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

Grant No. DE-FE0007272

(Oct 1, 2011-Sept 30, 2014)

Program Manager: Patricia Rawls

Fumio S. Ohuchi[1] (PI) and Rajendra K. Bordia[2](Co-PI)

Department of Materials Science and Engineering

[1]University of Washington, Seattle, WA

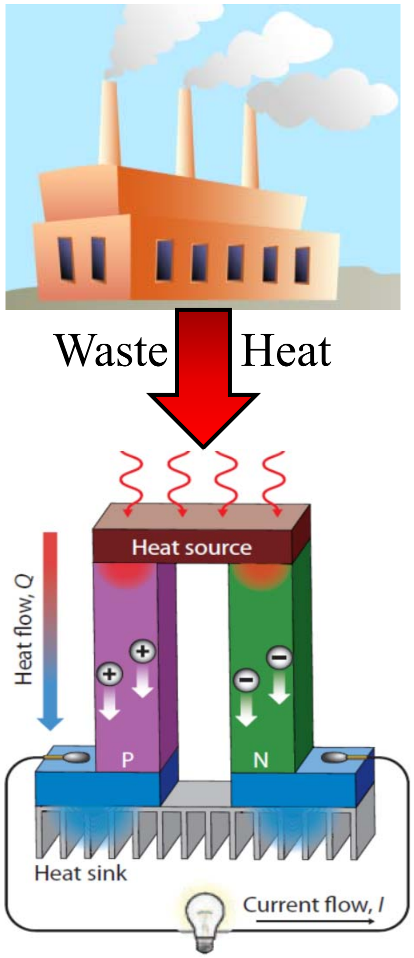
[2]Clemson University, Clemson, SC

Graduate Students: Christopher Dandeneau and YiHsun Yang

May 21, 2014

NETL Crosscutting Research Review Meeting

Introduction/Motivation for Research



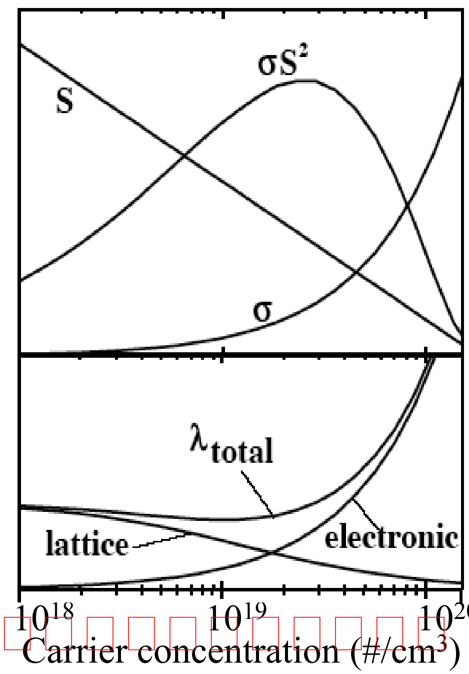
TE generator

- >60% of energy produced in U.S dissipated into environment as heat
- **Thermoelectric (TE) generator:** Convert waste heat into electrical power via the Seebeck effect

Interplay of three conflicting parameters:

- Seebeck coefficient S
- Electrical conductivity σ
- Thermal conductivity κ

$$Efficiency \equiv \frac{\sigma \bullet S^2}{\kappa}$$



You want *Efficiency* ⇑

You need σ⇑ , S⇑ κ⇓ at all T

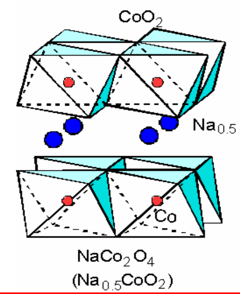
But normally σ⇑ , S⇓, κ⇑ (conflicting)

Searching materials/conditions that exhibit σ⇑, S⇑ and κ⇓ is an outstanding problem in Materials Science and Physics.

Current Thermoelectric Materials

	Materials	S (μV/K	ρ (Ω cm)	K (W/mK)	zT
p-Type	$Yb_{14}MnSb_{11}$	185	0.0054	0.7	~1 (1200 K)[38]
	$0.23B–0.77Si_{0.8}Ge_{0.2}$	168	0.001219	4.1	~0.62 (1200 K)[39]
	$NaCo_2O_4$ (crystal)	100	0.0002	2 (poly)	0.75
	$Na_xCo_2O_4$	100	0.0063		
	(plate morphology cera	177	0.0073		
	$Na_{1.5}Co_{1.8}Ag_{0.2}O_4$	101	0.0066		
	$LaCoO_3$	635	15.6		
	$La_{0.98}Sr_{0.02}CoO_3$	330	0.265		
n-Type	Bi_2Te_3	−200	0.001		1.2[44]
	$0.59P–0.41Si_{0.8}Ge_{0.2}$	−171	0.00074	4.2	~1.15 (1200 K)[39]
	$Sr_{0.98}La_{0.02}TiO_3$	−260	0.001	11	0.18[45]
	$Sr_{0.9}Dy_{0.1}TiO_3$	−190	~0.0028	~2.6	0.22 (573 K)[46]
	Thin film	−200		3	0.37 (1000 K)[33]
	$SrTi_{0.8}Nb_{0.2}O_3$				
	$Zn_{0.98}Al_{0.02}O$	−220	0.001	8 (1073 K)	0.65(1250K)[47] ~0.16 (550 K)

Non-stoichiometric $Na_xCo_2O_{4-\delta}$ is so far a champion material in p-type.
(PRB56(1997)R12685)



***p*-type oxides**

Holes generated by oxygen excess

$$\frac{1}{2}O_2 \rightarrow V_M'' + 2h^{\bullet\bullet} + O_O^x$$

Good stability in air at high T

***n*-type oxides**

Oxygen deficiency results in excess electrons

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

Stability often poor at high T in air

Development of n-type oxide materials is still behind.

This Project (DE-FE0007272)

(Oct 01, 2011 – Sept 30, 2014)

Overall Goal:

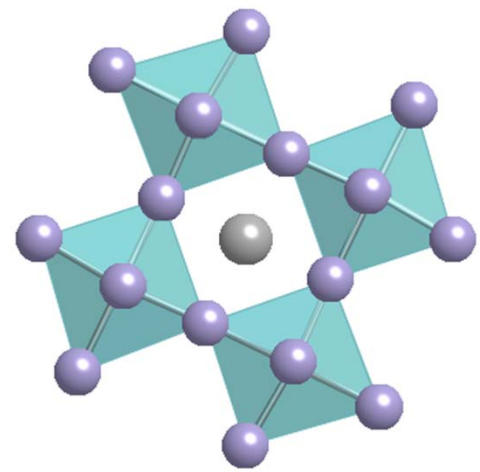
Investigate potential materials and processing technology of n-type oxides with high TE performance using combination of the developed material compositions and hierarchical designed microstructures.

Technical Objective:

- Exploit unique crystallographic structure to optimize the thermo-electric properties of oxide materials.
- **Tungsten-bronze** crystal structure represented by ferroelectric strontium-barium-niobate ($Sr_xBa_{1-x}Nb_2O_6$) as a prototype system.
- Develop processing routes to make desired crystalline phases and aniso-tropic porous structure to evaluate the effect of micro- and macro-pores on thermoelectric properties.

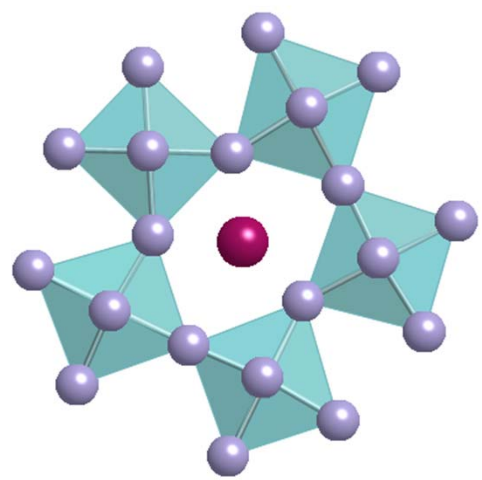
Presentation Outline

After 2.5 years of research under this grant



- **Materials development**
  - Strontium barium niobate (SBN)
  - Processing and structure
  - Understanding cation site occupancy

- **Thermoelectric properties of SBN**
  - TE behavior
  - Local electronic environment/structure
  - Conductivity and stability

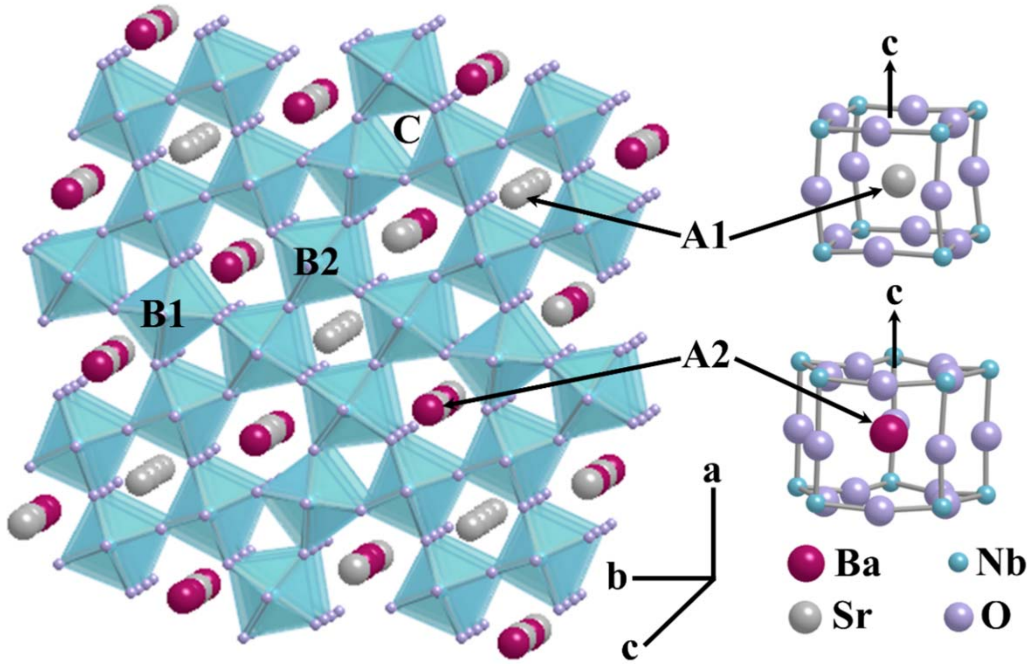


- **Materials engineering**
  - Microstructural aspects
  - Multi-length scale engineering

- **Future perspectives (i.e. rest of 6 months)**

Tetragonal Tungsten Bronze(TTB) Structure

Strontium-Barium Niobate: $Sr_xBa_{1-x}Nb_2O_6$



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

- Tetragonal A1: Sr only
- Pentagonal A2: Sr or Ba
- Octahedral B1, B2: Nb
- Trigonal C = Vacant

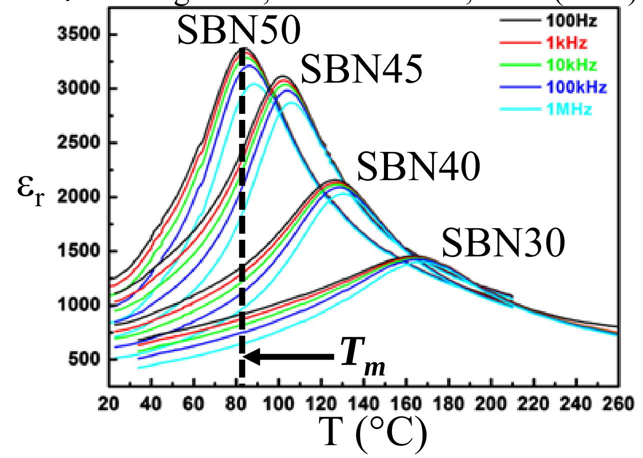
*1/6 of total A1+A2 sites vacant

- Complex disordered structure for **low κ**
- Wide range of compositions by varying *x* or doping
- Polarization occurs along polar c-axis: explore possible ferroelectric-TE coupling

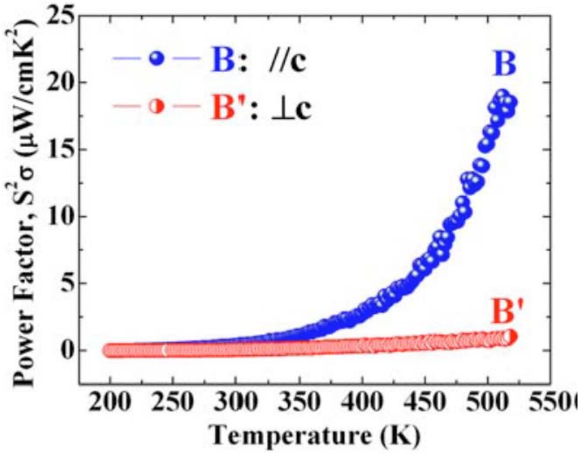
Strontium Barium Niobate (SBN)

- $Sr_xBa_{1-x}Nb_2O_6$ (SBN100*x*): *n*-type relaxor ferroelectric with broad ferroelectric to paraelectric transition
  - Extensively studied for electro-optic/photorefractive applications
  - Congruent composition: $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN61)
  - Phase stability region: $0.25<x<0.75$ **(?)**
  - Composition-dependent phase transition temp.
  - Electrically conductive with annealing in reducing environment

Zhang *et al.*, *Ceram. Int.* **39**, 1971 (2013)



- Reduced SBN for TE applications
  - High power factor (PF = 20 μW/cm·K²) parallel to polar *c*-axis in $SBN61_{SC}$*



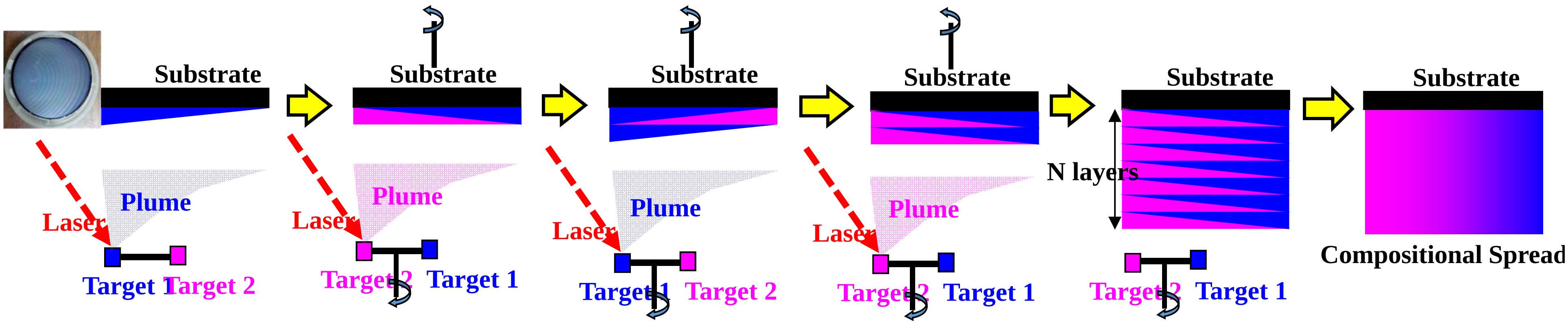
Motivation to study TE behavior of polycrystalline SBN: Start with structure

