Realise Low-toxic, High-Performance Thermoelectric Materials for Energy Conversion

Curtin-UQ ElectroMaterials Workshop
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Outline

- Introduction
- Methodologies for enhancing thermoelectrics
  A. Full length phonon scattering
  B. Band Engineering
- Conclusions and outlooks
Thermoelectric motivation

- Exhausting of fossil fuels
- Heat engines still provide 90% of power consumption
- 70% of energy (45TW/ year) was wasted in heat engines
Thermoelectrics

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

- **S**: Seebeck coefficient
- **\( \sigma \)**: electrical conductivity
- **K**: thermal conductivity


\[ \eta = \frac{T_h - T_c}{T_h} \cdot \frac{\sqrt{1 + zT} - 1}{\sqrt{1 + zT} + T_c / T_h} \]

- \( T_{(hot)} = 500 \, ^\circ C, \, T_{(cold)} = 50 \, ^\circ C \)
- \( ZT = 1, \, \text{Efficiency} = 8 \% \)
- \( ZT = 2, \, \text{Efficiency} = 17 \% \)
- \( ZT = 5, \, \text{Efficiency} = 22 \% \)

Controlled Side Ceramic Substrate (Component or Heat Source)

Uncontrolled Side Ceramic Substrate (Heat Sink)

External Leads to:
- Resistive Load \( (R_L) \) in Generation Mode
- Bipolar Power Supply (in Cooling and Heating Modes)
# Thermoelectric Materials and Challenges

![Graph showing ZT and Efficiency vs. Carrier Concentration](image)

<table>
<thead>
<tr>
<th>TE materials / approaches</th>
<th>ZT</th>
<th>Conversion efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1st generation</strong></td>
<td>Bi₂Te₃, PbTe, SiGe-based</td>
<td>~1</td>
</tr>
<tr>
<td><strong>2nd generation</strong></td>
<td>Nanostructure built-in, Hybrid system, Valence band convergence, band energy offset minimization, all length-scale photon scattering</td>
<td>ZT=2~3</td>
</tr>
<tr>
<td><strong>3rd generation</strong></td>
<td>Novel Condense Materials; Atomic Network; Structural Control; Synergetic System</td>
<td>ZT≥ 3</td>
</tr>
</tbody>
</table>

