from different compositions with higher Tc?
- For practical applications, we need polycrystalline powder materials.

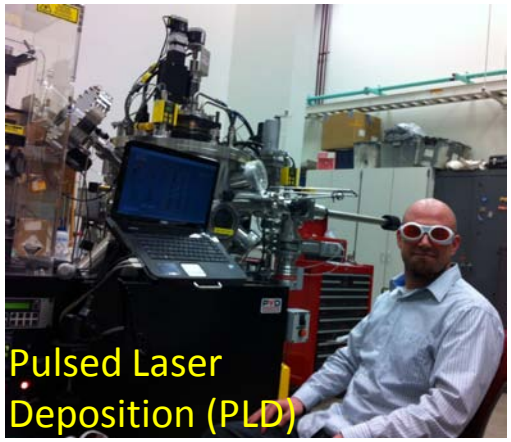
Combinatorial Material Exploration (CME)

A paradigm to explore large multi-variant materials spaces that enables both screening and understanding complex material systems in a time/cost-effective manner.

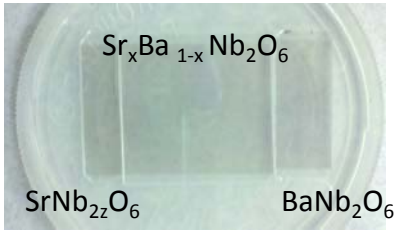
$Sr_xBa_{1-x}Nb_2O_6$ (SBN)





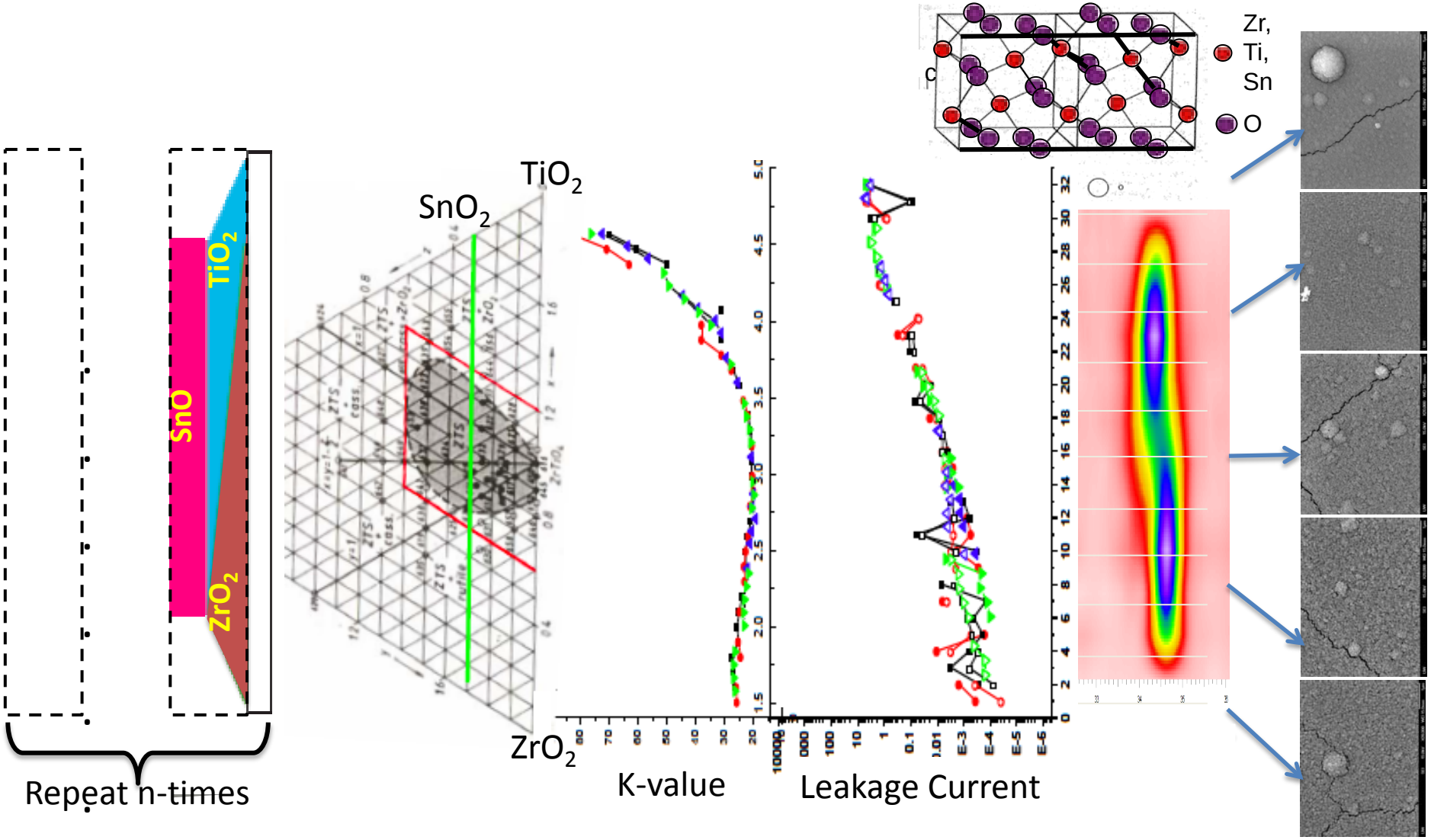


Graduate student: Chris Dandeneau



Type of information we can learn from CME

Example from our previous investigation on high-K materials



Bulk Synthesis of SBN(x)

- Need single phased and nano-sized homogeneous powders for fabricating dense textured polycrystalline pellets.
- Conventional solid-state synthesis suffers from presence of secondary phases.

Solution Combustion Synthesis (SCS)

Fabrication method that involves the exploitation of a self-sustaining exothermic reaction to form a desired material.

- Reactions occur between metal salts (nitrates) and a suitable fuel (urea) in a **homogenous solution**
- Sufficient intermixing of metal cations due to the use of liquid precursors.
- Fast reaction times and ability to produce nano-powders with uniform particle size and high phase purity

