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

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(June 1, 2012-May 31, 2013)

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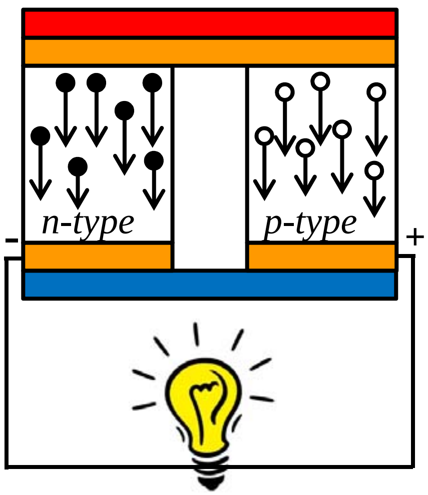
June 10, 2013
The UCR Contractors Review Conference

Introduction/Motivation for Research

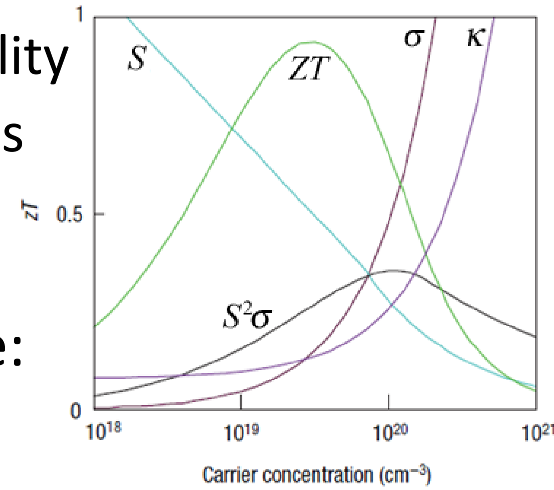
Waste Heat

TE generator



Electrical power

- Thermoelectric (TE) oxides for waste heat recovery
  - Good high-temperature stability
  - Stable in hostile environments
  - Low cost/toxicity



- Oxides with complex structure:
  - Low thermal conductivity, κ
  - Tailor stoichiometry to maximize $S^2\sigma$ with low κ
- Significant progress in the development of the *p*-type TE oxides (e.g., $NaCo_2O_4$)
- Similar breakthroughs not yet achieved for *n*-type TE oxides
- **Search for high-performance *n*-type oxides**

Overall Goal of This Project (DE-FE0007272):

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

Specific Objectives:

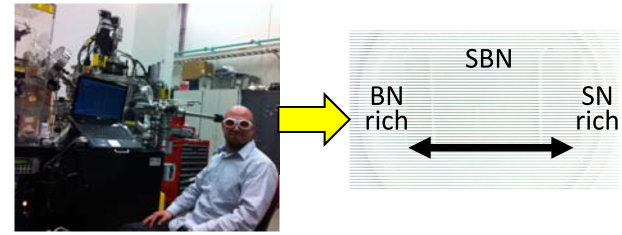
- Investigate potential materials and processing technology of n-type oxides with high TE performance using hierarchical designed microstructures.
- Develop processing routes to make desired crystalline phases and anisotropic porous structures to evaluate the effect of micro- and macro-pores on thermoelectric properties.

Technical Objective:

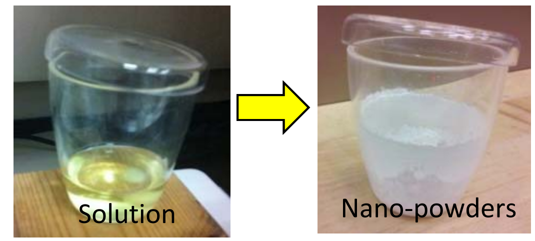
Establish beneficial combination of ferro-electricity (FE) and thermo-electricity (TE) to improve the TE performance of materials.

Summary of Progress from FY-1 (Oct 1, 2011-May 31, 2012)

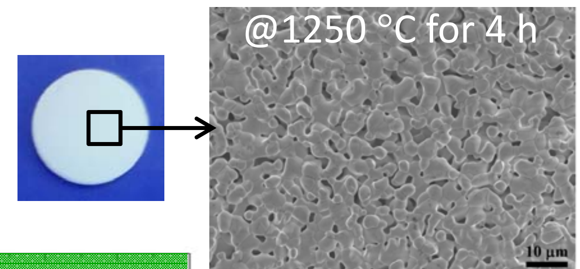
- Combinatorial Materials Exploration (CME), to select compositions of $Sr_xBa_{1-x}Nb_2O_6$ (SBN).



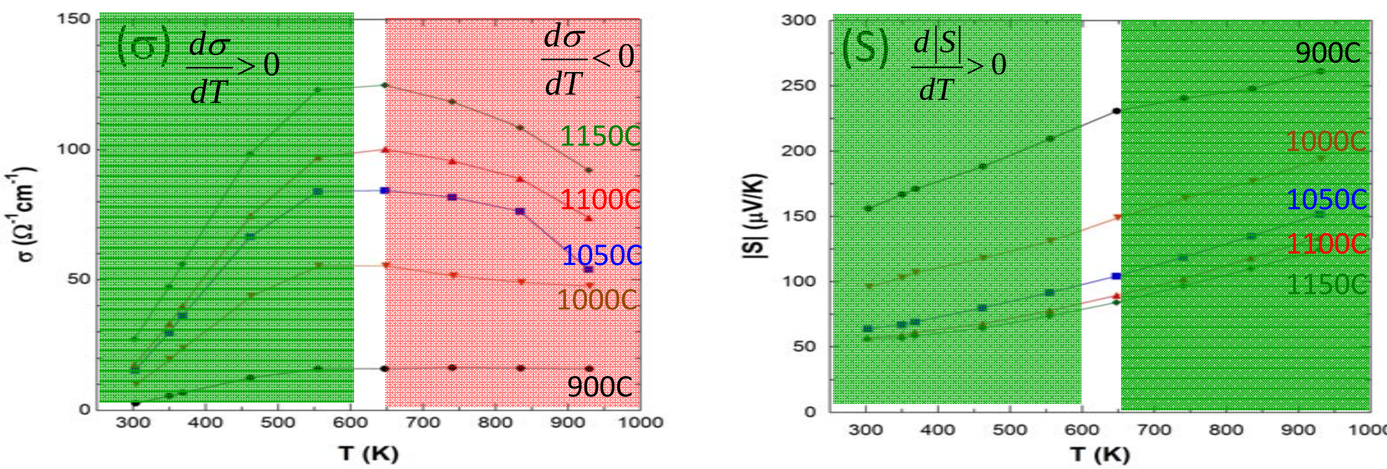
- Solution Combustion Synthesis (SCS) to produce nano-powders with a high degree of crystallinity and phase purity.



- Preliminary tests of thermoelectric performance from pressure-less sintered pellets (SBN50).



- Significant findings: $\sigma\uparrow \& |S|\uparrow$



- Publication: *Journal of the American Ceramic Society* Thermoelectric Properties of Reduced Polycrystalline $Sr_{0.5}Ba_{0.5}Nb_2O_6$ Fabricated Via Solution Combustion Synthesis (2013)

Summary of Progress During This Period

(June 1, 12-May 31, 13)

Scientific Achievement

- Reduction of SBNx and TE effect.

$$Sr_xBa_{1-x}Nb_2O_6 \rightarrow Sr_xBa_{1-x}Nb^{5+}_{2-y}Nb^{n+}_yO_{6-\delta} + \frac{\delta}{2}O_2$$

- Site specific occupancy in SBNx.
- Electronic and phonon effects of of SBNx on thermal conductivity.
- Better understanding of change in sign of dσ/dT and $\sigma \uparrow \& |S| \uparrow$
- XPS to ascertain optimum cond. of reduction for high TE effect.

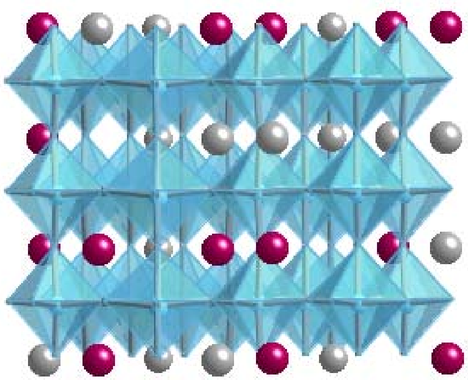
Technological Development

- Further refinement of SCS, and production of large quantities of nano-powders.
- Exploration of other niobate compositions with Higher Tc.

  M:$(Sr, Ba)_2Nb_2O_7$ (M:SBN)

  $Sr_xBi_{2-x}Nb_2O_9$ (SBiN)
- Controlled microstructures, grain texture, densification and pores to control TE properties.

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



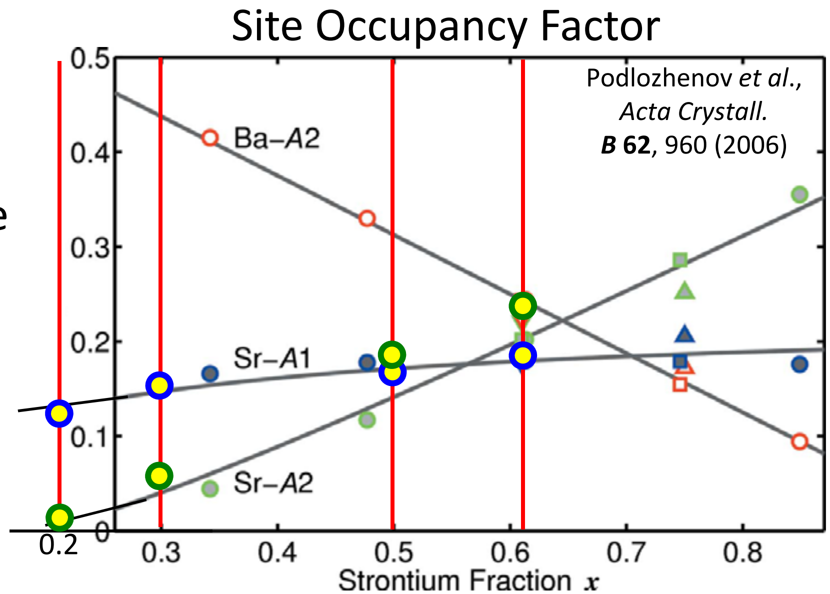
- Ferroelectric relaxor
- Tungsten tetragonal bronze
- Ion occupancy

