Thermoelectric Materials and Devices for Power Generation

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Outline

• Introduction to University of Malaya
• Thermoelectric
  • Introduction and fundamental principle
  • Current state of development and applications
  • Works at the lab of NanoMicro Engineering
University of Malaya

- Established in 1949
Campus View
The King Edward VII College of Medicine was founded in 1905 to train the first Malaysian (Malayan) doctors. The College later became known as the University of Malaya in Singapore.

The University of Malaya Kuala Lumpur campus was established in 1959.

The University Hospital was opened in 1968.

Present day University of Malaya.
UM Profile

- 12 Faculties
- 2 Academies
- 3 Centers
- 3 Institutes
- 4 Research Clusters
- >50 Research Centres
- 1 Private University
- 1 Continuing Education Centre
- >6,000 Total Staff Strength
- >2,300 Academic Staff (13.5% International)
- >2,900 Support Staff
- >670 Management & Professional
- >17,000 Undergraduate Students
- >13,000 Postgraduate Students
- >30,000 Total Number of Students
- >3,700 International Students from over 90 Countries
- Over 200 Academic Programmes

International Academic Staff from more than 60 countries includes:

- Algeria
- Australia
- Austria
- Bangladesh
- Brazil
- Canada
- China
- France
- Germany
- India
- Indonesia
- Iraq
- Iran
- Italy
- Japan
- Jordan
- Netherlands
- Nigeria
- Philippines
- South Korea
- Thailand
- United Kingdom
- United States
- Yemen

Note: Figures as at 31 December 2018
Broad-based Research-Intensive University

12 Faculties
1. Arts & Social Sciences
2. Built Environment
3. Business & Accountancy
4. Computer Science & IT
5. Dentistry
6. Economics & Administration
7. Education
8. Engineering
9. Languages & Linguistics
10. Law
11. Medicine
12. Science

2 Academies
1. Islamic Studies
2. Malay Studies

3 Academic Centres
1. Foundation Studies
2. Sport & Exercise Sciences
3. Cultural

3 Institutes
1. Institute for Advance Studies (IAS)
2. Asia-Europe Institute (AEI)
3. International Institute of Public Policy and Management (INPUMA)

4 Research Clusters
1. Social Advancement & Happiness
2. Health & Well-Being
3. Frontiers of The Natural World
4. Innovative Industry & Sustainability Science

~100 Undergrad Programmes
~180 Masters Programmes
4 Doctoral Programmes
2 Double Degree
8 Dual/Double Masters
25 Joint /Dual PhDs
Thermoelectrics??
Thermoelectricity - known in physics as the "Seebeck Effect"

- In 1821, Thomas Seebeck, a German physicist, twisted two wires of different metals together and heated one end.

- Discovered a small current flow and so demonstrated that heat could be converted to electricity.
Thermoelectric Effect

- Interconversion of electrical energy and thermal gradients in materials.
  - in a thermal gradient, an electromotive force (emf) is produced
  - a thermal gradient is induced when a current is made to flow

The more energetic electrons at the hot side (Th) of the material have a longer mean free path compared with electrons at the cold side (Tc) of the material.

These more energetic electrons (denoted by white dots) then diffuse to the cold side, which induces the development of an electric field (E) to resist further diffusion.

**SEEBECK EFFECT**

- A temperature difference between two points in a conductor or semiconductor results in a voltage difference between these two points

- The Seebeck effect arises when charge carriers—electrons or holes—are excited to higher energy levels at the hot contact/sources and then diffuse throughout the material toward cooler areas.

**Seebeck Coefficient**

\[
S = \frac{dV}{dT}
\]
Thermoelectric device

• Generally, most metals possess Seebeck coefficients of 10 μV/K or less, but semiconductor materials are promising in constructing the thermocouples because they have Seebeck coefficients in excess of 100 μV/K.

• Electron/hole pairs excited when in contact with heat sources.
• Pairs recombine and reject heat at the cold end.
• The net voltage appears across the bottom of the thermoelectric legs.

