Advanced Thermoelectric Materials and Generator Technology for Automotive Waste Heat at GM

Gregory P. Meisner

General Motors Global Research & Development

Warren, MI

2011 Thermoelectrics Applications Workshop

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Hotel Del Coronado

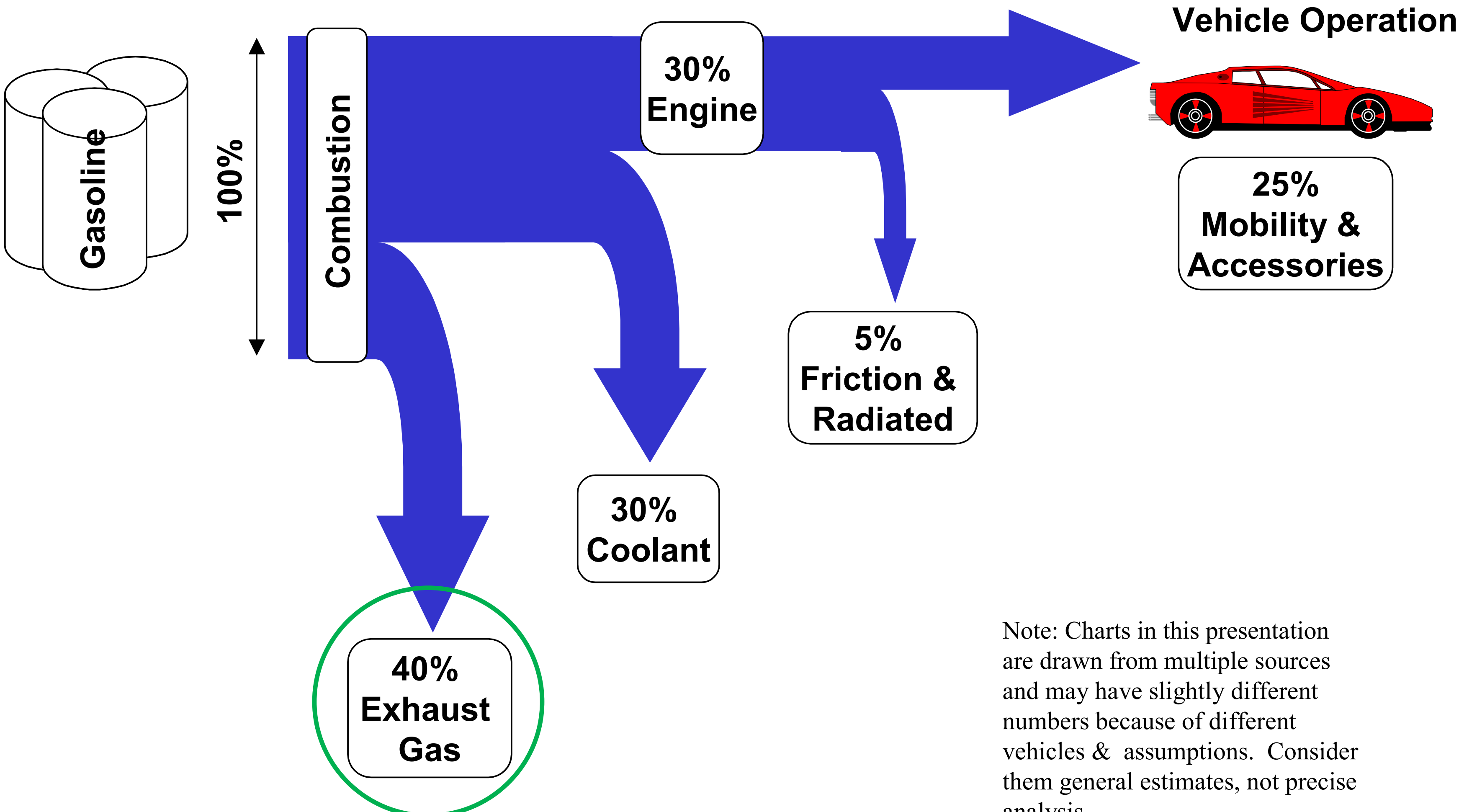
San Diego, CA

Outline

- Thermoelectric Research and Development Projects at GM Global R&D
- Introduction: TE Technology for Waste Heat Recovery
- Acknowledgements
- Thermoelectric Materials Research
- Thermoelectric Generator Development
- Results
- Summary: Current/Future Work

Opportunity for TE Waste Heat Recovery

Automotive Energy Flow Diagram



Note: Charts in this presentation are drawn from multiple sources and may have slightly different numbers because of different vehicles & assumptions. Consider them general estimates, not precise analysis.

Francis Stabler, Future Tech, (GM Powertrain , Ret.)

Develop Thermoelectric Technology for Automotive Waste Heat Recovery

Project lead: *General Motors*

Timeline

Start date – May 2005

End date – August 31, 2011

Budget

Total funding: $12,779,610

– DOE share: $7,026,329

– Contractor share: $5,753,281

Barriers & Targets

- Integrating new advanced TE materials into operational devices & systems
- Integrating/Load Matching advanced TE systems with vehicle electrical networks
- Verifying device & system performance under operating conditions

Partners (Interactions/collaborations)

Marlow – Thermoelectric module development and fabrication

Oak Ridge National Lab – High T transport & mechanical property measurements

University of Nevada – Las Vegas:– Computational materials development

Faurecia – Exhaust subsystem fabrication and integration

NSF/DOE Thermoelectrics Partnership: Thermoelectrics for Automotive Waste Heat Recovery