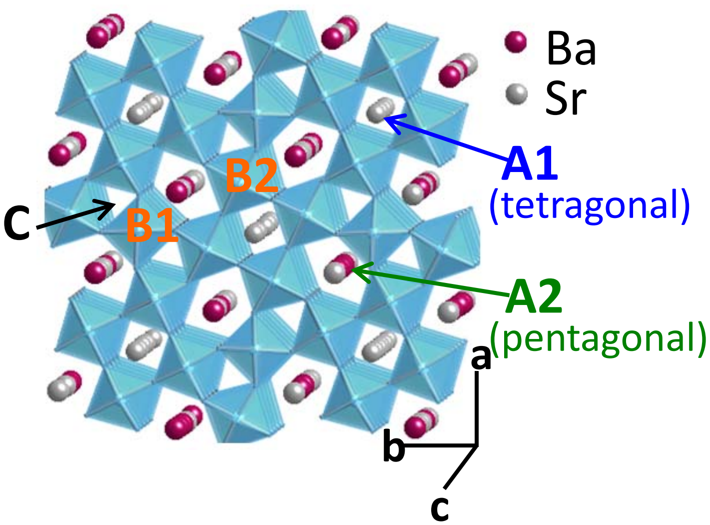
$(A1)_2(A2)_4(C)_4(B1)_2(B2)_8O_{30}$

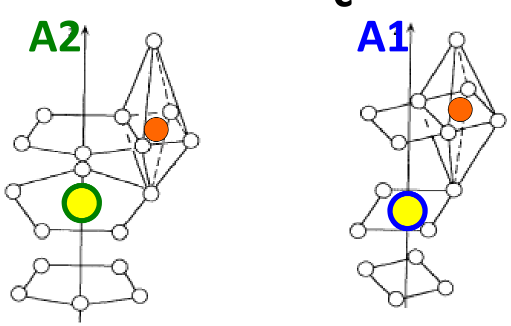
A1 = Sr^{+2}

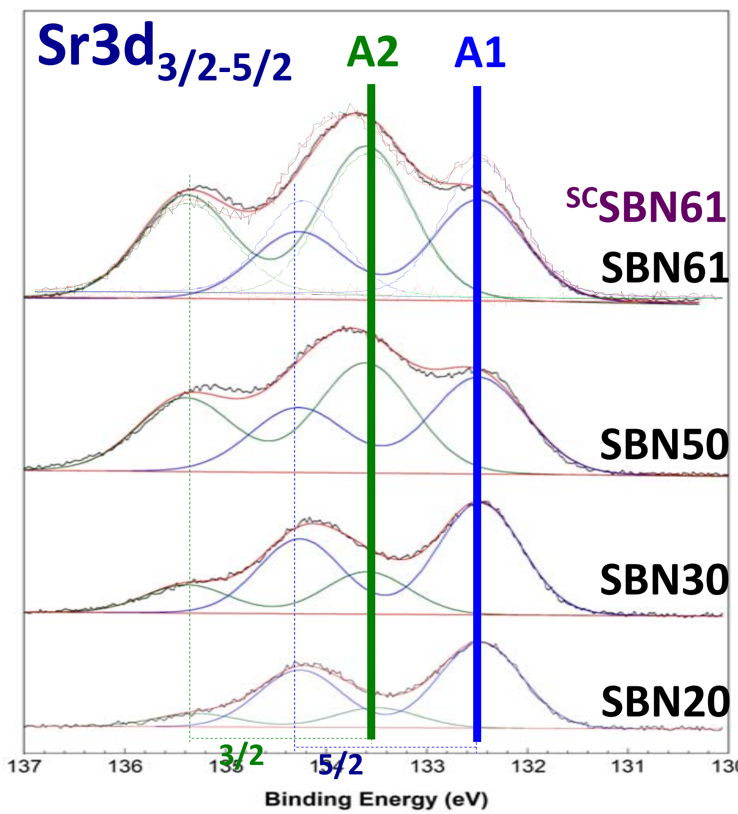
A2 = Sr^{+2} and Ba^{+2}

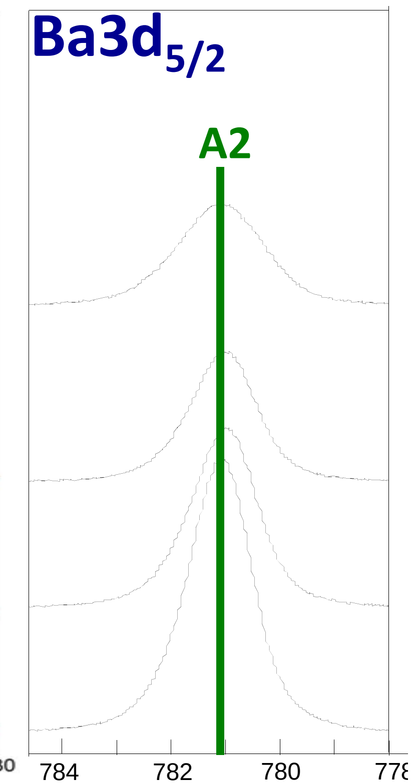
B1 and B2 = Nb^{+5}



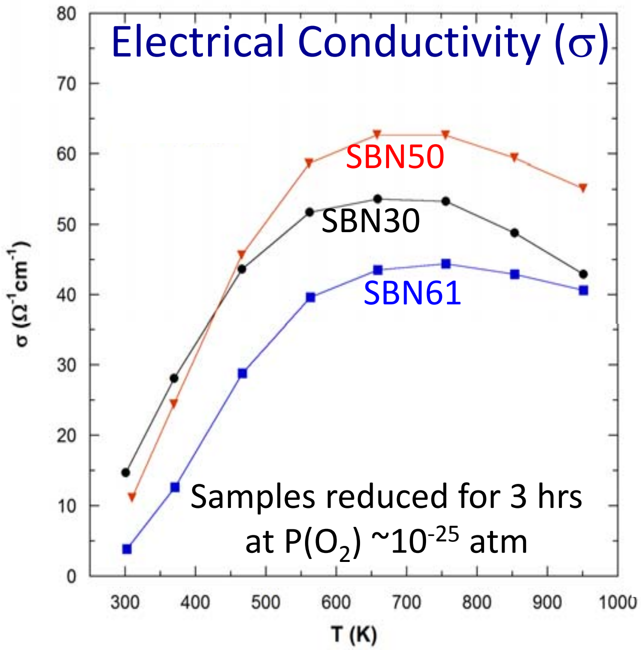


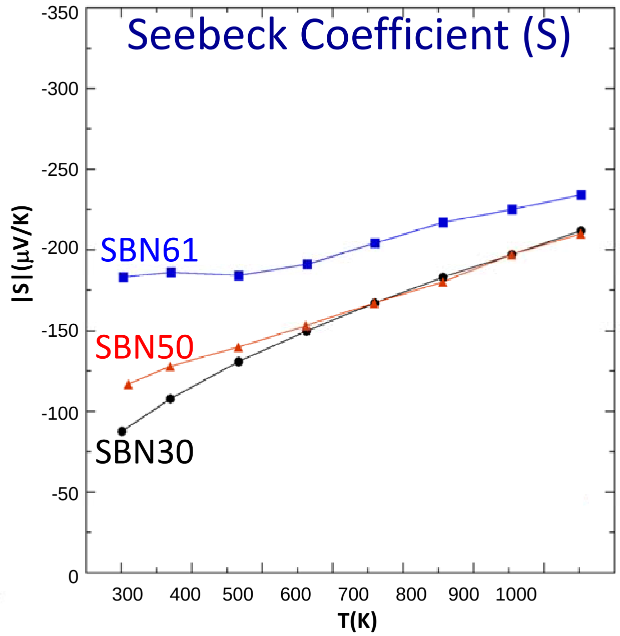


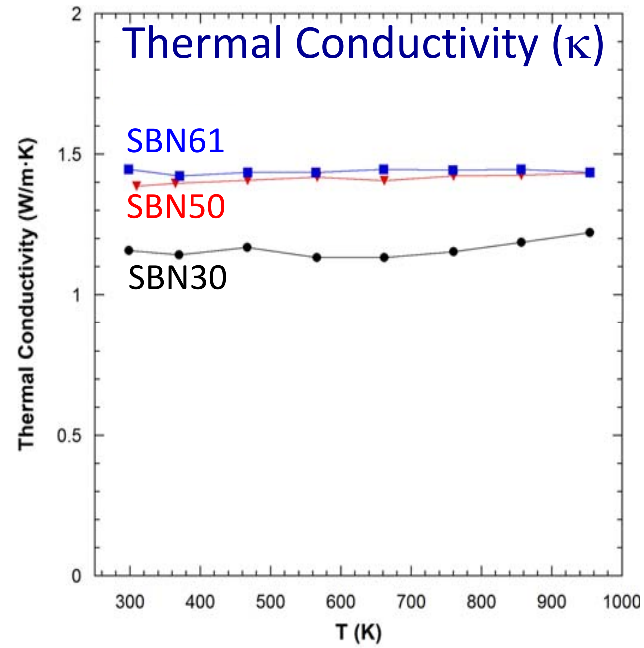


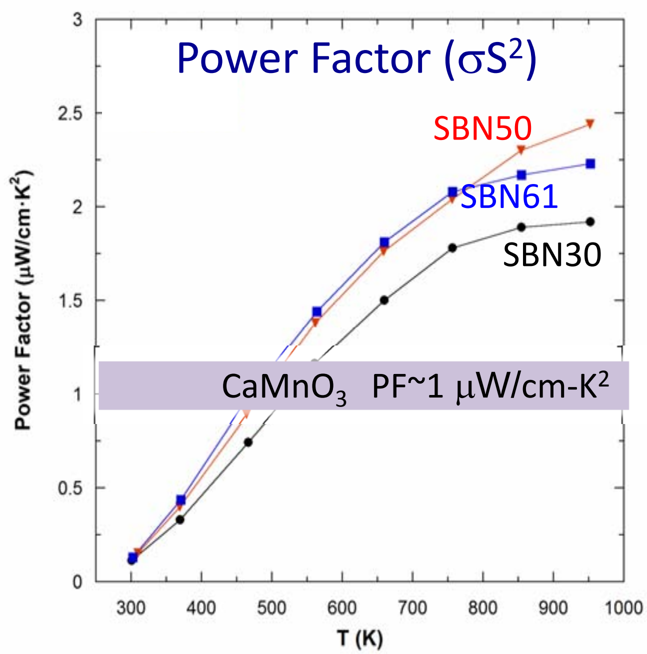


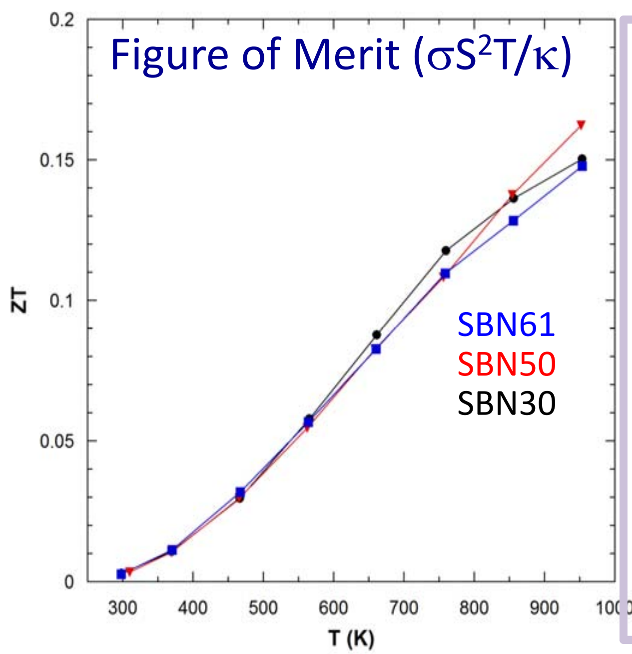
TE Results from $Sr_xBa_{1-x}Nb_2O_6$

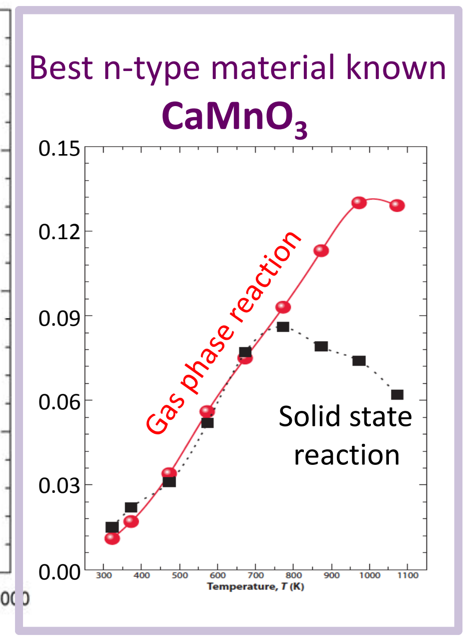












SBN50 as a model compound to investigate:

