NSF/DOE Thermoelectric Partnership: High-Performance Thermoelectric Devices Based on Abundant Silicide Materials for Vehicle Waste Heat Recovery

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Overview

Timeline
• Project start date: October 1, 2010
• Project end date: September 30, 2013
• Percent complete: 15%

Budget
• Total project funding: $1,499,984
  – DOE share: $749,992
  – NSF share: $749,992
• Funding received in FY10: $499,991
• Funding for FY11: $499,993

Partners
• Collaboration:
  Hsin Wang,
  Oak Ridge National Lab

Barriers
• Barriers
  - Cost
  - Scale-up to a practical thermoelectric device
  - Thermoelectric device/system packaging

• Targets:
  • Earth-abundant silicide thermoelectric materials with performance competitive with the state of the art found in materials that contain rare elements
  • Single-body silicide TE legs with gradient doping instead of a segmented design to eliminate interfaces
  • Silicide interface and interconnect materials to further enhance thermomechanical durability
Objectives and Tasks

Objectives:

a) To increase the ZT of abundant, low cost, and bulk scale 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-dependant 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 computational 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
Approach: Higher Manganese Silicides (HMS) or MnSi$_{1.75}$

- Novotony Chimney Ladder Phase

- Peak ZT close to ~0.7 at near 800 K reported in complex doped HMS by Zaitsev et al., in CRC Handbook of Thermoelectrics, 1994, Ed. Rowe

Higgins & Jin, JACS, 130, 16086 (2008)
Accomplishments: Synthesis and Characterization of HMS Nanowires


- Nanoribbon (NR) or NWs of $\text{Mn}_{39}\text{Si}_{68}$ or $\text{Mn}_{19}\text{Si}_{33}$
- $c \approx 17$ nm
- Growth direction perpendicular to \{121\} planes, or $63^\circ$ from the c axis
Accomplishments: Discovery of Amorphous Thermal Conductivity in HMS NRs and NWs

- Calculated amorphous thermal conductivity limit $\kappa_\alpha \approx 0.7 \text{ W/m-K}$.

- 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.
Accomplishments: Modeling Size Effect on Electron Transport in MnSi$_{1.75}$ Nanowires

Approach: Bulk HMS Synthesis via Two-step Solid-State Reaction

Mn + Si → Mn, Si mixture

1 h

Sealed in a tube 973 k, 48 h → ingot

HMS

Sealed in a tube 1473 k, 48 h → mixture

Ball milling 1 h → powder

Ball milling 1 h → 1149°C

Grinding

Si Concentration / at%
Accomplishments: Synthesis of Bulk HMS With MnSi Phases

SEM s 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
Accomplishments: TE Properties of Bulk Un-doped HMS with MnSi phases

![Graphs showing S (μV/K), σ (Ω cm⁻¹), κ (Wm⁻¹K⁻¹), and P (Wm⁻¹K⁻¹) vs. T (K) for different orientations.]

Accomplishments: Synthesis of Pure HMS without MnSi and Si Phases

- MnSi\(_x\) was synthesized by solid state reaction in a vacuumed quartz tube (700\(^\circ\)C, 48 h).
- The amount of MnSi decreased with increase of Si, and pure HMS was obtained at x=1.83.

[Diagram showing X-ray diffraction patterns with peaks labeled a to e, and Mn\(_{15}\)Si\(_{26}\) (PDF# 20-0724) with intensity and 2θ values.]

- a: MnSi1.74
- b: MnSi1.77
- c: MnSi1.80
- d: MnSi1.83
- e: MnSi1.89
Accomplishments: Synthesis and TE Property of Pure HMS

Synthesis method:

HMS obtained at 700 °C for 48h → cold press → Pellets → annealed in vacuum 700 °C, 10 h → Sample for TE measurement

XRD after annealing

Seebeck coefficient of cold-pressed HMS

Literature [001] and [100] data from Zaitsev et al, in CRC Handbook of Thermoelectrics, 1994, Ed. Rowe
Future Work in HMS Materials Research

• Converting MnSi microlayers and microparticles in HMS into nanoparticles to scatter long wavelength phonons
• Ball milling / solution synthesis of HMS nanoparticles for making bulk nanocomposites
• Tuning the $ZT$ peak position via position-dependant doping
• Converting diatomaceous earth into bulk nanostructured silicides
Future Work:
Converting Diatomaceous Earth into Bulk Nanostructured Silicides

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

Expand to doped MnSi$_{1.75}$ and Mg$_2$Si$_{1-x}$Sn$_x$
Approach: Integration of TE Devices in a 6.7 liter Cummins Diesel Engine

Exhaust after-treatment (DOC/DPF)
Approach: 
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

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

\[
\eta_{sys} = \frac{\eta_{TE} \dot{Q}_h - \dot{W}_{pumping}}{m\psi}
\]
Future Work: 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
Accomplishments:
Preliminary System Level Analysis Results

- 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

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
Collaborations

• Partners
  We plan to collaborate with Dr. Hsin Wang of Oak Ridge National Lab to employ their high-temperature TE characterization facility to validate our in-house measurement results.
Summary

• **Relevance:** The cost, scale-up, and packaging barriers for thermoelectric vehicle waste heat recovery devices are being addressed by fabricating abundant silicide materials-based thermoelectric devices with enhanced device efficiency and heat exchanger system performance.

• **Approaches:** 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 to fabricate single-body silicide TE legs with gradient doping instead of a segmented design to eliminate interfaces. Silicide interface and interconnect materials are investigated to enhance thermomechanical durability. New heat exchanger designs are investigated to enhance thermal management performance.

• **Accomplishments:** In nanostructured complex MnSi$_{1.75}$, the contributions to κ from high-frequency phonons and low-frequency phonons have been found to be suppressed by the complex structure and interface scattering, respectively, to obtain glass-like thermal conductivity. Pure MnSi$_{1.75}$ bulk samples have been synthesized and the properties have been measured. Preliminary exhaust temperature measurements and thermodynamic modeling results have been obtained.

• **Collaboration:** We will collaborate with Dr. Hsin Wang of Oak Ridge National Lab to employ their high-temperature TE characterization facility to validate our in-house measurement results.

• **Future Work:** We will conduct theoretical modeling and experiments to investigate various heat exchanger configurations for enhancing heat transfer to the TE devices, and continue our investigation of synthesis techniques to produce single-body TE legs based on nanostructured bulk silicides with gradient doping.