Analysis of Advanced Thermoelectric Materials and Their Functional Limits

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Presentation Goal & Outline

- Help audience to establish a strong foundation in fundamental concepts of Thermoelectric
- Share NIA / NASA Langley Research Center TE research

Thermoelectric

Current trends in the physics of TE materials

Measuring TE transport properties

Summary

Strategy
National Institute of Aerospace

- An Independent Non-profit Research and Graduate Education Institute formed in 2002 by a Consortium of Research Universities and the AIAA Foundation
- Conceived by NASA Langley Research Center and established to serve as LaRC’s Collaborative Partner
- Conducts Collaborative Research in Engineering and Science relevant to Aerospace
- Offers Full- and Part-time Resident Graduate Education in Engineering and the Sciences from Member Universities
- Leads and Participates in a wide range of Outreach Programs to enhance the nation’s Science and Technology Workforce
Structures, Materials, Measurement Sciences
Aerodynamics, Hypersonics, Acoustics
Flight Dynamics, Aviation Safety and Aerospace Operations
Planetary Exploration, Atmospheric Science, and Global Environmental Change

Materials
Synthesis & Processing

Analytical & Computational Methods

Durability & Damage Tolerance

Nondestructive Evaluation

Structural Health

Advanced Sensing & Optics

Structural Concepts

All images credit: NASA
Energy and Thermoelectric
(Potential of TE)

“Waste Heat” Can Be Utilized Using Thermoelectrics

Thermoelectrics (TE) and background physics

Thermoelectric materials are a group of electronic materials which can interconnect gradients in electrical potential and temperature.

Physics of TEs are governed by **three thermodynamics effects**

- **Seebeck effect (1822)**: Heat → electric current
- **Peltier effect (1834)**: Current → cooling
- **Thomson effect (1850s)**: Released or absorbed internally in a material if the Seebeck coefficient depends on temperature, balancing for the flowing Peltier heat.

\[ V = \alpha \Delta T \]

where
- \( V \) = Voltage
- \( \alpha \) = **Seebeck coefficient**
- \( \Delta T \) = Temperature difference

All effects are related to heat being transported by the charge carriers.
Historic development of TE materials based on applications

- RTG power system for deep space exploration

- VW and BMW announced TE on exhaust in 2008:
  - 24 Bi$_2$Te$_3$ modulus
  - 600W under motorway driving → 30% of car’s electrical requirement
  - 5% reduction in fuel consumption through removing alternator

- Hybrid low cost power sources
  - Advanced TE system in tandem mode for high gain of cascade efficiency
  - Solar thermal applications (Photovoltaic + TE)

Why use Thermoelectrics?

- No moving part → no maintenance
- Peltier Coolers: fast feedback control mechanisms → $\Delta T < 0.1^\circ C$
- Scalable to the nanoscale → physics still works (some enhancement) but power $\propto$ area

- Most heat sources are “static”
- Waste heat from many systems could be harvested
  
  home, Industry, background
Efficiency of the TE materials and conversion efficiency

- Efficiency determined by Dimensionless figure of merit

\[ ZT = \frac{\sigma S^2}{\kappa} T \]

\( S \) = seebeck coefficient
\( \sigma \) = electrical conductivity
\( \kappa \) = thermal conductivity
\( \varepsilon \) = efficiency of a TE device for electricity generation

\[ \varepsilon = \frac{T_H - T_C}{T_H} \left( \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}} \right) \]

\( \varepsilon \) = Carnot
\( \times \) Joule losses and irreversible processes
Different material harvest optimally at different temperature ranges

- Bulk $n$-$\text{Bi}_2\text{Te}_3$ and $p$-$\text{Sb}_2\text{Te}_3$ used in most commercial Peltier coolers
- Bulk $\text{Si}_{1-x}\text{Ge}_x$ ($x$~0.2 to 0.3) used for high temperature satellite applications

Conflicting Materials Requirements

**S (Seebeck coefficient)**
Need small \( n \), large \( m^* \)
- Semiconductor (valence compound)
  \[
  S = \frac{8\pi^2 k_B^2}{3e\hbar^2} \frac{m^*}{n^2} \left( \frac{\pi}{3n} \right)^3 T
  \]

**\( \sigma \) (Electrical conductivity)**
Need large \( n \), high \( \mu \), low \( m^* \)
- Metal
  \[
  \sigma = ne\mu
  \]

**k (Thermal conductivity)**
Desire small \( k_{ph} \), small \( n \)
\[
{k} = k_{ph} + L T n e \mu
\]

L: Lorentz constant, \( K_e \) and \( K_{ph} \) correspond to carrier and phonon contribution to thermal conductivity, respectively. \( m^* \): carrier effective mass
For most bulk materials...

\[ ZT = \frac{S^2 \sigma T}{\kappa} = \frac{S^2 \sigma}{\kappa_e + \kappa_{ph}} T = \frac{S^2}{L + (\kappa_{ph} / \sigma T)} \]