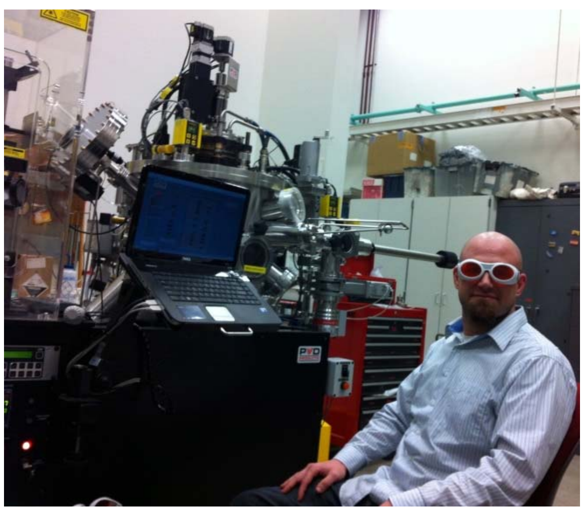
*Lee *et al.*, *Appl. Phys. Lett.* **93**, 031910 (2010)

Combinatorial Materials Exploration(CME)

FY-1

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

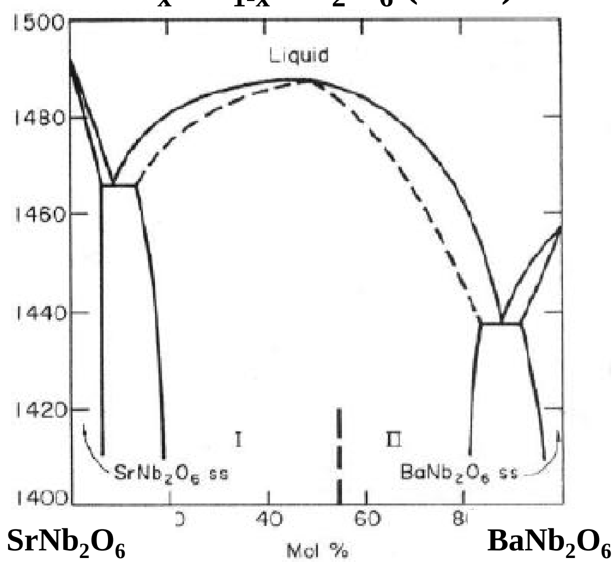


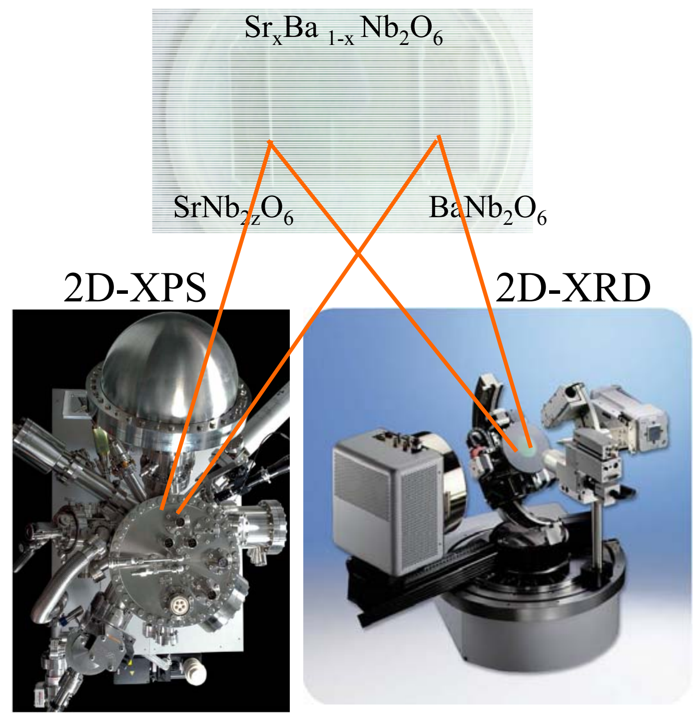


Pulsed Laser Deposition (PLD)

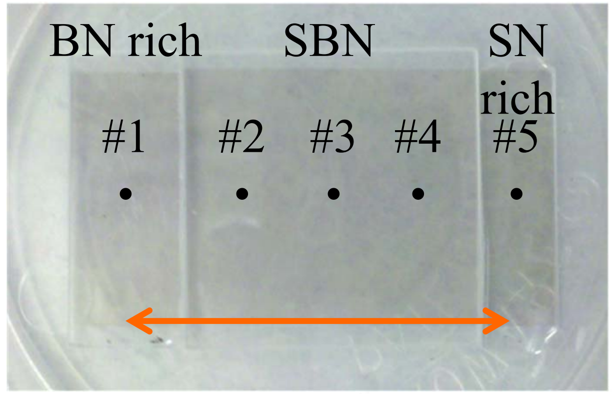
Graduate student: Chris Dandeneau

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

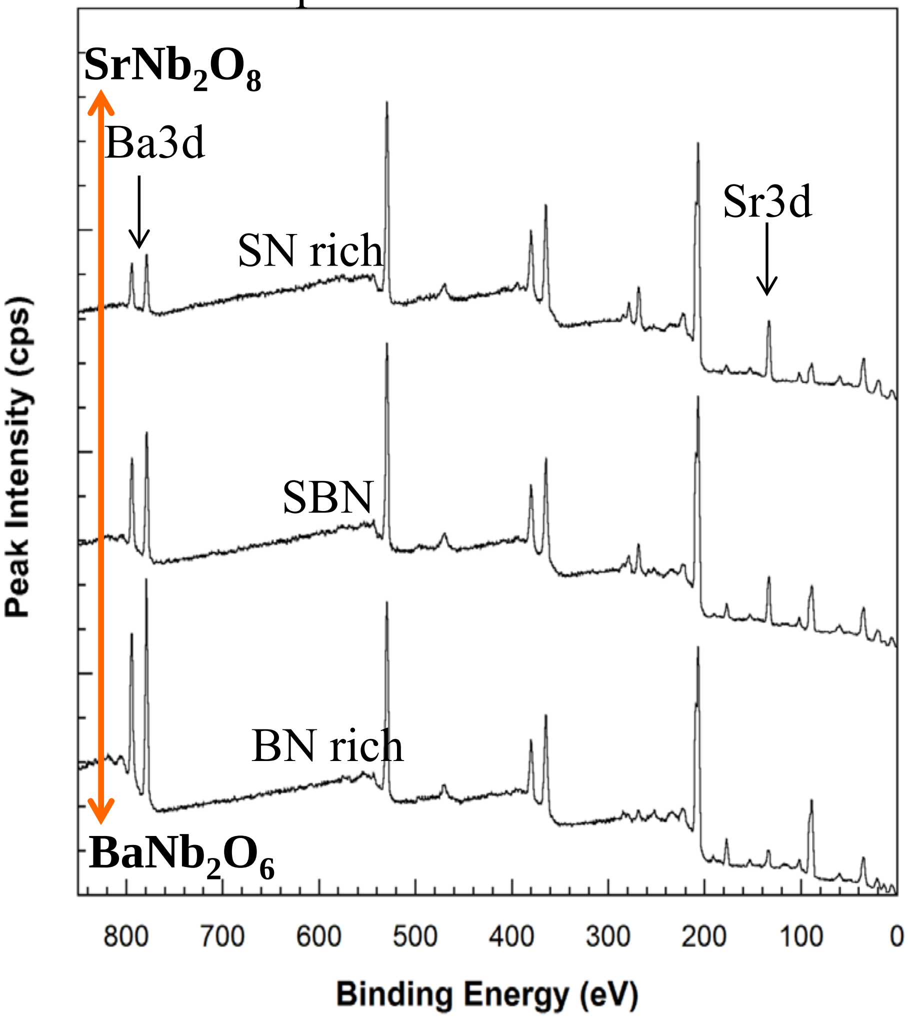




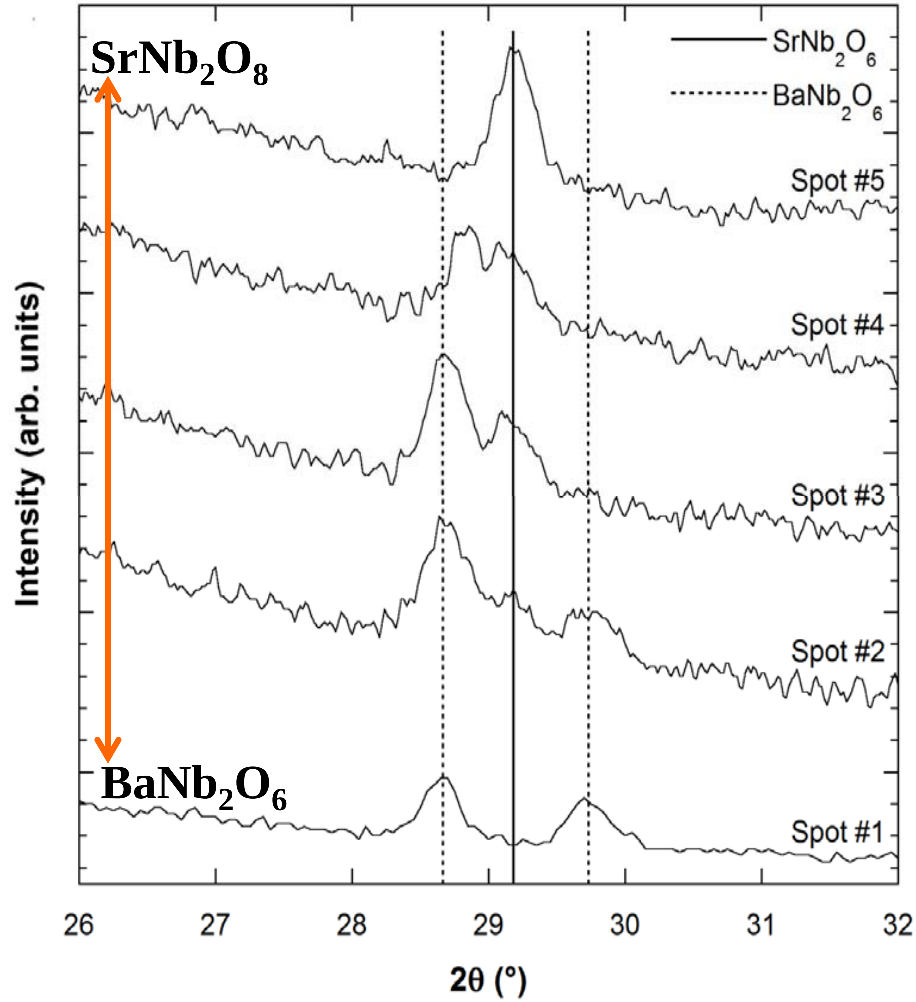
CME Library of SBN(x)



XPS: composition



XRD: structure



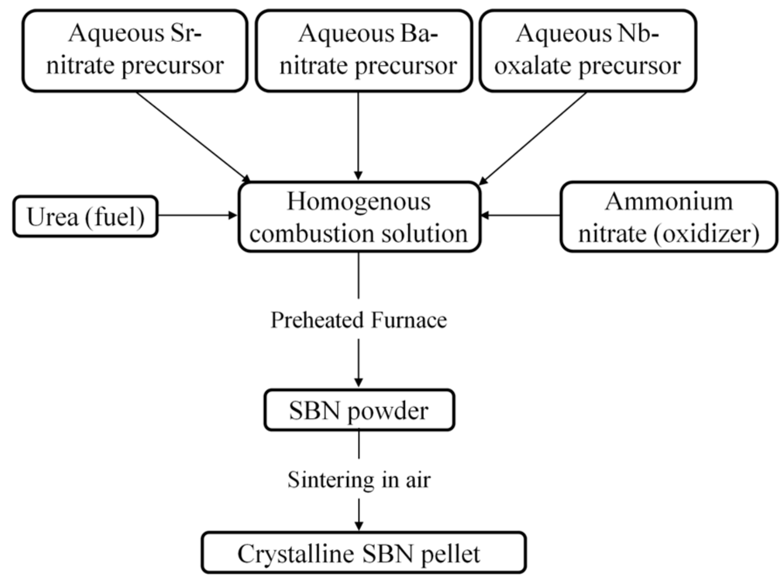
Bulk Synthesis of SBN(x)

- Need single phase and nano-sized homogeneous powders for fabricating dense textured polycrystalline pellets.
- Conventional solid-state synthesis suffers from issues related to phase purity and efficiency.

Solution Combustion Synthesis (SCS)

A self-sustaining exothermic reaction to form a desired material

- Reactions 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

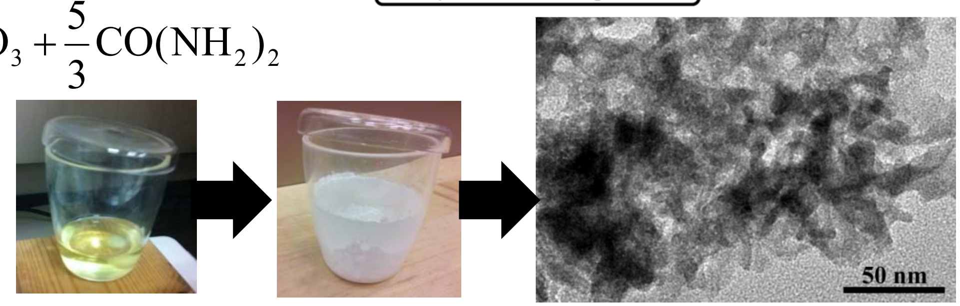


Example: $Sr_xBa_{1-x}Nb_2O_6$ (SBN50)

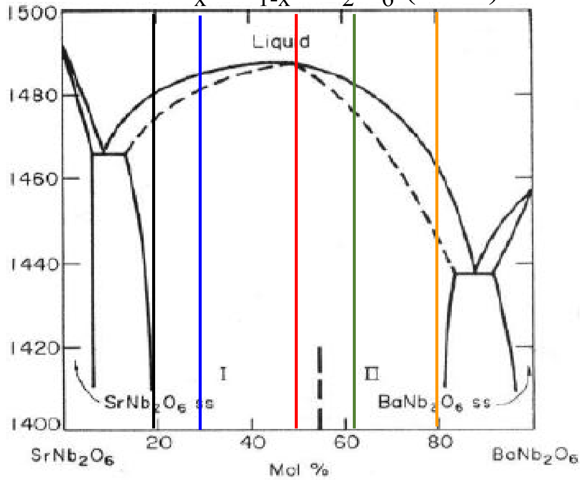
$$0.5Sr(NO_3)_2 + 0.5Ba(NO_3)_2 + Nb_2(C_2O_4)_5 + 5NH_4NO_3 + \frac{5}{3}CO(NH_2)_2$$

$$\Downarrow$$

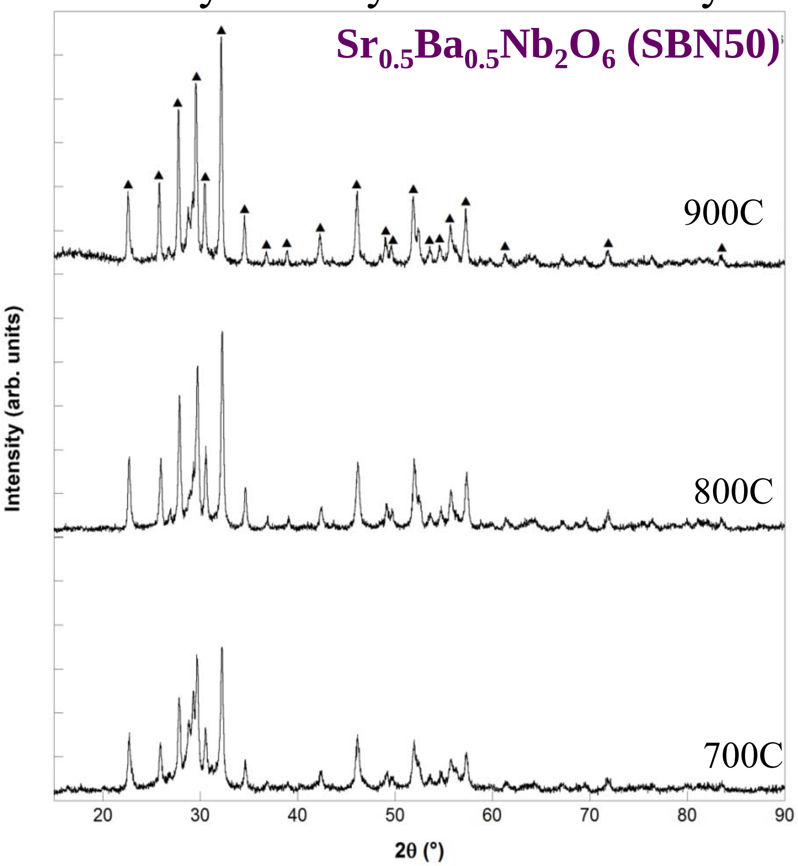
$$Sr_{0.5}Ba_{0.5}Nb_2O_6 + \frac{35}{3}CO_2 + \frac{40}{3}H_2O + \frac{23}{3}N_2$$