1. Reduction of SBNx and TE effect.

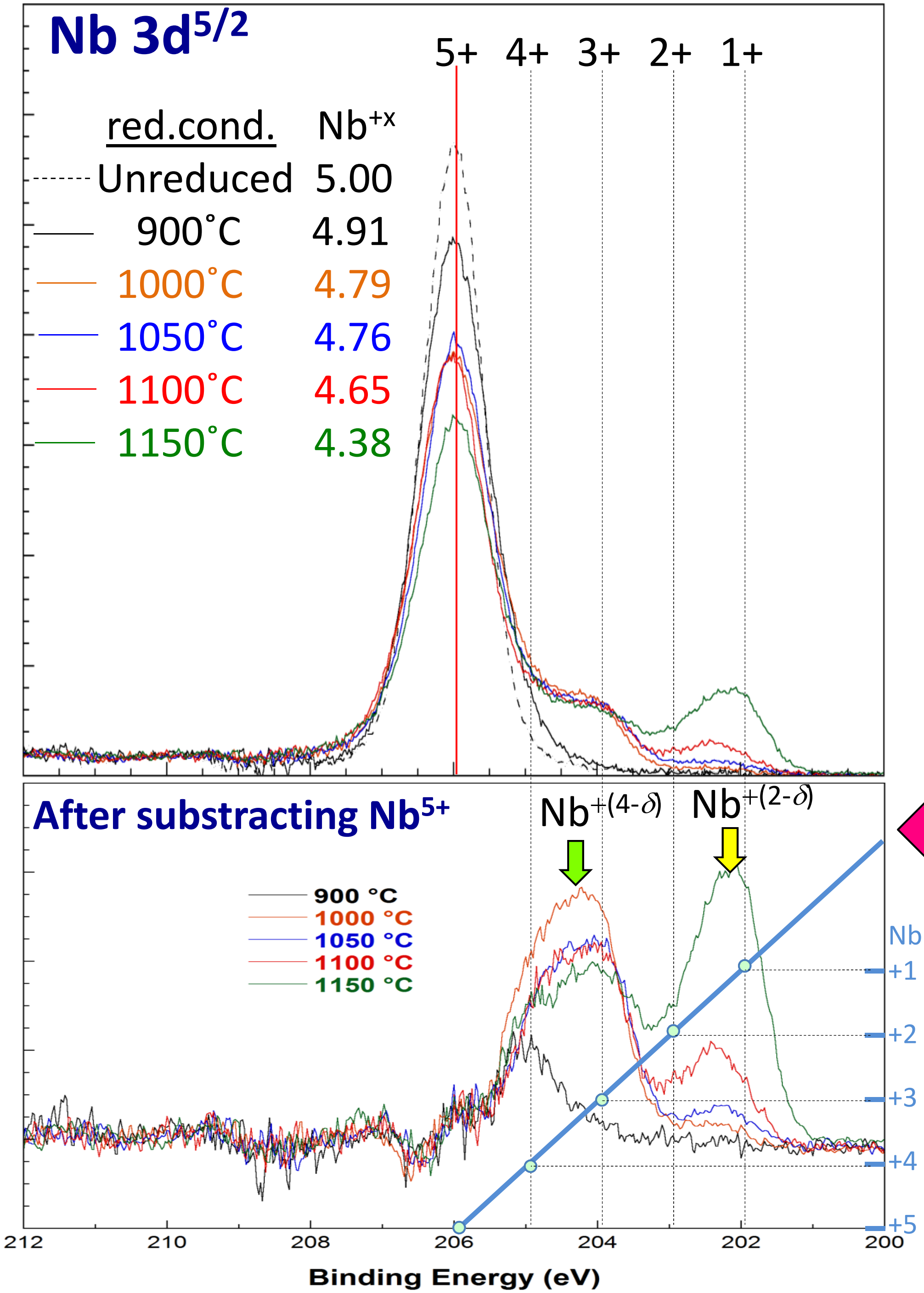
1. Site specific occupancy of Sr^{+2} ions, and reduction of Nb^{+5} ions in SBNx.

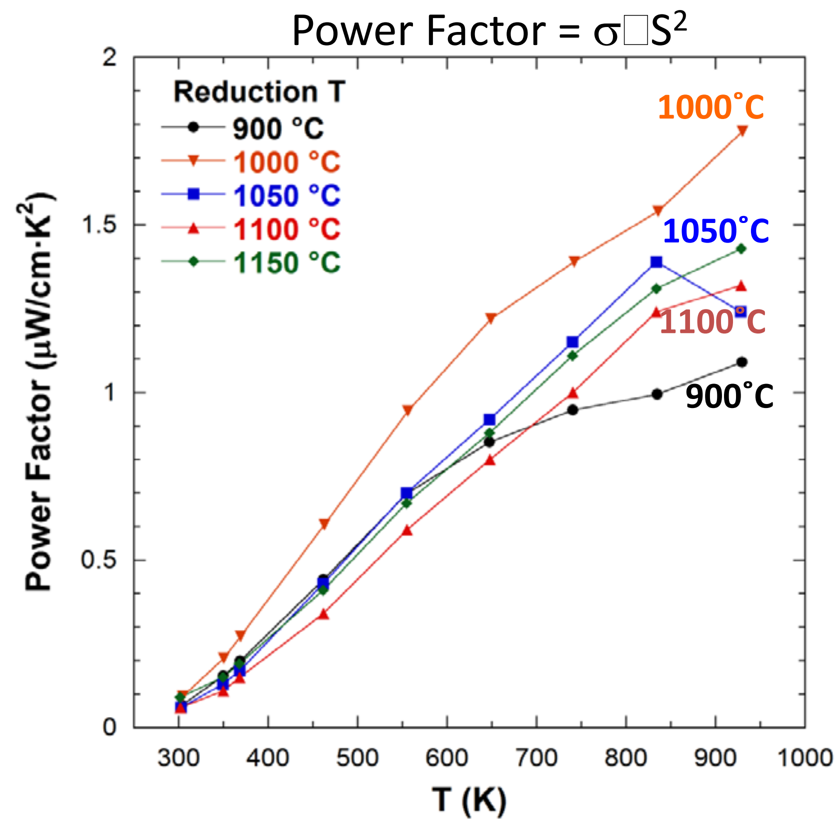
3. Electronic and phonon contribution in thermal conductivity of SBNx.

4. Mechanistic understanding of change in sign of $d\sigma/dT$ and parallel trend of σ and S.

5. XPS as a tool to ascertain optimum reduction conditions for high TE effect.

6. Microstructural aspects on TE property.



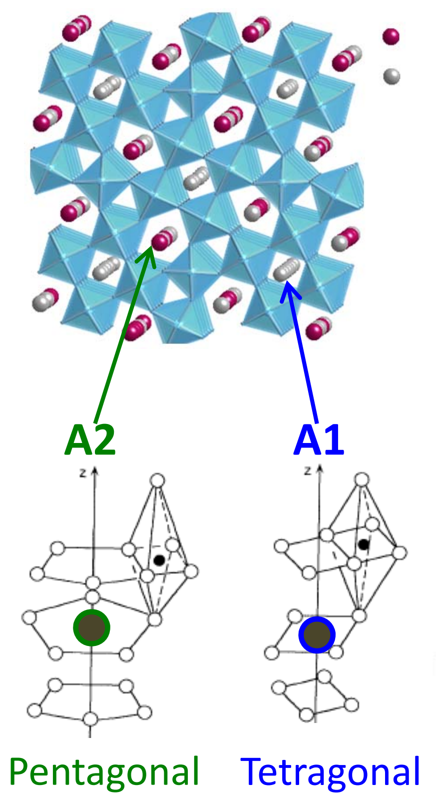


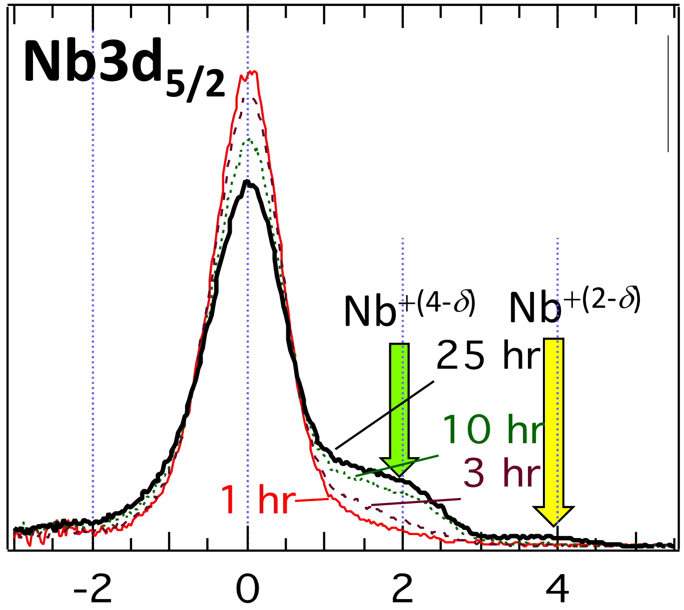
- $Nb^{+(4-\delta)}$ to $Nb^{+(2-\delta)}$ ratio becomes maximum after 1000 °C reduction
- PF becomes maximum before $Nb^{+(2-\delta)}$ switches on.