Important Properties

**Figures of merit, ZT**

- The coefficient of performance (e) for a thermoelectric power generator or cooler depends on the active thermoelectric material through:

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

- \( \sigma \) = Electrical Conductivity
- \( S \) = Seebeck Coefficient
- \( K \) = Thermal Conductivity

**Thermal Conductivity, \( k \)**

\[ k = k_e + k_l \]

\[ k_e = L\sigma T = n e \mu L T \]

- \( n \) – carrier concentration
- \( m^* \) - effective mass of carrier
- \( \mu \) – carrier mobility
Figure of Merit - Conflicting Properties

Figure of Merit - $zT$

$$zT = \frac{S^2\sigma T}{\kappa} \Rightarrow z = \frac{S^2\sigma}{\kappa}$$

$S$ - Seebeck Coefficient

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

$\sigma$ - Electron Conductivity

$$\sigma = \frac{1}{\rho} = ne\mu$$

$\kappa$ - Thermal Conductivity

$$\kappa = \kappa_e + \kappa_l$$

$$\kappa_e = L\sigma T = ne\mu LT$$

$n$ - carrier concentration

$m^*$ - effective mass of carrier

$\mu$ - carrier mobility

Figure of Merit - Conflicting Properties

Figure of Merit - \( zT \)

\[
zT = \frac{S^2 \sigma T}{\kappa} \quad \Rightarrow \quad z = \frac{S^2 \sigma}{\kappa}
\]

S - Seebeck Coefficient

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

\( m^* \) - effective mass of carrier

\( \kappa \) - Thermal Conductivity

\[
\kappa = \kappa_e + \kappa_l
\]

\[
\kappa_e = L \sigma T = ne\mu L T
\]

\( n \) - carrier concentration

\( \sigma \) - Electron Conductivity

\[
\sigma = \frac{1}{\rho} = ne\mu
\]

\( \rho \) - electrical resistivity

\( \mu \) - carrier mobility

Effect of Temperature

Figure of Merit - Conflicting Properties

Figure of Merit - $zT$

$$zT = \frac{S^2 \sigma T}{\kappa} \implies z = \frac{S^2 \sigma}{\kappa}$$

$S$ - Seebeck Coefficient

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

$\sigma$ - Electron Conductivity

$$\sigma = \frac{1}{\rho} = ne\mu$$

$\kappa$ - Thermal Conductivity

$$\kappa = \kappa_e + \kappa_l$$

$$\kappa_e = L \sigma T = ne\mu LT$$

- Best micro-scale materials operate at $ZT = 1$ (10% of Carnot efficiency)
- To run at 30% efficiency (home refrigeration) need a $ZT=4$. 

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TE Materials

Thermoelectric materials research is an application-driven multidisciplinary topic of fundamental research, which involves the charge, spin, orbital, and lattice degrees of freedom of material.

\[ ZT = \frac{\alpha^2 T}{\rho \kappa} \]

\(ZT\) is the primary parameter of the thermoelectric potential of a material. The vertices denote four degrees of freedom that can be optimized to improve \(ZT\).
Materials of Choice

<table>
<thead>
<tr>
<th>TE Parameters</th>
<th>Electrical Conductivity (G)</th>
<th>Seebeck Coefficient (S)</th>
<th>Thermal Conductivity (κ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td>Very High (\sim 10^7) S/m</td>
<td>Low (\sim 10) μV/K</td>
<td>High (\sim 10^2) W/m-K</td>
</tr>
<tr>
<td>Insulators</td>
<td>Extremely low (\sim 10^{-10}) S/m</td>
<td>High</td>
<td>Low (\sim 10^{-2}-10^{-4}) W/m-K</td>
</tr>
<tr>
<td>Semiconductors</td>
<td>Moderate (10^{-3}) S/m</td>
<td>High (\sim 120) μV/K</td>
<td>Low (\sim 10) W/m-K</td>
</tr>
</tbody>
</table>

Semiconductors most suitable TE material. Allow separate control of \(\sigma\) (electrons) and \(\kappa\) (phonons).
Some TE Materials Performances

- PbTe/Bi$_2$Te$_3$ (room to mid temperature)
- Alloy Si-Ge (high temperature)
- Mixed chalcogenides with complex structures (mid to high temperature)
- Thallium compounds (mid temperature)
- Phonon glass-electron crystals (mid to high temperature)
Efficiency relation with ZT
TEG Applications Roadmap

- Large scale central TEG
- Smart grid cogeneration TEG
- TEG car
- OTEC, LNG cold, low-grade heat from plants
- Synergy Nano
- Structure control of complex compounds

Module Efficiency (%)
- Large scale waste heat recovery from industry
- Solar thermal
- Geothermal
- Waste heat recovery (industrial, private, vehicle)
- Solid waste combustion

2010-2040

Scale of TEG systems
- 10MW
- 1MW
- 100kW
- 10kW
- 1kW
- 1W
- 1mW
- 1μW

η = 15%
- Quantum effect
- Structure Control
- Synthesis of Atomic Network/Cluster Materials
- Energy harvesting TEG (bio-heat, ground heat, air, solar)
- Robust Nanostructured
- PGEC

η = 20%
- Solid waste combustion

η > 30%
- Natural SL

η = 8%
- Phonon Scattering
TE Performances Progress

- \( \text{Cu}_2\text{Se} \) at \( \leq 850\text{K} \)
- \( \text{PbTe} \) at \( 820\text{K} \)
- \( \text{InSb} \) at \( 773\text{K} \)
➢ In **1821**, the thematron’s technology developed watches at Centre electronique horloger (CEH) in Neuchatel, Switzerland;

➢ In **1988**, Seiko developed a thermic watch;
In 2010, Skinny Player was designed by Chinese engineers Chih-Wei Wang and Shou-His Fu.