Project lead: *Purdue University*

Timeline

Start date – Jan. 1, 2011
End date – Dec. 31, 2013

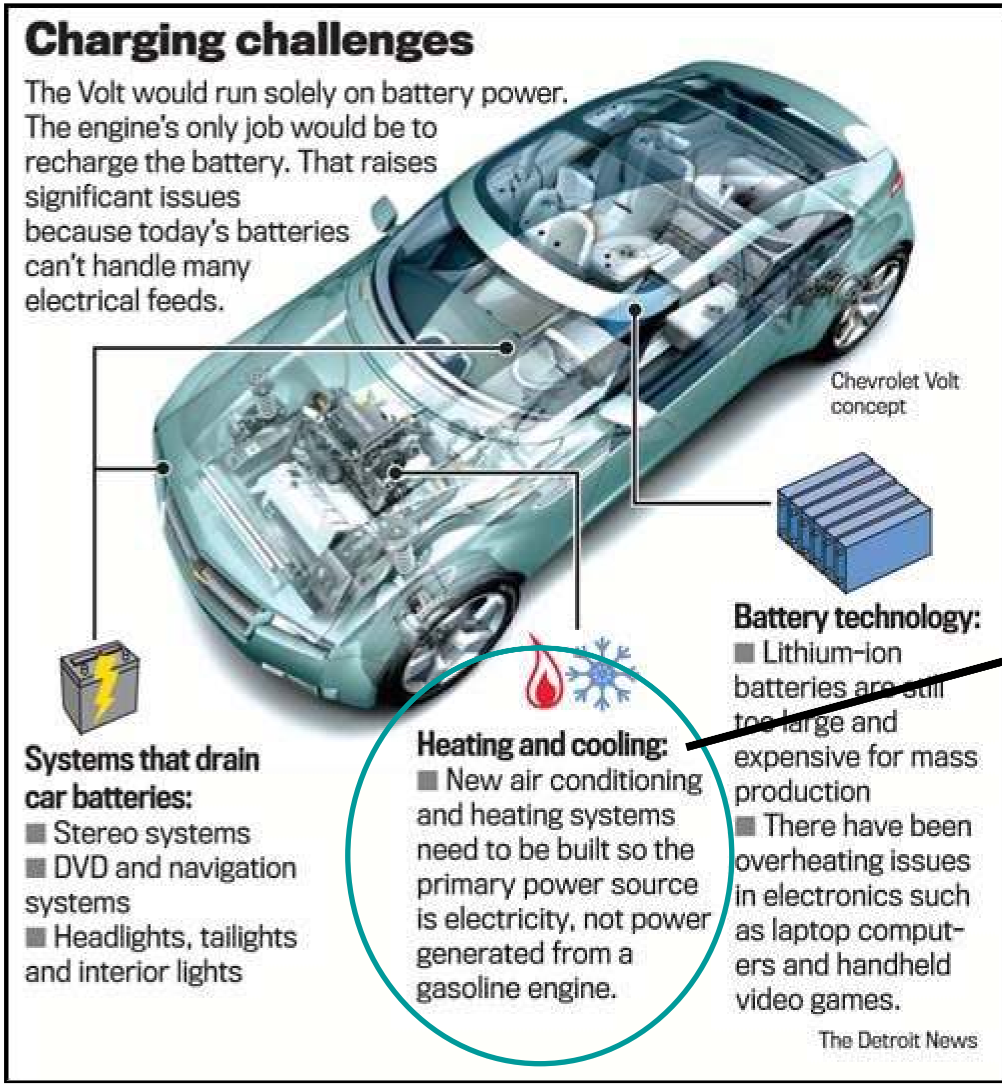
Budget

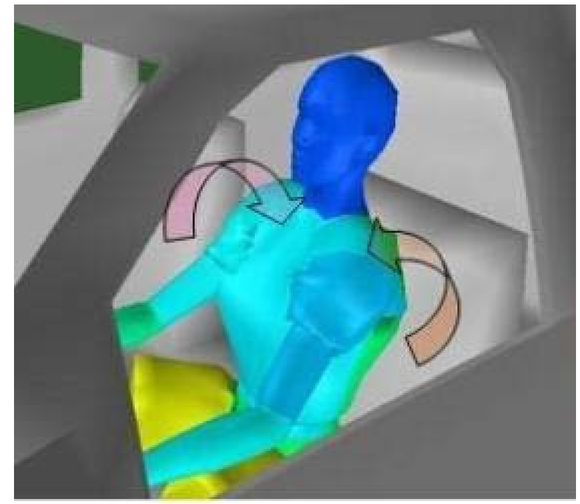
Total funding: $1,391,824

Key Research Elements

- TE materials development
- Systems-level thermal management design and modeling
- TEG prototype construction & evaluation
- Durability design & testing
- Efficient heat exchangers for transferring heat from hot gas to TE materials
- Thermal interface materials
- Measurements and characterization: TE materials, interfaces, TEG power output

Opportunity for TE Cooling/Heating





Distributed Cooling (and Heating) for High Efficiency HVAC System

Improving Energy Efficiency by Developing Components for Distributed Cooling and Heating Based on Thermal Comfort Modeling

Project lead: *General Motors*

Timeline

Start date – November 2009

End date – October 31, 2012

Budget

Total funding: $5,097,592

- DOE* share: $2,548,796
- Contractor share: $2,548,796

* We thank the California Energy Commission and the DOE Vehicle Technologies Program for their support and funding of this project