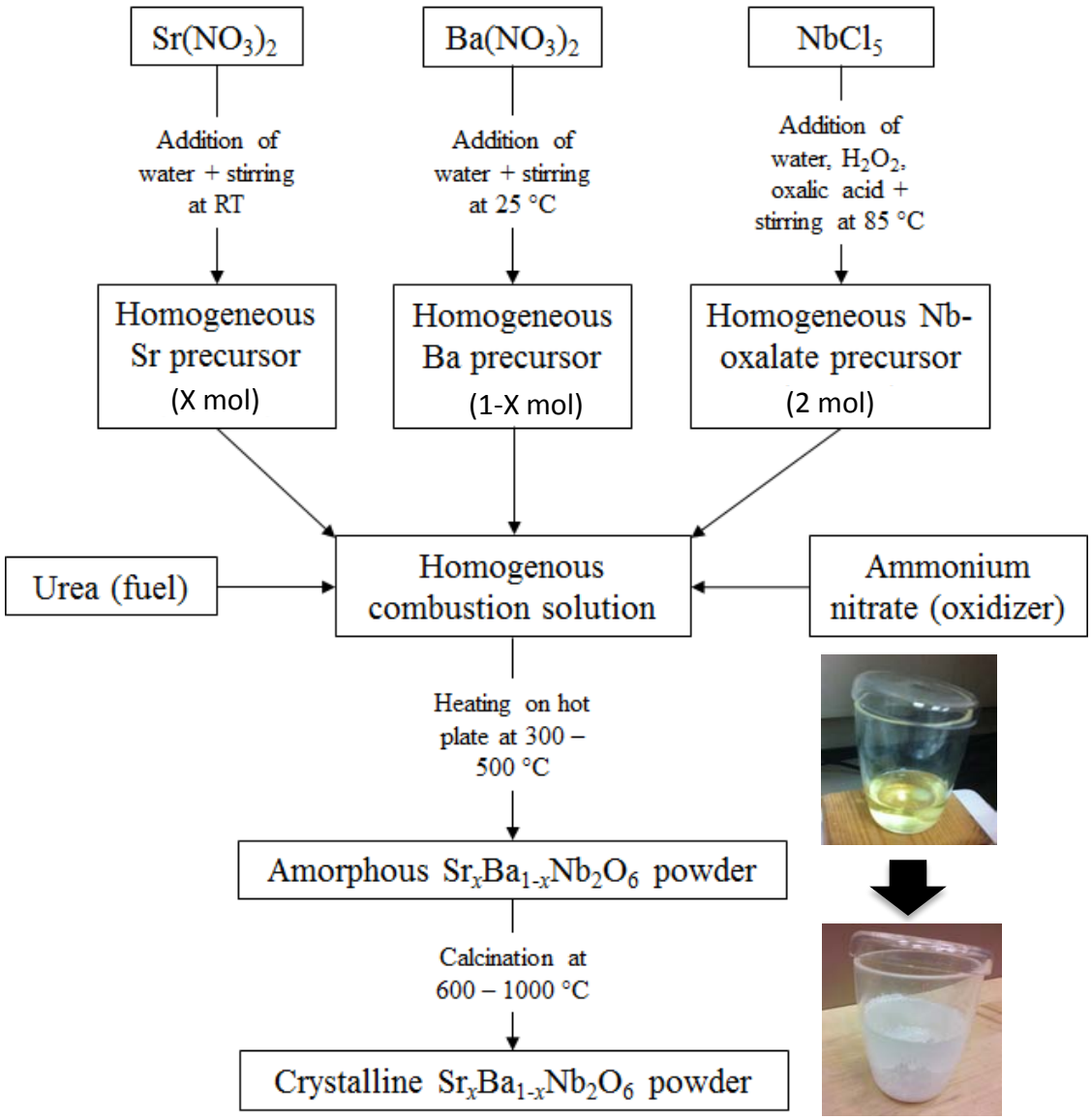
Example: $Sr_xBa_{1-x}Nb_2O_6$ (SBN50)

$$0.5Sr(NO_3)_2 + 0.5Ba(NO_3)_2 + Nb_2(C_2O_4)_5 + 5NH_4NO_3 + \frac{5}{3}CO(NH_2)_2$$

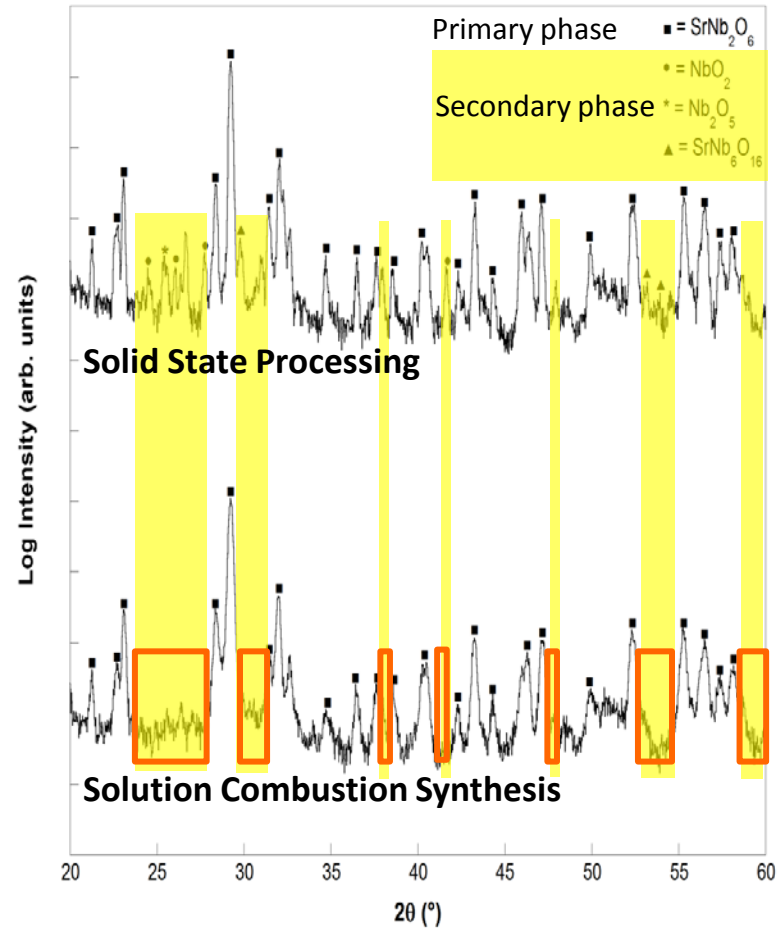
$$\Downarrow$$

$$Sr_{0.5}Ba_{0.5}Nb_2O_6 + \frac{35}{3}CO_2 + \frac{40}{3}H_2O + \frac{23}{3}N_2$$

