High-Performance Thermoelectric Devices Based on Abundant Silicide Materials for Vehicle Waste Heat Recovery

Investigators:
Li Shi, John Goodenough, Matt Hall, Jianshi Zhou
Department of Mechanical Engineering & Texas Materials Institute
University of Texas at Austin

&

Song Jin
Department of Chemistry
University of Wisconsin-Madison

Participating Students:
Chad Baker, Xi Chen, Arden Moore, Annie Weathers (Texas)
Jeremy Higgins, Ankit Pokhrel (Wisconsin)

Collaboration:
Hsin Wang, Oak Ridge National Lab
Objectives:

a) To increase the ZT of abundant silicides to a level competitive with the state of the art found in materials containing much more scarce and expensive elements

b) To enhance the thermal management system performance for silicide TE devices installed in a diesel engine

Tasks:

a) Investigate methods for scalable synthesis and position-dependent doping of bulk nanostructured silicides

b) Explore silicide and alloy interface materials with low contact resistance and improved thermomechanical compliance

c) Characterize the TE properties of silicides at temperatures between 300 and 900 K

d) Develop computation models to guide the heat exchanger design and the placement of the TE elements of spatially varied TE properties

e) Test silicide TE waste heat recovery devices in a 6.7 liter Cummins diesel engine
Complex doped MnSi$_{1.75}$
Nanocrystalline BiSbTe
BiSbTe alloy
AgPb$_m$SbTe$_{2+m}$
TI doped PbTe
Ba$_{0.30}$Ni$_{0.05}$Co$_{3.95}$Sb$_{12}$
Zn$_4$Sb$_3$
Mg$_2$Si$_{0.6}$Sn$_{0.4}$
Mg$_2$Si$_{0.4}$Sn$_{0.6}$
PbTe
Complex doped MnSi$_{1.75}$
Nanocrystalline p-Si$_{80}$Ge$_{20}$

ZT of Bulk Thermoelectric Materials

J. Mater. Chem., 2011, DOI: 10.1039/C0JM02755C
Index of Abundance of Elements

Relative abundance of the chemical elements in Earth’s upper continental crust (in log scale)

Higher Manganese Silicides (HMS), $\text{Mn}_n\text{Si}_{2n-m}$ or $\text{MnSi}_{1.75}$

- Novotony Chimney Ladder Phase

Data of Zaitsev et al., in CRC Handbook of Thermoelectrics, 1994, Ed. Rowe

Higgins & Jin, JACS, 130, 16086 (2008)
• Very long $c$ gives small first Brillouin zone, long minimum wavelength.

• The low group velocity of numerous optical phonon modes and enhanced phonon-phonon scattering results in low $\kappa = 2–4 \text{ W/m-K}$ and $ZT = 0.7$ at 800 K in bulk MnSi$_{1.75}$.

• The low frequency acoustic phonons are not suppressed effectively by the complex structures.
HMS Nanowires Synthesis and Characterization


- Nanoribbon (NR) or NWs of Mn$_{39}$Si$_{68}$ or Mn$_{19}$Si$_{33}$
- c ≈ 17 nm
- Growth direction perpendicular to {121} planes, or 63° from the c axis
• Calculated amorphous thermal conductivity limit $\kappa_\alpha \approx 0.7$ W/m-K.

• The transition from the phonon-crystal behavior in bulk to amorphous thermal conductivity in the MnSi$_{1.75}$ nanostructures reveals effects of surface scattering, especially for long-wavelength phonons.
Size Effect on Electron Transport in MnSi_{1.75} NWs

\[ \sigma = \frac{q^2}{3\pi^2 m^*} \left( \frac{2k_B T m^*}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{x^{3/2} e^{x - \varsigma}}{\left(e^{x - \varsigma} + 1\right)^2} dx \]

Relaxation Time:
\[ \frac{1}{\tau} = \frac{1}{\tau_{e-p}} + \frac{1}{\tau_{imp}} + \frac{1}{\tau_b} \]