In 2013, Fujifilm has developed the flexible polymer TE conversion module.

2016, Embr Wave body thermostat developed by Sam Shames.
**INORGANIC MATERIALS:**

The last 5 years

<table>
<thead>
<tr>
<th>Material</th>
<th>Seebeck (µV/K)</th>
<th>T (°C)</th>
<th>ZT</th>
<th>P. Factor (µW/mK²)</th>
<th>Thermal Conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgPb₁₈SbTe₂₀</td>
<td>-370</td>
<td>527</td>
<td>2.19</td>
<td>29.57</td>
<td>1.08</td>
</tr>
<tr>
<td>AgPb₁₈SbTe₂₀</td>
<td>-335</td>
<td>427</td>
<td>1.99</td>
<td>31.42</td>
<td>1.1</td>
</tr>
<tr>
<td>(Sr₀.2₅Ba₀.2₅Yb₀.5₀)₀.₅Co₄Sb₁₂.₅</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In₀.₂Ce₀.₂Co₄Sb₁₂</td>
<td>295</td>
<td>327</td>
<td>1.7</td>
<td>28.46</td>
<td>1</td>
</tr>
<tr>
<td>PbTe–SrTe (2%)</td>
<td>285</td>
<td>527</td>
<td>1.7</td>
<td>285</td>
<td>0.95</td>
</tr>
<tr>
<td>Na-doped PbTe–5 mol% CaTe</td>
<td>265</td>
<td>527</td>
<td>1.7</td>
<td>24.57</td>
<td>1.15</td>
</tr>
<tr>
<td>In₀.₂Ce₀.₁Co₄Sb₁₂</td>
<td>340</td>
<td>327</td>
<td>1.6</td>
<td>26.58</td>
<td>1</td>
</tr>
<tr>
<td>Pb₀.₉₆Mn₀.₀₄Te:Na</td>
<td>263</td>
<td>427</td>
<td>1.6</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>AgSbTe₂</td>
<td>242</td>
<td>377</td>
<td>1.57</td>
<td>8.6</td>
<td>0.38</td>
</tr>
<tr>
<td>(Tl₀.₃₀Zr₀.₃₅Hf₀.₃₅)₂₉Ni₃₃(Sn₀.₉₉₄Sb₀.₀₀₆)₃₈</td>
<td>-275</td>
<td>427</td>
<td>1.51</td>
<td>60.5</td>
<td>2.8</td>
</tr>
<tr>
<td>p-type Bi₂Te₃</td>
<td>225</td>
<td>117</td>
<td>1.5</td>
<td>31.64</td>
<td>0.8</td>
</tr>
<tr>
<td>Tl₀.₅(Zr₀.₅Hf₀.₅)₉ₕNi₁S₁Y₁Sb₁Y (Y=0.002)</td>
<td>-280</td>
<td>527</td>
<td>1.5</td>
<td>52.21</td>
<td>2.9</td>
</tr>
<tr>
<td>AgSbSe₀.₀₂Te₁.₉₈</td>
<td>250</td>
<td>327</td>
<td>1.36</td>
<td>14.06</td>
<td>0.62</td>
</tr>
</tbody>
</table>
### FLEXIBLE HYBRID TE MATERIALS:

#### The last 5 years

<table>
<thead>
<tr>
<th>Device/ method and substrates</th>
<th>Materials</th>
<th>Δ T</th>
<th>OCV</th>
<th>$P_{\text{max}}$</th>
<th>Year, Author</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Flexible TEG (flexible plastic substrate)</strong></td>
<td>SWNT/PEDOT:PSS</td>
<td>20 K</td>
<td></td>
<td>335 nW</td>
<td>2018, Wang et al.</td>
</tr>
<tr>
<td><strong>Flexible TEG (solution casting method, polyimide substrate)</strong></td>
<td>LiClO$_4$ doped poly(ether-b-amide 12)/CNT</td>
<td>60 K</td>
<td>OCV: 120 mV</td>
<td></td>
<td>2018, Luo et al.</td>
</tr>
<tr>
<td><strong>Flexible TEG (inkjet printing method, 25 m thick polyimide substrate)</strong></td>
<td>PEDOT:PSS/Ag</td>
<td>5 K</td>
<td>OCV ~50 V</td>
<td>~0.24 pW</td>
<td>2017, Beretta et al.</td>
</tr>
<tr>
<td><strong>Flexible and foldable standard paper based TE generator (micromachining and microfabrication method)</strong></td>
<td>Sb$_2$Te$_3$</td>
<td>75 K</td>
<td>OCV: 190.7 mV</td>
<td>~24 nW</td>
<td>2017, Rojas et al.</td>
</tr>
<tr>
<td><strong>Wearable TEG (Welded method, flexible printed circuit board substrate)</strong></td>
<td>Bi$_2$Te$_3$-based TE materials</td>
<td>12 K</td>
<td>Output voltage: 48 mV</td>
<td>8.3 W (0.67 W/cm$^2$) at ΔT = 11K</td>
<td>2017, Liu et al.</td>
</tr>
</tbody>
</table>
## FLEXIBLE HYBRID TE MATERIALS: The last 5 years

<table>
<thead>
<tr>
<th>Device/method and substrates</th>
<th>Materials</th>
<th>$\Delta T$</th>
<th>OCV</th>
<th>$P_{\text{max}}$</th>
<th>Year, Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexible TEG (drop casting method, 2 $\mu$m thick polyethylene terephthalate substrate)</td>
<td>SWCNTs</td>
<td>SWCNTs</td>
<td>27.5K</td>
<td>OCV: 11.3 mV</td>
<td>2.51 W (167 W/cm$^2$)</td>
</tr>
<tr>
<td>Silk fabric-based TEG (repeatedly depositing)</td>
<td>Sb$_2$Te$_3$</td>
<td>Bi$_2$Te$_3$</td>
<td>35 K</td>
<td>OCV: ~10 mV</td>
<td>~15 nW</td>
</tr>
<tr>
<td>Flexible TEG (dispense-printing, polyimide substrate)</td>
<td>PEDOT:PSS SV3 (Ag paste)</td>
<td>Ti$<em>2$S$<em>2$H$</em>{0.01}$NMF$</em>{0.003}$</td>
<td>20 K</td>
<td>OCV: ~1.3 mV</td>
<td>24 nW (32 W/cm$^2$)</td>
</tr>
<tr>
<td>Free-standing flexible TE foil (solution-based synthesis process)</td>
<td>Bi$_2$Te$_3$</td>
<td>Bi$_2$Te$_3$</td>
<td>20 K</td>
<td>OCV: ~15 mV</td>
<td>~100 nW</td>
</tr>
<tr>
<td>Wearable TEG</td>
<td>PEDOT:PSS coated polyester fabric strips connected with silver wire</td>
<td>75.2 K</td>
<td>OCV: 4.3 mV</td>
<td>12.29 nW</td>
<td>2015, Du et al.</td>
</tr>
</tbody>
</table>
Typical fabrication process for the rolled modules using PEDOT:PSS as p-type and CPE/CNT nanocomposite as n-type legs, respectively. (Fang et al., 2017. J. Appl. Polym. Sci. 134, 44208.)
(a) Layer arrangement for the multilayered fabric. CNT/PVDF conduction layers (B and D) are alternated between PVDF insulation layers (A, C, and E). Every other conduction layer contains p-type CNTs (B), while the others contain n-type CNTs (D).

(a) Schematic illustration of the fabric-based TE generators Positive (b) and negative face (c) of the 5-strip fabric-based TE generators connected with Constantan wires.

APLICATIONS: Combustion drive vehicle

- TEG in Porsche exhaust (944 model)
- Hi-Z technology integrated TEG capable of generating 200 W (1991)
- TEG tested in truck reached 1068 W electric energy
- BMW 5 series of 3000cc generate 500 W, $\Delta T=207^\circ C$ [BSST, BMW, Visteon and Marlow Industries 2005]
- Hybrid phase (generate electric power and charging the battery)
- TEG generate between 300 to 330 W electric and capable of charging 12 & 24 V (Hi-Z technology, 2004)

Thermoelectric generator in a BMW
Some studies indicate that using thermoelectric converters with an efficiency of 5% would increase the electric energy in a car by 6%.

In the United States, it is intended in 2020 to have 90% of cars with thermoelectric generators for internal cooling systems, and thus to replace air conditioners. This would save about 5% of the country's current daily average gasoline consumption and reduce greenhouse gas emissions.
TE modules in Voyager I by NASA. Radioisotopes TEG (RTG), nuclear batteries convert heat into electricity. 

