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

Program Manager: Patricia Rawls

Fumio S. Ohuchi (PI) and Rajendra K. Bordia (Co-PI)

Department of Materials Science and Engineering
University of Washington
Box 352120
Seattle, WA 98195

Grant No. DE-FE0007272
(June 1, 2012-May 31, 2013)

Graduate Students: Christopher Dandeneau and YiHsun Yang

June 10, 2013
The UCR Contractors Review Conference
Introduction/Motivation for Research

• 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, $\kappa$
  ➢ Tailor stoichiometry to maximize $S^2\sigma$ with low $\kappa$

• Significant progress in the development of the $p$-type TE oxides (e.g., NaCo$_2$O$_4$)

• 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 \( \text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6 \) (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 \( \text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6 \) 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.
  \( \text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6 \rightarrow \text{Sr}_x\text{Ba}_{1-x}\text{Nb}_{2-y}\text{Nb}_y^{5+}\text{O}_{6-\delta} + \frac{\delta}{2}\text{O}_2 \)

• Site specific occupancy in SBNx.

• Electronic and phonon effects of SBNx on thermal conductivity.

• Better understanding of change in sign of \(d\sigma/dT\) 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.
  \( \text{M:}(\text{Sr, Ba})_2\text{Nb}_2\text{O}_7 \) (M:SBN)
  \( \text{Sr}_x\text{Bi}_{2-x}\text{Nb}_2\text{O}_9 \) (SBN)

• Controlled microstructures, grain texture, densification and pores to control TE properties.
$\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBNx)

- Ferroelectric relaxor
- Tungsten tetragonal bronze
- Ion occupancy

$(A1)_2(A2)_4(C)_4(B1)_2(B2)_8\text{O}_{30}$

$A1 = \text{Sr}^{+2}$
$A2 = \text{Sr}^{+2}$ and $\text{Ba}^{+2}$
$B1$ and $B2 = \text{Nb}^{+5}$

Site Occupancy Factor


SR3d$_{3/2}$-$5/2$

Ba3d$_{5/2}$
TE Results from $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$

**Electrical Conductivity ($\sigma$)**

- SBN30
- SBN50
- SBN61

Samples reduced for 3 hrs at $P(\text{O}_2) \sim 10^{-25}$ atm

**Seebeck Coefficient ($S$)**

- SBN61
- SBN50
- SBN30

**Thermal Conductivity ($\kappa$)**

- SBN61
- SBN50
- SBN30

**Power Factor ($\sigma S^2$)**

- SBN50
- SBN61
- SBN30

CaMnO$_3$ $PF \sim 1 \mu\text{W/cm-K}$

**Figure of Merit ($\sigma S^2T/\kappa$)**

- SBN61
- SBN50
- SBN30

Best n-type material known: CaMnO$_3$
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 $\sigma$ and $S$.

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

6. Microstructural aspects on TE property.
Reduction of SBN50 at various temperatures under H2/Ar flowing condition.

• \( \text{P(O}_2\text{)} \approx 10^{-25} \text{ atm} \)

After substracting Nb\(^{5+}\)

\( \text{Nb}^{+(4-\delta)} \) to \( \text{Nb}^{+(2-\delta)} \) ratio becomes maximum after 1000 °C reduction

• PF becomes maximum before \( \text{Nb}^{+(2-\delta)} \) 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

Seebeck
Elec. Cond.
Power Factor

Removal of oxygen from A2 site?
X-ray Diffraction Analysis of SBN50

Forbidden

Sr$^{+2}$ $-$ $\delta$

Nb$^{+4}$ $-$ $\delta$

A2

(321) Forbidden

(520)

(530) Forbidden

(600)
X-ray Diffraction Analysis of Reduced SBN50

O$_0$ → V$_0^{**}$ + 2e' + $\frac{1}{2}$O$_2$(g)

Sr$_{0.5}$Ba$_{0.5}$Nb$_{2-a}$[Nb$_a$$^+$O$_6$]$_{6-d}$O$_{6-d}$ + $\frac{\delta}{2}$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?