## Challenge - thermoelectric Cost

Summary of composition, synthesis condition, cost (in $/kg), and major progress of the best $n$- and $p$-type Bi–Te, Pb–Te, skutterudites, half-Heusler, and Si–Ge nanocomposites. DC-HP, RF-HP, and SPS correspond to direct current induced-hot press, RF induction-hot press, and spark plasma sintering, respectively.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Powder synthesis</th>
<th>Sintering</th>
<th>Cost</th>
<th>Major progress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{0.01}$Bi$</em>{2.7}$Te$_{0.35}$</td>
<td>Mechanical alloying by ball milling</td>
<td>DC-HP</td>
<td>171</td>
<td>Cu stabilizes the structure, enhances power factor and reduces thermal conductivity</td>
</tr>
<tr>
<td>Bi$<em>{x}$Sb$</em>{2-x}$Te$_{3}$</td>
<td>Ball milling bulk alloy ingots</td>
<td>DC-HP</td>
<td>231</td>
<td>Grain boundaries and defects result in low thermal conductivity</td>
</tr>
<tr>
<td>PbTe$<em>{0.9985}$I$</em>{0.0012}$</td>
<td>Furnace melting $\rightarrow$ quenching $\rightarrow$ annealing $\rightarrow$ hand grinding</td>
<td>RF-HP</td>
<td>135</td>
<td>Iodine as efficient dopant to improve ZT</td>
</tr>
<tr>
<td>K$<em>{0.02}$Pb$</em>{0.98}$Te$<em>{0.15}$Se$</em>{0.85}$</td>
<td>Furnace melting $\rightarrow$ slow cooling $\rightarrow$ hand grinding</td>
<td>DC-HP</td>
<td>59</td>
<td>Enhanced Seebeck coefficient via heavy-hole band activation by potassium doping</td>
</tr>
<tr>
<td>Ba$<em>{0.08}$La$</em>{0.05}$Yb$<em>{0.04}$Co$</em>{0.5}$Sb$_{12}$</td>
<td>Induction melting $\rightarrow$ annealing $\rightarrow$ grinding</td>
<td>SPS</td>
<td>64</td>
<td>Multiple-filling to enhance power factor and reduce thermal conductivity</td>
</tr>
<tr>
<td>Ce$<em>{0.45}$Nd$</em>{0.45}$Fe$<em>{3.5}$Co$</em>{0.5}$Sb$_{12}$</td>
<td>Furnace melting $\rightarrow$ quenching $\rightarrow$ ball milling</td>
<td>DC-HP</td>
<td>103</td>
<td>Replacing time-consuming annealing by ball milling for fast process</td>
</tr>
<tr>
<td>Hf$<em>{0.32}$Zr$</em>{0.75}$Ni$<em>{0.99}$Sb$</em>{0.01}$</td>
<td>Arc melting $\rightarrow$ ball milling</td>
<td>DC-HP</td>
<td>114</td>
<td>Hf reduction without ZT degradation by enhanced alloying scattering</td>
</tr>
<tr>
<td>Hf$<em>{0.44}$Zr$</em>{0.44}$Ti$<em>{0.12}$Co$</em>{0.88}$Sb$_{0.2}$</td>
<td>Arc melting $\rightarrow$ ball milling</td>
<td>DC-HP</td>
<td>166</td>
<td>Ternary composition for stronger phonon scattering and lower Hf usage</td>
</tr>
<tr>
<td>(Si$<em>{0.65}$Ge$</em>{0.35}$)$<em>{0.65}$ (Si$</em>{0.2}$Ge$<em>{0.0}$P$</em>{0.3}$)$_{0.3}$</td>
<td>Mechanical alloying by ball milling</td>
<td>DC-HP</td>
<td>430</td>
<td>Modulation doping to enhance power factor</td>
</tr>
<tr>
<td>(Si$<em>{0.8}$Ge$</em>{0.2}$)$<em>{0.8}$ (Si$</em>{1.0}$P$<em>{0.2}$)$</em>{0.7}$</td>
<td>Mechanical alloying by ball milling</td>
<td>DC-HP</td>
<td>423</td>
<td>Modulation doping to enhance power factor</td>
</tr>
</tbody>
</table>

### Materials Selections - Cheap, High Performance System

The Periodic Table

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**Table**: Elements arranged in order of atomic number, showing their periodic properties and positions in the periodic table. The highlighted elements are copper (Cu) and zinc (Zn), along with indium (In), tin (Sn), antimony (Sb), tellurium (Te), and iodine (I), which are often used in various applications due to their unique properties.
Methodologies for enhancing TEs

ACS Nano 2015 9, 8843
Nano Lett. 2015, 15, 5830
Adv. Elect. Mater. 2015, 1, 20150025
Nature Nanotech. 2011, 6, 216.

Nano Energy 2016, 20, 144
J. Mater. Chem. C, 2016, 4, 521
ACS Appl. Mater. Inter. 2015, 7, 989.

CrystEngComm 2014, 16, 393.
Crystal Growth & Design 2013, 13, 5092.
Appl. Phys. Lett. 2013, 103, 031605