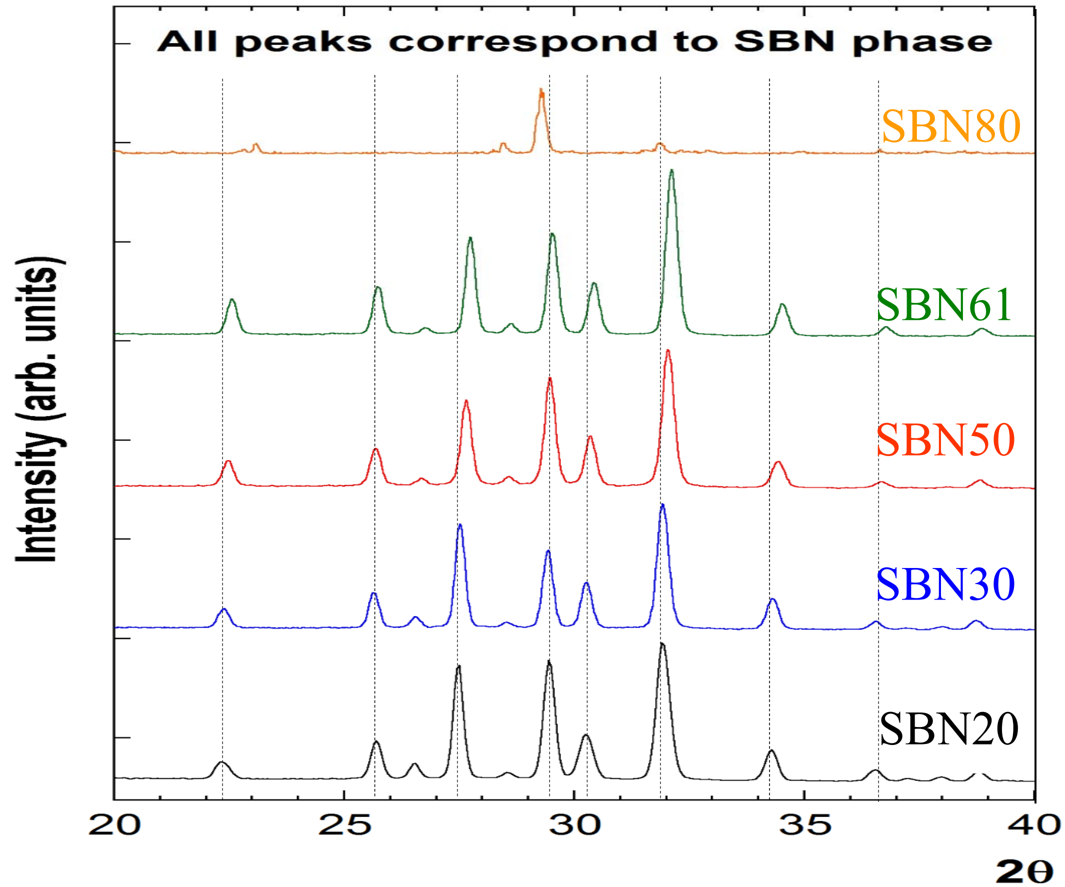
$Sr_xBa_{1-x}Nb_2O_6$ (SBN)



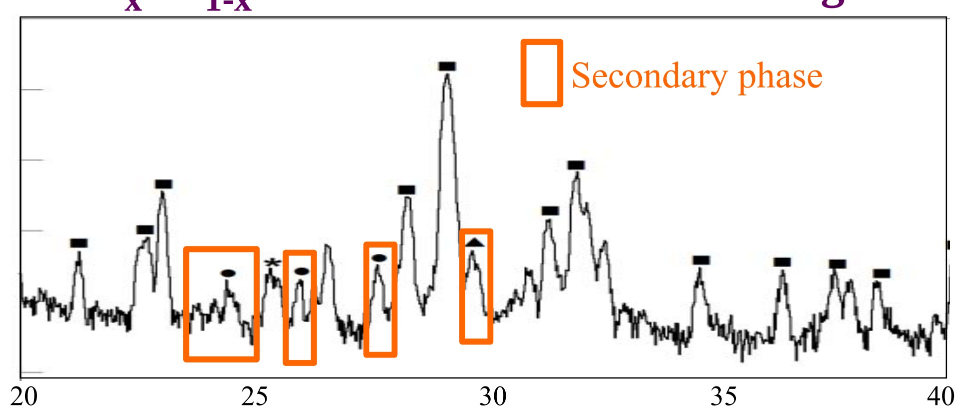
Crystallinity and Phase Purity



$Sr_xBa_{1-x}Nb_2O_6$ via SCS

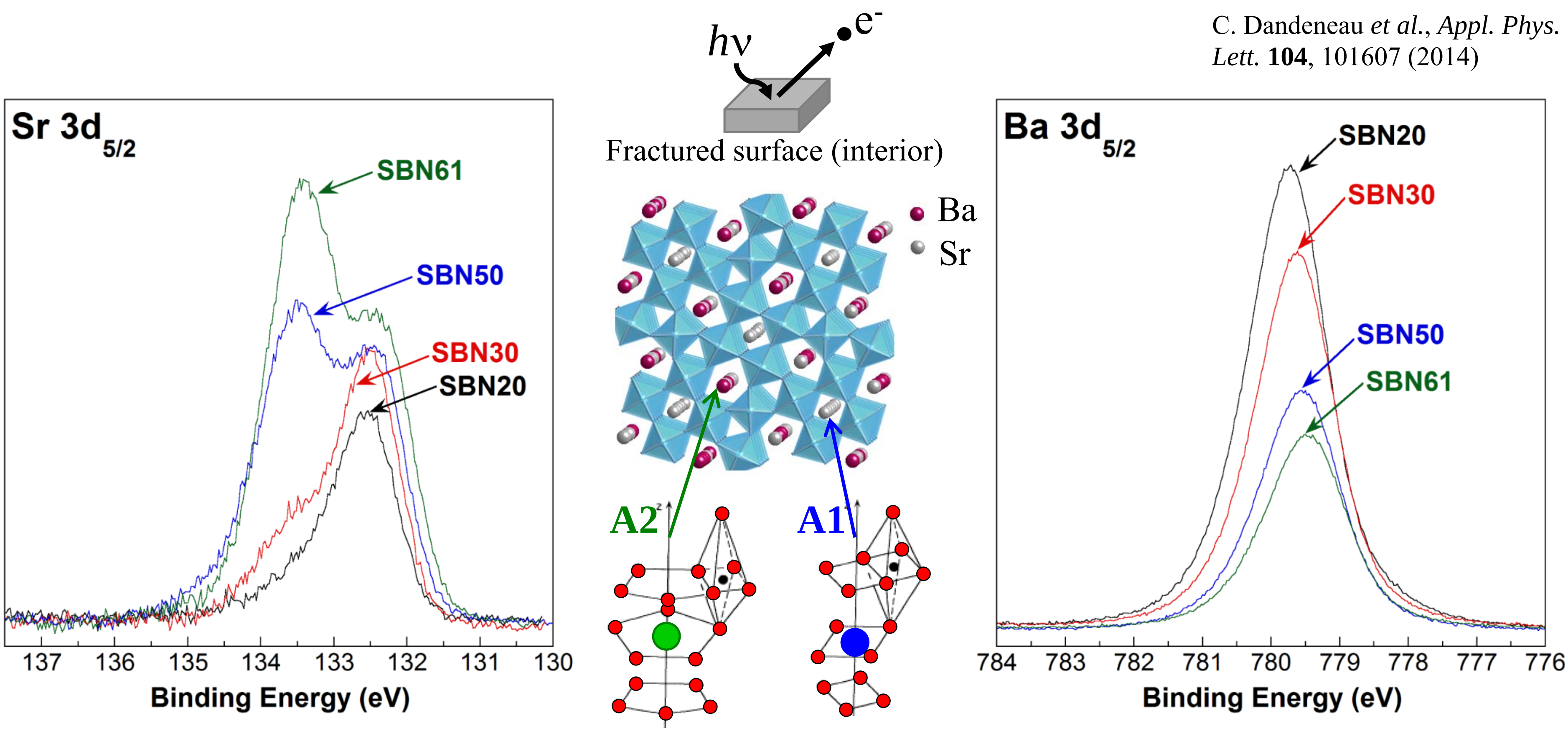


$Sr_xBa_{1-x}Nb$ via Solid State Processing



Cation Site Occupancy in SBN

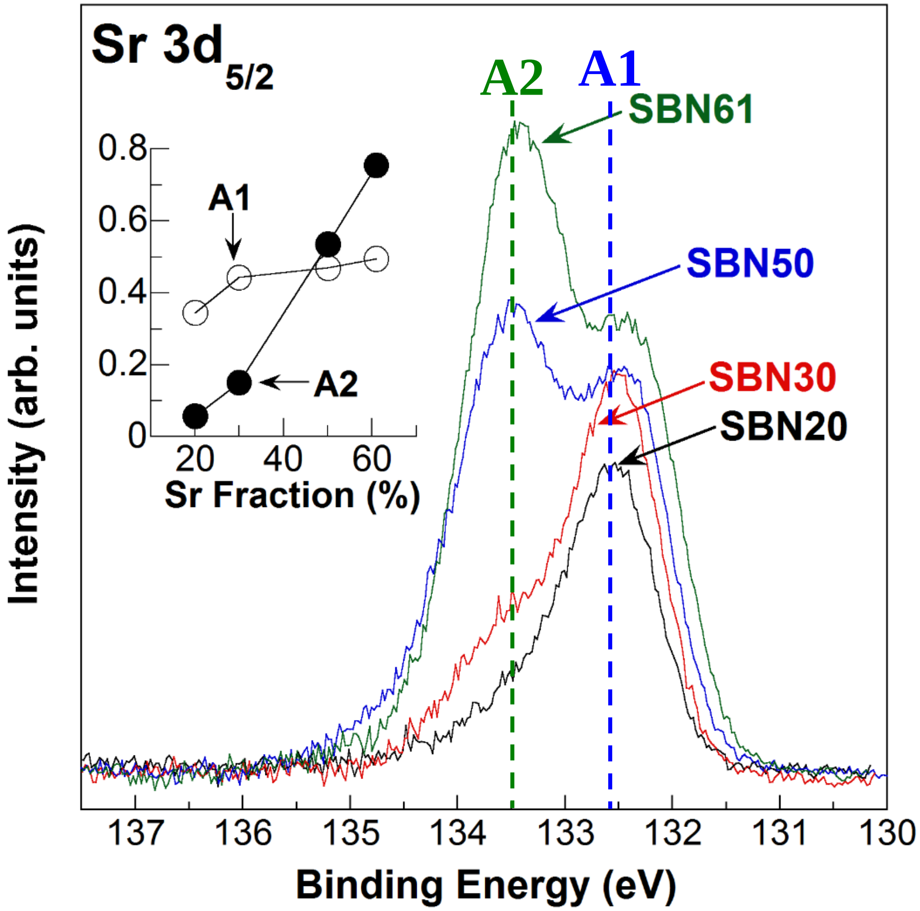
C. Dandeneau *et al.*, *Appl. Phys. Lett.* **104**, 101607 (2014)

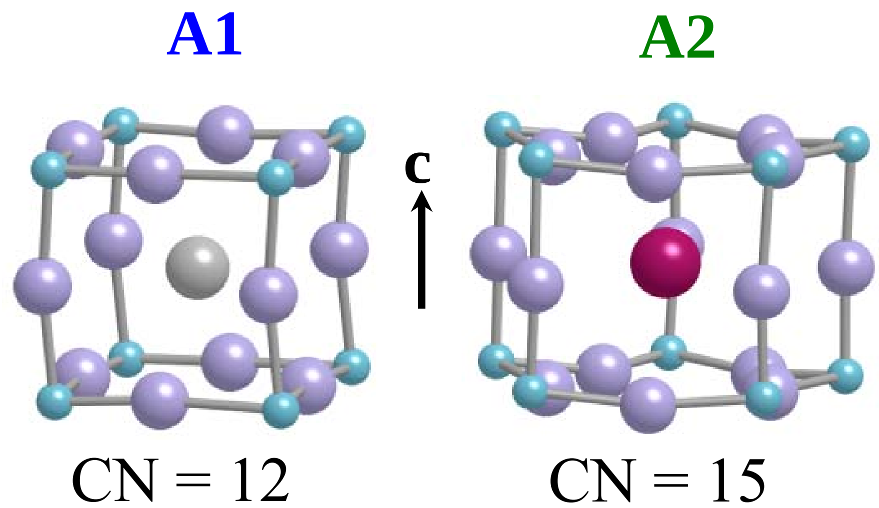


- Only one Ba $3d_{5/2}$ peak observed: Ba occupying A2 site only
- Two Sr $3d_{5/2}$ peaks appear: Sr occupying both A1 and A2 sites with BE difference of ~1eV

Which Sr site corresponds to higher BE peak?