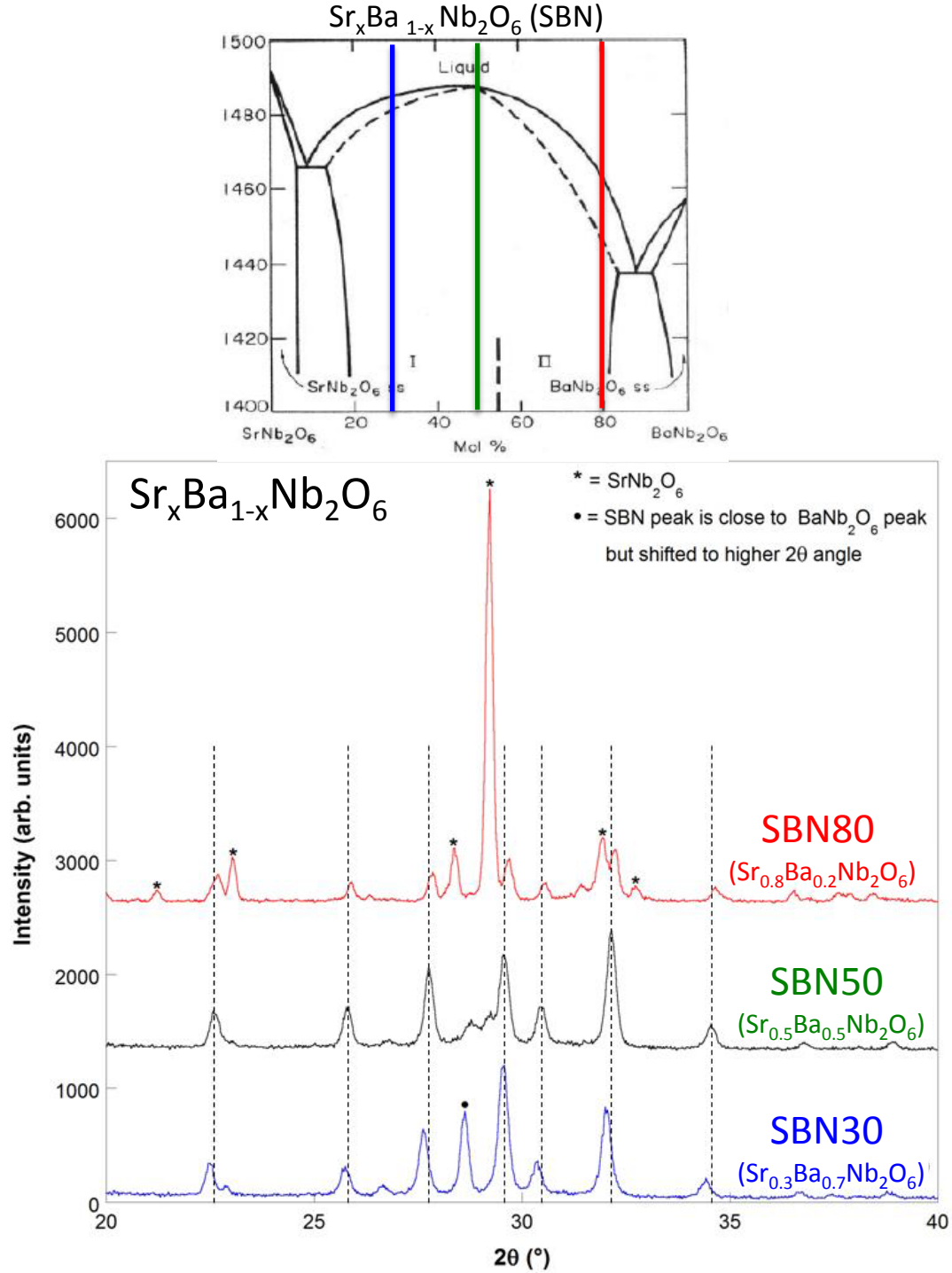
Solution Combustion Synthesis (SCS)

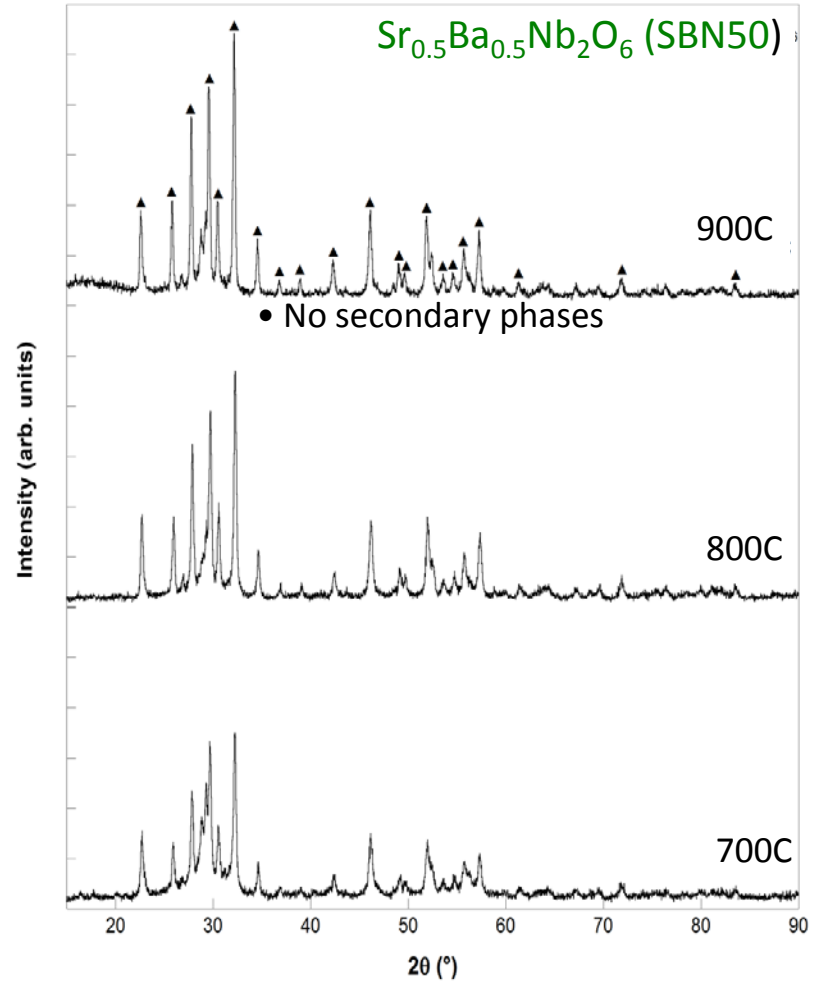


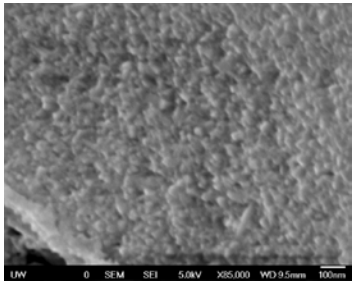
XRD-Comparison for $SrNb_2O_6$



Crystallinity and Phase Purity







Thermoelectric Evaluation of SBN50

- Full characterization of CME thin-film library is still in progress. Optimum composition(s) have not yet been determined for further exploration.