\[ \text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_{2-\alpha}^{+5} \text{Nb}_{\alpha}^{+n} \text{O}_{6-\delta} + \frac{\delta}{2} \text{O}_2 (g) \]

**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
  \[ \text{O}_\text{o} \rightarrow \text{V}_{\text{o}}^\bullet \bullet + 2e^\prime + \frac{1}{2} \text{O}_2(g) \]
  \[ K = [V_{\text{o}}^\bullet \bullet] n^2 (p\text{O}_2)^{\frac{1}{2}} = \exp\left(-\frac{\Delta G^\circ}{kT}\right) \]

- Electrical conductivity \[ \sigma = en\mu_e \]
  \[ \ln \sigma = \left(\frac{1}{T}\right) \left(-\frac{\Delta G^\circ}{3k}\right) + \ln B \]

- \( \Delta G_0 \sim 3.6\text{-}3.9\text{eV} \)

Planned Experiment (FY-3)
- EXAFS and hard X-ray diffraction analysis at DOE-APS Facility.
Electrical Conductivity
Test of Polaron Hopping Models

\[ \frac{d\sigma}{dT} > 0 \]
\[ \frac{d\sigma}{dT} < 0 \]

1-D hopping
3-D hopping

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

Fit to 1-D or 3-D hopping model equally well:
Not conclusive → Planned Experiment (FY-3)
SBN50: Thermal Conductivity

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

Development of an entirely new reduction scheme:
“Irreversible Chemical Reduction” (FY-3)
SBN50 Powder Processing

Conventional Sintering (CS)  Spark Plasma Sintering (SPS)  Sinter-Forging (SF)

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

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

$\rho \approx 80\% \rho_{\text{th}}$

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

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

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.
  \[ T_B \] Burns Temp. (PRB28, 2527 (1983))

- Strategy for widening \( \sigma \uparrow \& |S| \uparrow \) region
  Comp. \( T_C \) \( T_B \)
  SBNx \( 0 \sim 200^\circ C \) \( 200 \sim 400^\circ C \)
  \( \text{Sr}_2\text{Nb}_2\text{O}_7 \) \( \sim 1300^\circ C \) \(?\)
  \( \text{SrBi}_2\text{Nb}_2\text{O}_9 \) \( \sim 450^\circ C \) \(?\)

- The strontium niobate \((\text{Sr}_n\text{Nb}_n\text{O}_{3n+2})\) systems
  - A pseudo 1-D system
  - Perovskite structure
  - Highly anisotropic
Progress so far (May 31, 2013):

1. Completed SCS of Sr$_2$Nb$_2$O$_7$ (SN) and basic characterization

\[
\text{Nb}_2(\text{C}_2\text{O}_4)_3 + 2\text{Sr(NO}_3)_2 + 10\text{NH}_4\text{NO}_3 + 5\text{CO(NH}_2)_2 \rightarrow \text{Sr}_2\text{Nb}_2\text{O}_7 + 15\text{CO}_2 + 30\text{H}_2\text{O} + 17\text{N}_2
\]

SBN50 vs. Sr$_2$Nb$_2$O$_7$

2. SN-TE characterization still in progress

3. Bi-doped SN and SrBi$_2$Nb$_2$O$_9$ in progress

4. Development of Seebeck tester, capable of measuring TE prop at $T>1000^\circ$C.

Planned Experiment (FY-3)
Summary of Findings
(June 1, 2012-May 31, 2013)

1. Demonstrated $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_{6-\delta}$ (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 $\frac{ds}{dT}$ 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


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

3. Exploration of $(\text{Sr, Ba})_2\text{Nb}_2\text{O}_7$ and $\text{Sr}_x\text{Bi}_{2-x}\text{Nb}_2\text{O}_9$ (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
   2. SBNx: TE
   4. High T Seebeck tester
**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

Thank you!