(1977)

RTG thermocouples use natural decomposition of radioactive plutonium-238 as a source of heat and use cold outer space to produce a low T at the junction of thermocouple

https://rps.nasa.gov/
APPLICATIONS: A new model of RTG is the MultiMission Radioisotope Thermoelectric Generator (MMRTG)

- Designed to operate on planetary bodies with atmospheres like Mars as well as in space vacuum.
- Flexible and capable to generate electricity in small increments, quickly reaching 100 W.
- A heat source composed of eight modules with General Purpose Heat Source of 4.8 kg (10.6 lb.) of plutonium dioxide which initially supplies about 2000 W of thermal power and 120 W of electrical power.

https://rps.nasa.gov/
APPLICATIONS: Residential facilities

Hi-Z technology (2002) able to generate 20 W with output voltage of 12-14 V

The hottest area of the stove is at the top of the furnace and the cooler region is below the ash

The best location for the thermoelectric module would be near the upper right corner next to the stove, where it will allow the highest temperature gradient

The measured open circuit voltage, a single module provides the highest output of $4.2 \pm 0.08$ W

The modules were thermoset coated at both ends and placed in the middle of an aluminum plate with the pressure applied thereto by means of a heat sink, which was held in place by an adjustable fastening mechanism.
APPLICATIONS: Building & Industrial

- The model of a device for industrial heat recovery, where the residual heat is absorbed by the heating collection block.
- The modules are fixed to the outside of the device, exposed to a hot side and a cold side.

- Device for heat recuperation in an industry

Green TEG, no moving parts, does not require burning fuels to generate powers

Demonstration of the Green TEG

TEG in commercial rooms. The temperature difference is due to the outside temperature in relation to the interior, roughly 18 °C

Scheme of a thermoelectric module on the wall
APPLICATIONS: Portable equipment

TEG for network of body sensors. Bi$_2$Te$_3$ in the system was able to store an average power of 100 μW on the battery and 2.4 V of output voltage. [Gyselinckx's group]

- a wireless pulse oximeter by J. Penders group, powered by a pulse-type generator and also a wireless monitoring system.
- The power is 30 μW/cm$^2$ for a voltage greater than 4 V when positioned on the wrist.
Design & Development

A Novel Self-Powering Ultrathin TEG Device Based on Micro/nano Emitter for Radiative Cooling (2018)

A highly integrated ultrathin TEG-RC can output voltage continuously. TEG-RC exhibited a continuous average 0.18 mV output for 24 hours.
High-performance self-powered wireless sensor node driven by a flexible thermoelectric generator (2018)

flexible-TEG for a particular wireless sensor application, harvested 272 mW of energy from a heat pipe at a temperature of 70 °C
Optimization of thermoelectric generator (TEG) integrated with three-way catalytic converter (TWC) for harvesting engine’s exhaust waste heat (2018)

A novel design of TEG integrated with TWC.

On the condition of maintaining high conversion efficiency of TWC, a moderate height of hollow center body contributes to higher maximum output power of TEG with reasonable pressure drop. Compared with a single TEG, the maximum output power of present TEG is increased by 16%, and the maximum net output power is increased by 37% with considering the power loss caused by the additional pressure drop and increased weight.
Design & Development

- Evaluating thermoelectric modules in diesel exhaust systems: potential under urban and extra-urban driving conditions (2018)

- TEG applied to light duty diesel engines working under like urban and extra-urban driving conditions
Quarternary alloys of $\text{Pb}_{1-x}\text{Mg}_x\text{Te}_{0.8}\text{Se}_{0.2}$

ZT values as high as 2.2 can be achieved at 820K

Large size bulk materials and TE performance

Fu et al. (2016). J. Materiomics 2, 141–149.
ZT of 1.28 at 773K InSb-based material

- By addition of excess Sb into the InSb matrix, an InSb-Sb eutectic structure has been introduced.
- ZT value increases almost 3 times in comparison with the eutectic-free matrix.

Schematic illustration of the solid-state transformation of the CuSe₂ template into (1-x)Cu₂Se/(x)CuInSe₂ nanocomposites.


ZT values as high as 2.6 can be achieved at temperatures \( \leq 850K \)
TE MATERIALS: Recent Development

Graphene/Cu$_2$Se at 870K

Pb$_{0.9}$/Na$_{0.03}$Te–1 mol% Ba$_{0.5}$/Ca$_{0.5}$Te

In$_{0.25}$/Co$_{0.75}$/Sb$_{12}$

Pb$_{14}$/Sn$_4$/Ag$_2$/Te$_{20}$

Mg$_{3-x}$/0.0125$/Zn$_x$/Na$_{0.0125}$/Sb$_2$
Research at the Lab
Skutterudite Structure

• **$N_2M_8Pn_{24}$**
• **or** **$NM_4Pn_{12}$**

- Metal Atom (Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir)
- Pnicogen Atom (P, As, Sb)
- Void Space/Filler Ion
Methodology

Mix of Co, In, La, Sb powders

Planetary Ball Milling (10h)

SPS

Characterizations

XRD

SEM

TGA& DSC

TE (k, S, ρ) ZT

Ball milling condition:
✓ Zirconia Jar 50 ml,
✓ Zirconia balls 5 mm in diameter,
✓ The weight ratio of balls to powders 20:1,
✓ The speed 400 rpm,
✓ Time 10 hrs.