Barriers & Targets

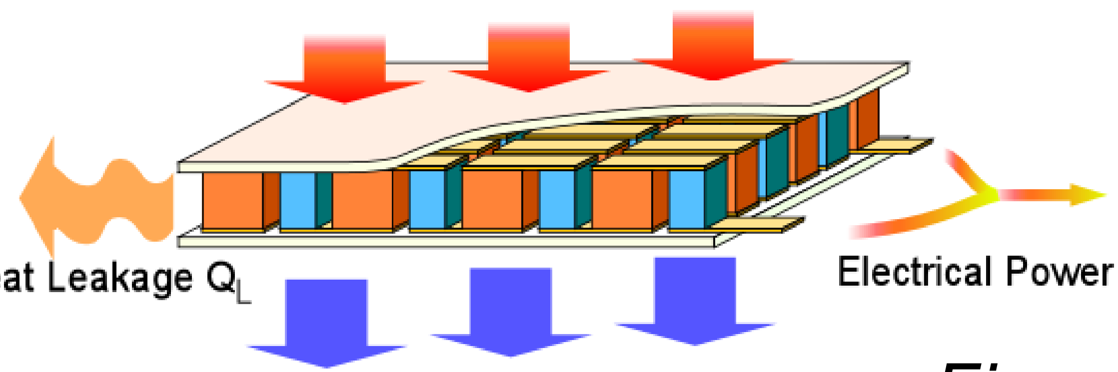
- Early stage of development for thermoelectric (TE) devices in automotive HVAC applications
- TE CoP: > 1.3 (cool), > 2.3 (heat)
- Reduce HVAC energy by > 30%
- New TEs for Waste Heat TEGs

Partners

- *University of California – Berkeley:* Thermal Comfort testing & modeling
- *Delphi Thermal Systems:* HVAC component development
- *University of Nevada – Las Vegas*: TE materials research

Introduction

Thermoelectrics for Waste Heat Recovery



Efficiency:

$$\varepsilon = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_C}{T_H}}$$

Figure of Merit:

$$ZT = S^2 T/\kappa_T \rho$$

S = *Seebeck Coefficient (Thermoelectric Power)*

κ_T = *Thermal Conductivity*

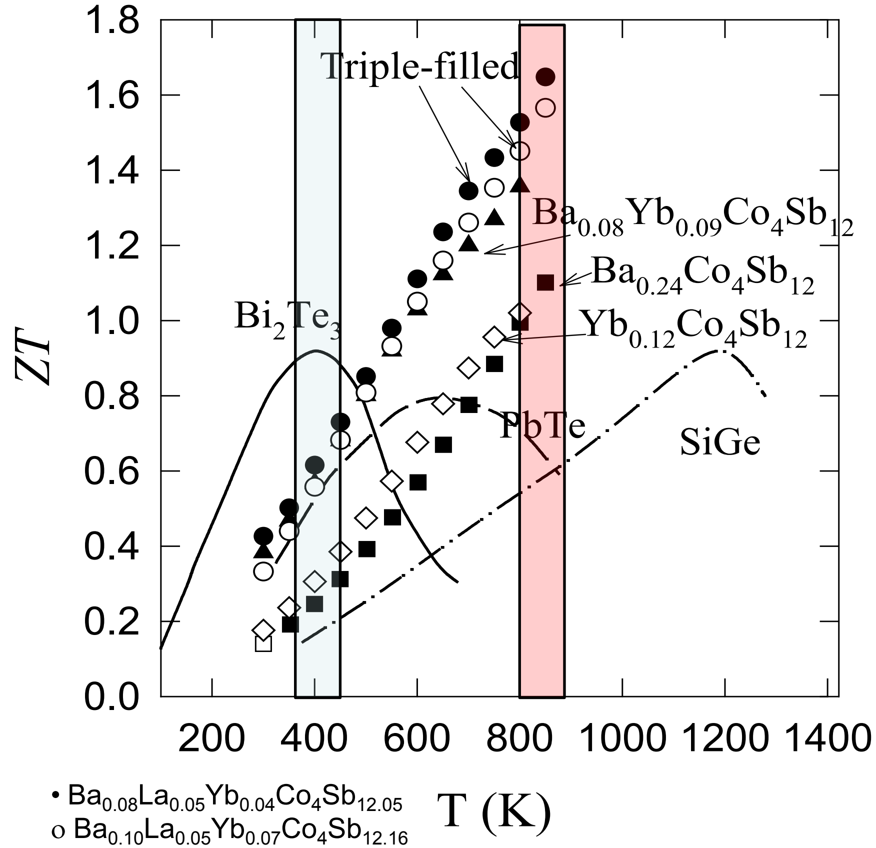
ρ = *Electrical Resistivity*

Introduction

Insulators: *S* can be very high, but electrical resistance is very high
$\Rightarrow$ *ZT* too small.

Metals: Electrical resistance very low, but *S* is very low, and thermal conductivity is too high
$\Rightarrow$ *ZT* too small

Semiconductors: Can find materials with adequate *S*, acceptable resistance that can be tuned by doping, and low thermal conductivity. Optimized material properties can give large *ZT*.



X. Shi, et al. Appl. Phys. Lett. **92**, 182101 (2008).
X. Shi, et al, Electronic Materials 38, 930 (2009).

Material Requirements:

Bulk material (i.e., not thin film or nanostructured); Operating temperatures of 400-800 K (125-525°C); Both p- and n-type TEs, Low lattice thermal conductivity κ_L, High values of ZT > 1; Good mechanical properties; Readily available and inexpensive raw materials. Environmentally friendly.

