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

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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
Efficiency

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

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

Shakouri, 
Lessons From Light Emitting Diodes (LEDs)

- LED lights are much more expensive than incandescent bulbs
- Why do organizations buy them?

![Paying the Light Bill](chart)

- Life cycle cost is lower than for incandescent bulbs
- Situation is similar for thermoelectric devices

*Year 2011*
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
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
Figure of Merit of Existing Materials: Data

“Conventional” Thermoelectrics

Oxide Thermoelectrics

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.
Today’s Best Thermoelectric Compounds

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

Tober, Synder
“Data Driven Review of Thermoelectric Materials”,
Materials Scarcity: Herfindahl-Hirschman Index

Large scale, high volume use requires abundant (blue) elements

“Data Driven Review of Thermoelectric Materials”,
“Data Driven Review of Thermoelectric Materials”,
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/Tm.

For a single diffusional process,

\[ r = A \exp(-Q/RT) \]

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

\( C \) is the Larson-Miller parameter.

**Conclusion:**

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

\[ \text{In}_2\text{O}_3(\text{ZnO})_k \]

\[ \text{SrTiO} \]
Ruddleston-Popper

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

STEM-ADF image

Monolayer InO\(_2\) sheets

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

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

Phase diagram adapted from Moriga et al., J. Am Ceram 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**

\[ Z_{Device} \cdot T = \frac{S^2}{\kappa_{Device} R_{Device}} \]

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

**K Device**

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

**R Device**

\[ R_{Device} = R_{legs} + R_{contact} + R_{interconnect} \]

\[ = \frac{L}{A_n} \rho_n + \frac{L}{A_p} \rho_p + R_{contact} + R_{interconnect} \]
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
Problem: \[ q_{hc} = q_{hot} - q_{cold} = A \sigma \left( \varepsilon_h T_h^4 - \varepsilon_c T_c^4 \right) \approx A \sigma \left( T_h^2 + T_c^2 \right) \left( T_h + T_c \right) \Delta T \]

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
Output Power

- 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

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

- But what sets size?
- Internal resistance:

$$R \approx \frac{4L \rho}{A_T}$$

$$P_o = \frac{S^2}{\rho} \frac{A_T}{16L} (\Delta T)^2$$

*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

Cutting, dicing and soldering

$\text{Bi}_2\text{Te}_3$, $\text{PbTe}$

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 interconnect

0.34 W at \( T_h = 1000^\circ\text{C} \)

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Funahashi, unpublished. (Quoted by Kuomoto, Annual Reviews of Materials Res, 2010)

*p*-type: \( \text{Ca}_{2.7}\text{Bi}_{0.3}\text{Co}_4\text{O}_9 \)

*n*-type: \( \text{Ca}_{0.9}\text{Mn Yb}_{0.1}\text{O}_3 \)

\( L = 5 \text{ mm}, 100 \text{ pairs of legs} \)

silver interconnect

12 W at \( T_h = 800^\circ\text{C} \). \( \Delta T = 400 \text{ C} \)

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**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

Injection molding. Kyocera, Silicon nitride

Transient liquid bonding

Direct spray writing

Mesoscribe, Inc

Low temperature hybrid manufacturing

Additive manufacturing

Net shape forming and cofiring
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

Fraunhofer Institute

Split, clam-shell design with annular arrays of junctions
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