Cation Site Occupancy in SBN





Larger coordination number (CN) for Sr at A2 site

↓

Lower electron density, higher BE

- Five formula units per $(A1)_2(A2)_4(C)_4(B1)_2(B2)_8O_{30}$ unit cell
- For $Sr_{0.2}Ba_{0.8}Nb_2O_6$ (SBN20): Ba occupying all A2 sites
- No higher BE peak for SBN20 ⟶ corresponds to A2 site

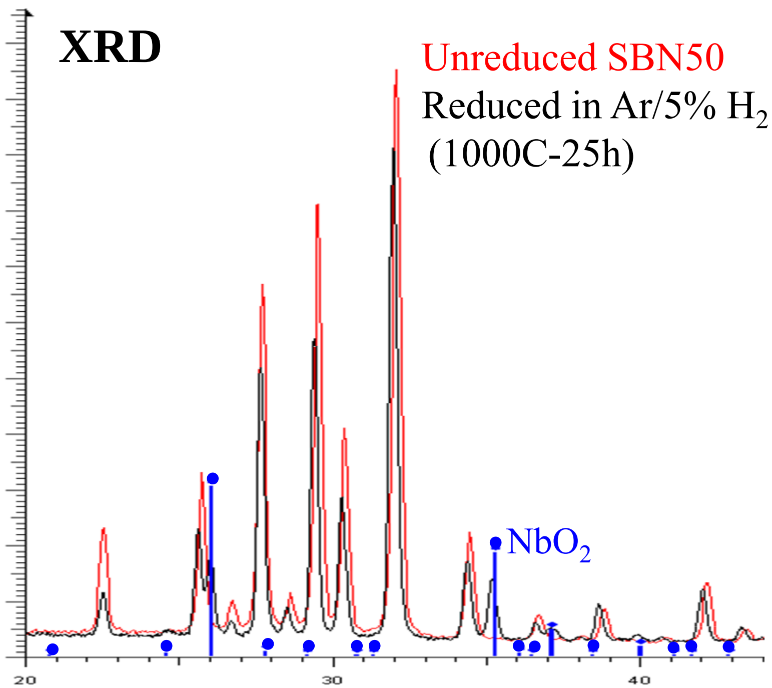
Reduction of SBN in Ar/5%-H_2

- As-sintered SBN samples possess very low σ
- Annealing in reducing environment creates oxygen vacancies:

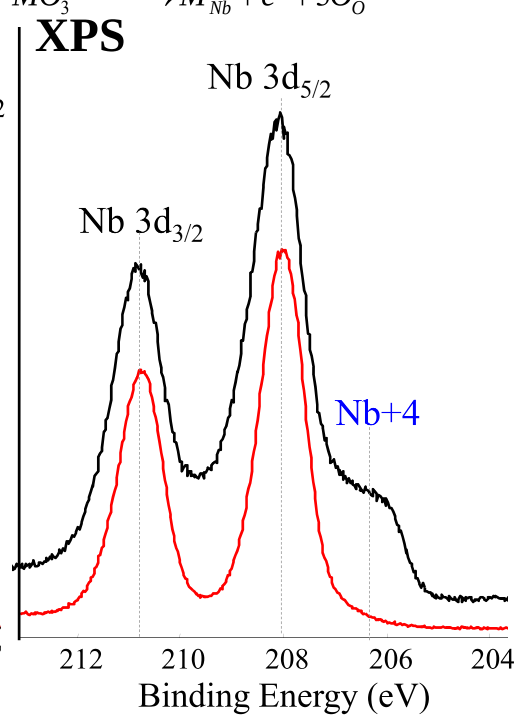
$$O_O \rightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g)$$

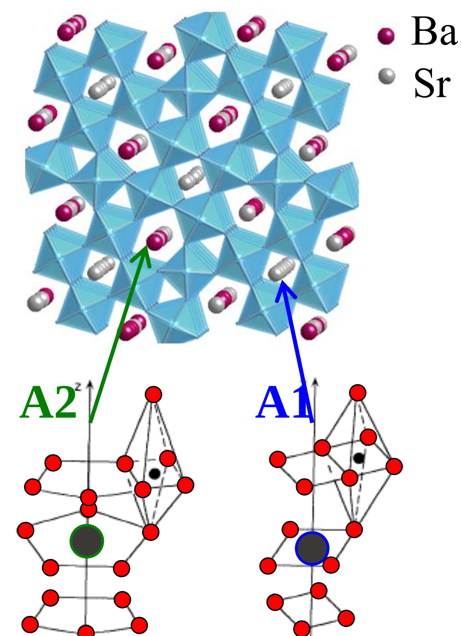
- Increase of σ by *e*- donated back to Nb to preserve electroneutrality.

- For SBN50: $Sr_{0.5}Ba_{0.5}Nb_2O_6 \rightarrow Sr_{0.5}Ba_{0.5}Nb^{5+}_{2-y}\boxed{Nb^{n+}_y}O_{6-\delta} + \frac{\delta}{2}O_2$



$$MO_3 \xrightarrow{SBN} M^{\bullet}_{Nb} + e^- + 3O_O^x$$

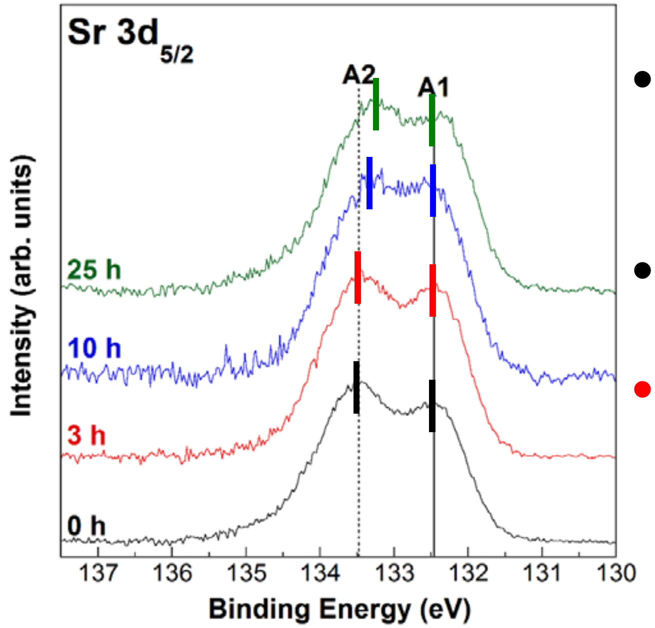


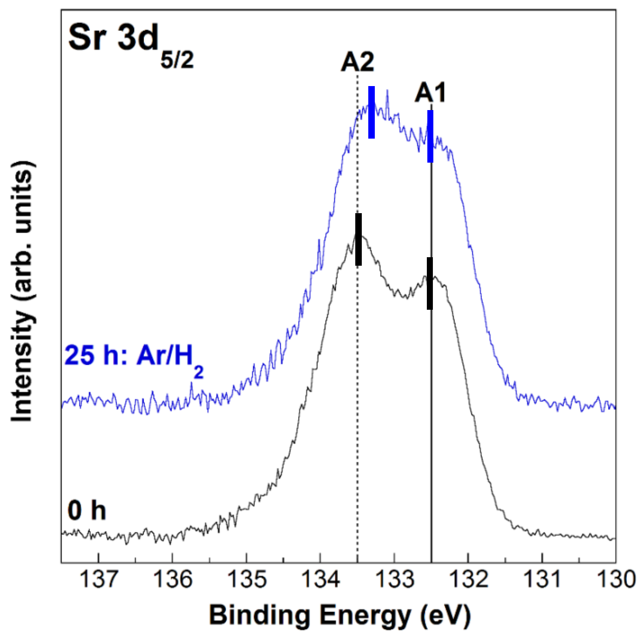


Which oxygen(s)?

Reduced SBN: Sr/Ba XPS Spectra

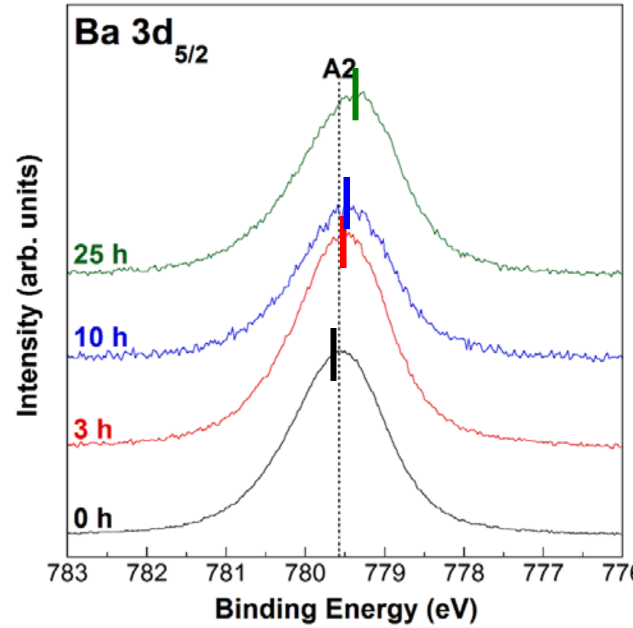
1000 °C reduction

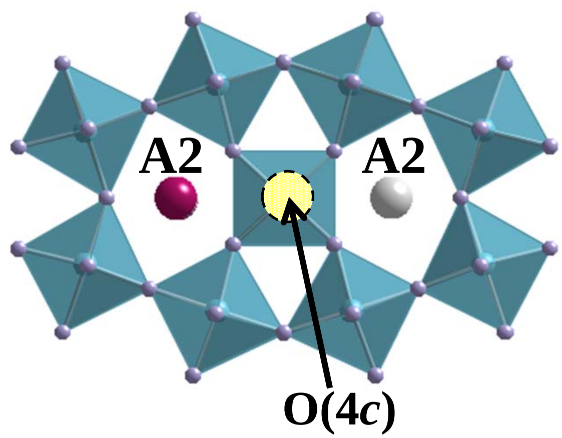


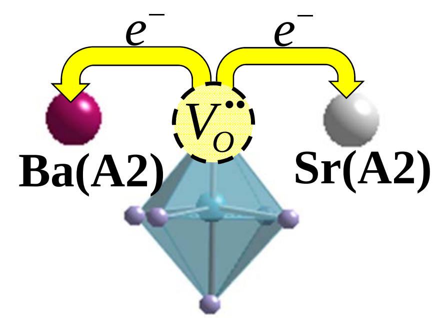


- Only **A2** peaks shift to lower BE for Sr, Ba.
- No shift in **A1** peak.
- **Suggest which O is removed**

1000 °C reduction



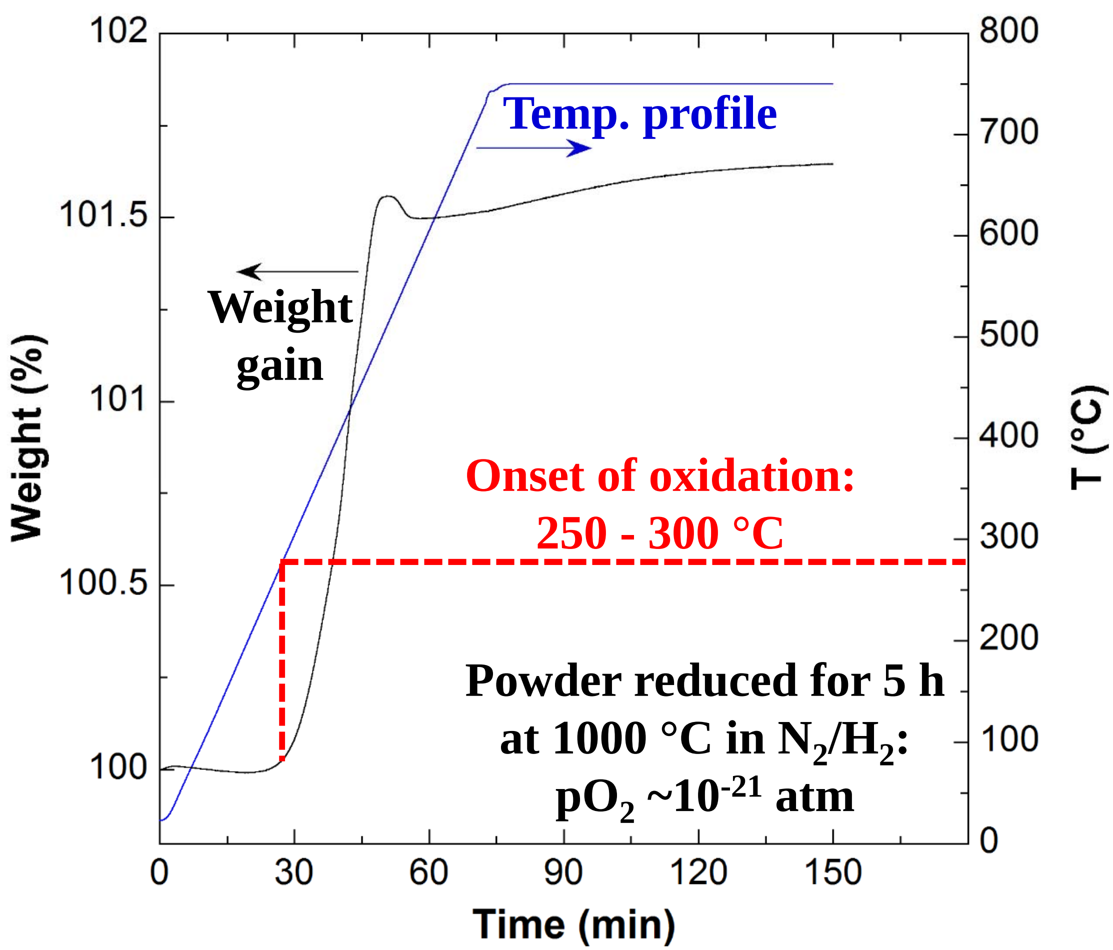




- Preferential oxygen vacancy formation at 4c site could increase electron density.
- Oxygen in 4c site calculated to have lowest vacancy formation energy*

*Baetzold *et al.*, *Phys. Rev. B* **48**, 9 (1993)

TGA: Oxygen Uptake



Weight gain due to oxygen uptake: 1.52%

Value of δ in $Sr_{0.5}Ba_{0.5}Nb_2O_{6-\delta}$: 0.36

Valence of Nb from charge balance: 4.64

- TGA gives us two key pieces of information:

1) Maximum reduction in Nb valence (powder vs. dense pellet)
2) Temperature at which reduced state degrades in air

Vacancy Formation Enthalpy

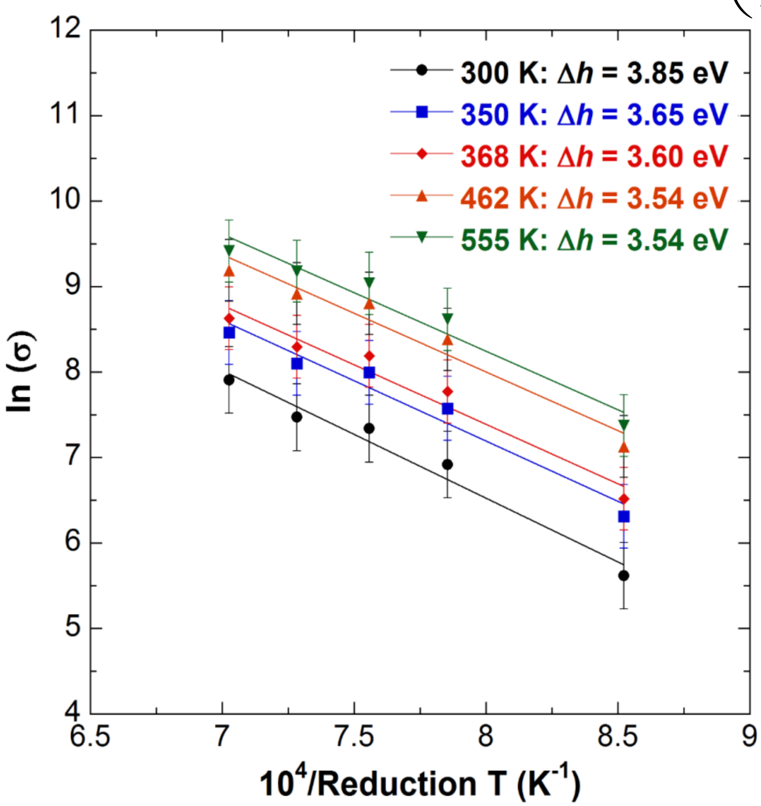
$$O_O \rightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g)$$

- Equilibrium constant (K_{re}) and electroneutrality condition gives:

$$[V_O^{\bullet\bullet}] = K_2 \exp\left(-\frac{\Delta h}{3kT_{Re}}\right) \quad \text{where} \quad K_2 = K_1^{\frac{1}{3}} 4^{-\frac{1}{3}} (pO_2)^{-\frac{1}{6}}$$

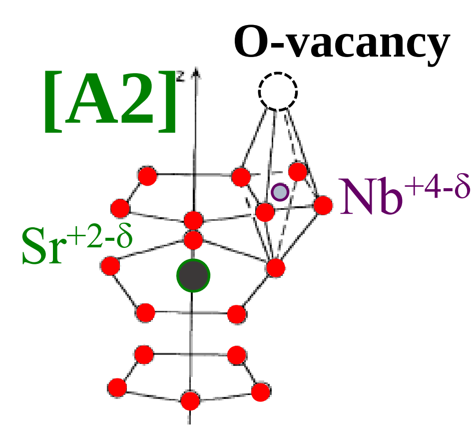
- From $\sigma = en\mu_e$

$$\ln\sigma = \left(\frac{1}{T_{Re}}\right)\left(-\frac{\Delta h}{3k}\right) + \ln K_3 \quad \text{where} \quad K_3 = 2K_2 e\mu_e$$



Assumptions:

1) Defect state is "frozen" in upon quenching
2) Mobility does not vary significantly among samples at measuring T
3) Δh~3.6-3.9eV



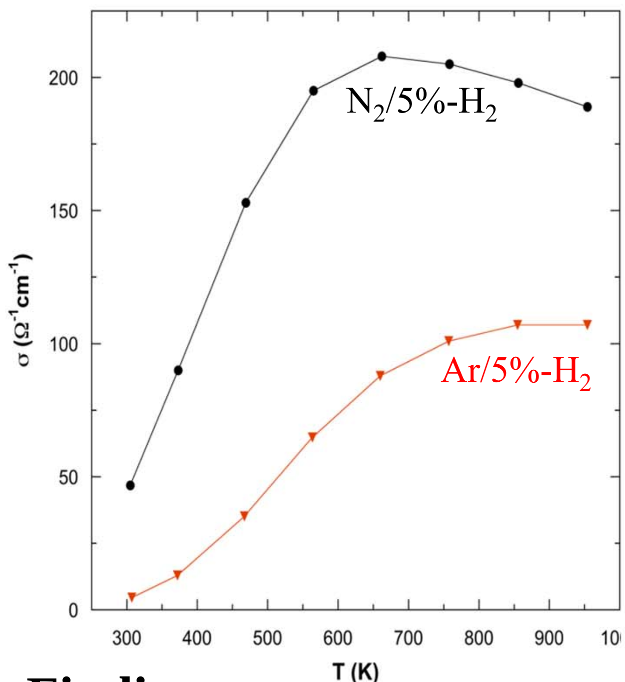
Ref.