Introduction

US Department of Energy:

Funding Opportunity Announcement No. DE-PS26-04NT42113, “Energy Efficiency Renewable Energy (EERE) - Waste Heat Recovery and Utilization Research and Development for Passenger Vehicle and Light/Heavy Duty Truck Applications”

Achieve 10% improvement in fuel economy (FE) by 2015 without increasing emissions

- Demonstrate FE improvement for a Federal Test Procedure (FTP) driving cycle (~3%)
- Demonstrate that actual FE improvement for real world driving is closer to DOE goal

Demonstrate commercial viability

- Assemble, install, and test prototype TEG on a production vehicle
- Collect performance data, show viability
- Identify specific design, engineering, and manufacturability improvements for path to production

Approach:

- Thermoelectric Materials Research: discover, investigate, optimize advanced TEs
- Incorporate new advanced TE materials into operational devices & vehicle systems
- Integrate/Load Match advanced TE systems with vehicle electrical networks
- Verify device & system performance under operating conditions

Introduction

GOALS & OBJECTIVES:

Initial TEG Prototype Construction

- Translate conceptual design from GE into buildable unit
- Fabricate subsystem parts and complete assembly

Test Vehicle Modification and Integration

- Modify exhaust system for temperature and back pressure management
- Complete integration of electronic systems and controls for TEG output power management

TEG Installation

TEG Performance Data Collection (FTP and Real World drive testing)

TE and Thermo-Mechanical Property Improvements

- Adjust composition & processing for best performance
- Synthesize material batches for TE module production

Skutterudite TE Module Production

- Complete metallization and fabrication method studies
- Complete fabrication of Skutterudite TE modules for the TEG

Acknowledgements

U.S. Department of Energy Grant # DE-FC26-04NT 42278
John Fairbanks (DOE), Carl Maronde (NETL)

GM R&D Thermoelectrics Team:

Researchers:
- Jim Salvador
- Jihui Yang
- Mike Reynolds

Postdocs:
- Xun Shi, Jung Cho, Zuxin Ye

Engineering Operations:
- Kevin Rober
- John Manole

Gov. Contracts:
- Ed Gundlach,
- Amanda Demitrish
- Rick Leach

Management:
- Jan Herbst
- Mark Verbrugge

GMPT Integration & Testing:
- Greg Prior (Retired)
- Joshua Cowgill

Collaborators/Subcontractors:

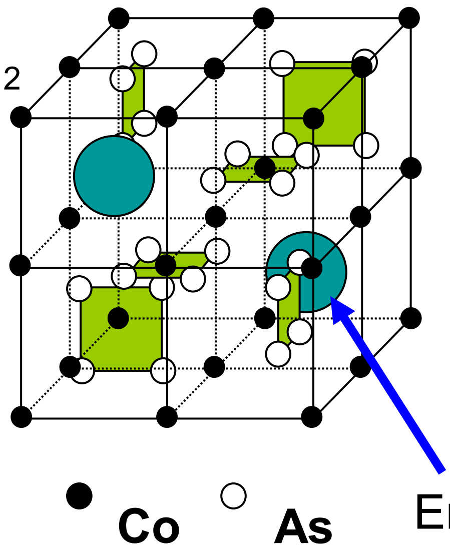
- Marlow Industries: Jeff Sharp, Jim Bierschenk, Josh Moczygemba
- Oak Ridge National Laboratory: Hsin Wang, Andy Wereszczak
- University of Nevada, Las Vegas: Changfeng Chen, Yi Zhang
- Future Tech: Francis Stabler
- Heat Technology, Inc
- Emcon (Faurecia)
- Shanghai Institute of Ceramics: Lidong Chen
- University of Michigan: Ctirad Uher
- University of South Florida: George Nolas
- Brookhaven National Laboratory: Qiang Li
- Michigan State University: Don Morelli
- General Electric Global Research: Todd Anderson, Peter DeBock

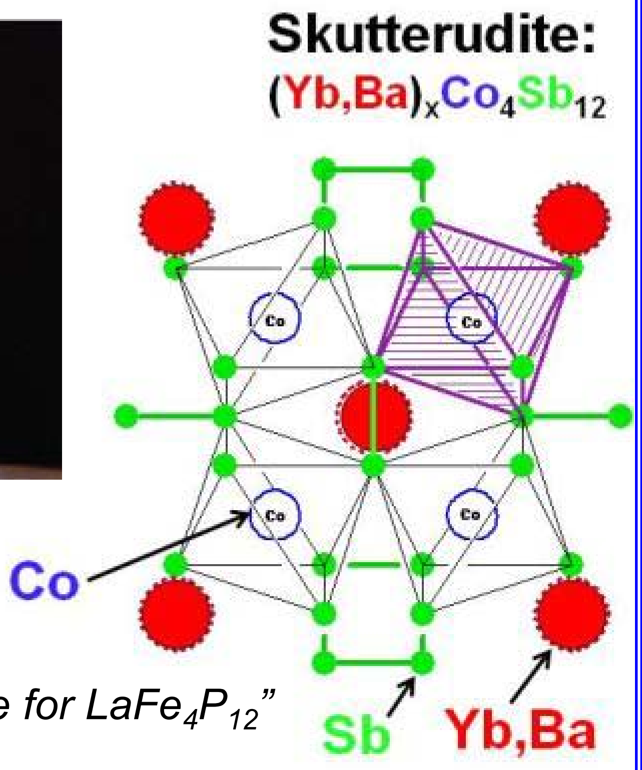
TE Materials Research

Skutterudites: Technologically Important, Scientifically Fascinating

Skutterudite: a $CoAs_3$ mineral found near Skutterud, Norway, in 1845, and compounds with the same crystal structure (body-centered cubic, *Im3,* Oftedal (1928): *Zeitschrift für Kristallographie* 66: 517-546) are known as “skutterudites”

