Oxide Thermoelectric Devices:
A Major Opportunity for the Global Ceramics Community

David R. Clarke
Materials Discovery and Application Laboratory
School of Engineering and Applied Sciences
Harvard University

5th International Congress on Ceramics, Beijing, August 2014
Despite low efficiencies, there are opportunities for thermoelectric devices at high temperatures.

Lessons from the development of Light Emitting Diodes (LEDs)

Oxides have intrinsic advantages at high temperatures

Use of Data mining

Natural superlattice compounds as alternatives to nanostructuring engineering

Materials challenges in high temperature thermoelectrics

Ceramics processing offers new manufacturing paradigms for thermoelectric devices

International collaboration is highly desirable and essential


**Basics: Energy Efficiency of Thermoelectric Materials**

**Efficiency**

\[
\eta = \frac{P}{Q} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT_m} - 1}{\sqrt{1 + ZT_m} + \frac{T_C}{T_H}}
\]

**Seebeck coefficient**

\[
ZT = \frac{S^2 \sigma}{(\kappa_{el} + \kappa_L)} \cdot T
\]

**Electrical conductivity**

**Thermal conductivity due to electrons in material**

**Thermal conductivity due to lattice vibrations**

**Need to both minimize thermal conductivity and maximize power factor, \( S^2 \sigma \)**

*Synder, JPL*
High efficiencies are not so important to life-cost of thermoelectrics because:

1. Absence of moving parts means there are no long-term maintenance cost
2. Long life expectancy 20-30 years
3. Waste heat is currently discharged
• LED lights are much more expensive than incandescent bulbs
• Why do organizations buy them?

- Life cycle cost is lower than for incandescent bulbs
- Situation is similar for thermoelectric devices
Examples of High Temperatures in Industry

- Exhaust manifolds of combustion engines
  - Small segments of hot pipes but millions of cars.
  - Disadvantage -- Complex geometry
- Chemical plants -- exothermic reactions
  - Kilometers of pipes,
  - Simpler geometry, typically circular pipes
- Metallurgical industries
  - smelting, casting
- Gas and steam turbines
  - Tens of thousands of turbines.
- Nuclear reactors
  - Few reactors but kilometer of pipes
- Solar thermal
  - Potential market not known yet

Mercedes AMG
Why Oxide Thermoelectrics?

- Only oxides are stable in air at high temperatures
- No oxidation protection needed → packaging cost is lower
- Huge number of trivalent and quadra-valent oxides (~ $10^5$) are known to exist
  but very few have been studied in detail
- Many oxides are highly refractory → use at low homologous temperatures
- Cation diffusion rates are low in oxides → so they more resistant to coarsening
- Refractory oxides form from abundant elements and, furthermore,
  scarce element oxides are generally not stable at high-temperatures
None of these materials is stable in air at high temperatures. Many are also not stable and melt at high temperatures. Far fewer oxides have been studied. No nanostructuring so far.
Remarkable materials but ..... they combine scarce elements and the high ZT’s are based on microstructural refinement !

Need ..... Commonly occurring elements in compounds that also don’t depend on microstructural refinement for high ZT’s
Data Mining

“Data Driven Review of Thermoelectric Materials”,
Large scale, high volume use requires abundant (blue) elements

“Data Driven Review of Thermoelectric Materials”,
Materials Selection Tool

High-Temperature Diffusion: Achilles' Heel of Nanostructuring

- Many of the high values of ZT are achieved as a result of nano-structuring (refining the microstructure scale to reduce thermal conductivity).
- All microstructures coarsen (Ostwald ripening).
- Coarsening is a thermally-activated diffusional process.
- Key temperature is the homologous temperature, $T/T_m$.
- For a single diffusional process, the nanostructural coarsening rate, $r$

$$r = A \exp(-Q/RT)$$

$$\text{LMP} = \frac{Q}{R} = T[C + \ln(t)]$$

Larson-Miller parameter $C$

- Conclusion:
  - High-temperature thermoelectric devices cannot rely on nanostructuring
  - Thermodynamically-stable nanostructuring is required.
Natural Superlattices
(Polysomes – Modular Phases – Homologous series)