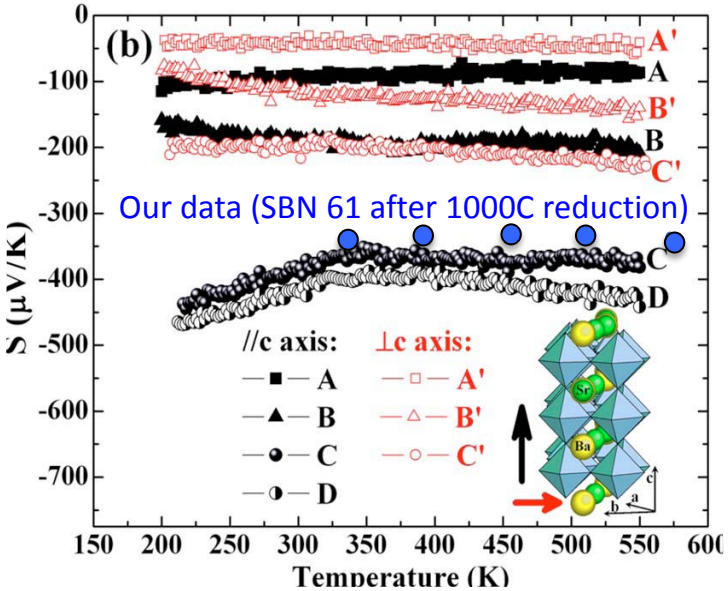
- **SBN61** (single-crystal) for cross-check.

  -ULVAC ZEM-3 for TE measurements

  -Comparison with published data

  -Evaluation of reduction conditions

  N2/H2(5%) flowing through 900-1150C heated zone

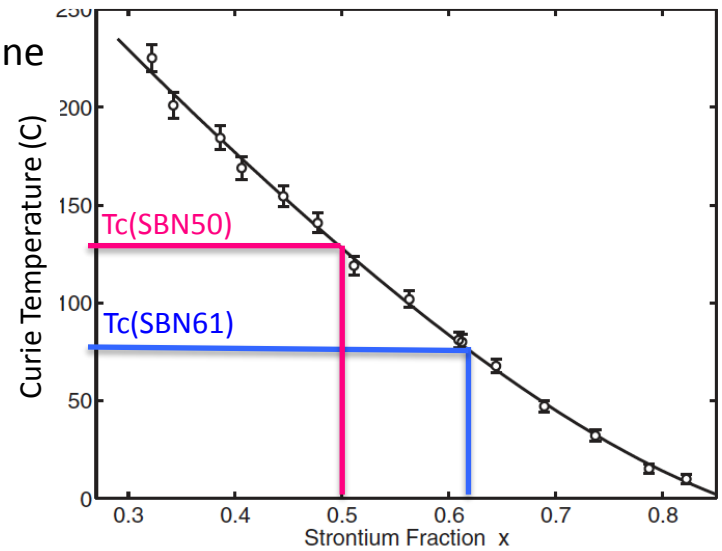


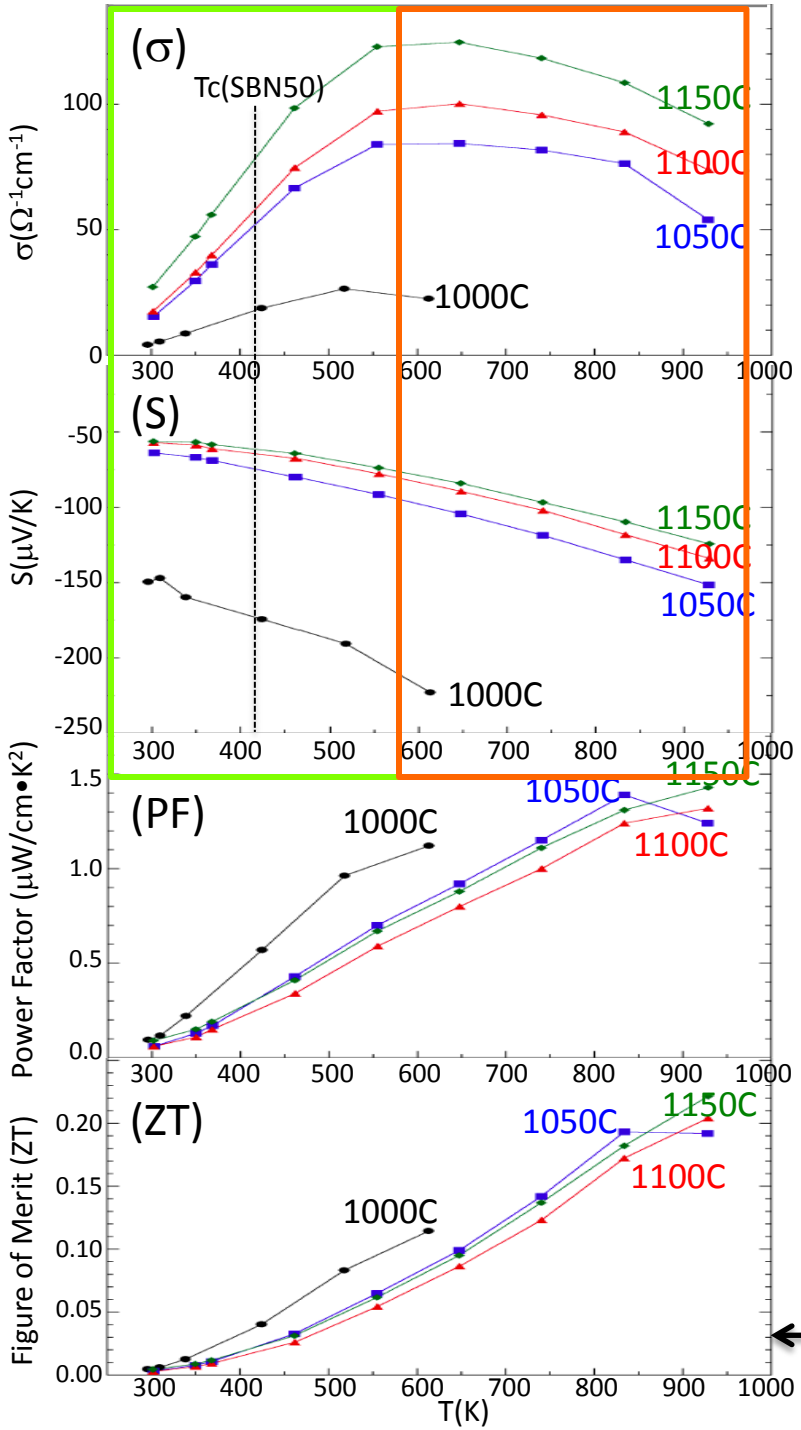
- **SBN50** in bulk form to investigate factors that determine the TE performance.