Electron-Phonon Scattering:
\[ \tau_{e-p} = \frac{\hbar^4 v^2 \rho}{\left(8\pi^2\right)^{3/2} k_B T \Delta^2} \left(\frac{\varepsilon v}{m^*}\right)^{1/2} \]

Boundary Scattering:
\[ \tau_b = \frac{d [1 + p]}{v_h [1 - p]} \]

Impurity Scattering:
\[ \tau_{imp} = \left(\frac{2m^*}{\pi^3}\right)^{1/2} \frac{8\varepsilon_0 E^{3/2}}{n_i q^4 \log \left(1 + \left(3\varepsilon_0 k_B T / q^2 n_i^{1/3}\right)^2\right)} \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference</th>
<th>Parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m_h^* = 15 m_e)</td>
<td>[1]</td>
<td>(E_g = 0.84 \text{ eV})</td>
<td>[7]</td>
</tr>
<tr>
<td>(n = 2 \times 10^{27} \text{ m}^{-3})</td>
<td>[1]</td>
<td>(\Delta = 8 \text{ eV})</td>
<td>[6]</td>
</tr>
<tr>
<td>(n_{imp} = 2.24 \times 10^{24} \text{ m}^{-3})</td>
<td>fitted</td>
<td>(\rho = 5000 \text{ kg/m}^3)</td>
<td>[10]</td>
</tr>
<tr>
<td>(v_s = 10^5 \text{ m/s})</td>
<td>fitted</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Bulk HMS Synthesis via Two-step Solid-State Reaction

1. **Mn** + **Si**: Ball milling **1 h** → **Mn, Si mixture**
2. **Mn, Si mixture**: Sealed in a tube **973 K, 48 h** → **ingot**
3. **HMS**: Sealed in a tube **1473 K, 48 h** → **mixture**
4. **mixture**: Ball milling **1 h** → **powder**

Diagram showing the solid-state reaction temperatures and phases involved in the synthesis process.
XRD and Microstructures of Bulk HMS

SEM of HMS sample surface after polishing and 60-s selective etching of MnSi in HF:HNO₃:H₂O=1:6:13

MnSi layers etched away

MnSi particles etched away
TE Properties of Bulk Undoped HMS

Literature data from Zaitsev et al, in CRC Handbook of Thermoelectrics, 1994, Ed. Rowe
Future Directions in HMS Materials Research

- Turn MnSi micro-layers and particles in HMS into nanoparticle inclusion to scatter long wavelength phonons
- Bulk nanostructured HMS via conversion (see next slide)
- Ball milling / solution synthesis of HMS nanoparticles for making bulk nanocomposites
- To tune the $ZT$ peak position via position-dependant doping

Converting Diatomaceous Earth into Bulk Nanostructured Silicidess

SiO$_2$ (s) + 2 Mg (g) $\rightarrow$ Si (s) + 2 MgO (s)
Si (s) + 2 Mg (g) $\rightarrow$ Mg$_2$Si (s)

Mg$_2$Si/MgO composite with nanoscale grains

Future work: Expand to doped MnSi$_{1.75}$ and Mg$_2$Si$_{1-x}$Sn$_x$
Improved thermoelectric properties of Mg$_2$Si$_x$Ge$_y$Sn$_{1-x-y}$ nanoparticle-in-alloy materials

S. Wang$^{1,a}$ and N. Mingo$^2$

APPLIED PHYSICS LETTERS 94, 203109 (2009)

FIG. 1. (Color online) Calculated thermal conductivities ($\kappa$) of different Mg$_2$Si$_x$Ge$_y$Sn$_{1-x-y}$ NEAT materials as a function of particle diameters at 300 K and 800 K with 3.4% nanoparticle volume fraction. The horizontal lines denote calculated $\kappa$ of [(a) and (d)] Mg$_2$Si$_{0.4}$Ge$_{0.6}$, [(b) and (e)] Mg$_2$Ge$_{0.4}$Sn$_{0.6}$, [(c) and (f)] and Mg$_2$Si$_{0.4}$Sn$_{0.6}$ matrices for comparison.
Implementation in a 6.7 liter Cummins Diesel Engine

Exhaust after-treatment (DOC/DPF)
Preliminary Thermodynamic Systems Model

- Primary constraints: maintain temperature of 250°C into exhaust after-treatment system, maintain acceptable pressure drops throughout exhaust system.