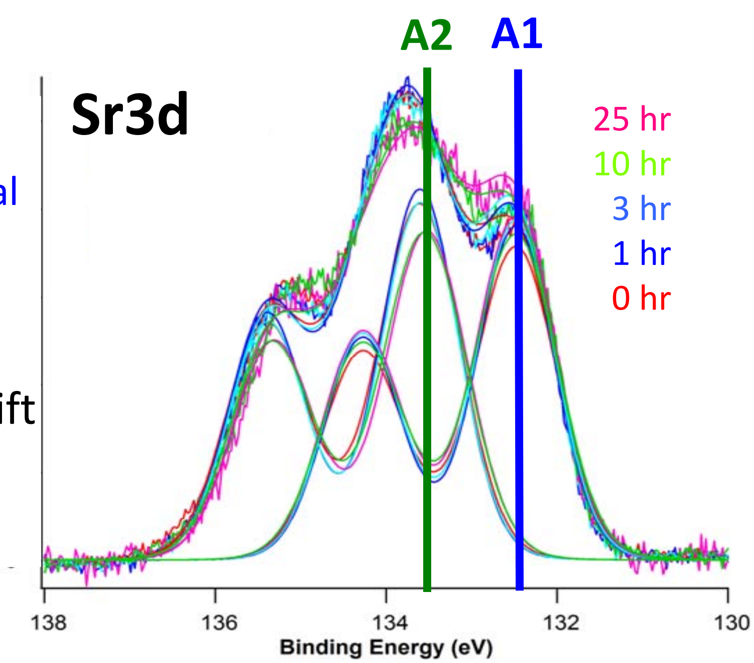
XPS as a protocol to ascertain ideal reduction conditions

Testing Protocol : SBN50

Reduction @1000 °C for different times





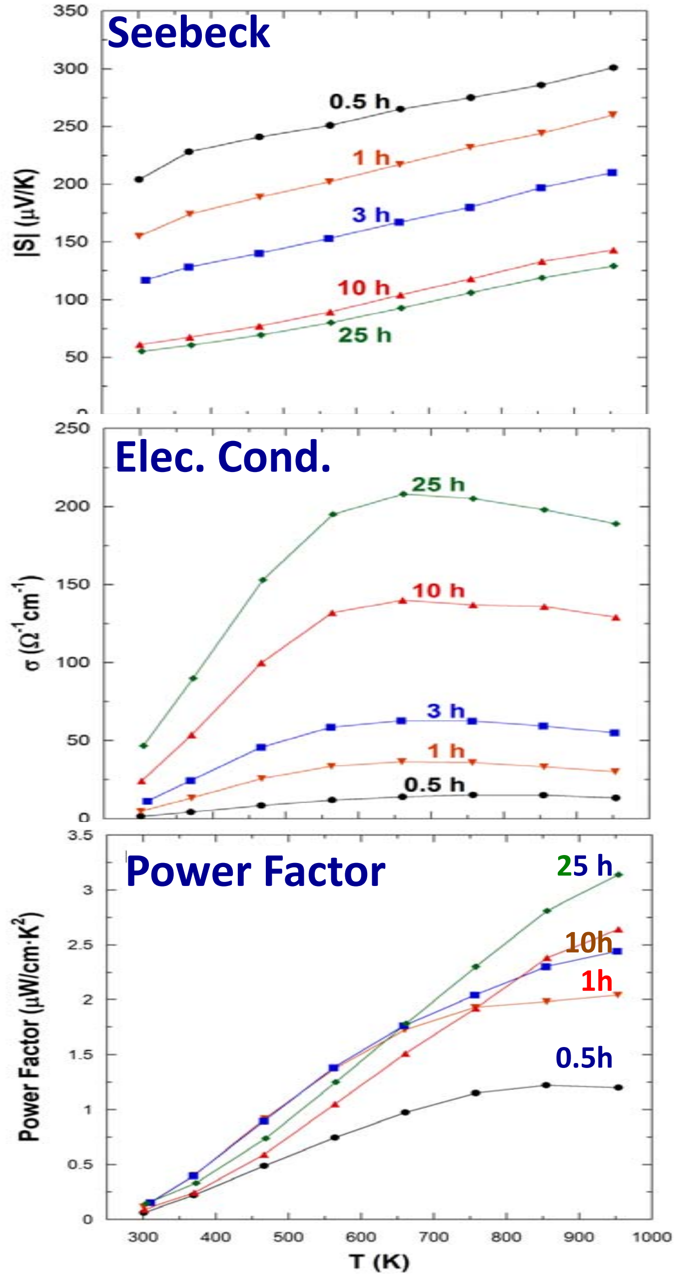


Reduction causes:

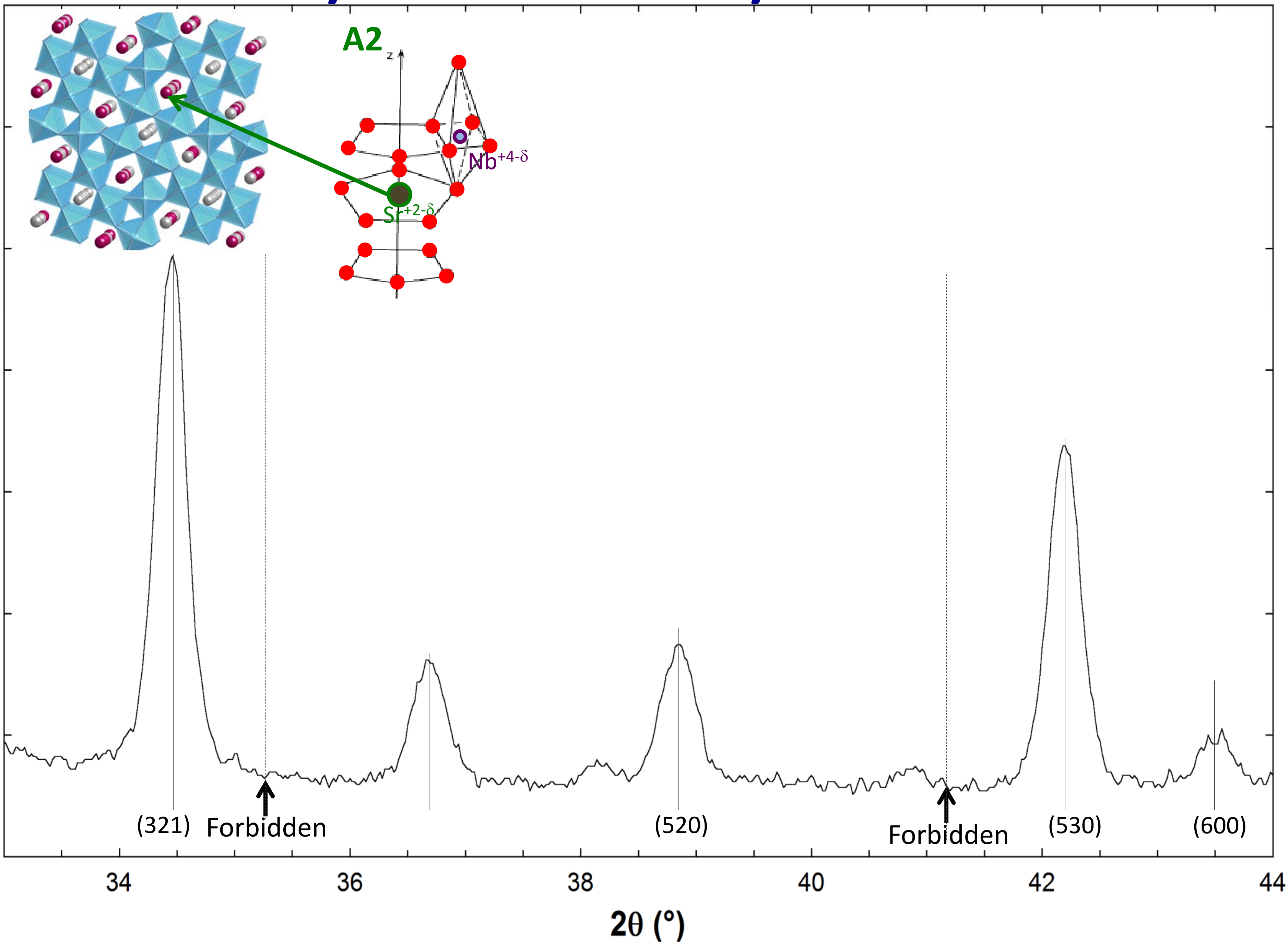
- **A1**: Unchanged
- **A2**: Broadening/shift

Removal of oxygen from A2 site?