  -Mid composition in $Sr_xBa_{1-x}Nb_2O_6$ series

  -Higher Tc

  -Higher Ba content for lower κ





- Electrical conductivity (σ) ↑ as reduction temp ↑
- Seebeck coefficient (S) ↑ as reduction temp ↓
- Electrical conductivity (σ) ↑ and Seebeck(S) ↑ in □

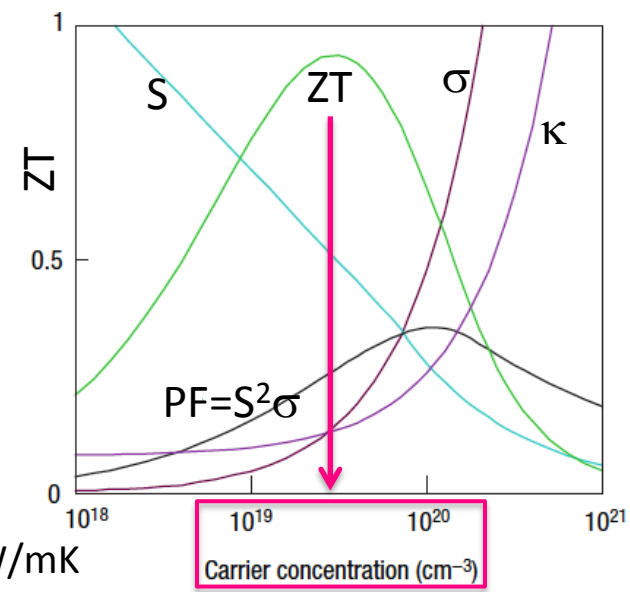
- SC-metal transition: If Mott transition, n_e~ 10^{20}#/cm^3
- Oxygen vacancies due to reduction

$$O_O \rightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g)$$

- Carrier concentration n_e~ 10^{19}-10^{20}#/cm^3 based on $[n_e]=2[V_O^{\bullet\bullet}]$ defect equilibria.

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

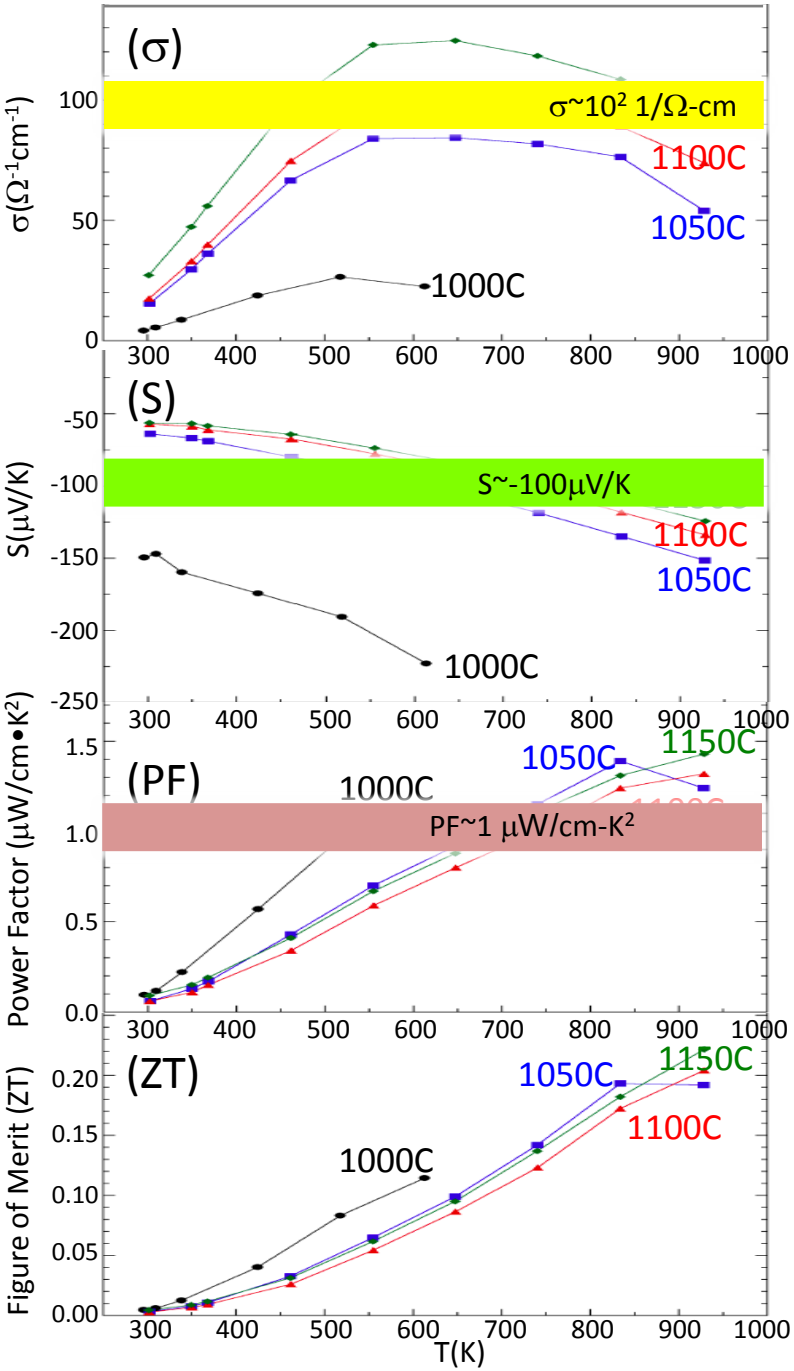
Assuming κ = 0.6 W/mK (single x'tal data)