To increase \( ZT \), we want

\[ S \uparrow, \quad \sigma \uparrow, \quad \kappa \downarrow \quad \text{but} \quad S \uparrow \Leftrightarrow \sigma \downarrow \]

- Empirical law from experimental observation that
  \[ \frac{k}{\sigma T} = \text{constant for metals} \]
- For low carrier densities in semiconductors, \( k_e \ll k_{ph} \)
- For high carrier densities in semiconductors, \( k_e \gg k_{ph} \)
- Good TE materials should ideally have \( k_e \ll k_{ph} \)
Current trends in the physics of TE materials
(Main strategies for optimizing ZT)

\[
ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_{ph}} T
\]

“Electron Crystal (crystalline semiconductor) – Phonon Glass (insulator)”

\[
S = \frac{8\pi^2 k_B^2}{3e\hbar^2} m^* T \left( \frac{\pi}{3n} \right)^{\frac{2}{3}}
\]

\[
S = -\frac{\pi^2}{3} \frac{k_B}{e} k_B T \left[ \frac{d \ln(\sigma)}{dE} \right] E_F
\]

\[
S_i = \frac{1}{(eT)} \left[ \frac{\langle E\tau \rangle}{\langle \tau \rangle} - E_f \right]
\]

\[
\sigma = n e \mu
\]

- Low-dimensional structures:
  - Quantum confinement effect
  - Increase S through enhanced DOS
  - Make S and \( \sigma \) almost independent

- Energy filtering

Main strategies for optimizing ZT (cont.)

\[ ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_{ph}} T \]

“Electron Crystal (crystalline semiconductor) – Phonon Glass (insulator)”

\[ k = k_{ph} + LTne\mu \]

- Reducing thermal conductivity faster than electrical conductivity
  - Skutterudite structure: filling voids with heavy atoms

- Low-dimensional structures:
  - Reduce \( k \) through numerous interfaces to increase phonon scattering

- In metals, the thermal conductivity is dominated by \( \kappa_e \)
  - Exceptions
    - some pure metals at low temperatures
    - certain alloys where small \( \kappa_e \) results in significant \( \kappa_{ph} \) contribution
    - certain low dimensional structures where \( \kappa_{ph} \) can dominant
NIA / NASA Results
1st Approach:
SiGe twin crystal for high temperature application

- Thermal conductivity
- Electrical conductivity

Material Design

Highly Twinned SiGe Layer
Phonon-scattering for Thermoelectric Material Application

{220} pole-figures of [111]-oriented SiGe on trigonal substrate

85% Single-Crystalline SiGe Layer
High-Mobility Semiconductor Device Application

X-ray diffraction measurement on two-samples—
(1) grown at 820°C and (2) 850°C.

SiGe – TE performance at 300K and 1000K
2nd Approach:
SiGe twin crystal for high temperature application

Hyun Jung Kim et al., RSC Advances, C2RA21567E, 2012
Scanned Seebeck coefficient results

(a) Table of Seebeck coefficients:

<table>
<thead>
<tr>
<th>Not Irradiated</th>
<th>Irradiated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not Irradiated</td>
<td>Irradiated</td>
</tr>
<tr>
<td>143.5 156.2 151.8 156.4 144.2</td>
<td>164.3 153.3 154.1 161.3 171.1</td>
</tr>
<tr>
<td>163.3 162.3 140.4 162.1 155.2</td>
<td>179.4 139.3 146.3 180.4 169.2</td>
</tr>
<tr>
<td>151.1 151.2 158.6 150.2 152.5</td>
<td>166.4 132.4 163.5 167.4 168.7</td>
</tr>
<tr>
<td>160.0 162.2 167.2 161.4 163.2</td>
<td>179.5 152.5 148.4 178.3 168.3</td>
</tr>
<tr>
<td>159.5 162.4 160.2 153.5 141.2</td>
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<td>167.2 151.5 153.3 161.4 152.3</td>
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</tr>
<tr>
<td>160.2 148.9 157.5 162.4 162.3</td>
<td>158.4 149.3 145.4 158.2 152.4</td>
</tr>
<tr>
<td>153.5 142.4 150.2 155.5 149.3</td>
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</tr>
</tbody>
</table>

(b) Graph showing distribution of Seebeck coefficient:

- Without e-beam
- With e-beam

(c) Graph showing Seebeck coefficient vs. Temperature:

- As deposited
- After 1 hour E-beam irradiation
Bi$_2$Te$_3$ and Ag$_2$Te nano-bridge for intermediate / low temperature application

Nano-crystals: Ag$_2$Te, Bi$_2$Te$_3$

Metal nanoparticle: Ag or Au (Phonon Mean Free Path control)

K$_{ph}$

0.5 wt% Ag / BiTe

Test results and comparison of Bi$_2$Te$_3$

TE Inks for roll-to-roll process

By auspice of Dr. Varadan

Mass production
Inexpensive
Solar-tandem mode
Measuring TE transport properties of materials

“In order to direct material development, high precision measurement of ZT as well as good estimates of error is necessary”