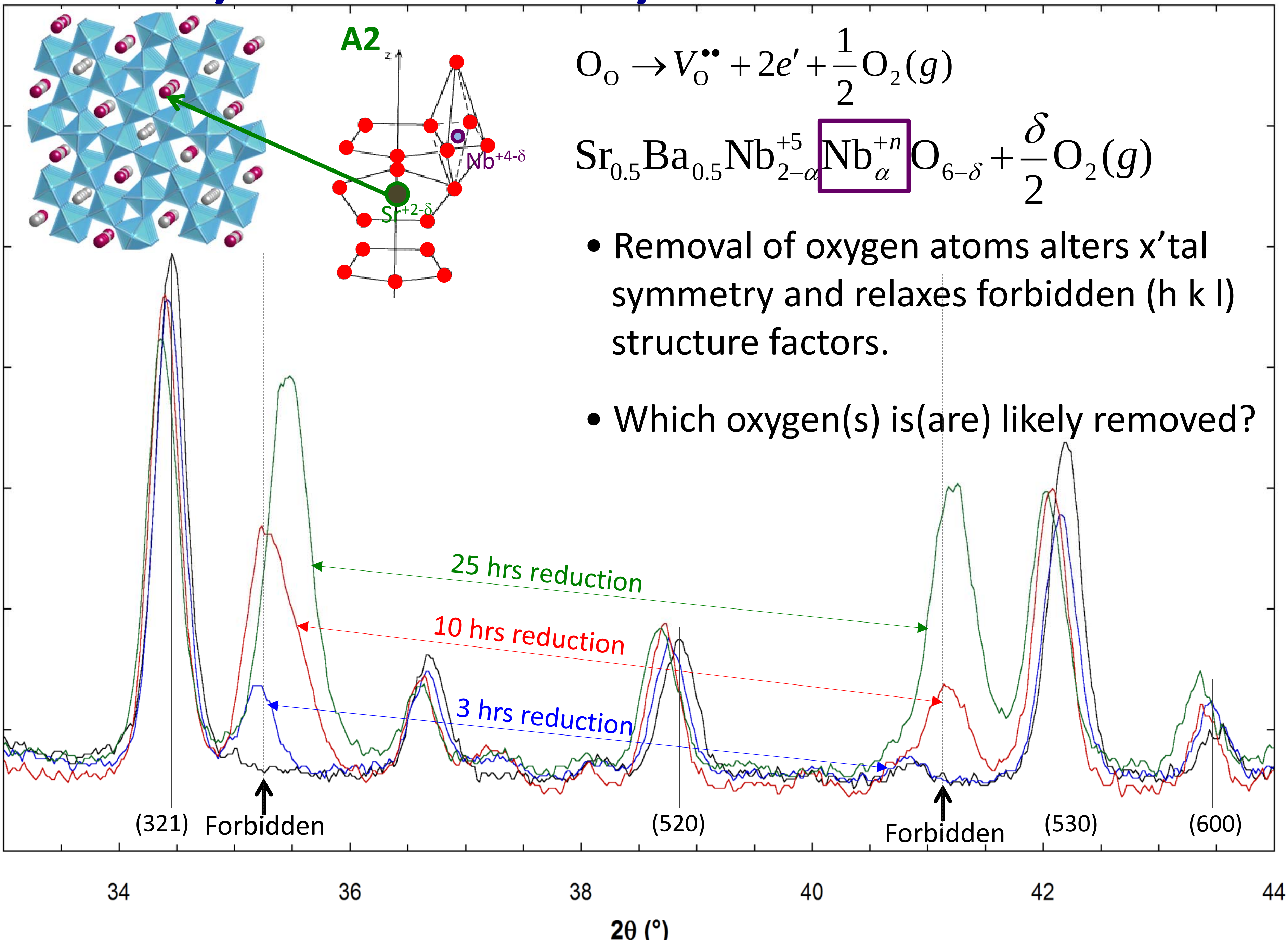
Corresponding TE properties



X-ray Diffraction Analysis of SBN50



X-ray Diffraction Analysis of Reduced SBN50

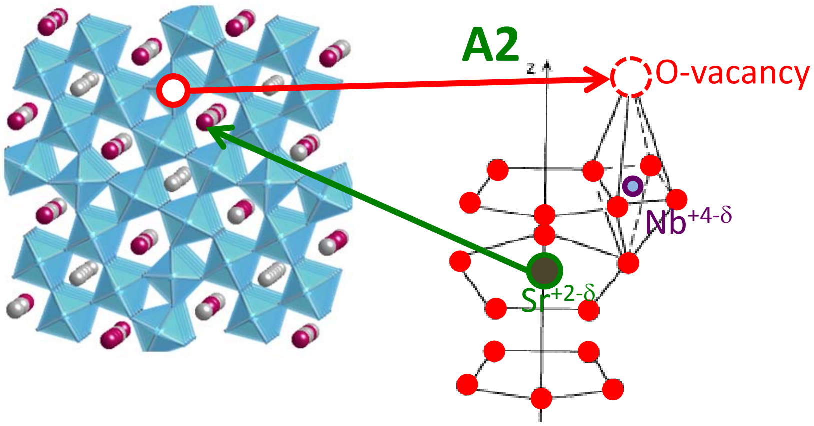


$$O_O \rightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g)$$

$$Sr_{0.5}Ba_{0.5}Nb^{+5}_{2-\alpha}\boxed{Nb^{+n}_{\alpha}}O_{6-\delta} + \frac{\delta}{2}O_2(g)$$

- Removal of oxygen atoms alters x'tal symmetry and relaxes forbidden (h k l) structure factors.
- Which oxygen(s) is(are) likely removed?

Which Oxygen(s) is(are) removed?



$$Sr_{0.5}Ba_{0.5}Nb^{+5}_{2-\alpha}\boxed{Nb^{+n}_{\alpha}}O_{6-\delta}+\frac{\delta}{2}O_2(g)$$

TABLE IV. Point defect formation energies in $Sr_{0.6}Ba_{0.4}Nb_2O_6$.

Ion	Position	Vacancy energy (eV)
Nb	2*b*	133.84
Nb	8*d*	131.65
O_1	8*d*	20.22
O_2	8*d*	20.66
O_3	4*c*	21.83
O_4	4*c*	18.14
O_{5a}	8*d*	21.17
O_{5b}	8*d*	21.18
Sr	2*a*	19.74
Ba	4*c*	18.47

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Calculations of defect properties important in photorefractive $Sr_{0.6}Ba_{0.4}Nb_2O_6$

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Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2001
(Received 8 April 1993; revised manuscript received 11 June 1993)

An interatomic potential model for $Sr_{0.6}Ba_{0.4}Nb_2O_6$ (SBN) has been developed by transfer of potentials from similar oxide crystals. The model has been used to examine defect properties of SBN important in the photorefractive effect. Our calculations indicate randomness on the Ba/Sr sublattice, and the possibility of O^- and Nb^{4+} small polarons when extra carriers are present. A self-compensation reaction is found to be a preferred incorporation model for tetravalent and trivalent impurities giving substitution on Nb and Ba/Sr sites. Our calculations indicate that Ce^{3+}, Fe^{2+}, and Mn^{2+} substituted on Ba/Sr sites can act as a donor to facilitate the photorefractive effect in SBN.

Planned Experiment (FY-3)

Neutron diffraction (at DOE-Oak Ridge Neutron Diffraction Facility)

Energy for Oxygen Vacancy Formation

Reduction and Electrical Conductivity of SBN

- Reaction to form oxygen vacancy

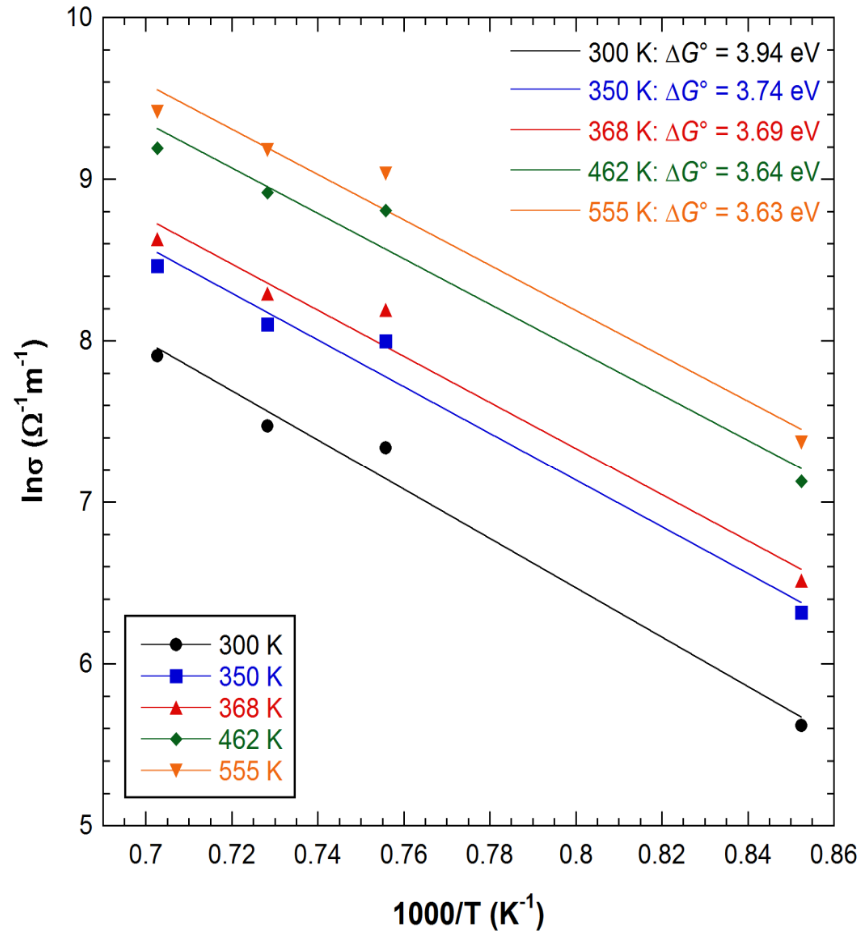
$$O_O \rightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g)$$

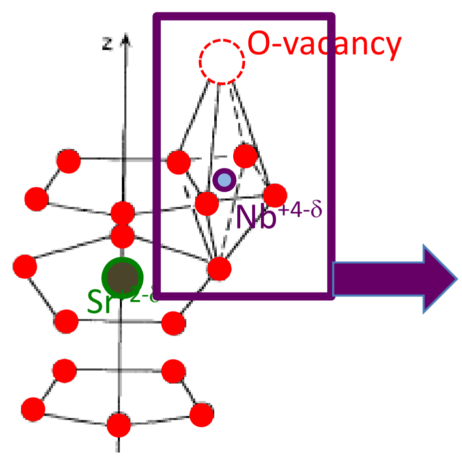
$$K = [V_O^{\bullet\bullet}]n^2(pO_2)^{\frac{1}{2}} = \exp\left(-\frac{\Delta G^\circ}{kT}\right)$$

- Electrical conductivity $\sigma = en\mu_e$

$$\ln\sigma = \left(\frac{1}{T}\right)\left(-\frac{\Delta G^\circ}{3k}\right) + \ln B$$

- ΔG_0~3.6-3.9eV



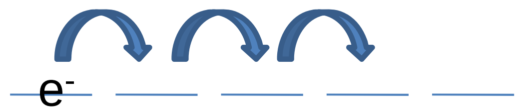


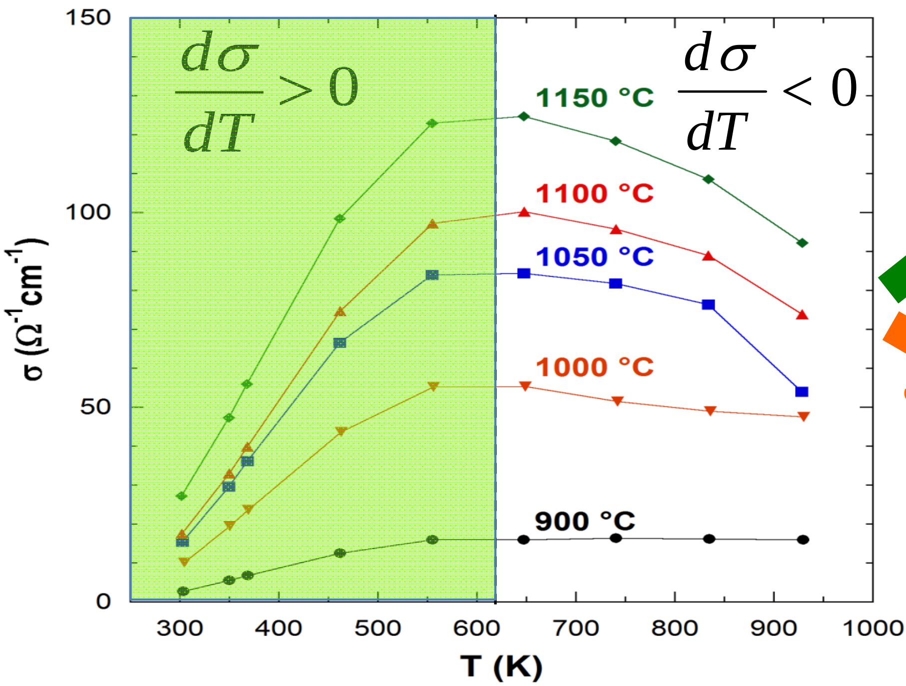
Planned Experiment (FY-3)

- EXAFS and hard X-ray diffraction analysis at DOE-APS Facility.