For $BaTiO_3$: $\Delta h = 5.24$ eV at pO_2 at 10^{-12} and T_{Re} between 1100 – 1300 °C

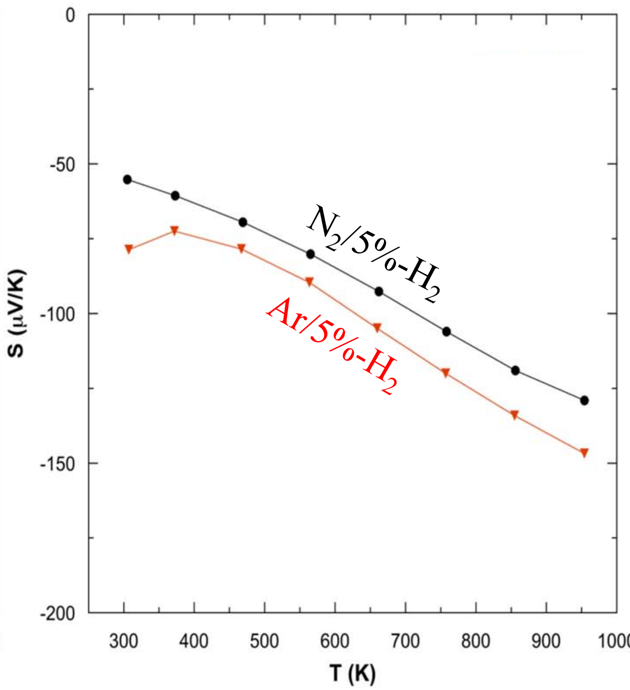
TE Properties of Reduced SBN50

Reduction in Ar/5% H_2 versus N_2/5%H_2

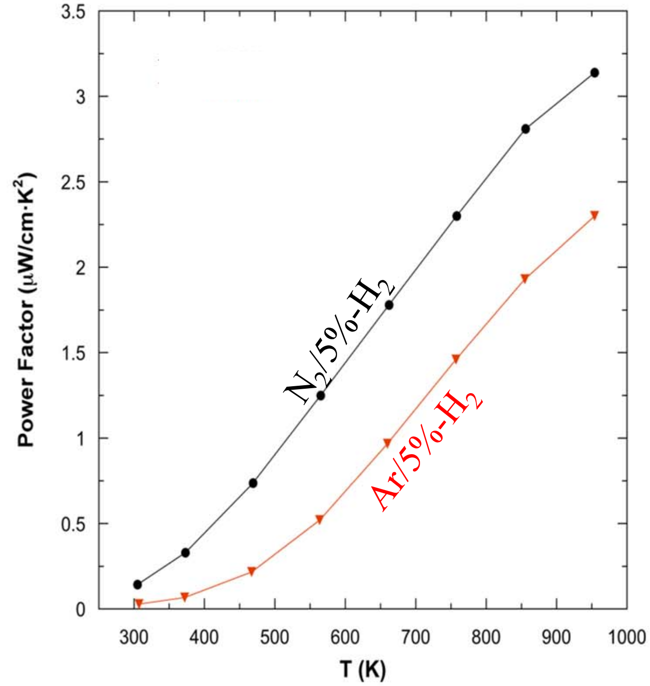
Electrical conductivity (σ)



Seebeck Coefficient (S)



Power factor ($P=\sigma \cdot S^2$)



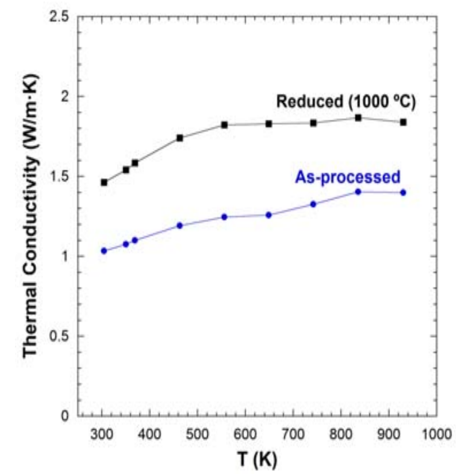
Findings

(1) Overall TE performance: (N_2/5%-H_2 red) > (Ar/5%-H_2 red)

(2) Around T~600K, sign of σ changes from $\frac{d\sigma}{dT} > 0$ to $\frac{d\sigma}{dT} < 0$

(3) For T to ~600K (N_2 red), $\sigma \Uparrow$ along with $|S| \Uparrow$

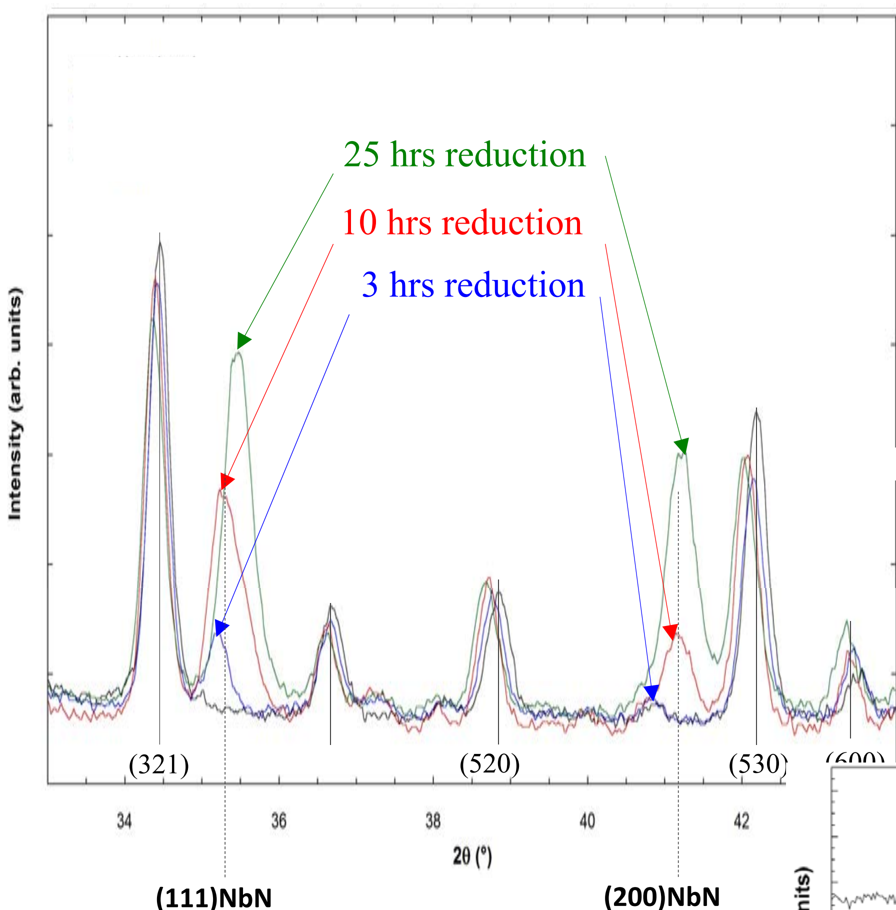
(4) κ after reduction increases by ~50% due to increases in the free carriers.



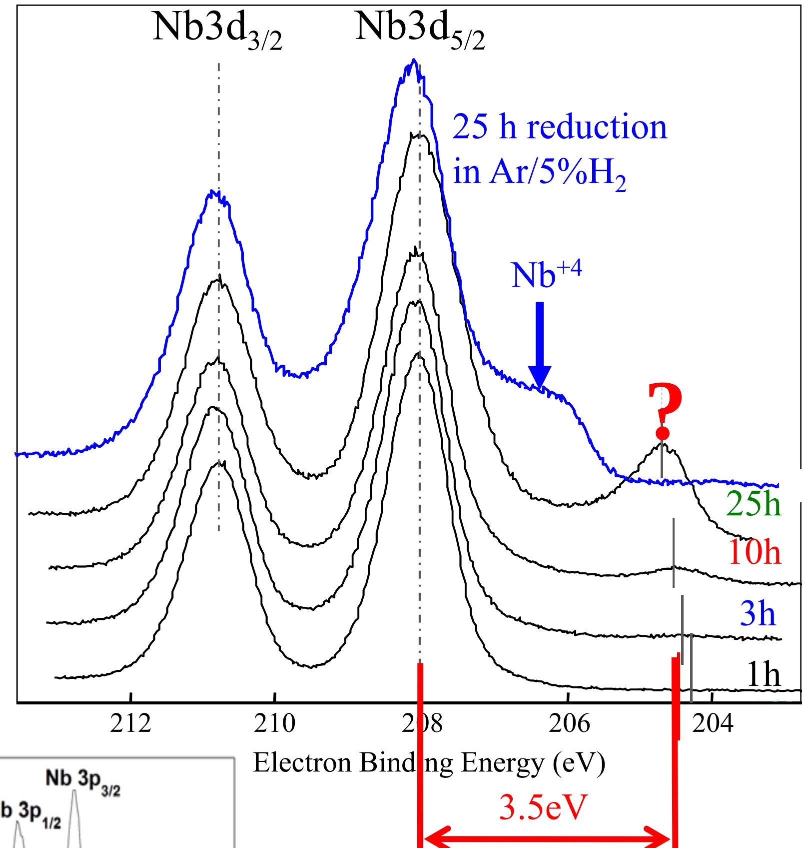
Difference Between N_2/H_2 and Ar/H_2 Reduction

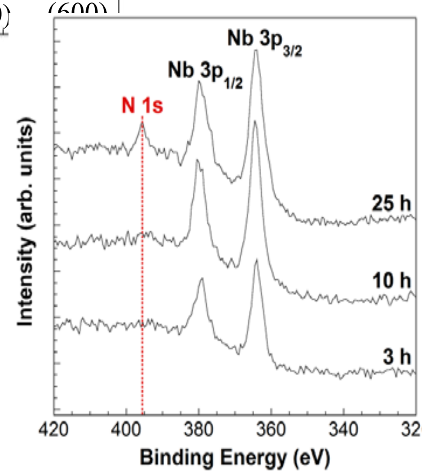
FY-2, 3

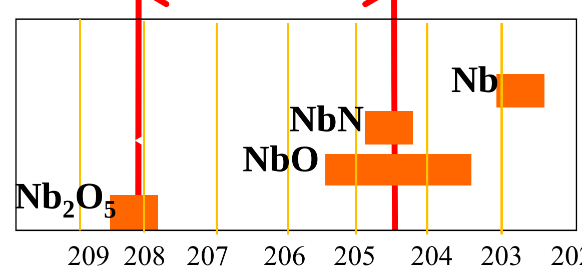
XRD before and after reduction in N_2/H_2



XPS : different degree of reduction







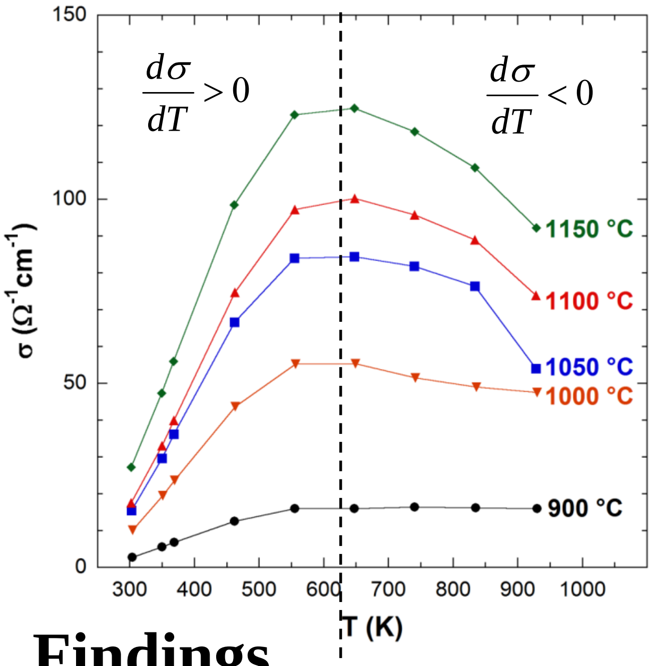
XPS Reference E_b for Nb compounds

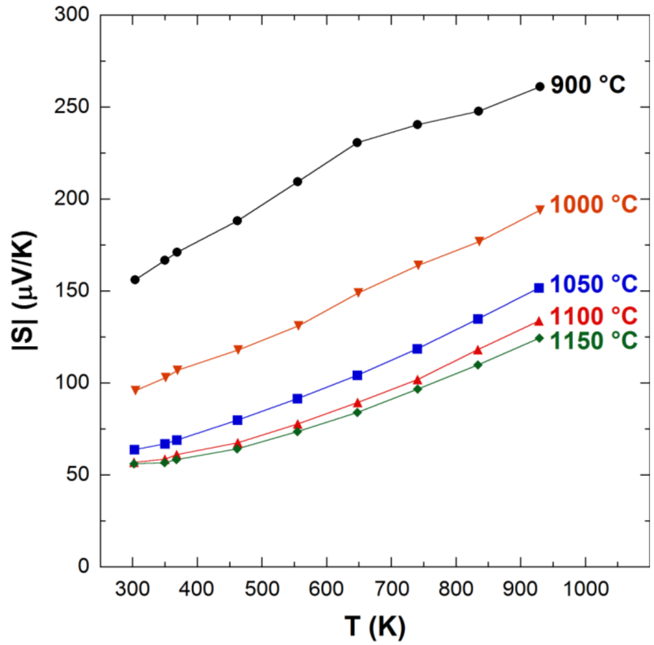
SBN (SC) and NbN: (Metallic)

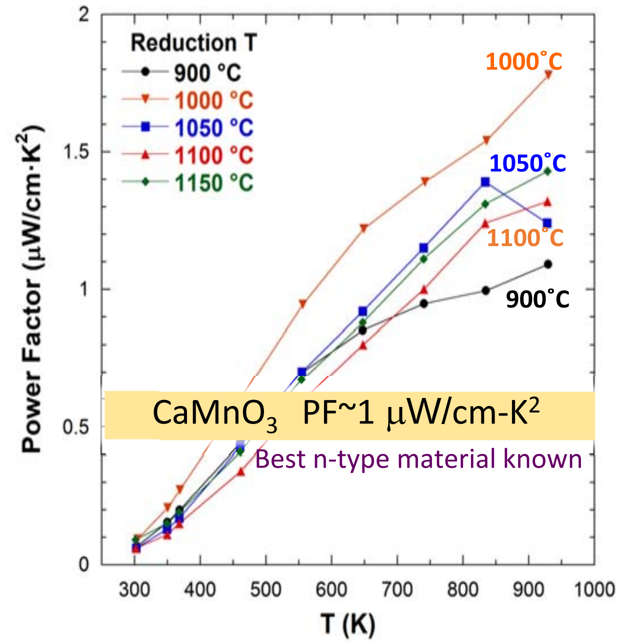
Enhancement of TE performance via "<u>Composite Effect</u>"?