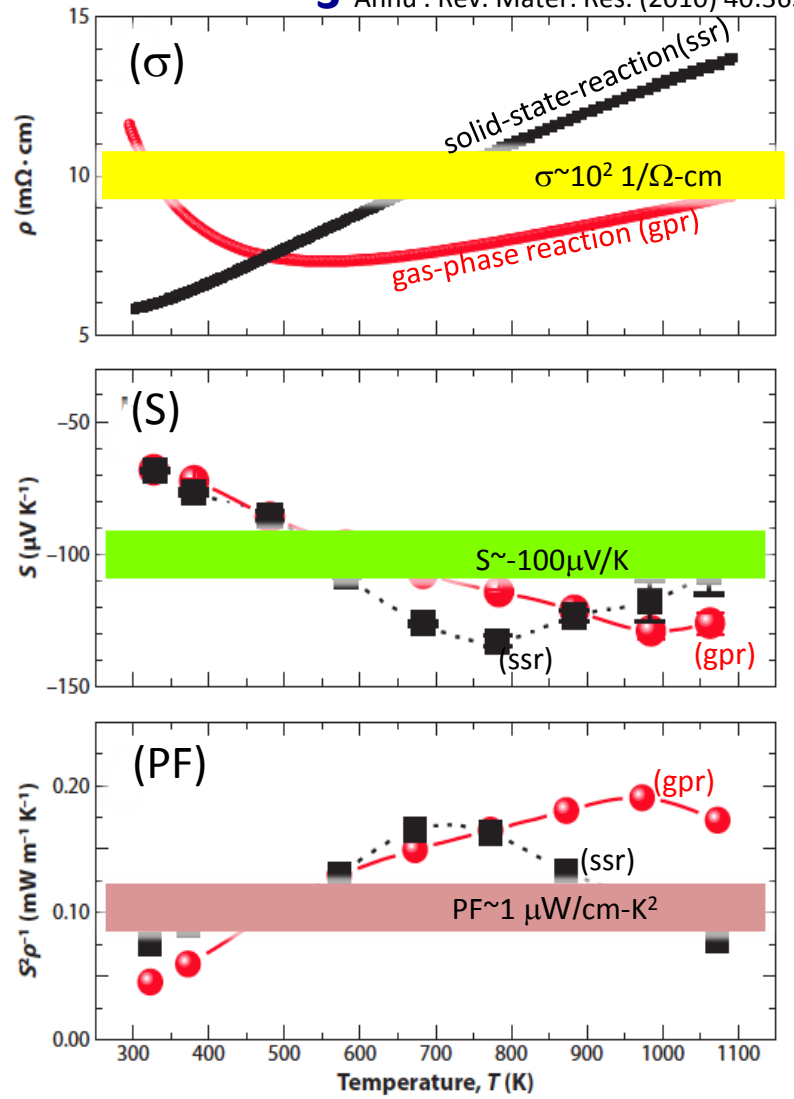


Snyder and Toberer
Nature Mat. 7, 105(2008)

SBN50 vs. $CaMnO_3$

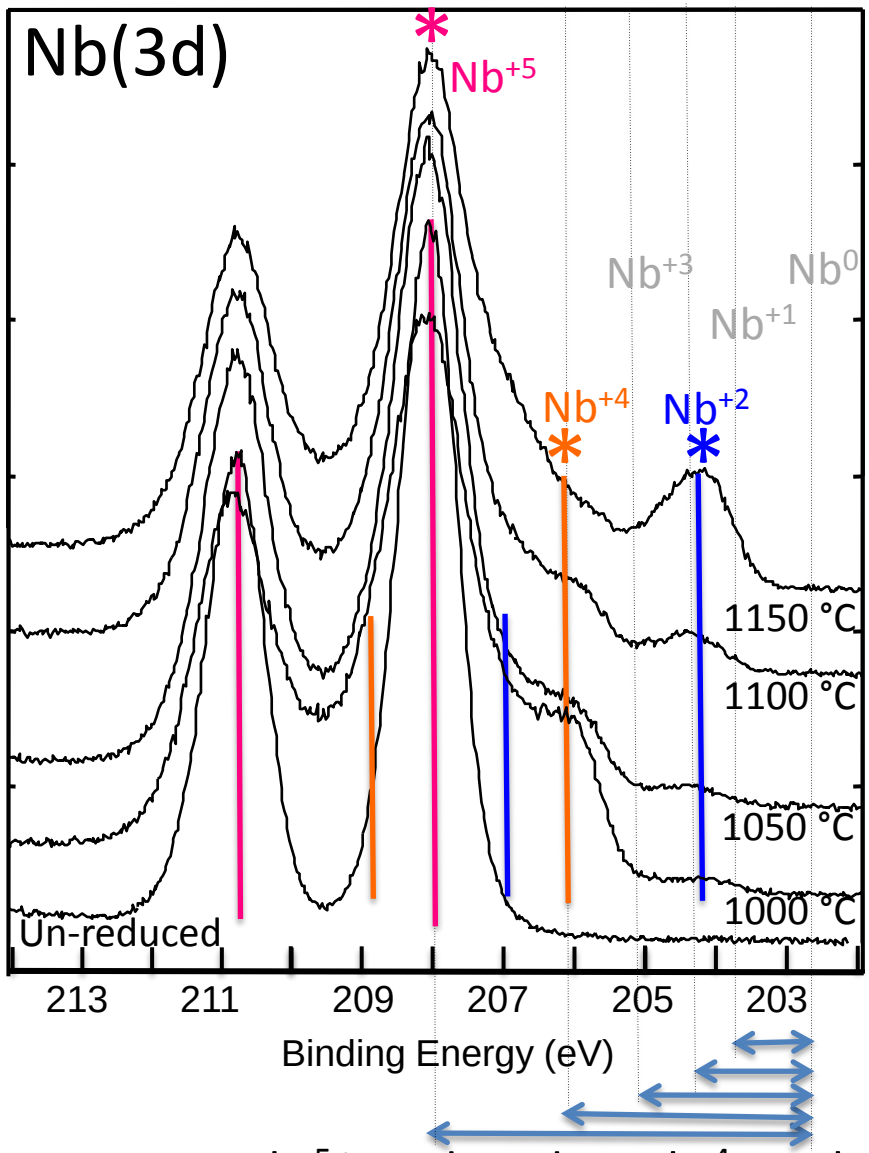
Annu . Rev. Mater. Res. (2010) 40:363-94

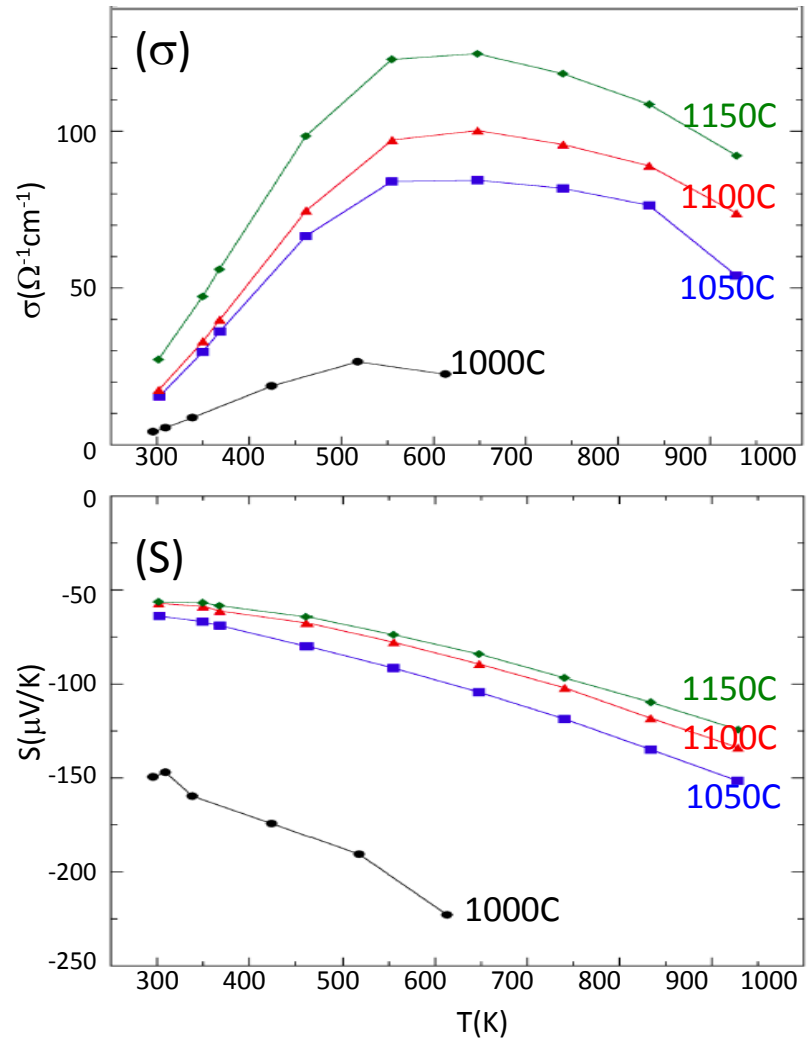




- So far $CaMnO_3$ is the best n-type material known.
- Un-optimized SBN50 shows similar performance.
- Optimization would give better performance.
- Very promising!