Spark plasma sintering (SPS) condition:
✓ Temperature 600°C,
✓ Time for 10 min,
✓ Pressure of 36MPa,
✓ Cylindrical graphite die 10mm diameter,
✓ Heating rate 100°C/min,
✓ Vacuum atmosphere ~ 4 Pa.
Methodology

- Ball Milling
- Spark plasma sintering (SPS)
- ZEM-3 system device
- A laser flash system (TC-7000H)
- Scanning Electron microscopy (SEM)
- Simultaneous thermal analysis (STA)
Results and Discussion ... (Cont.)

In-added $\text{La}_{0.25}\text{Co}_4\text{Sb}_{12}$ compositions ($0 \leq x \leq 0.5$)

Microstructure properties

The dominated $\text{CoSb}_3$ structure of skutterudite phase

The space group of $\text{Im}-3$

$\text{InSb}$ and $\text{CoSb}_2$ secondary phases.

$\text{InSb}$ phase was observed in most filled samples except $\text{In}_{0.1}\text{La}_{0.25}\text{Co}_4\text{Sb}_{12}$ sample.
Results and Discussion ... (Cont.)

The main phase of skutterudite CoSb₃
Secondary phases including; CoSb₂ and CoSb.
Results and Discussion ... (Cont.)

In-filled La$_{0.25}$Co$_4$Sb$_{12}$ compositions (0 ≤ x ≤ 0.5)

Microstructure properties

✓ The dominated CoSb$_3$ structure of skutterudite phase
✓ The space group of Im-3
✓ InSb and CoSb$_2$ secondary phases.
In was successfully filled the voids.

Atomic radius:

In (1.57 Å)
Void (1.892 Å)

The Jana Refinement images of (a) $I_n = 0$, (b) $I_n = 0.1$, (c) $I_n = 0.3$ and (d) $I_n = 0.5$
Thermoelectric Properties

Electrical resistivity
The lowest electrical resistivity value obtained was 9.67 μΩm which was achieved for In=0.5 sample at room temperature, this is mainly due to the presence of InSb phase and is relatively highly conductive as mentioned previously.
S was changed from p-type to n-type

In atoms act as electron donors

The absolute **Seebeck** reached to a maximum value over measured samples of 252 μV/K at 495 K for \( x = 0.1 \) sample.

The **power factor** to the highest value of \( 3.85 \times 10^{-3} \) W/mK\(^2\) has been obtained for \( \text{In}_{0.5}\text{La}_{0.25}\text{Co}_4\text{Sb}_{12} \) sample at 543 K
The \textbf{thermal conductivity} was greatly minimized to 1.27 W/mK for In$_{0.1}$La$_{0.25}$Co$_4$Sb$_{12}$ sample at 495K.

The In$_{0.1}$La$_{0.25}$Co$_4$Sb$_{12}$ compound shows the lowest \textbf{lattice thermal conductivity} value of 1.14 W/mK which is obtained at 495K.

The average of electronic contribution $k_e$ is 18\% from the total thermal conductivity.
The maximum value of $ZT$ was $1.25$ observed at 688 K for $\text{In}_{0.5}\text{La}_{0.25}\text{Co}_4\text{Sb}_{12}$ sample, due to the substantial reduction in the lattice thermal conductivity.

The improvement is 8% higher than $\text{In}_x\text{La}_{0.5}\text{Co}_4\text{Sb}_{12}$ system.
### Summary