□Co_4As_{12}

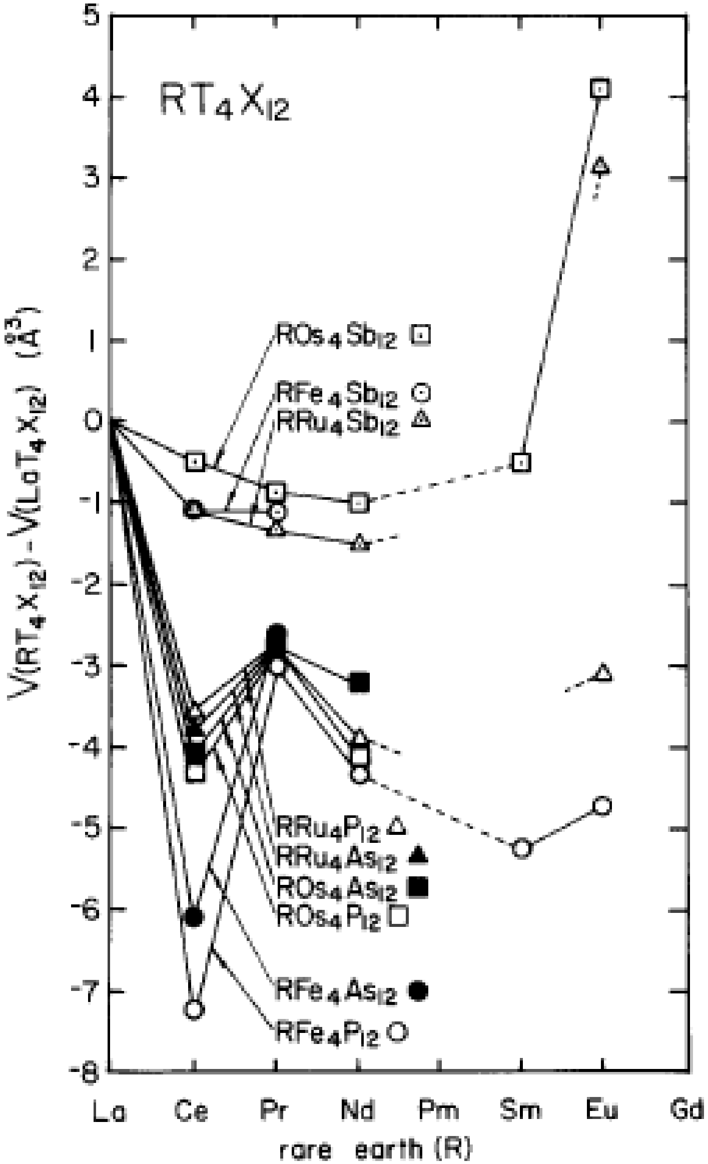




W. Jeitschko, D. J. Braun, “Filled Skutterudite Crystal Structure for $LaFe_4P_{12}$” Acta Crystallogr. ***B33*** *(1977) 3401:*

G. P. Meisner, “Superconductivity and Magnetic Order in Ternary Transition Metal Phosphides” Physica ***108B*** *(1981) 364.*

TE Materials Research



Filled Skutterudites

Change in unit cell volume $\Delta V = V(RT_4X_{12}) - V(LaT_4X_{12})$ versus R for T = Fe, Ru, or Os, and X = P, As, or Sb.

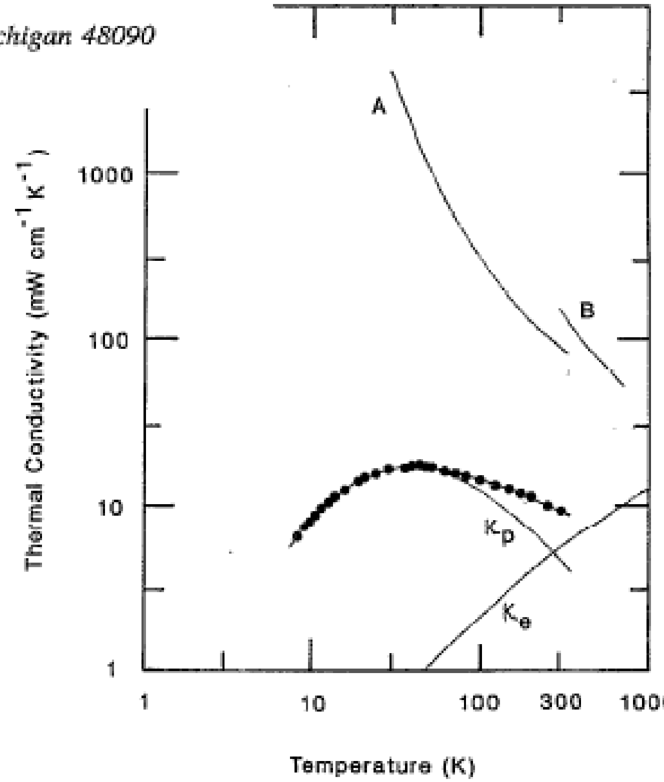
L. E. DeLong and G. P. Meisner, "The Pressure Dependence of the Superconducting Transition Temperature of LaT_4P_{12} (T = Fe, Ru, Os)" Solid State Commun. ***53*** *(1985) 119.*

TE Materials Research

Low temperature properties of the filled skutterudite $CeFe_4Sb_{12}$

Donald T. Morelli[a] and Gregory P. Meisner
Physics Department, General Motors Research and Development Center, Warren, Michigan 48090

(Received 10 October 1994; accepted for publication 30 December 1994)
Journal of Applied Physics (1995)



High Figure of Merit in Ce-Filled Skutterudites

Jean-Pierre Fleurial, Alex Borshchevsky, Thierry Caillat
Jet Propulsion Laboratory/ California Institute of Technology, Pasadena, California, USA