Degree of Reduction vs. Thermoelectric Performance





- Nb^{+5} is reduced to Nb^{+4} or Nb^{+2}; Not to Nb^{+3} nor Nb^{+1}
- Reduction to Nb^{+4} and Nb^{+2} improves σ , but Nb^{+2} affects S
- Peculiar electronic and crystal structural effect?

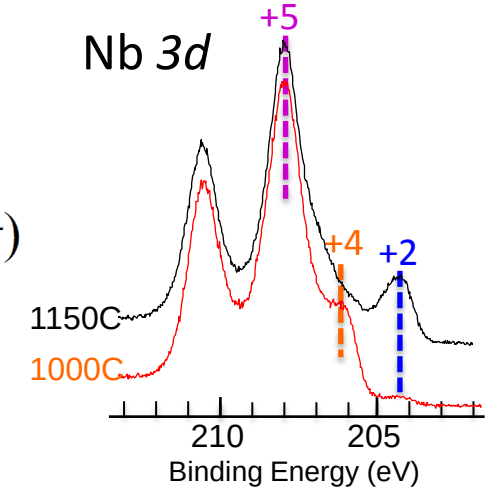
Non-stoichiometric SBN

- An oxygen vacancy created in a reduced environment through:

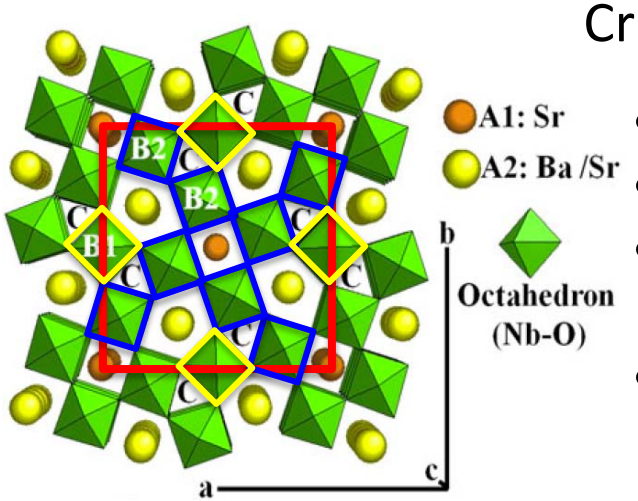
$$O_O \rightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g)$$

$$Sr_{0.5}Ba_{0.5}Nb_2O_6 \xrightarrow{Reduction} Sr_{0.5}Ba_{0.5}\boxed{Nb_{2-\alpha}^{+5}}\boxed{Nb_{\alpha}^{+n}}O_{6-\delta} + \frac{\delta}{2}O_2(g)$$

Nb^{+4} and Nb^{+2}



- Tetragonal Tungsten Bronze



Criteria for CN # and R(Cation/Anion) ratios suggest:

- Nb^{+5} and Nb^{+4} (Nb^{+3}) can form stable CN=6 octahedrons
- Nb^{+2} does not form Nb-O octahedrons
- In $CaO\text{-}SiO_2\text{-}NbO_x$, Nb^{+2} is known to occur
  (Metallurgical Materials Transactions ***41B***, 1038 (2010)

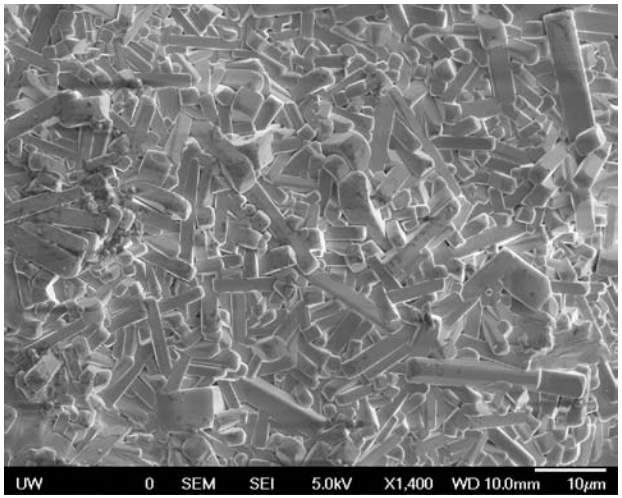
- **Hypothesis:**
  Local break-down of the Nb-O octahedrons may affect site occupancy of Sr and Ba ions and increase carrier density, causing reduction of the Seebeck effect.

- Need to conduct systematic study on "reduction process".

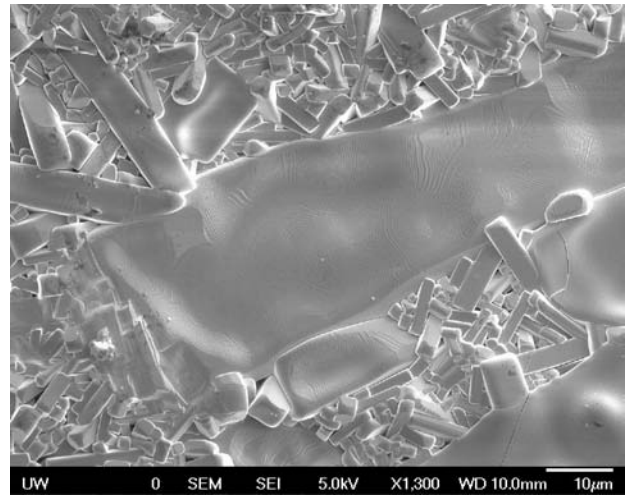
Microstructural Effect

- Micostructure of the present SBN50 sintered sample was not optimized

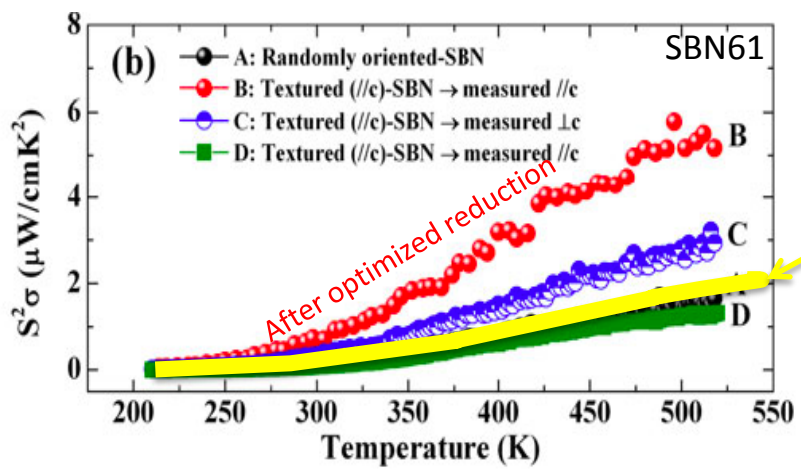
Random distribution of c-axis oriented phase



