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

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Introduction/Motivation for Research

- >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 \( \sigma \)
- Thermal conductivity \( \kappa \)

\[
\text{Efficiency} = \frac{\sigma \cdot S^2}{\kappa}
\]

You want **Efficiency** \( \uparrow \)
- You need \( \sigma \uparrow \), \( S \uparrow \), \( \kappa \downarrow \) at all \( T \)
- But normally \( \sigma \uparrow \), \( S \downarrow \), \( \kappa \uparrow \) (conflicting)

Searching materials/conditions that exhibit \( \sigma \uparrow \), \( S \uparrow \) and \( \kappa \downarrow \) is an outstanding problem in Materials Science and Physics.
## Current Thermoelectric Materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>$S$ (μV/K)</th>
<th>$\rho$ (Ω cm)</th>
<th>$K$ (W/mK)</th>
<th>$zT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb$<em>{14}$MnSb$</em>{11}$</td>
<td>185</td>
<td>0.0054</td>
<td>0.7</td>
<td>~1 (1200 K)$^{38}$</td>
</tr>
<tr>
<td>0.23B–0.77Si$<em>{0.8}$Ge$</em>{0.2}$</td>
<td>168</td>
<td>0.001219</td>
<td>4.1</td>
<td>~0.62 (1200 K)$^{39}$</td>
</tr>
<tr>
<td>Na$_x$Co$_2$O$_4$ (plate morphology cera)</td>
<td>177</td>
<td>0.0073</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$<em>{1.5}$Co$</em>{1.8}$Ag$_{0.2}$O$_4$</td>
<td>101</td>
<td>0.0066</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>635</td>
<td>15.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.98}$Sr$</em>{0.02}$CoO$_3$</td>
<td>330</td>
<td>0.265</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$_2$Te$_3$</td>
<td>−200</td>
<td>0.001</td>
<td></td>
<td>1.2$^{44}$</td>
</tr>
<tr>
<td>0.59P–0.41Si$<em>{0.8}$Ge$</em>{0.2}$</td>
<td>−171</td>
<td>0.00074</td>
<td>4.2</td>
<td>~1.15 (1200 K)$^{39}$</td>
</tr>
<tr>
<td>Sr$<em>{0.98}$La$</em>{0.02}$TiO$_3$</td>
<td>−260</td>
<td>0.001</td>
<td>11</td>
<td>0.18$^{45}$</td>
</tr>
<tr>
<td>Sr$<em>{0.9}$Dy$</em>{0.1}$TiO$_3$</td>
<td>−190</td>
<td>~0.0028</td>
<td>~2.6</td>
<td>0.22 (573 K)$^{46}$</td>
</tr>
<tr>
<td>Thin film</td>
<td>−200</td>
<td></td>
<td>3</td>
<td>0.37 (1000 K)$^{33}$</td>
</tr>
<tr>
<td>SrTi$<em>{0.8}$Nb$</em>{0.2}$O$_3$</td>
<td>−220</td>
<td>0.001</td>
<td>8 (1073 K)</td>
<td>0.65(1250K)$^{47}$</td>
</tr>
<tr>
<td>Zn$<em>{0.98}$Al$</em>{0.02}$O</td>
<td>−220</td>
<td>0.001</td>
<td>8 (1073 K)</td>
<td>~0.16 (550 K)</td>
</tr>
</tbody>
</table>

### $p$-type oxides

Holes generated by oxygen excess

\[ \frac{1}{2} O_2 \rightarrow V'_M^{''} + 2h^{'''} + O_O^x \]

Good stability in air at high $T$

### $n$-type oxides

Oxygen deficiency results in excess electrons

\[ O_O^x \rightarrow V'_O^{'''} + 2e' + \frac{1}{2} O_2 \]

Stability often poor at high $T$ in air

**Development of n-type oxide materials is still behind.**
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 ($\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$) 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: \( \text{Sr}_x \text{Ba}_{1-x} \text{Nb}_2 \text{O}_6 \)

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

\((\text{A1})_2(\text{A2})_4(\text{C})_4(\text{B1})_2(\text{B2})_8 \text{O}_{30}\)
- Tetragonal A1: Sr only
- Pentagonal A2: Sr or Ba
- Octahedral B1, B2: Nb
- Trigonal C = Vacant
*1/6 of total A1+A2 sites vacant
Strontium Barium Niobate (SBN)