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>Exp. density (g/cm³)</th>
<th>Th. density (g/cm³)</th>
<th>$\rho_{\text{min}}$ (µΩm)</th>
<th>$S_{\text{max}}$ (µV/K)</th>
<th>$P.F_{\text{max}}$ (10⁻³ x W/K².m)</th>
<th>$K_{\text{tot, min}}$ (W/mK)</th>
<th>$K_{L\text{min}}$ (W/mK)</th>
<th>ZT$_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>La$_{0.25}$Co$<em>4$Sb$</em>{12}$</td>
<td>7.53</td>
<td>7.78</td>
<td>42.1 @ 789 K</td>
<td>124 @ 495 K</td>
<td>0.14 @ 591 K</td>
<td>1.98 @ 495 K</td>
<td>1.92 @ 400 K</td>
<td>0.04 @ 591 K</td>
</tr>
<tr>
<td>2</td>
<td>In$<em>{0.1}$La$</em>{0.25}$Co$<em>4$Sb$</em>{12}$</td>
<td>7.43</td>
<td>7.82</td>
<td>36.5 @ 789 K</td>
<td>-252 @ 495 K</td>
<td>1.09 @ 543 K</td>
<td>1.27 @ 495 K</td>
<td>1.07 @ 495 K</td>
<td>0.44 @ 543 K</td>
</tr>
<tr>
<td>3</td>
<td>In$<em>{0.3}$La$</em>{0.25}$Co$<em>4$Sb$</em>{12}$</td>
<td>7.66</td>
<td>7.89</td>
<td>17.5 @ 400 K</td>
<td>-243 @ 688 K</td>
<td>3.2 @ 591 K</td>
<td>1.98 @ 495 K</td>
<td>1.29 @ 543 K</td>
<td>0.94 @ 639 K</td>
</tr>
<tr>
<td>4</td>
<td>In$<em>{0.5}$La$</em>{0.25}$Co$<em>4$Sb$</em>{12}$</td>
<td>7.88</td>
<td>7.99</td>
<td>9.7 @ 314 K</td>
<td>-231 @ 688 K</td>
<td>3.85 @ 543 K</td>
<td>1.92 @ 495 K</td>
<td>0.83 @ 639 K</td>
<td>1.25 @ 789 K</td>
</tr>
</tbody>
</table>
### Summary of results

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition</th>
<th>$\rho_{\text{min}}$ (µΩ.m)</th>
<th>$\alpha_{\text{max}}$ (µV/K)</th>
<th>PF (10^{-3} W/m.K^2)</th>
<th>$K_{\text{min}}$ (W/m.K)</th>
<th>$K_{\text{Lmin}}$ (W/m.K)</th>
<th>ZT</th>
<th>HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn-added CoSb$_3$</td>
<td>33.2 @ 577 °C</td>
<td>242 @ 127 °C</td>
<td>0.39 @ 277 °C</td>
<td>3.3 @ 500 K</td>
<td>3.3 @ 500 K</td>
<td>0.06 @ 600 K</td>
<td>639</td>
</tr>
<tr>
<td>2</td>
<td>Hf-added CoSb$_3$</td>
<td>52.1 @ 546 °C</td>
<td>153 @ 153 °C</td>
<td>0.14 @ 300 °C</td>
<td>1.8 @ 400 K</td>
<td>1.8 @ 400 K</td>
<td>0.04 @ 500 K</td>
<td>331</td>
</tr>
<tr>
<td>3</td>
<td>Al$_{0.3}$-added CoSb$_3$</td>
<td>31.5 @ 527 °C</td>
<td>-251 @ 27 °C</td>
<td>0.4 @ 377 °C</td>
<td>4.6 @ 600 K</td>
<td>4.4 @ 600 K</td>
<td>0.05 @ 600 K</td>
<td>499</td>
</tr>
<tr>
<td>4</td>
<td>Al$_{0.6}$-added CoSb$_3$</td>
<td>38.4 @ 527 °C</td>
<td>218 @ 127 °C</td>
<td>0.4 @ 327 °C</td>
<td>3.3 @ 500 K</td>
<td>3.2 @ 500 K</td>
<td>0.07 @ 600 K</td>
<td>469</td>
</tr>
<tr>
<td>5</td>
<td>Al$_2$-added CoSb$_3$</td>
<td>56.5 @ 527 °C</td>
<td>218 @ 127 °C</td>
<td>0.34 @ 277 °C</td>
<td>2.7 @ 500 K</td>
<td>2.6 @ 500 K</td>
<td>0.06 @ 600 K</td>
<td>436</td>
</tr>
<tr>
<td>6</td>
<td>Al$<em>{0.1}$-added Yb$</em>{0.25}$Co$<em>4$Sb$</em>{12}$</td>
<td>5.5 @ 27 °C</td>
<td>-217 @ 577 °C</td>
<td>4.9 @ 377 °C</td>
<td>3.3 @ 300 K</td>
<td>2 @ 400 K</td>
<td>0.93 @ 800 K</td>
<td>475</td>
</tr>
<tr>
<td>7</td>
<td>Al$<em>{0.2}$-added Yb$</em>{0.25}$Co$<em>4$Sb$</em>{12}$</td>
<td>5.4 @ 27 °C</td>
<td>-208 @ 577 °C</td>
<td>4.7 @ 327 °C</td>
<td>3 @ 300 K</td>
<td>1.3 @ 500 K</td>
<td>0.87 @ 850 K</td>
<td>456</td>
</tr>
<tr>
<td>8</td>
<td>Al$<em>{0.3}$-added Yb$</em>{0.25}$Co$<em>4$Sb$</em>{12}$</td>
<td>7.6 @ 27 °C</td>
<td>-213 @ 577 °C</td>
<td>4.3 @ 577 °C</td>
<td>1.7 @ 300 K</td>
<td>0.7 @ 500 K</td>
<td>1.36 @ 850 K</td>
<td>441</td>
</tr>
<tr>
<td>9</td>
<td>Bi$<em>{0.1}$-added Yb$</em>{0.25}$Co$<em>4$Sb$</em>{12}$</td>
<td>30 @ 427 °C</td>
<td>307 @ 77 °C</td>
<td>1.3 @ 277 °C</td>
<td>2.4 @ 850 K</td>
<td>1.8 @ 850 K</td>
<td>0.4 @ 850 K</td>
<td>430</td>
</tr>
<tr>
<td>10</td>
<td>Al$<em>{0.1}$Bi$</em>{0.05}$-added Yb$_{0.25}$Co$<em>4$Sb$</em>{12}$</td>
<td>22 @ 27 °C</td>
<td>-409 @ 277 °C</td>
<td>5 @ 277 °C</td>
<td>3.6 @ 600 K</td>
<td>3.2 @ 600 K</td>
<td>0.9 @ 600 K</td>
<td>442</td>
</tr>
</tbody>
</table>
Themoelectrochemical Energy Harvesting