Further look into reduction with N_2/5%-H_2

FY-2

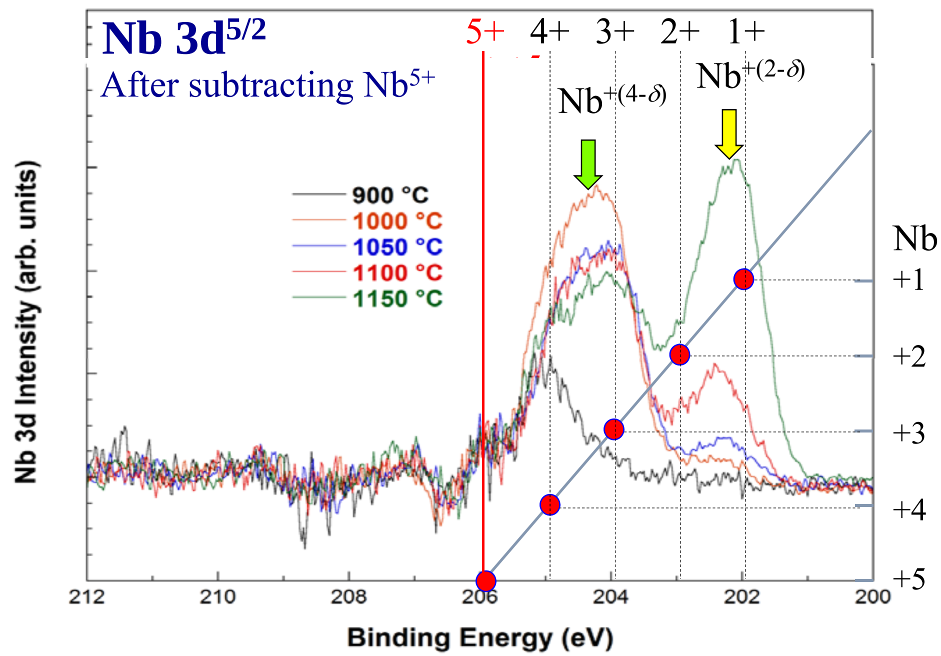




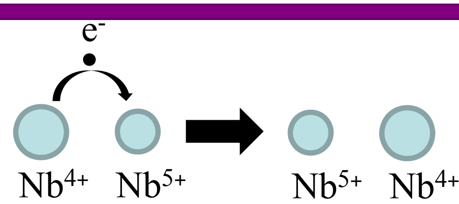


Findings

- Power Factor ($\sigma \cdot S^2$) max. at 1000C-red
- Parallel rise in $|S|$ and σ up to ~630 K
- Change in sign of $d\sigma/dT$ at higher T
- Loss of nanodomains?
- T_B for SBN61 = 620 – 650 K*
- Appearance of $Nb^{+(2-\delta)}$ as a protocol to ascertain "ideal" reduction conditions.



Electrical Conductivity Behavior(1)

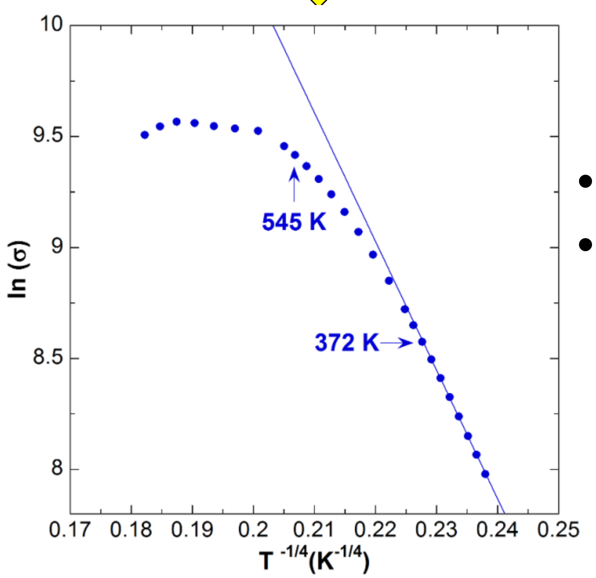


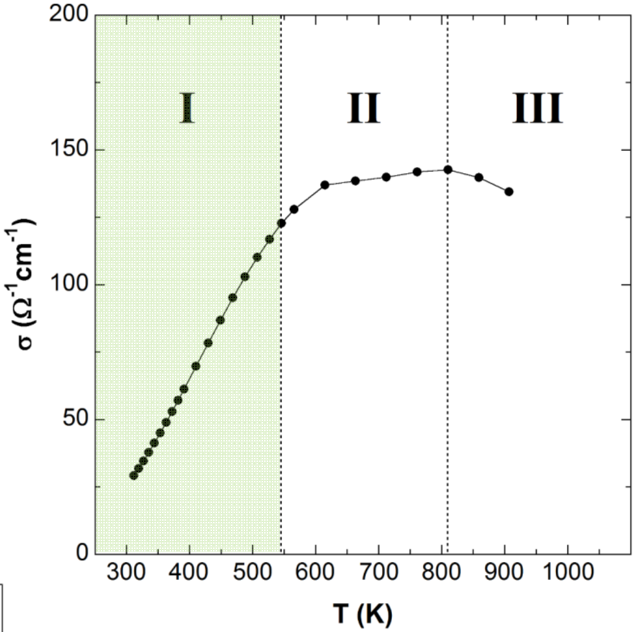
Variable range hopping (VRH)

$$\sigma = \sigma_0 \exp[-(T_0 / T)^{\frac{1}{d+1}}]$$

T_0 = Characteristic T coeff.
σ_0 = Pre-exponential factor
d = Dimensionality of hopping

At low T, electrons hop to more distant site with smaller potential barrier



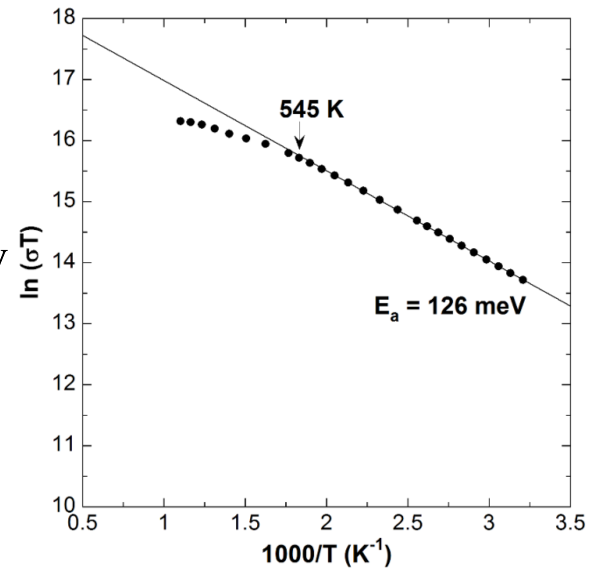


Nearest-neighbor small polaron hopping (SPH)

$$\sigma = \frac{A}{T^m} \exp\left(\frac{-E_a}{k_B T}\right)$$

A = Pre-exponential factor
E_a = Activation E for hopping
m = 1 (adiabatic) or 3/2 (non-adiabatic)

Electrons migrate by hopping out of self-induced potential well to neighboring site



- Adiabatic small polaron hopping:
- Charge carrier density and mobility

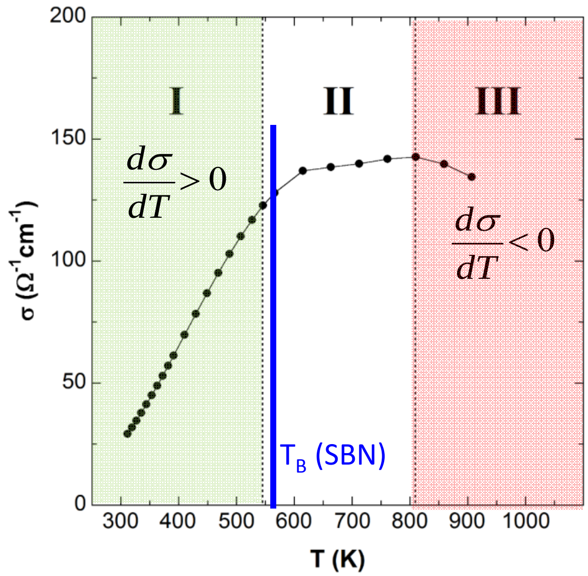
  $n = 1.7 \times 10^{21}$ cm^{-3}

  $\mu_e = 0.1$ cm^2/V·s

  at 400K for N2 reduction

Electrical Conductivity Behavior(2)

Why change in sign: $d\sigma/dT>0$ to $d\sigma/dT<0$?



Possibility (1)

At higher T, σ decreases with decreased mobility by scattering?

Mobility measurement with T
(Currently in progress)

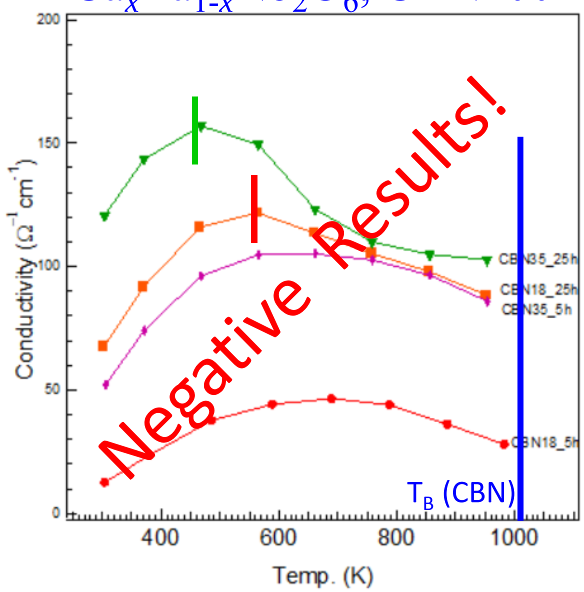
CBN materials	T_c	T_B
$Ca_{0.18}Ba_{0.78}Nb_2O_6$	~600	~1200
$Ca_{0.35}Ba_{0.65}Nb_2O_6$	~493	~1050

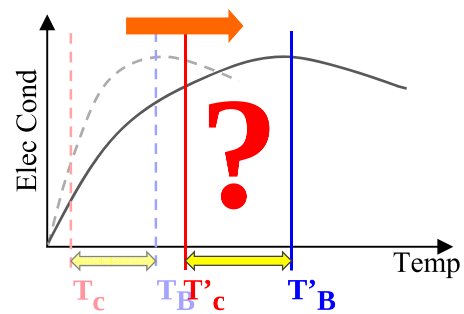
Possibility (2)

- Mott insulator-metal transition?
  Ferroelectric nanodomains
  Paraelectric regions
- For $T>T_B$, left with metal-like paraelectric phase

Use FE materials with higher Tc to test T_B effect.