- $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN100$x$): $n$-type relaxor ferroelectric with broad ferroelectric to paraelectric transition
  - Extensively studied for electro-optic/photorefractive applications
  - Congruent composition: $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ (SBN61)
  - Phase stability region: $0.25 < x < 0.75$ (?)
  - Composition-dependent phase transition temp.
  - Electrically conductive with annealing in reducing environment

- Reduced SBN for TE applications
  - High power factor ($\text{PF} = 20 \, \mu\text{W/cm} \cdot \text{K}^2$) 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)

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

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**Sr\(_x\)Ba\(_{1-x}\)Nb\(_2\)O\(_6\) (SBN)**

Pulsed Laser Deposition (PLD)

Graduate student: Chris Dandeneau
CME Library of SBN(x)

XPS: composition

- SrNb$_2$O$_8$
- Ba3d
- SN rich

- SBN
- Sr3d

- BN rich

XRD: structure

- SrNb$_2$O$_8$
- BaNb$_2$O$_6$
- Spot #1
- Spot #2
- Spot #3
- Spot #4
- Spot #5
**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: \( \text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6 \) (SBN50)**

\[
0.5\text{Sr(NO}_3\text{)}_2 + 0.5\text{Ba(NO}_3\text{)}_2 + \text{Nb}_2(\text{C}_2\text{O}_4)_5 + 5\text{NH}_4\text{NO}_3 + \frac{5}{3}\text{CO(NH}_2\text{)}_2
\]

\[
\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6 + \frac{35}{3}\text{CO}_2 + \frac{40}{3}\text{H}_2\text{O} + \frac{23}{3}\text{N}_2
\]
Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ (SBN)

Crystallinity and Phase Purity

Sr$_{0.5}$Ba$_{0.5}$Nb$_2$O$_6$ (SBN50)

Intensity (arb. units)

900°C

800°C

700°C

Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ via Solid State Processing

Secondary phase

All peaks correspond to SBN phase

SBN20

SBN30

SBN50

SBN61

SBN80
Cation Site Occupancy in SBN

- 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 $\sim 1$ eV

Which Sr site corresponds to higher BE peak?
Cation Site Occupancy in SBN

- Five formula units per \((A1)_{2}(A2)_{4}(C)_{4}(B1)_{2}(B2)_{8}O_{30}\) unit cell
- For \(Sr_{0.2}Ba_{0.8}Nb_{2}O_{6}\) (SBN20): Ba occupying all A2 sites
- No higher BE peak for SBN20 corresponds to A2 site

Larger coordination number (CN) for Sr at A2 site

Lower electron density, higher BE

\[CN = 12\]  \[CN = 15\]
Reduction of SBN in Ar/5%-H₂

- As-sintered SBN samples possess very low \( \sigma \)
- Annealing in reducing environment creates oxygen vacancies:

\[
O_0 \rightarrow V_{O} + 2e' + \frac{1}{2}O_2(g)
\]

- Increase of \( \sigma \) by \( e^- \) donated back to Nb to preserve electroneutrality.

- For SBN50: \( \text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6 \rightarrow \text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}^{5+}_{2-y}\text{Nb}^{n+}_y\text{O}_{6-\delta} + \frac{\delta}{2}O_2 \)

XRD

Unreduced SBN50
Reduced in Ar/5% H₂
(1000C-25h)

XPS

Nb 3d\( _{5/2} \)

Which oxygen(s)?
Reduced SBN: Sr/Ba XPS Spectra

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

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

TGA: Oxygen Uptake

- 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

**Powder reduced for 5 h at 1000 °C in N₂/H₂:**
- \( pO₂ \sim 10^{-21} \text{ atm} \)
- Onset of oxidation: 250 - 300 °C
- Weight gain due to oxygen uptake: 1.52%
- Value of \( \delta \) in \( \text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_{6-\delta} \): 0.36
- Valence of Nb from charge balance: 4.64
Vacancy Formation Enthalpy

\[ O_0 \rightarrow V_0^{**} + 2e' + \frac{1}{2}O_2(g) \]

- Equilibrium constant \( (K_{Re}) \) and electroneutrality condition gives:
  \[ [V_0^{**}] = K_2 \exp \left( -\frac{\Delta h}{3kT_{Re}} \right) \]
  where \( K_2 = K_1^3 4^{\frac{1}{3}} \left( pO_2 \right)^{\frac{1}{6}} \)

- From \( \sigma = e\mu_e \)
  \[ \ln \sigma = \left( \frac{1}{T_{Re}} \right) \left( -\frac{\Delta h}{3k} \right) + \ln K_3 \]
  where \( K_3 = 2K_2e\mu_e \)

**Assumptions:**

1) Defect state is “frozen” in upon quenching

2) Mobility does not vary significantly among samples at measuring \( T \)

3) \( \Delta h \sim 3.6-3.9\text{eV} \)

Ref.