- Alternative to solid-state Thermoelectrics is **Liquid Thermoelectrics**.
- Liquid Thermoelectric cells are referred to as Thermo-electrochemical Cells. (*Thermocells* or *TECs*)
- Constituents of Thermocells

![Fig 2. Two-beaker Thermocell](image1)

![Fig 3. Cell Config. Thermocell](image2)

Fig 5. Polar solvent increases the ionic conductivity and Electrochemical Seebeck; however; it simultaneously increases the thermal conductivities. Therefore, reducing the output power density from 120 to 40 μW.cm\(^{-2}\).
Experimental Details

**Electrolyte Preparation:** The I⁻/I₃⁻ redox solution (0.7 M) was prepared in 50 ml distilled water by dissolution of Iodine (5g) and Potassium Iodide (10g).

**PVDF Membrane Synthesis:** Commercially available Poly(Vinylidene Fluoride) (PVDF, Kynar® K-761, molecular weight of 440,000, density=1.7 g/ml and melt temperature ~ 165°C) powder was mixed with 1-Methyl-2-Pyrrolidinone (NMP) in a ratio of 18% by wt.

**Cell Fabrication:**

![Diagram of cell fabrication with dimensions](a) 13 mm
(b) 10 mm
(c) 8 mm
(d)
Results & Discussion

Fig 7. Infrared Thermography

Fig 8. Thermal Histograms

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Conclusions

• The presence of the membrane is significantly useful to enhance the TEC performance.

• The open-circuit voltage of MTEC is almost **2 times** higher than the without membrane TEC.

• The maximum power density of the MTEC is **245 nWcm**⁻² which is **78%** higher than the membrane-less case.

• The reason of this high performance is rooted in the thermal gradient improved by the PVDF membranes. The experiments show that the best MTEC (i.e. the membrane at the centre) simultaneously has highest thermal gradient of **8.8 K**.
Strategies to Increase ZT

All approaches fall into one of three categories:

1. Decrease the lattice thermal conductivity
   - Focus on phonons
   - larger unit cell and higher mass to decrease sound velocity
   - Increase disorder to decrease phonon mean free path

2. Increase the carrier mobility
   - New, covalently bonded materials
   - Heterostructures to physically separate carriers from scattering centers

3. Increase the thermopower
   - Larger effective mass materials
   - Barriers to inhibit transport of low energy carriers
   - Novel band structures and/or scattering mechanisms
Summary

The future of thermoelectricity relies on several important aspects:

1) One must find new mechanisms for balancing electron and phonon transport to maximize TE properties (high zT),
2) TE materials must be readily available and at low cost, and their processing must be simple and rapid to suit large-scale industrial operation,
3) It is important to focus on the design of high-performance TE materials that meet the actual application demands, especially to possess high average values of zT and have their performance peaking in the desired regime of operation temperatures,
4) It is imperative that the modules are thermally and mechanically stable and have a long lifetime,
5) It is important to specify proper and efficient synthesis routes and module fabrication processes to make thermoelectricity economically viable.