Donald T. Morelli and Gregory P. Meisner
General Motors Research and Development Center, Warren, Michigan, USA

Proc. 15th Inter. Conf. Thermoelectrics

United States Patent [19] — **Fleurial et al.**

[11] **Patent Number: 6,069,312**
[45] **Date of Patent: May 30, 2000**

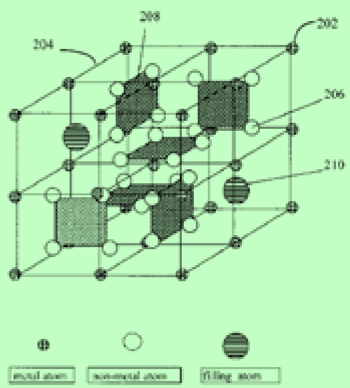
[54] **THERMOELECTRIC MATERIALS WITH FILLED SKUTTERUDITE STRUCTURE FOR THERMOELECTRIC DEVICES**

[75] Inventors: **Jean-Pierre Fleurial**, Duarte; **Alex Borshchevsky**, Santa Monica; **Thierry Caillat**, Pasadena, all of Calif.; **Donald T. Morelli**, White Lake; **Gregory P. Meisner**, Ann Arbor, both of Mich.

[73] Assignee: **California Institute of Technology**, Pasedena, Calif.