Electrical Conductivity

Test of Polaron Hopping Models

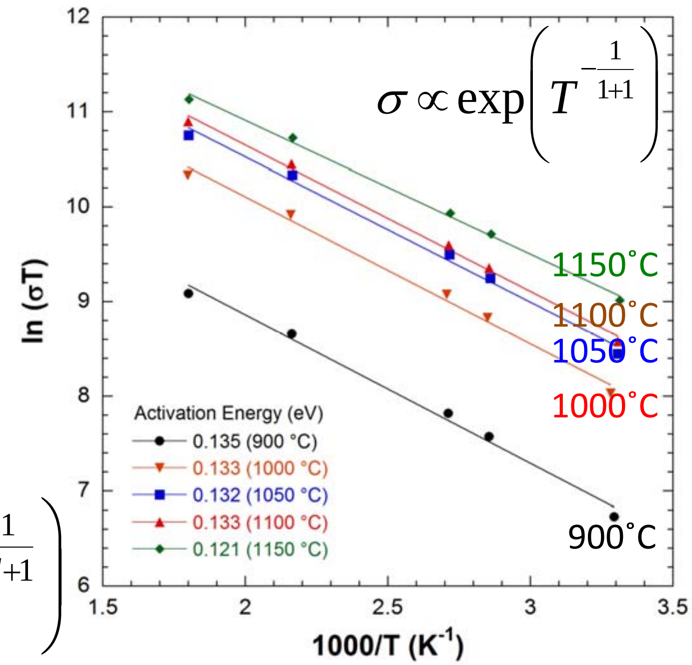


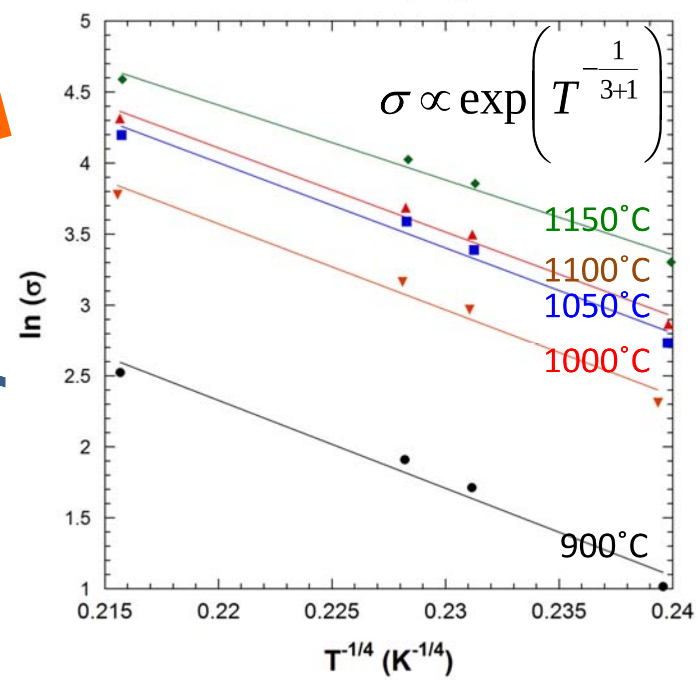


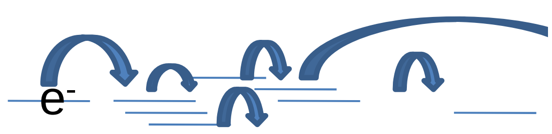
1-D hopping

$$\sigma \propto \exp\left(T^{-\frac{1}{d+1}}\right)$$

3-D hopping



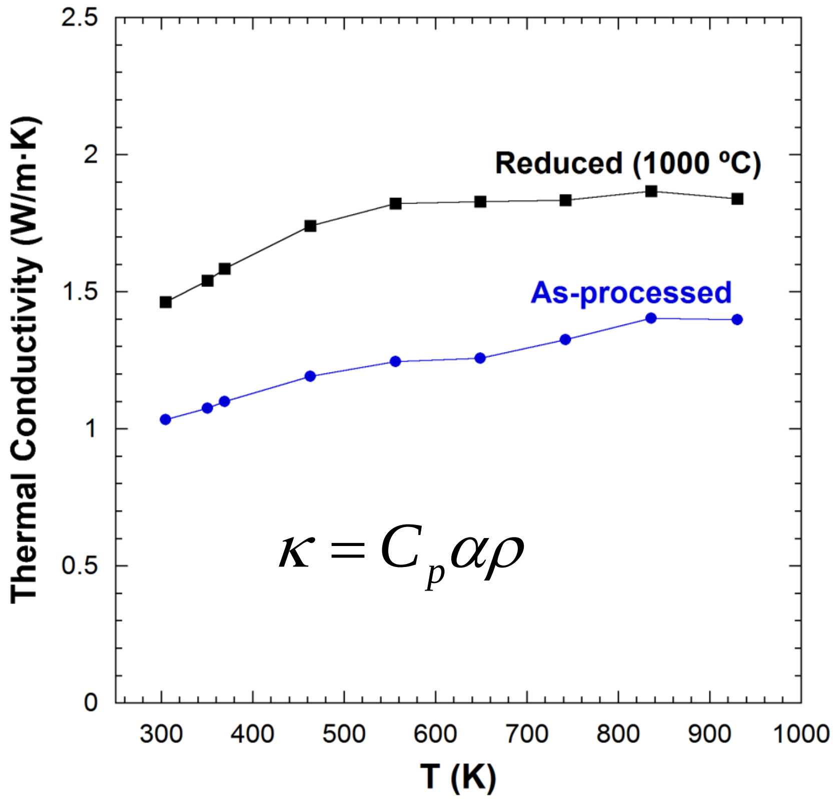


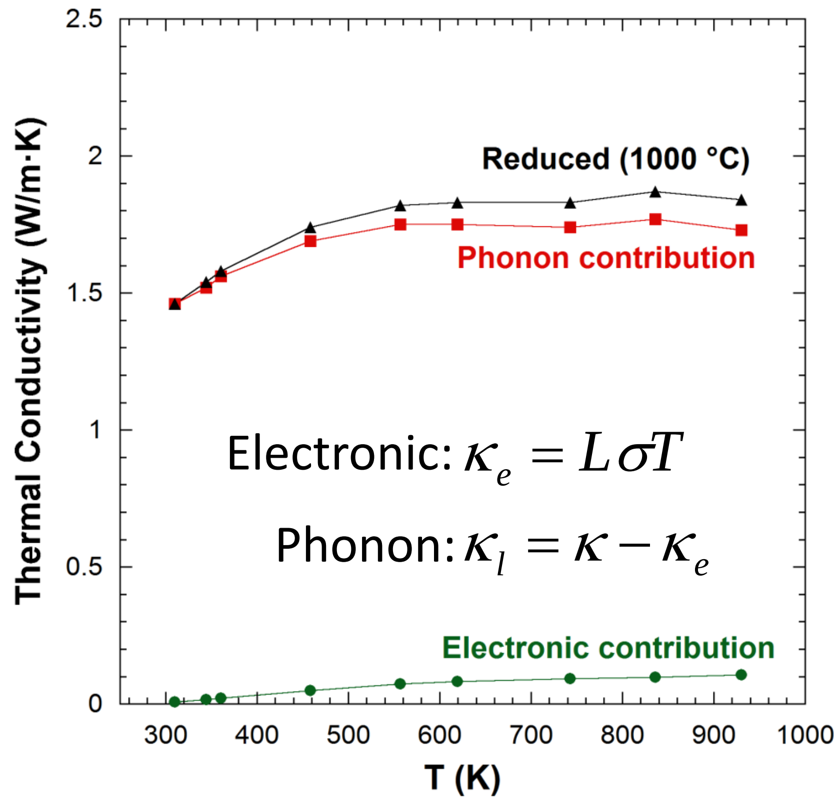


Fit to 1-D or 3-D hopping model equally well:

Not conclusive ⇨ **Planned Experiment (FY-3)**

SBN50: Thermal Conductivity



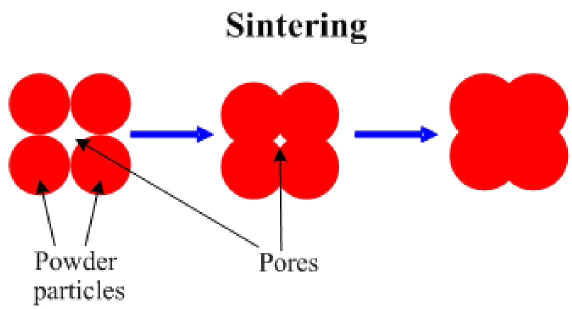


- Unreduced SBN50 $\longrightarrow$ low RT κ of ~1 W/m·K
- After reduction at 1000 °C – 40% average increase in κ
  - Density (ρ) increased from 74% to ~79%
  - Large increase in thermal diffusivity (α)
  - Lattice conduction is dominated.

Development of an entirely new reduction scheme: "Irreversible Chemical Reduction" (FY-3)

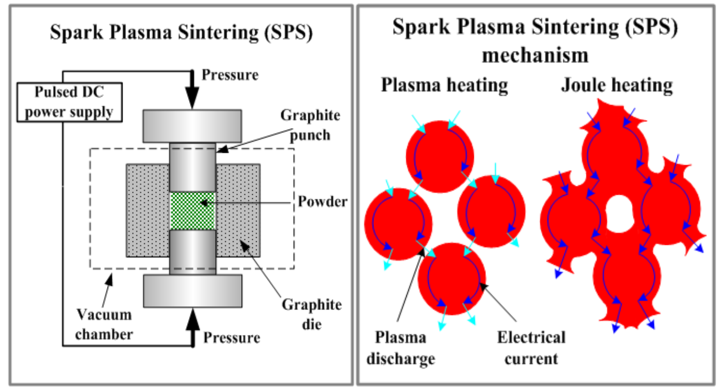
SBN50 Powder Processing

Conventional Sintering (CS)



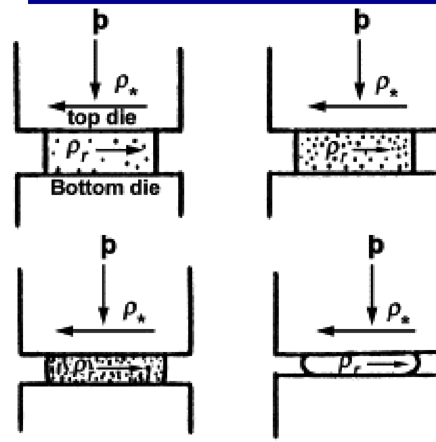
- Pressureless-sintering
- Varied density
- Possible grain growth (abnormal grain growth)

Spark Plasma Sintering (SPS)