For BaTiO₃: \( \Delta h = 5.24 \text{ eV} \) at \( pO_2 \) at \( 10^{-12} \) and \( T_{Re} \) between 1100 – 1300 °C

\[ [A2]^* \]

O-vacancy

\[ \text{Sr}^{2-\delta} \]

\[ \text{Nb}^{4-\delta} \]
**TE Properties of Reduced SBN50**

Reduction in Ar/5% H₂ versus N₂/5%H₂

**Findings**

1. Overall TE performance: \((\text{N}_2/5\%-\text{H}_2 \text{ red}) > (\text{Ar}/5\%-\text{H}_2 \text{ red})\)

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

3. For \(T \sim 600\)K (N₂ red), \(\sigma \uparrow\) along with \(|S| \uparrow\)

4. \(\kappa\) after reduction increases by \(\sim 50\%\) due to increases in the free carriers.
**Difference Between N\textsubscript{2}/H\textsubscript{2} and Ar/H\textsubscript{2} Reduction**

XRD before and after reduction in N\textsubscript{2}/H\textsubscript{2}

SBN (SC) and NbN: (Metallic) Enhancement of TE performance via “Composite Effect”?

XPS : different degree of reduction

FY-2, 3

XPS Reference Eb for Nb compounds
Further look into reduction with N$_2$/5%-H$_2$

**Findings**

- Power Factor ($\sigma \cdot S^2$) max. at 1000°C-red
- Parallel rise in $|S|$ and $\sigma$ up to $\sim$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.

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*CaMnO$_3$ PF~1 $\mu$W/cm-K$^2$ Best n-type material known*
Electrical Conductivity Behavior

Variable range hopping (VRH)

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

- \( T_0 \) = Characteristic \( T \) coeff.
- \( \sigma_0 \) = 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)

\[ \sigma = \frac{A}{T^m} \exp\left(\frac{-E_a}{k_BT}\right) \]

- \( A \) = 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:
  \( n = 1.7 \times 10^{21} \text{ cm}^{-3} \)
  \( \mu_e = 0.1 \text{ cm}^2/\text{V} \cdot \text{s} \)
  at 400K for N2 reduction
Why change in sign: $d\sigma/dT > 0$ to $d\sigma/dT < 0$?

**Possibility (1)**

At higher $T$, $\sigma$ decreases with decreased mobility by scattering?

Mobility measurement with $T$ (Currently in progress)

**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 $T_c$ to test $T_B$ effect.

CBN materials

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

FY-3
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 $\sigma$ of polycrystalline SBN begin to degrade?

- Upon cooling from 450, 550 K, almost no change in $\sigma$ observed
- Above 550 K, notable decrease in $d\sigma/dT$ and degradation of $\sigma$ 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)

**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

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Sintered 25°C above previous T

\[ \rho \approx 80\% \rho_{th} \]

\[ \rho = 93\% \rho_{th} \]

\[ \rho > 97\% \rho_{th} \]
Sintering of SCS Powder: SBN50

Sintered at 1250 °C for 4 h

- ~74% relative density

Sintered at 1250 °C for 24 h

- ~88% relative density
On-going work (1): Nano-Micro Composites

- Reduction in grain size adversely affects electron mobility

- Research into nano-micro composites to scatter phonons and preserve $\sigma$

- 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

- 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).

*Lee et al., Appl. Phys. Lett. 93, 031910 (2010)*
On-going work (3): Chemical Reduction

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

\[
MO_3^{SBN} \rightarrow MB^{+6} + e^- + 3O_O^x
\]

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

Chemical reduction without removing O

Physical reduction by removing O

New Mechanism of Reduction
Overall Summary

• Suitable methods to fabricate and reduce polycrystalline SBN specimens with range of compositions were devised
• 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 $|S|$, $\sigma$ were observed
• Thermally activated polaron hopping was shown to be a likely $\sigma$ mechanism in SBN
• A degradation in $\sigma$ 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 Sr0.5Ba0.5Nb2O6 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.


“Correlation of thermoelectric properties with local electronic and chemical environments in reduced polycrystalline SrxBa1-xNb2O6” 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.