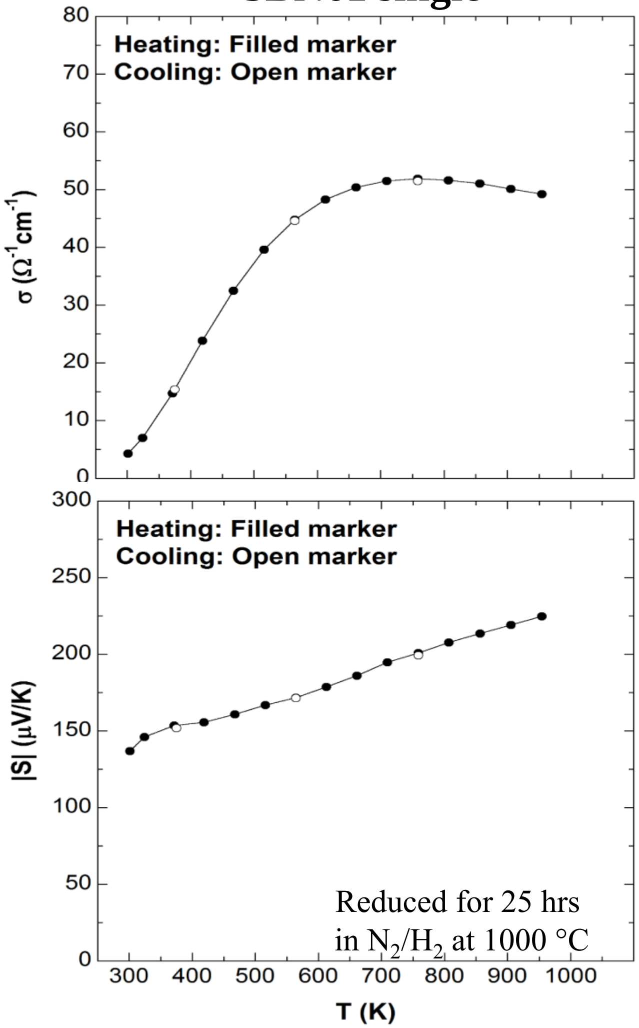
$Ca_xBa_{1-x}Nb_2O_6$, CBN100x



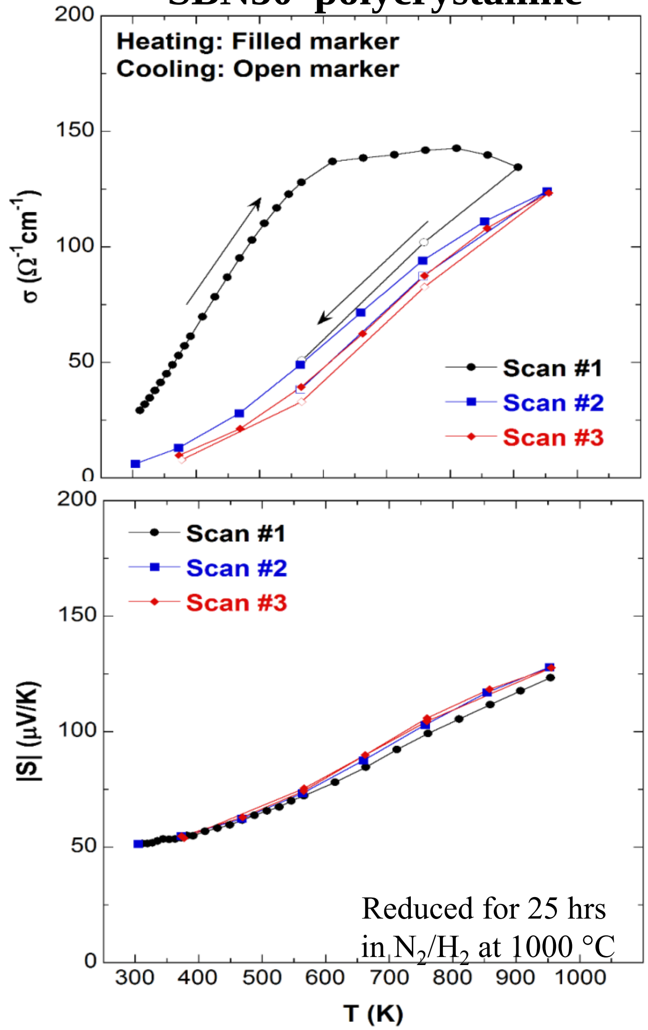


Stability: Repeated Testing

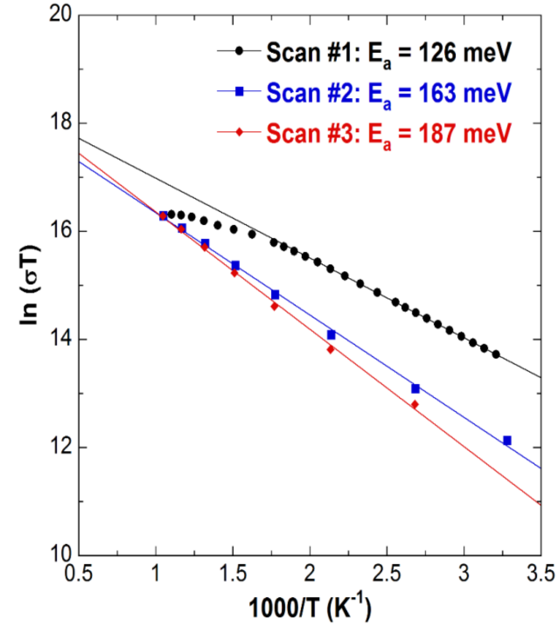
SBN61 single



SBN50 polycrystalline



Deviation from SPH fit decreases during retesting

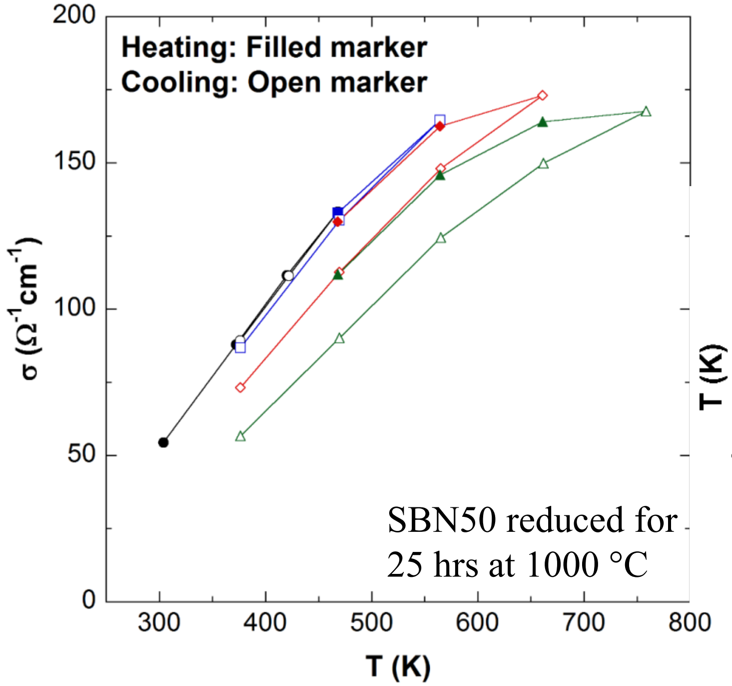


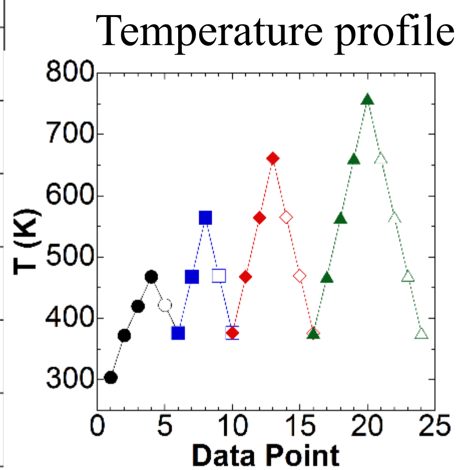
Factors contributing to the changes of polycrystalline sample

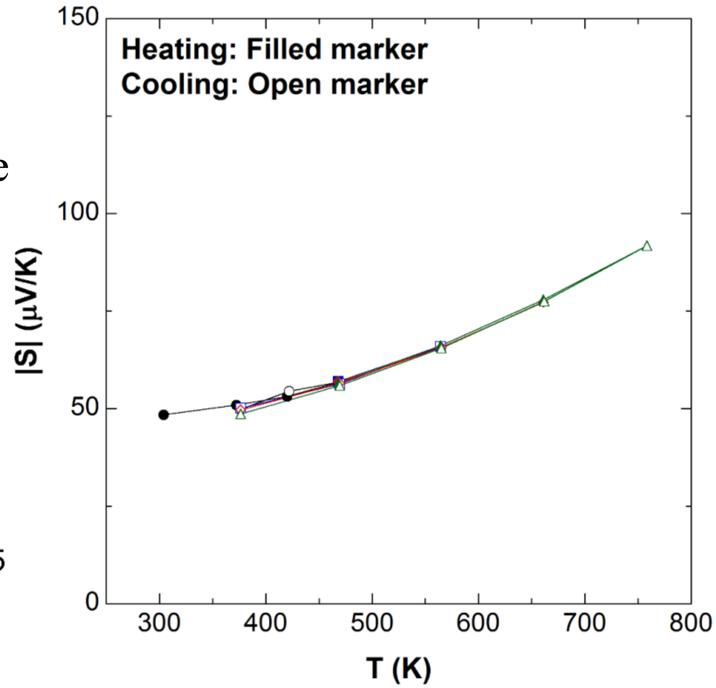
- Partial oxidation of the grain boundaries?
- Removal of the boundary passivation, such as hydrogen adsorbed at dangling bonds?

Stability: Incremental Heating/Cooling

At what point does σ of polycrystalline SBN begin to degrade?



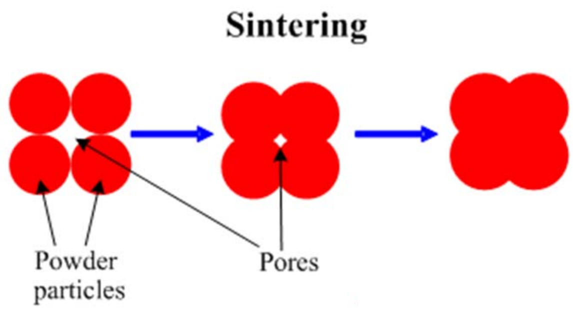




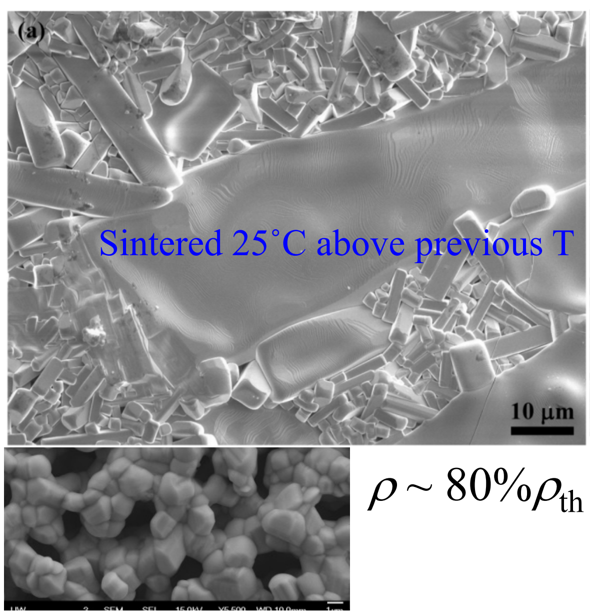
- Upon cooling from 450, 550 K, almost no change in σ observed
- Above 550 K, notable decrease in $d\sigma/dT$ and degradation of σ values with cooling are evident - $|S|$ exhibits no change
- Further experiments are planned to look at effects of time and reduction in hydrogen-free environments

SBN50 Powder Sinterability

Conventional Sintering (CS)

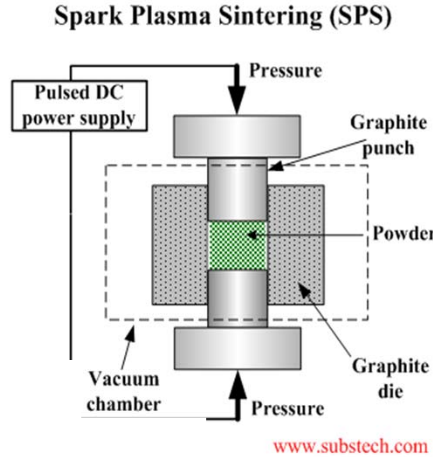


- Pressureless-sintering
- Varied density
- Possible grain growth (abnormal grain growth)

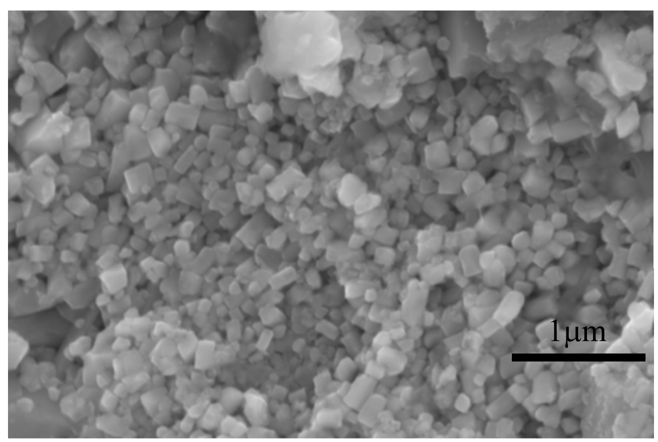


$\rho \sim 80\% \rho_{th}$

Spark Plasma Sintering (SPS)

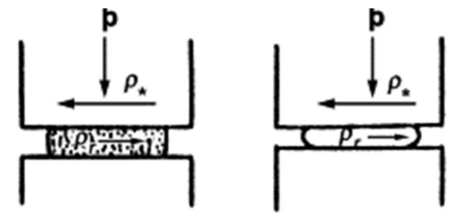


- Pressure + Electrical Current in vacuum
- Extremely fast sintering times (<10 min)
- High density with fine-grains (<250 nm)

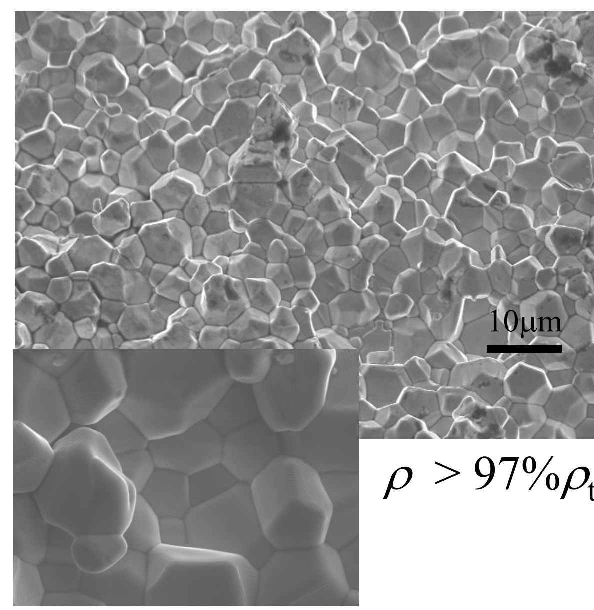


$\rho = 93\% \rho_{th}$

Sinter-Forging (SF)