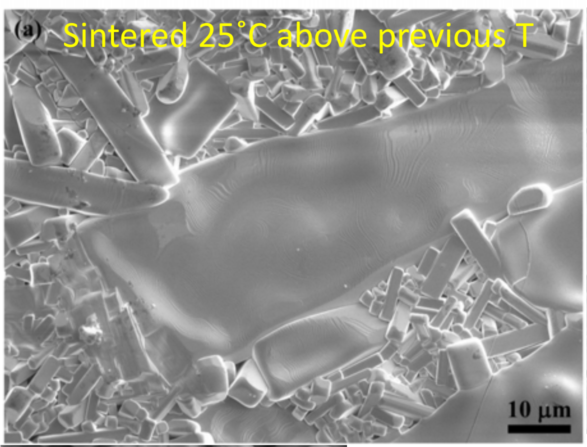


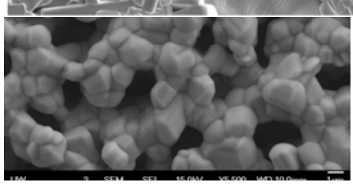
- Pressure + Electrical current in vacuum
- Extremely fast sintering times (<10 min)
- High density with fine-grains (<250 nm)

Sinter-Forging (SF)

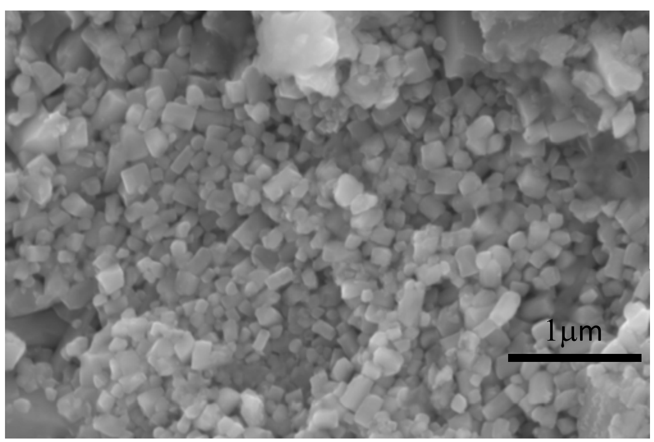


- CS + uniaxial pressure.
- High density.
- Textured grains

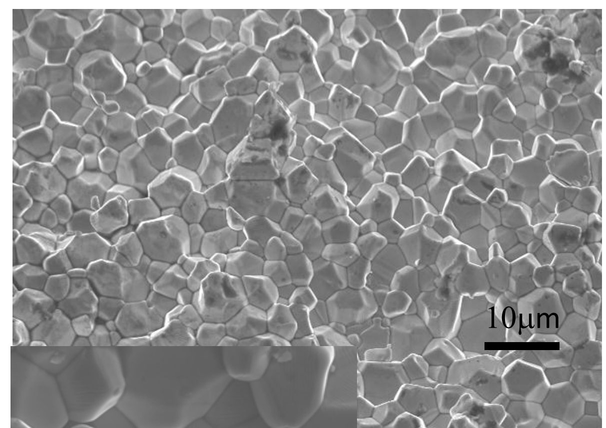


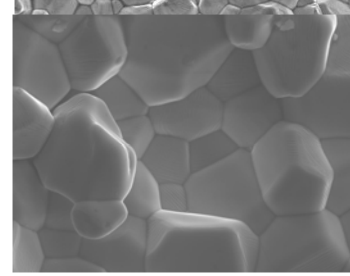


$\rho \sim 80\% \rho_{th}$



$\rho = 93\% \rho_{th}$

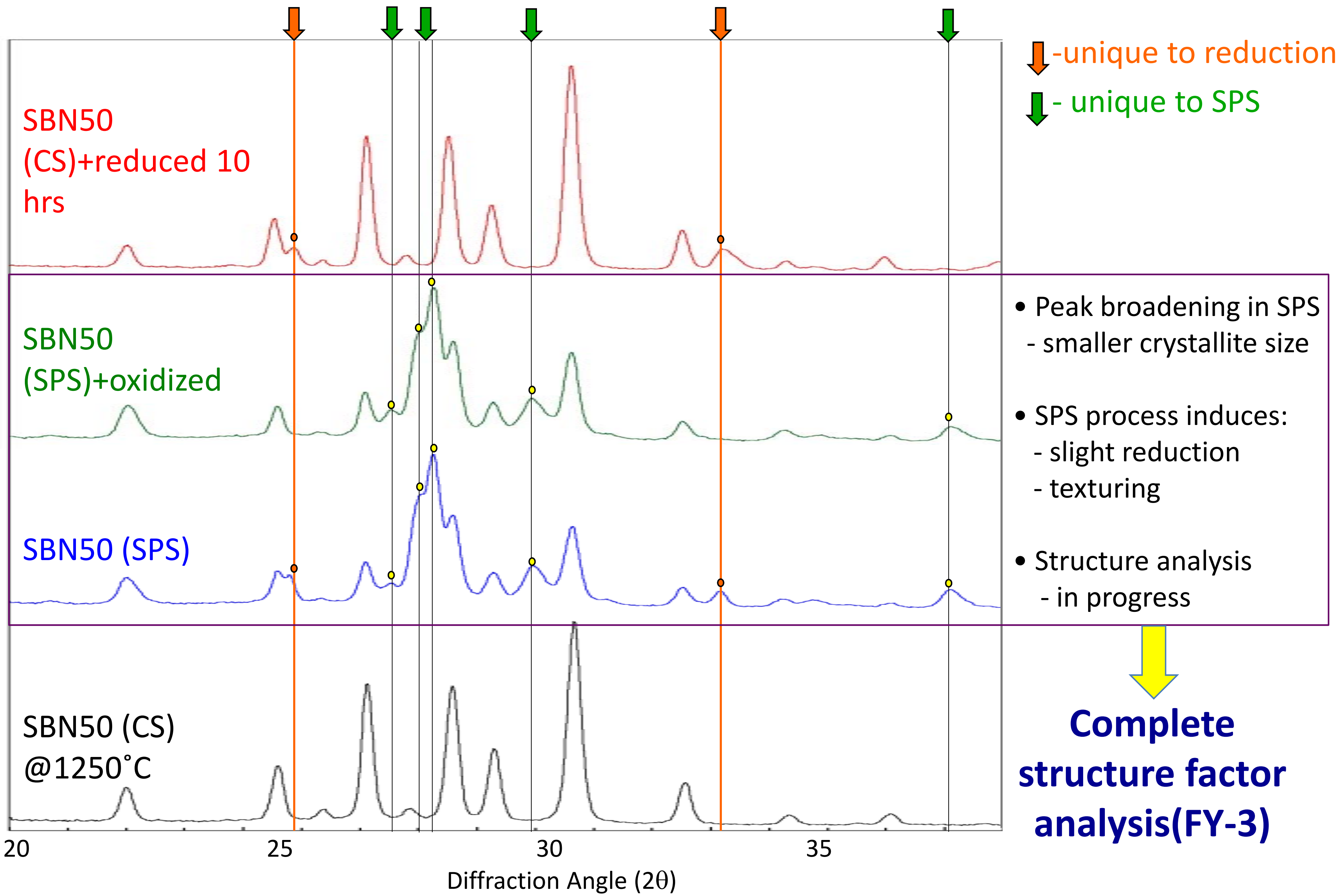




$\rho > 90\% \rho_{th}$

Focus on SPS and SF (FY-3)

XRD Comparison of CS and SPS Processes



- Peak broadening in SPS
  - smaller crystallite size
- SPS process induces:
  - slight reduction
  - texturing
- Structure analysis
  - in progress

Complete structure factor analysis(FY-3)

Ferroelectric Relaxor Materials for TE Applications

- Unique TE properties found in SBNx

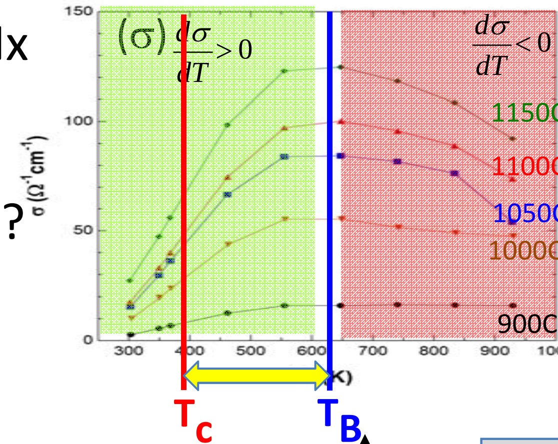
$$\sigma\uparrow \& |S|\uparrow$$

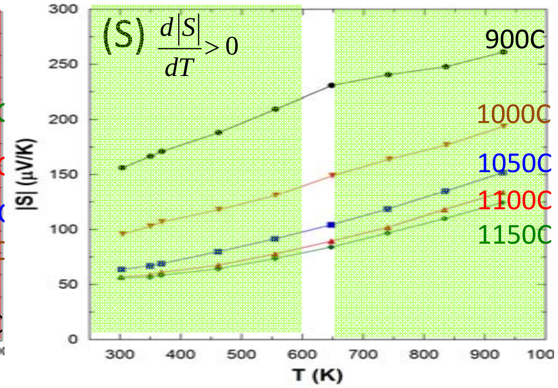
- Is this due to Ferroelectric Relaxors?

  T_C Curie Temp.

  Local polar domains

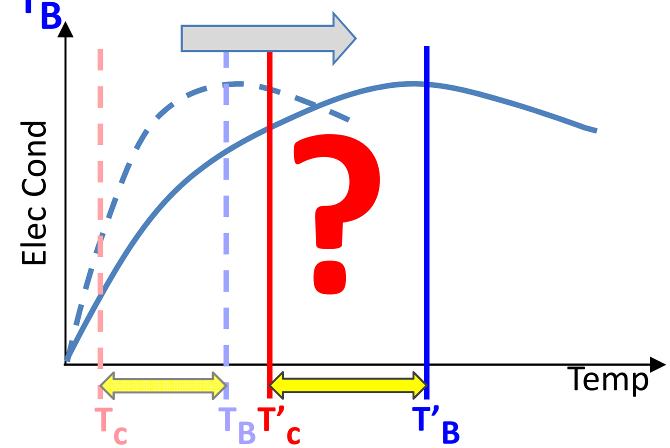
  T_B Burns Temp. (PRB28, 2527 (1983))





- Strategy for widening $\sigma\uparrow \& |S|\uparrow$ region

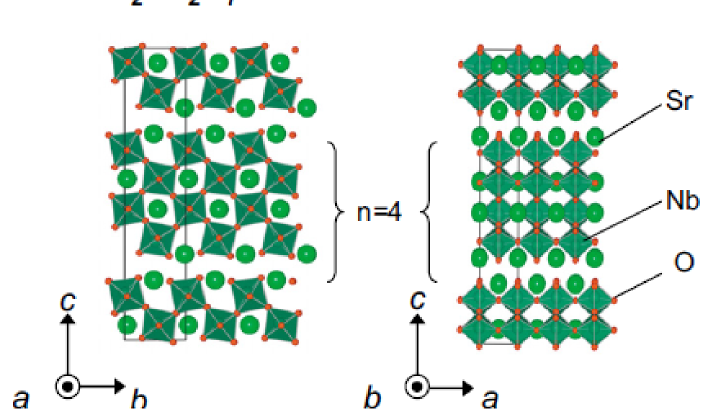
Comp.	T_C	T_B
SBNx	0~200˚C	200~400˚C
$Sr_2Nb_2O_7$	~1300˚C	?
$SrBi_2Nb_2O_9$	~450˚C	?