Small 2014, 10, 2747
Prog. Nat. Sci. 2012, 22, 535
Manufacturing strategies

Nano/Bulk Powders

Wet chemistry methods
High yield
High quality

Nanostructure and band engineering

Advanced Characterizations

Typical structures

Hot processing
SPS

Nano Bulk Pellets

Pellets 90-98% of theoretical density

Performance evaluations

Manufacturing strategies
Full Length Phonon scattering
Full Length Phonon scattering

\[ \kappa_i = \frac{k_B}{2\pi^2\nu} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \tau_{tot} \frac{z^4 \exp(z)}{[\exp(z) - 1]^2} dz \]

\[ \theta_D \] is the Debye temperature

\[ \nu = \left[ \frac{1}{3} \left( \frac{1}{v_\parallel} + \frac{2}{v_\perp} \right) \right]^{-1/3} \] the sound velocity

\[ \tau_{tot} \] is the total relaxation time,

\[ \tau_{tot}^{-1} = \tau_U^{-1} + \tau_E^{-1} + \tau_{PD}^{-1} + \tau_B^{-1} + A B^2 \tau_{DS}^{-1} + \tau_{DC}^{-1} \]

\[ z = \frac{\hbar \omega}{k_B T} \] is the reduced phonon frequency

U=Phonon-phonon scattering
E=electron-phonon scattering
PD=point defect scattering
B=grain boundary scattering
DC+DS= dislocation scattering

Min, Chen*, et al. Nano Energy 2016, 20, 144
Recorded high ZT p-type Cu$_2$Se

- *In-situ* TEM suggests that *in-situ* heating results in phase change.
- High density of low-angle grain boundaries result in super low $\kappa$.

Band engineering for Improving Power Factor

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

\[ \sigma = \frac{n e^2 \tau}{m^*} \]

\( n \): Doping or alloying

\( \eta \): Reduced Fermi level

Prog. Nat. Sci. 2012, 22, 535; Small 2014, 10, 2747
Few layer Bi2Se3 nanosheets

Few layer Bi2Se3 nanosheets

Few layer Bi2Se3 nanosheets

Few layer Bi$_2$Se$_3$ nanosheets

$$S = \frac{k_B}{e} \left[ \frac{F_{1,2}^1(\eta, \beta)}{F_{1,2}^0(\eta, \beta)} - \eta \right]$$

$$\sigma = \frac{3e^2 N_v \hbar C_l}{\pi m^*_l E_{def}^2} F_{1,2}^0(\eta, \beta) \quad \eta = \frac{E_v - E_f}{k_B T} \quad \beta = \frac{k_B T}{E_g}$$

In$_3$Se$_4$ – A new thermoelectric system

Australian Patent (AU2013900321)

**Discovery**

CrystEngComm 2014, 16, 393

**Controllable synthesis**

Cryst. Growth Des. 2013, 13, 5092

**Thermal stability**

Appl. Phys. Lett. 2013, 103, 263105

**Cation Exchange**

**Thermoelectrics**

J. Mater. Chem. A 2014, 2, 7109

Small 2014, 10, 2747
Industry investment commercialisation

Industry Investment from NEUSOFT/BAOLI/SUNPOWER
Conclusions


Prog. Nat. Sci. 2012, 22, 535
Small 2014, 10, 2747
Outlooks

Roadmap

- Large scale central TEG
- Smart grid cogeneration TEG
- TEG car
- OTEC/LNG cold, low grade heat from plants
- Waste heat recovery (industrial, private, vehicles)
- Solar thermal
- Geothermal
- Biomass
- Solid waste combustion
- Energy harvesting TEG (bio-heat, ground heat, air, solar)

Scale of TEG systems

- 10 MW
- 1 MW
- 100 kW
- 10 kW
- 1 kW
- 1 W
- 1 mW
- 1 μW

Module Efficiency (%)

- η=20%
- η=30%
- η=15%
- η=7%

2010 - 2020

Number of TEG systems

Mass production

Small and pilot series

Future material

Commercially available material

EUV CO₂ limit

85 g/km

EU CO₂ limit

120 g/km

Phases in

Today - 2010 - 2015 - 2020 - 2025

System costs

- < 0.25 €/W
- > 10% efficiency
- > 700 °C

System costs

- ~1.00 €/W
- ~ 10% efficiency
- up to 600 °C

System costs

- ~10.00 €/W
- < 10% efficiency
- up to 500 °C
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  1 Australian Academy of Science
  1 UQ Foundation Excellence Award
  3 UQ internal Funds
  1 Industry investment
Thank you for your attention