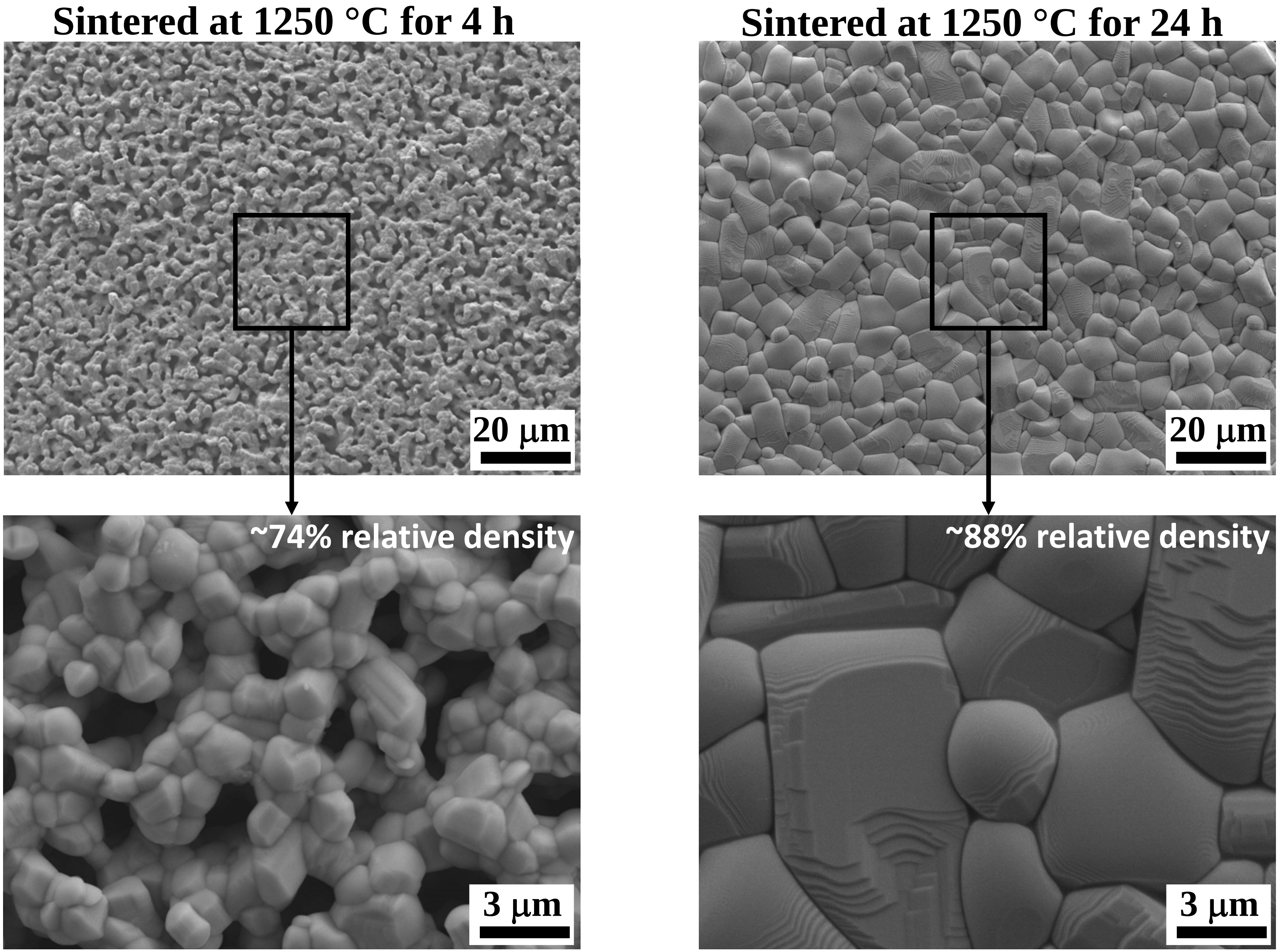


- CS + uniaxial pressure.
- High density.
- Textured grains

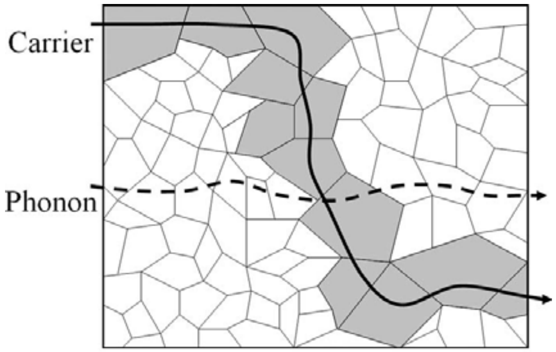


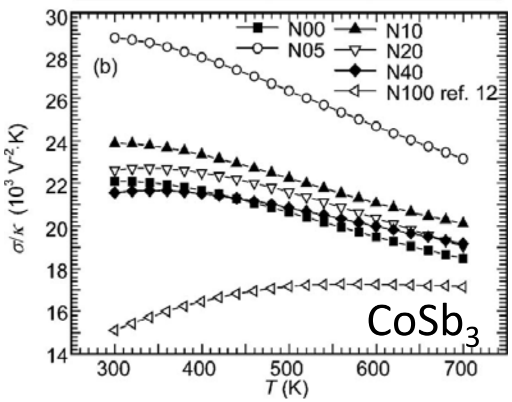
$\rho > 97\% \rho_{th}$

Sintering of SCS Powder: SBN50



On-going work (1): Nano-Micro Composites

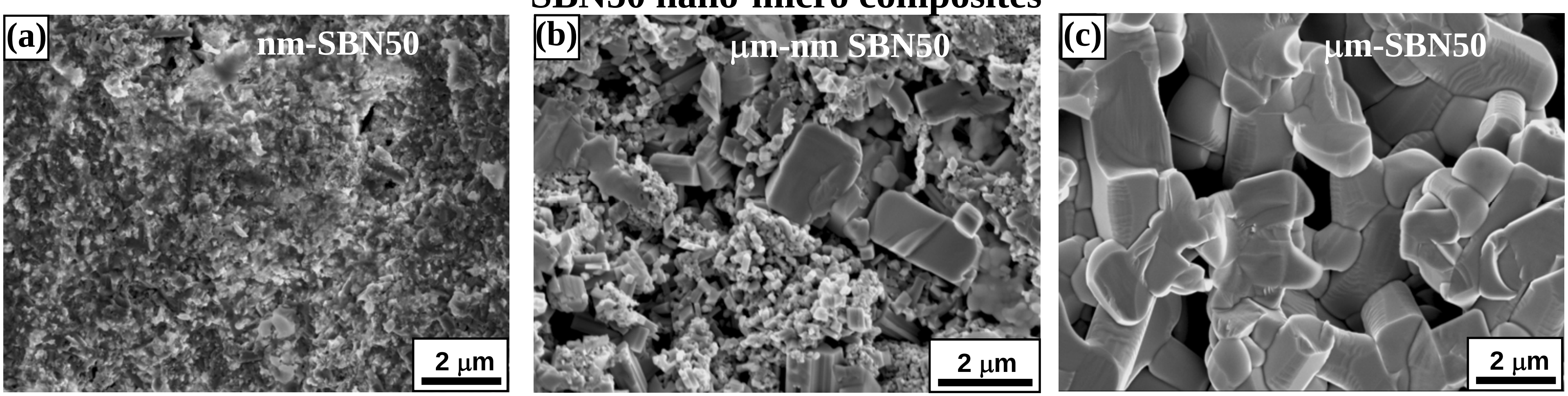




Mi *et al.*, *App. Phys. Lett.* **91**, 172116 (2007)

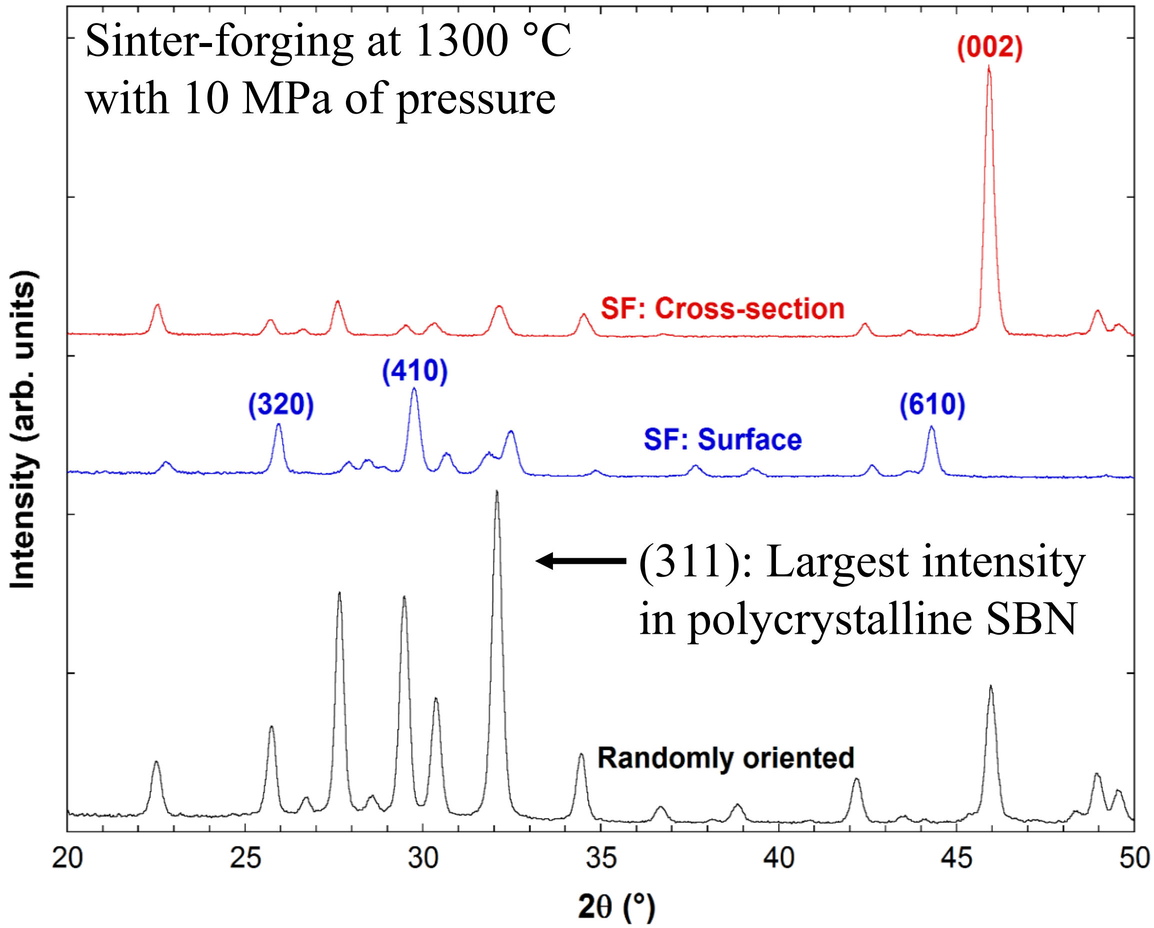
- Reduction in grain size adversely affects electron mobility
- Research into nano-micro composites to scatter phonons and preserve σ
- Percolation effect: Charge carriers “select” low resistivity path while phonons scattered by nanoparticles

SBN50 nano-micro composites

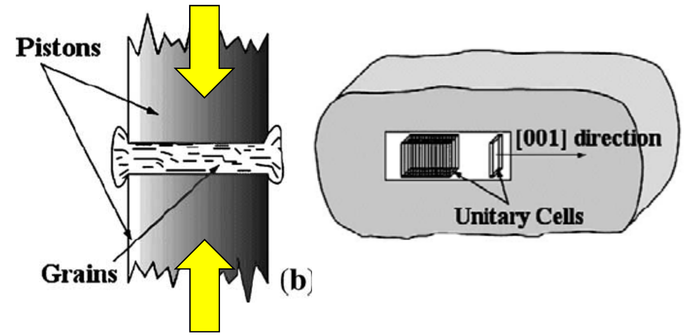


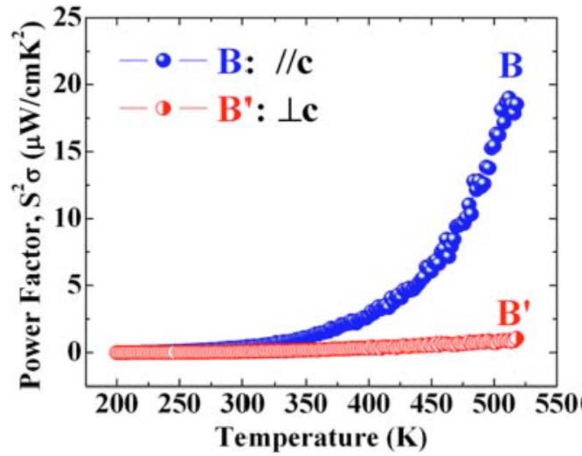
On-going work (2): Texture by Sinter-forging

FY-3



Anistropic grain growth and (00*l*) texturing induced by uniaxial loading





*Lee *et al*., *Appl. Phys. Lett.* **93**, 031910 (2010)

- Texturing successfully achieved by sinter-forging at 1300 °C
- **Increase in *T* from 1250 to 1300 °C; (311):(002) ratio decreased from 1.46 to 0.12**
- Enhanced TE properties expected for SBN along c-axis **(in progress)**.

On-going work (3): Chemical Reduction

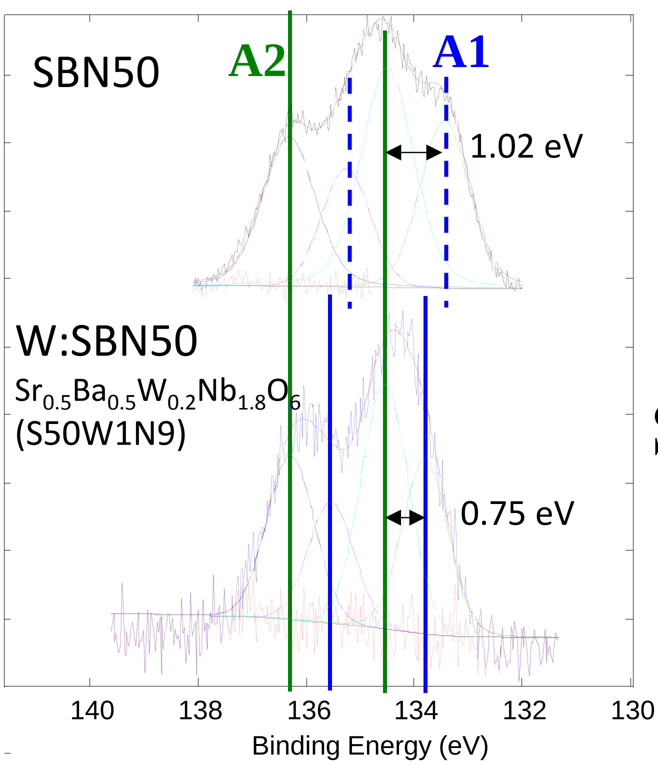
Currently developing strategy to chemically reduce SBN through incorporation of heteroatom dopants with higher valency than Nb.

$$MO_3 \xrightarrow{SBN} M_{Nb}^{\bullet} + e^{-} + 3O_O^{x} \quad \Leftrightarrow \quad O_O \rightarrow V_O^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g)$$

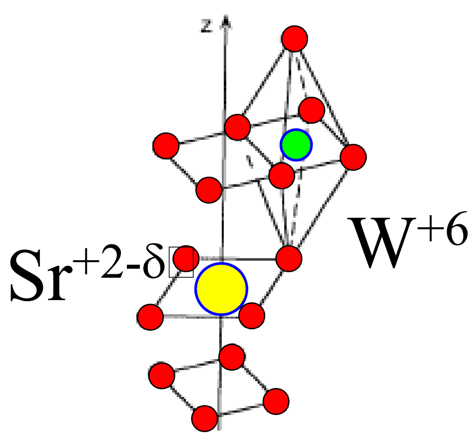
where M= +6 ion, such as W^{+6}, Mo^{+6}

Chemical reduction without removing O

Physical reduction by removing O



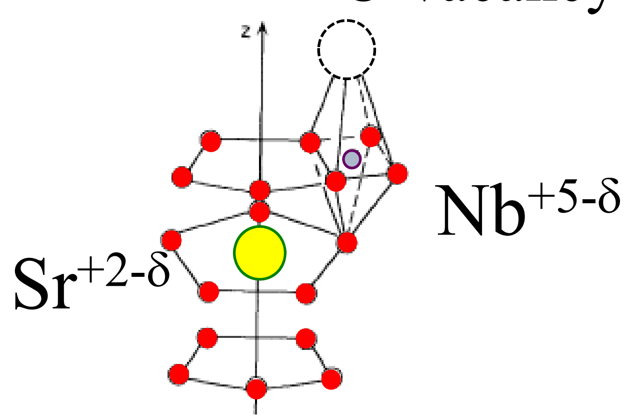
A1



New Mechanism of Reduction

A2

O-vacancy



Overall Summary

- Suitable methods to fabricate and reduce polycrystalline SBN specimens with range of compositions were devises
- Fundamental insight was gained into site occupancy and the effect of reduction on local cation environments
- TE data was successfully obtained; a change in sign of $d\sigma/dT$ was noted and a parallel rise in $|S|$, σ were observed
- Thermally activated polaron hopping was shown to be a likely σ mechanism in SBN
- A degradation in σ was noted for SBN after initial testing, and a possible mechanism related to grain boundary passivation from reduction was identified

To finish this project

- Micro-nano composites for optimizing TE properties
- Texturing experiments to exploit SBN anisotropy
- Chemical reduction (i.e dopants) to increase the electrical conductivity

List of Publications

"Thermoelectric properties of reduced polycrystalline $Sr_{0.5}Ba_{0.5}Nb_2O_6$ fabricated via solution combustion synthesis", authored by *Christopher S. Dandeneau, Tyler W. Bodick, Rajendra K. Bordia, and Fumio S. Ohuchi*, **Journal of the American Ceramic Society**, **96** (2013) 2230-7.

"Site occupancy and cation binding states in reduced polycrystalline $Sr_xBa_{1-x}Nb_2O_6$" Christopher S. Dandeneau, YiHsun Yang, Benjamin W. Krueger, Marjorie A. Olmstead, Rajendra K. Bordia and Fumio S. Ohuchi; ***Applied Physics Letter*** 104, 101607 (2014).

"Correlation of thermoelectric properties with local electronic and chemical environments in reduced polycrystalline $Sr_xBa_{1-x}Nb_2O_6$ " ***Journal of Applied Physics*** in preparation.

"Thermoelectric properties of reduced polycrystalline $Ca_xBa_{1-x}Nb_2O_6$ and the effect of polarized nanodomains" ***Journal of Vacuum Science and Technology A*** in preparation.

"High temperature Seebeck tester" ***Review of Scientific Instruments*** in preparation.

Thank you!