Consideration
- No standard reference material (Round-Robin project)
- Density of samples (>97% density)
- Sample homogeneity (scanning system)
- Geometry factor and coating

<table>
<thead>
<tr>
<th>Parameter</th>
<th>S</th>
<th>σ</th>
<th>k</th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Scatter (maximum spread in data / the average)</td>
<td>5% (at 300K)</td>
<td>10% (at 500K)</td>
<td>15% (specific heat) 5% (density) 7% (Thermal diffusivity, at 300K)</td>
<td>12% (at 300K) 21% (at 475K)</td>
</tr>
<tr>
<td>Note (comparing the data on the same material measured at several labs)</td>
<td>Geometry error Twice that in Seebeck coefficient</td>
<td></td>
<td></td>
<td>Above 475K, higher variation can be expected</td>
</tr>
</tbody>
</table>
Seebeck coefficient

- $S > 0$ for p-type, $S < 0$ for n-type

$$ S = -\frac{\Delta V}{T_2 - T_1} $$

- Difficulty and Solution: differences in thermocouple wires, reactive samples, cold finger effect

- Measure $T_1$, $T_2$, and $\Delta V$
Thermal conductivity

Difficulty: The difficulty in accurately correcting for radiation loss limits the accuracy at higher temperature.

Solution:
- The sample needs to be in good thermal contact with the heater, heat sink, and thermocouples while being thermally insulated from the surroundings
- Apply the radiation correction (heat loss) factor (Cowan, Cape and Lehman, etc. for laser flash method)

Angstroms method

Thermal diffusivity, \( \alpha = \frac{L^2}{2\Delta t \ln \frac{M}{N}} \)

Thermal conductivity, \( k = \alpha \rho C \)

\( \rho = \) density

\( C = \) specific heat
Electrical conductivity

Difficulty:
▪ Geometry error
▪ Inaccurate temperature determination
  -poor temperature determination
  -poor thermal contact between the sample and the thermocouples
  -cold or hot finger effect
  -varying voltage offset (vacuum, feedthrough, connections)

Solutions:
▪ Using an insulation shield to reduce the radiation loss from sample surface
▪ Direct attaching the thermocouples to the sample
NIA / NASA Results
The correction factor

$$y_{\text{cor}} = -3.945 \times 10^{-9} \cdot x^3 + 1.1039 \times 10^{-5} \cdot x^2 + 0.00428 \cdot x - 0.5843$$
The scanning Seebeck coefficient measurement system

- Motorized XYZ probe head
- Max scan area: 25 x 25 mm
- Min interval: 0.05μm
- LabVIEW interface
  - Keithley 740 Scanning voltage meter & DC servo motors

- Linear bearing
- Soft spring
Summary

► Waste heat is everywhere → enormous number of applications

► Seebeck coefficient can be increased by using the low dimensional structures and energy filtering effect

► Reducing $k_{ph}$ faster than $\sigma$ has been the most successful approach to improve ZT to date

► Heterointerface scattering of phonons has been successful in reducing $k$

► Need for reliable transport properties measurements
  - Simple technique to Seebeck coefficient, Electric conductivity, and Thermal conductivity for bulk, thin film and flexible samples
  - Need to solve the thermal contact issue

► TE materials and generators are not optimized → there is plenty of room for innovation
Strategy 1.  
(Data driven materials science)

<table>
<thead>
<tr>
<th>Data</th>
<th>+</th>
<th>Correlations</th>
<th>+</th>
<th>Theory</th>
<th>=</th>
<th>Knowledge Discovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Combinatorial experimentation</td>
<td>• Data mining</td>
<td>• Atomistic based calculations</td>
<td>• Materials discovery</td>
<td>• Structure-property-processing relationships</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Digital libraries &amp; data bases</td>
<td>• Dimensionality reduction</td>
<td>• Continuum based theories</td>
<td>• Hidden data trends</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Information is multivariate, diverse, very large and access/expertise is globally distributed

Strategy 2.
(Heat control for maximum output power)

- $F = \text{fabrication factor} = \text{perfect system} - R_{\text{contact}} - R_{\text{series}} - \text{Lost heat}$

- Practical system: both electrical and thermal impedance matching is required

\[
P_{\text{max}} = \frac{1}{2} FN A \Delta T^2 S^2 \sigma
\]

$A = \text{module leg area}$

$L = \text{module leg length}$

$N = \text{number of modules}$
Strategy 3. (New thermal conductivity measurement system)

- Fabricate the thermal conductivity based measurement /management system with a novel nanotube based phonon waveguide

- Thermal measurement/management systems are currently very slow and relatively inefficient, particularly when compared to advances in photon (light) transport and photon based measurement system
- Additionally inefficiencies in conversion to and from thermal to electrical, optical or other signals in most thermal measurement/management systems lead to further degraded performance.
- At each of the initial signal conversion steps, measurement accuracy and speed is being lost, while the later processing steps each tends to end to the amount of energy consumed in the process.
Strategy 4.
(Niche applications abound!)
Acknowledgements

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