Abnormal grain growth



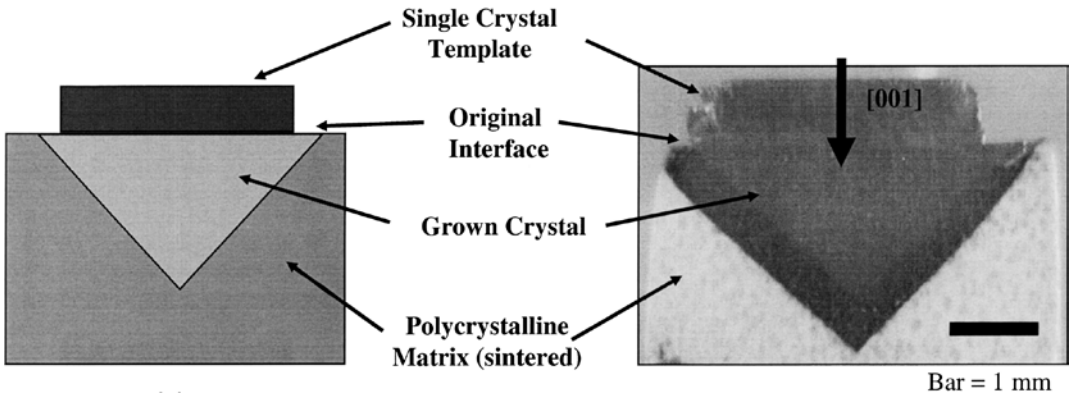
- Textured SBN significantly enhances SBN's TE performance



Our SBN50 data
- un-optimized
- random orientation

Lee et al., J. Mater. Res., ***26***(1) 26 (2011)

Templated Grain Growth (TGG)

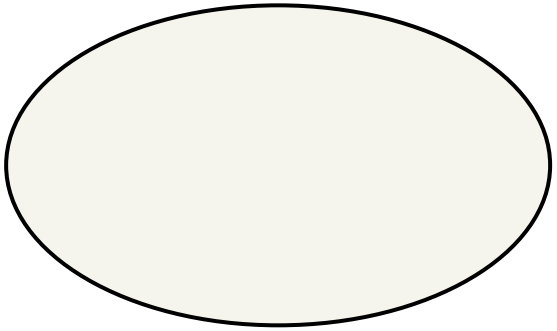


G.L. Messing et al., *Critical Reviews in Solid State and Materials Sciences* **29**, 45 (2004)

- Templated grain growth (TGG) –Oriented seed crystals are mixed with amorphous particles prior to growth
- Final product has same orientation as the seed crystals
- Experimental (next)

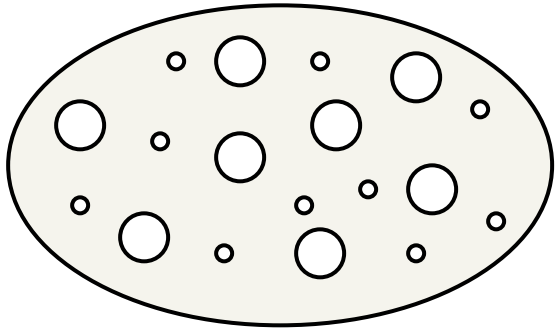
Effects of Porosity

Optimized composition



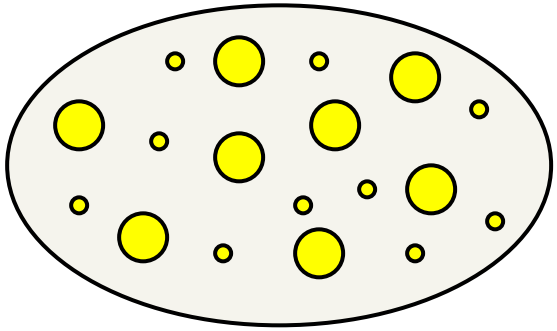
- Compositions with both high T_c and good TE performance

Optimized composition
+
Macro/micro pores



- Examine effect of hierarchical pore structure on TE behavior

Optimized composition
+
Macro/micro pores
+
CO_2



- Examine effects of CO_2 infiltration on thermoelectric properties

- CO_2 – low κ, by-product in many factory processes
- Infiltration of CO_2 into porous structure may improve *ZT*

Summary of Findings

(October 1, 2011-Present)

1. $Sr_xBa_{1-x}Nb_2O_{6-\delta}$ (SBN) as potential candidates for n-type TE oxide materials.
2. Combinatorial approach for screening the optimum compositions, structures, and TE properties, is in progress.
3. Solution combustion synthesis (SCS) produces SBN nano-powders with uniform particle size and high purity(no second phases).
4. Thermoelectric evaluation of SBN50, even in its un-optimized forms, showed comparable TE performance with those found in the best known materials so-far, such as n-type $CaMnO_3$.
5. Degree of reduction strongly influences the TE performance, and an experimental protocol to determine optimum condition(s) for reduction is established.
6. Preventing abnormal grain growth as well as controlling texture together with compositional optimization, SBN may become prime candidates for n-type TE oxide materials.

List of Future Plans for FY-1(rest) and FY-2

1. Compositional optimization of SBNs via CME screening

   FY-1 focus: $Sr_xBa_{1-x}Nb_2O_6$
   FY-2 focus: $M:(Sr, Ba)_2Nb_2O_7$

   } Particularly higher Ba side

   - Shift Mott-transition temperature higher
   - Increase phonon scattering through Ba
   - Use Nb^{+2} protocol for reduction

1. Bulk material fabrications of optimum SBN by SCS
2. Scale up process of 2.
3. Micro-structure control by textured growth via sinter forging.
4. Evaluation of hierarchical pore effect and environment.
5. <u>Attempt</u> to fabricate "proto-type TE device" using SBN based n-type materials with p-$NaxCoO_3$ or p-$CaCoO_3$.

Thank you!