In$_2$O$_3$(ZnO)$_k$

SrTiO
Ruddleston-Popper

Nano-scale spacing fixed by composition not processing. So they do not coarsen with time at high temperatures
Natural Superlattice in (ZnO)$_k$.In$_2$O$_3$

STEM-ADF image

Monolayer InO$_2$ sheets

Interface Thermal Resistance: $5 \times 10^{-10}$ m$^2$K/W

Liang and Clarke, In press, 2014
ZnO-InO$_{1.5}$ Phase Diagram

Phase diagram adapted from Moriga et al., J. Am Ceramic Soc 1998
Natural Superlattices Decrease Thermal Conductivity

Phase diagram adapted from Moriga et al., J. Am. Ceramic Soc. 1998

Liang and Clarke, APL, 2013
ZT of Natural Superlattices: $(\text{ZnO})_k\cdot\text{In}_2\text{O}_3$

Model system

Range over which NSL form

Liang and Clarke, Acta Materialia, 2014
Annular Thermoelectric Design For High-Temperature Pipes

Conformal geometry
Large scale
Contact resistances and interconnect resistances must be minimized. 

NB. Dependence on $L$ and $A$ of the TE legs.

Material ZT

$$ZT = \frac{S^2 \sigma}{(\kappa_{el} + \kappa_L)} \cdot T$$

Device / Module ZT

$$Z_{Device} \ T = \frac{S^2}{\kappa_{Device} R_{Device}}$$

Dimensions dictated by electrical and thermal resistances as well as temperature difference.

$$\kappa_{Device} = \frac{A_n}{L} \kappa_n + \frac{A_p}{L} \kappa_p + \frac{A}{\kappa_{contact}}$$

$$R_{Device} = R_{legs} + R_{contact} + R_{interconnect}$$

$$= \frac{L}{A_n} \rho_n + \frac{L}{A_p} \rho_p + R_{contact} + R_{interconnect}$$
High-Temperature Thermoelectric Devices: Some Challenges

Minimization of contact resistances -- electrical and thermal

Minimization of “thermal shorts” by radiative heat transfer

Identification of low resistivity metal oxide interconnect

Also, required: minimization of long-term chemical inter-diffusion
• Limited number of electrically conducting oxides exist, eg, ZnO, LaSrCrO
• Some guidance comes from electrode development for solid oxide fuel cells
• Identification of lower resistivity, high-temperature oxides should be a research priority
• Platinum is possible short-term solution but is far too expensive and also undergoes morphological instability and evaporation in air
The Challenge of Minimizing Radiative Heat Transfer

Problem:

\[ q_{hc} = q_{hot} - q_{cold} = A \sigma \left( \varepsilon_h T_h^4 - \varepsilon_c T_c^4 \right) \approx A \sigma \left( T_h^2 + T_c^2 \right) (T_h + T_c) \Delta T \]

Radiative exchange between hot and cold surfaces short-circuits the TE elements — gets worse at higher temperatures.
The Challenge of Minimizing Radiative Heat Transfer

Plasma-spray very porous YSZ into gaps to reduce radiative transfer
(technology transfer from TBC community)

Introduce micron-sized porosity into TE materials themselves
Radiation scattering is maximum when pore diameter $\sim$ IR wavelength
• Device design optimizes output power
• Design objective of conventional thermoelectric devices minimizes
  • weight, or
  • size, or
  • volume of TE material

• Industrial use of oxide thermoelectrics may require different design objectives
• Output power, $P_o$, is given by

$$P_o = \frac{S^2 (\Delta T)^2}{2 \left( R + R_{load} \right)} = \frac{S^2 (\Delta T)^2}{4 R}$$