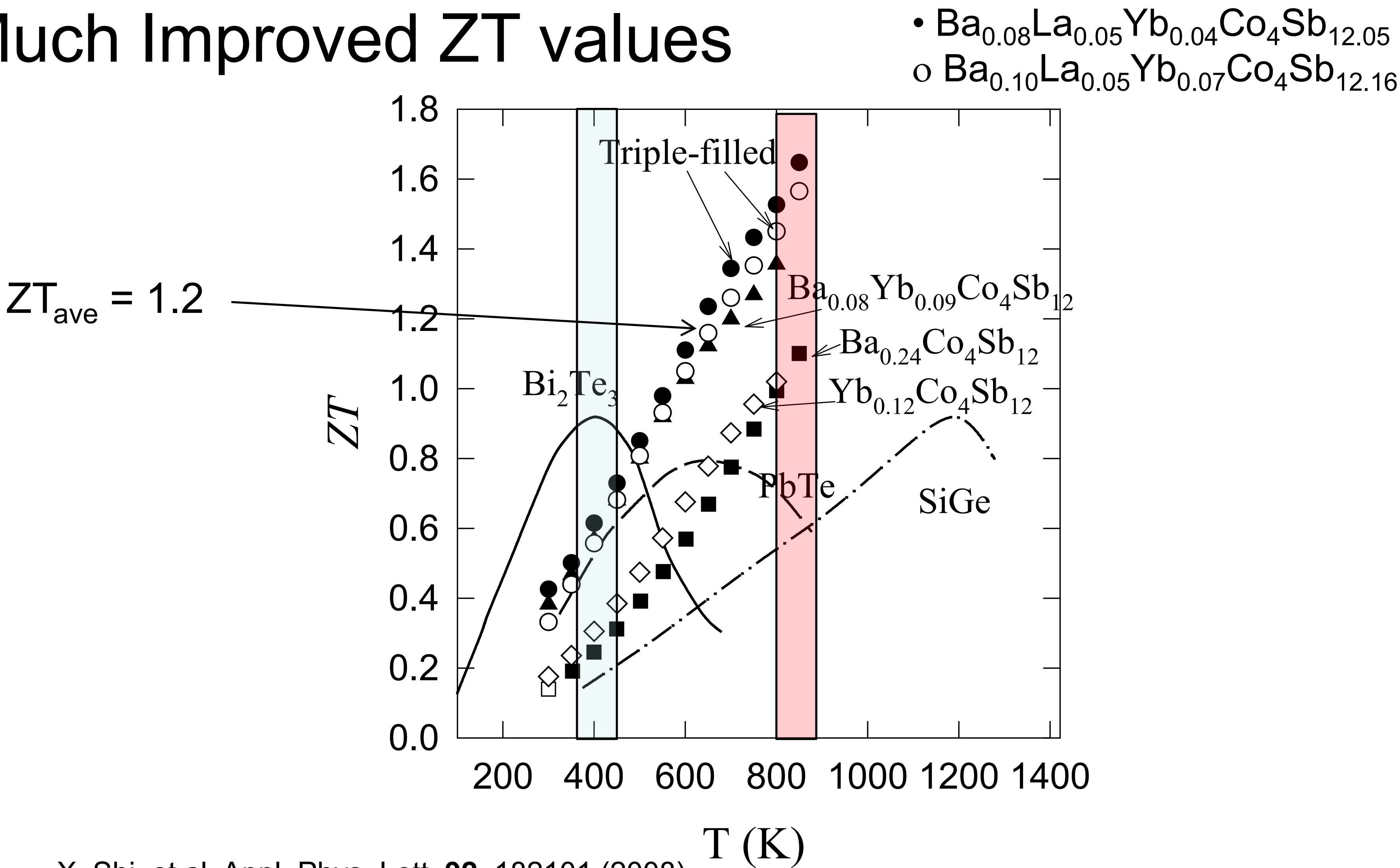
[21] Appl. No.: **08/908,814**

[22] Filed: **Aug. 7, 1997**



TE Materials Research

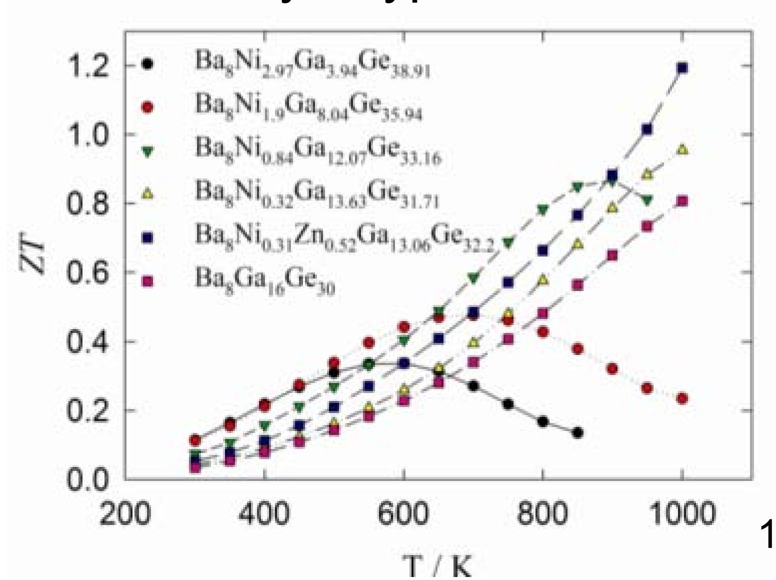
Much Improved ZT values



X. Shi, et al. Appl. Phys. Lett. **92**, 182101 (2008).
X. Shi, et al, Electronic Materials 38, 930 (2009).

TE Materials Research

- Validated measurements of transport and mechanical properties and performance at high temperature.
- Explored optimization of preferred materials for use in TE modules.
- Improvement in the synthesis, processing, and transport properties of Yb-filled skutterudites associated with specifically created nano-scale precipitates at grain boundaries and within grains.
- Achieved a figure of merit *ZT* = 1.6 for multiple filled skutterudites, highest value yet reached for any n-type filled skutterudite material.
- Improved TE properties of Type I clathrates by doping transition metals on the gallium sites.
- Investigated new TE materials: In_4Se_3, In_4Te_3, Cu-Ge-Se.



2010 Publications/Presentations

1. Shi, X.; Yang, Jiong; Bai, S. Q.; Yang, Jihui; Salvador, J. R.; Wang, H.; Chi, M.; Zhang, W. Q.; Chen, L.; Wong-Ng, W. “On the Design of High Efficiency Thermoelectric Clathrates through a Systematic Cross-substitution of Framework Elements”, Adv. Funct. Mater. **20**, 755 (2010).
2. Beekman, M., Shi, X., Salvador, J. R., Nolas, G. S., and Yang, J., "Characterization of delafossite-type $CuCoO_2$ prepared by ion exchange", J. Alloys Compounds **489**, 336 (2010).
3. Cho, J. Y.; Shi, X.; Salvador, J. R.; Yang, J.; and Wang, H.; “Thermoelectric properties of ternary diamond-like semiconductors $Cu_2Ge_{1+x}Se_3$”, J. Appl. Phys. **108**, 073713 (2010).
4. Shi, X.; Cho, J.; Salvador, J. R.; Yang, J.; Wang, H.; “Thermoelectric properties of polycrystalline In_4Se_3 and In_4Te_3”, Appl. Phys. Lett. **96**, 162108 (2010).
5. Salvador, J. R.; Yang, J.; Wang, H.; Shi, X.; “Double-filled skutterudites of the type $Yb_xCa_yCo_4Sb_{12}$: Synthesis and Properties,” J. Appl. Phys. **107**, 043705 (2010).
6. Meisner, G. P.: “Materials and Engineering for Automotive Thermoelectric Applications,” Global Powertrain Congress, Troy, MI, November 2009 (Invited).
7. Salvador, J. R.; “Engineering and Materials for Automotive Thermoelectric Applications,” U.S. Car, Troy MI, March 3, 2010 (Invited).
8. Yang, J.; “Neutron Scattering Studies of Thermoelectric Materials for Automotive Applications” American Physical Society Meeting, Portland, OR, March 2010. (Invited).
9. Yang, J.; “Thermoelectric Materials by Design,” 29th International Conference on Thermoelectrics, Shanghai, China, May 2010 (Invited).
10. Meisner, G. P.; “Automotive Waste Heat Recovery Using Advanced Thermoelectrics,” Complex and Nanostructured Materials for Energy Applications Conference, Michigan State University, Lansing, MI, June 2010 (Invited).
11. Meisner, G. P.; “Improving Energy Efficiency by Developing Components for Distributed Cooling and Heating Based on Thermal Comfort Modeling,” Vehicle Technologies Program Annual Merit Review Meeting, U.S. Department of Energy, Washington, DC, June 2010.
12. Meisner, G. P.; “Develop Thermoelectric Technology for Automotive Waste Heat Recovery,” Vehicle Technologies Program Annual Merit Review Meeting, U.S. Department of Energy, Washington, DC, June 2010.
13. Meisner, G. P.; “Thermoelectric Generator Development for Automotive Waste Heat Recovery,” 16^{th} Directions in Engine Efficiency & Emissions Research (DEER) Conference, Detroit, MI, September 2010.
14. Yang, J.; “Advanced Materials for Future Propulsion”. 2010 Frontiers of Renewable Energy Sciences & Technologies Conference, Harvard University, Cambridge, MA, September 2010 (Invited).