- **Assumptions**: TE heat exchanger is able to extract all available heat subject to temperature constraints and with cold side temperature of 25°C.

- Model has yet to account for spatial variation of TE properties along TE module

\[
\eta_{TE,max} = \frac{\Delta T}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_h}
\]

\[
\eta_{sys} = \frac{\eta_{TE} \dot{Q}_h - \dot{W}_{pumping}}{m \psi}
\]
Configuration 5

- EGR
- EGR Cooler
- Intake Manifold
- Engine Block
- Exhaust Manifold
- Turbo
- Intercooler
- TEM
- DOC
- DPF
- SCR
- Shaft Work
- 300 K
- 550 K
- 800 K
Maximum Possible Thermoelectric Power

Case 1: single TEM > turbo > after-treatment
Case 2: turbo > single TEM > after-treatment
Case 3: turbo > after-treatment > single TEM
Case 4: turbo > TEM > after-treatment > TEM
Case 5: TEM > turbo > after-treatment > TEM

- RPM = 2000
- Brake Torque = 300 lb-ft
- Charge flow rate = 7.8 kg/min
- Exhaust port temperature = 800 K
- Engine exhaust availability = 81.1 kW
Summary

• In nanostructured complex MnSi$_{1.75}$, the contributions to $\kappa$ from high-frequency phonons and low-frequency phonons are suppressed by the complex structure and interface scattering, respectively, to obtain glass-like thermal conductivity.

• While it remains to be verified, the large hole effective mass and large carrier concentration can potentially lead to effective screening of surface states/scattering, so that potentially the power factor is reduced as much as $\kappa_l$ suppression in MnSi$_{1.75}$ nanostructures, similar to our prior finding on CrSi$_2$ nanowires (Nano Lett 2007, 7, 1649).

• Bulk MnSi$_{1.75}$ and Mg$_2$Si$_{1-x}$Sn$_x$ with nano-grains or nanoparticle inclusion are being synthesized via both solid state reaction and chemical conversion from diatomaceous earth.

• Preliminary exhaust temperature measurements and thermodynamic modeling results suggest that two thermoelectric modules, one upstream of the turbo and the other downstream of the exhaust after-treatment equipment, would considerably increase the power output. Additional enhancement is expected by extracting the EGR flow downstream rather than upstream of the 1$^{st}$ stage module.
Configuration 2
Configuration 3
Configuration 4

- EGR Cooler
- Intake Manifold
- Engine Block
- Exhaust Manifold
- EGR

Temperature points:
- 300 K
- 575 K
- 680 K
- 800 K

Components:
- Turbo
- Shaft Work
- DOC
- TEM
Implementation in a 6.7 liter Cummins Diesel Engine

- Engine data currently being gathered as inputs to models.
- **Temperatures**: exhaust port and downstream of turbine
- **Pressures**: exhaust manifold, boost pressure, pressure between turbine and DOC/DPF
- **Flow rates**: air, fuel, and EGR
Systems Modeling

• Two computer models currently being developed
  – Thermodynamic systems model to optimize thermoelectric device locations in engine exhaust
  – Heat Transfer model for improving TE module performance
  – Both to be integrated as one model and to account for transient exhaust conditions

• Components include:
  – TE Module(s)
  – Turbocharger
  – Exhaust aftertreatment system
  – EGR cooler