• But what sets size?
• Internal resistance:

$$R \approx \frac{4 L \bar{\rho}}{A_T} \quad \Rightarrow \quad P_o = \frac{S^2}{\bar{\rho}} \frac{A_T}{16 L} (\Delta T)^2$$

*From Ure and Heikes, “Science and Engineering of Thermoelectrics”,*
Recipe For Commercial Success In The Materials Area

- Provide a product designer with a new functionality
- Ensure the designer has familiarity with the materials
- Absence of competing materials
- Ability to form complex shapes
- Availability of source materials
- Ability to join different materials
- Performance advantage
- Ability to amortize costs over several years so capital costs do not dominate life-cycle costs
Thermo-electric Generator Today

Flat geometry

COLD SIDE

HOT SIDE

Bi$_2$Te$_3$, PbTe

Cutting, dicing and soldering

Assembly required

Fabrication process is based on semiconductor wafer processing paradigm and packaging technologies. Also, relatively small in size, ~ centimeters
Two Examples of Oxide Thermoelectric Modules


- **p-type:** $\text{Ca}_{2.7}\text{Bi}_{0.3}\text{Co}_4\text{O}_9$
- **n-type:** $\text{Ca Mn}_{0.98}\text{Mo}_{0.02}\text{O}_3$

$L = 4.5 \text{ mm}, 8 \text{ pairs of legs}$
$silver \text{ interconnect}$
$0.34 \text{ W at } T_h = 1000^{\circ}\text{C}$


- **p-type:** $\text{Ca}_{2.7}\text{Bi}_{0.3}\text{Co}_4\text{O}_9$
- **n-type:** $\text{Ca}_{0.9}\text{Mn}\text{Yb}_{0.1}\text{O}_3$

$L = 5 \text{ mm}, 100 \text{ pairs of legs}$
$silver \text{ interconnect}$
$12 \text{ W at } T_h = 800^{\circ}\text{C}. \Delta T = 400 \text{ C}$

**Important first steps but ..... follows the wafer processing paradigm !**
Strengths of the Ceramics Community

- Expertise in processing powders to form intricate shapes
- Variety of powder processing technologies – sintering, hot forging, plasma spraying ……
- Understanding high-temperature phase equilibria
- Familiarity with complex crystal chemistry
- Manipulating electronic and ionic transport in oxides
- Familiarity with thermal stresses and thermal shock
- Knowledge and processing high-temperature materials, eg
  - Oxide fuel cells
  - Nuclear fuels
  - Thermal barrier coatings
  - Structural ceramics
- Understanding oxidation processes
Building on Ceramics Community Skills

- **Net shape forming**
- **Solid oxide fuel cell by spraying**
- **Thermal barrier coating**
- **Injection molding. Kyocera, Silicon nitride**
- **Transient liquid bonding**
- **Direct spray writing. Mesoscribe, Inc**
- **Low temperature hybrid manufacturing**
- **Net shape forming and cofiring**

Additive manufacturing
Possible Fabrication of Oxide Thermoelectric Devices

Guiding principles:
• Always fabricate devices at a higher temperature than they will be used at
• Preferred process technology determined by shape

- Electrophoretic deposition or direct write conducting metal oxide (CMO) onto mandrel
- Laser ablation patterning of CMO electrode
- Green shaping of rings of TE oxides
- Co-firing rings to conducting oxide electrode pads
- Deposition of outer electrodes by plasma spraying
- In-gap spraying of zirconia thermal barrier
- Air annealing to stabilize device
Concluding Remarks

- Oxide thermoelectric generators are a potential new application for high-temperature ceramics.
- As a community we should not wait for the “best” TE material before demonstrating devices and developing technology.
- We should begin to build high-temperature generators using existing TE oxide materials in parallel to identifying better oxide TE materials.
- Develop processes for fabricating cylindrical TE Devices.
- A major research effort in discovering low resistivity oxides is needed.
- Data mining is a powerful tool in selecting promising classes of materials for further study.
- International partnerships offer the opportunities to bring together essential skills and accelerate development.