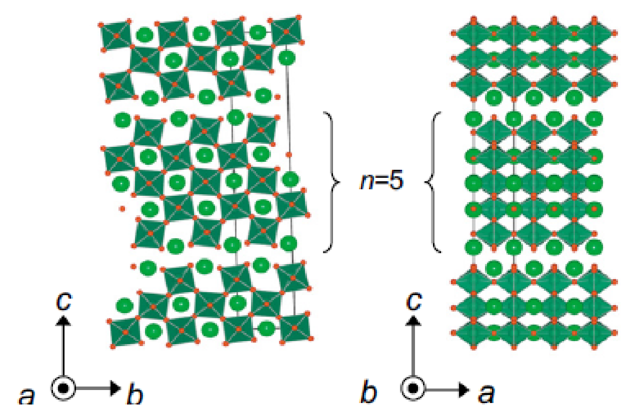
- The strontium niobate ($Sr_nNb_nO_{3n+2}$) systems

  - A pseudo 1-D system
  - Perovskite structure
  - Highly anisotropic

$Sr_2Nb_2O_7$



$Sr_5Nb_5O_{17}$

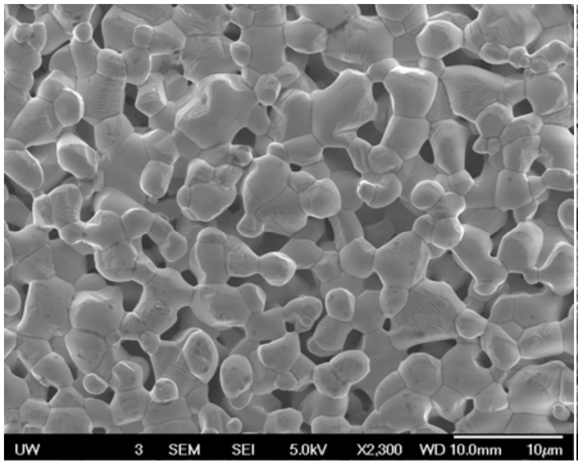


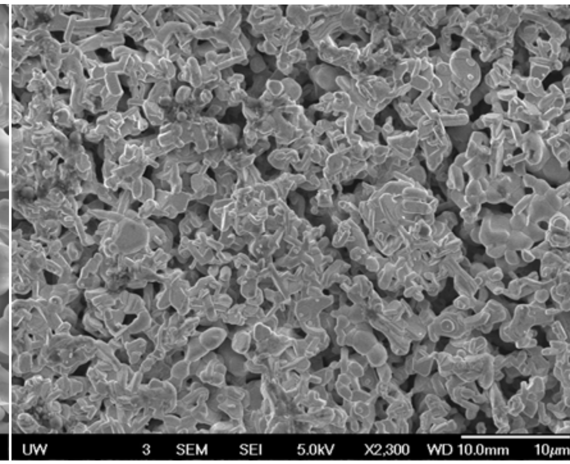
Progress so far (May 31, 2013):

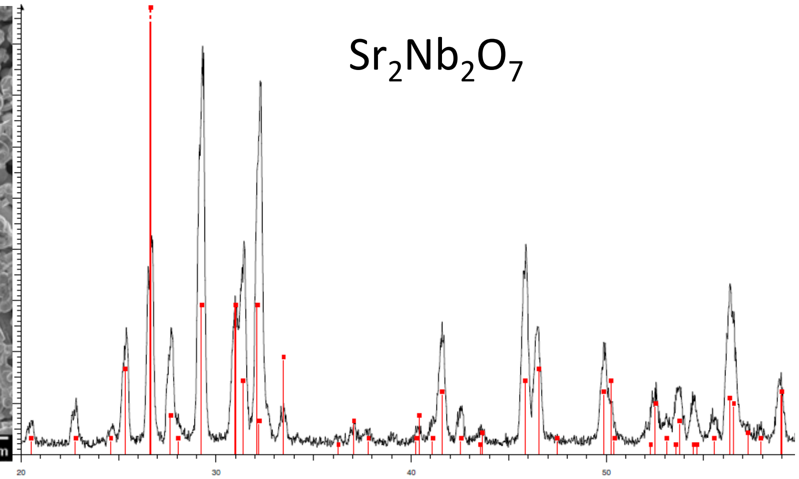
1. Completed SCS of $Sr_2Nb_2O_7$ (SN) and basic characterization

$$Nb_2(C_2O_4)_5 + 2Sr(NO_3)_2 + 10NH_4NO_3 + 5CO(NH_2)_2 \longrightarrow Sr_2Nb_2O_7 + 15CO_2 + 30H_2O + 17N_2$$

SBN50 vs. $Sr_2Nb_2O_7$





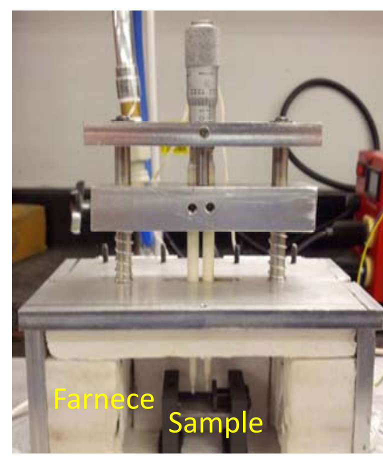


2. SN-TE characterization still in progress

3. Bi-doped SN and $SrBi_2Nb_2O_9$ in progress

4. Development of Seebeck tester, capable of measuring TE prop at T>1000˚C.

➡ **Planned Experiment (FY-3)**



Summary of Findings

(June 1, 2012-May 31, 2013)

1. Demonstrated $Sr_xBa_{1-x}Nb_2O_{6-\delta}$ (SBNx) as potential candidates for n-type TE oxide materials.
2. Thoroughly studied reduction processes of SBNx in relation to their TE effects.
   - Site specific occupancy in tungsten tetragonal bronze
   - Change in sign of ds/dT and parallel trend of S and s
   - Electronic and phonon contributions in electronic and thermal conductivity
3. Microstructural aspects using different sintering techniques
4. Exploration of niobate based other ferroelectric relaxors
5. Proved XPS as a tool to ascertain optimum reduction conditions for high TE effect.

Future Plans for FY-2(rest) and FY-3

1. SBNx: Further refinement of scientific issues
   - Neutron diffraction for site specific oxygen removal
   - EXAFS and hard x-ray diffraction for local bonding and coordination
   - TE transport mechanisms unique to relaxors
   - Crystallographic texture in relation to TE transport properties

2. Development of a new "**Chemical Reduction**" scheme.

3. SBNx: Engineering development
   - Multiple length scale engineering to enhance TE properties
   - Nano-micro composites concept*
   - Development of prototype TE devices

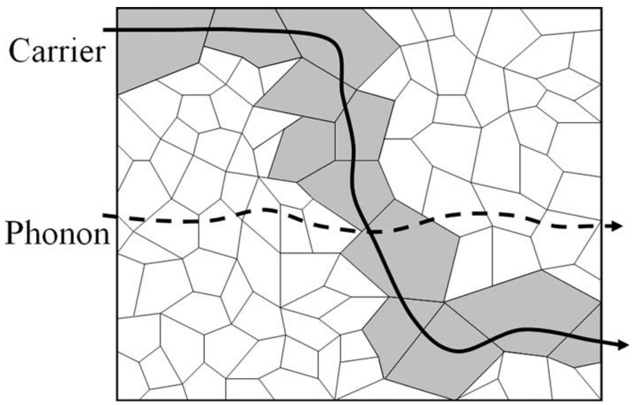
3. Exploration of $(Sr, Ba)_2Nb_2O_7$ and $Sr_xBi_{2-x}Nb_2O_9$ (SBiN)
   - Effect of local polar nano-domains b/w T_c and T_B of relaxors

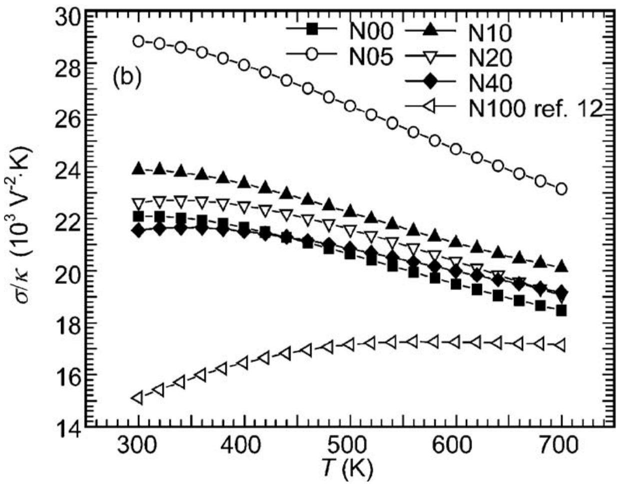
4. Publications in preparation (current)

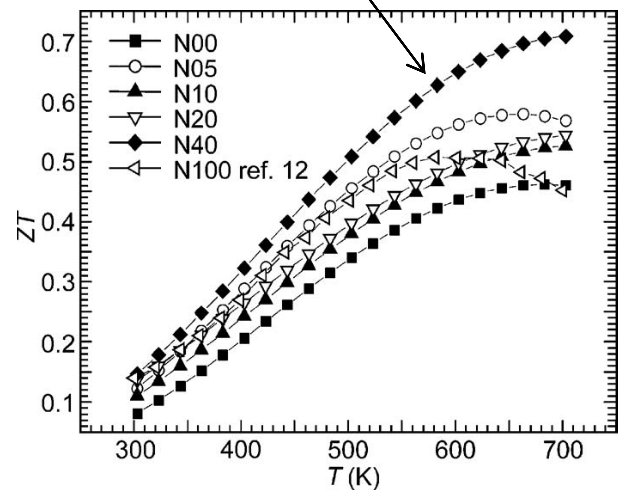
1, 2: SBNx: XPS related 3. SBNx: TE 4. High T Seebeck tester

*Nano-Micro Composites

N40: 40% $CoSb_3$ nanoparticles







- Reduction in grain size adversely affects electron mobility
- Research into nano-micro composites to scatter phonons and preserve σ
- Percolation effect: Charge carriers "select" low resistivity path while phonons scattered by nanoparticles

Mi *et al.*, *App. Phys. Lett.* **91**, 172116 (2007)

Thank you!