2010 Publications/Presentations (Cont.)

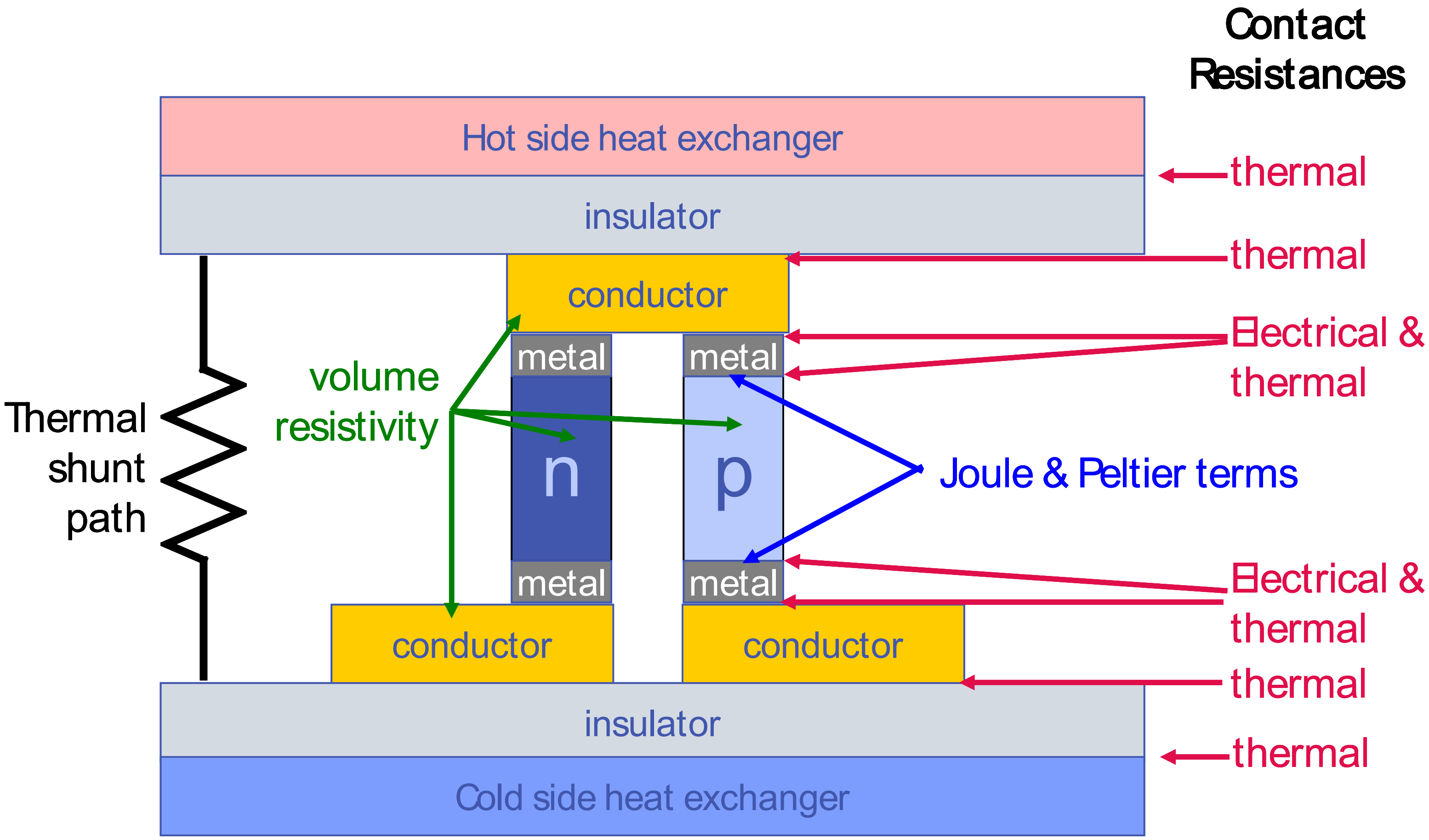
15. Yang, J.; "Advanced Materials for Future Propulsion". 2010 Frontiers of Renewable Energy Sciences & Technologies Conference, Harvard University, Cambridge, MA, September 2010 (Invited).
16. Salvador, J. R.; "Engineering and Materials for Automotive Thermoelectric Applications," Global Powertrain Congress, Troy, MI, November 2010 (Invited).
17. Yang, J. Shi, X.; Wang, H.; Chi, M.; Salvador, J. R.; Yang, Jiong; Bai, S.; Zhang, W. Q.; Chen, L.; Copley, J. R.; Leao, J.; Rush, J. J.; "Are Skutterudites Phonon Crystals or Phonon Glasses," Materials Research Society Fall Meeting, Boston, MA, December 2010 (Invited).
18. Meisner, G. P.; "Progress on Thermoelectric Generator Development for Automotive Exhaust Gas Waste Heat Recovery," Materials Research Society Fall Meeting, Boston, MA, December 2010.
19. Salvador, J. R.; "Mechanical and Elastic Property Evaluation of n and p-type Skutterudites," Materials Research Society Fall Meeting, Boston, MA, December 2010.
20. Cho, J. Y.; Salvador, J. R.; Wang, H.; Wereszcak, A. A.; Chi, M.; 'Thermoelectric Properties of Diamond-like Compounds $Cu_2Ga_xGe_{1+x}Se_3$ (x = 0 ~ 0.1)," Materials Research Society Fall Meeting, Boston, MA, December 2010.

ROIs/Patents

1. "Filled Skutterudites for Advanced Thermoelectric Applications," Yang, J.; Meisner, G. P.; U.S. Patent 7648552 Issued January 19, 2010.
2. "Optimal power determination for a Thermoelectric Generator by setpoint dithering," Reynolds, M. G.; Cowgill, J. D.; P011627, Record of Invention submitted January 29, 2010.
3. "Algorithms for Bypass Valve and Coolant Flow Controls for Optimum Temperatures in Waste Heat Recovery Systems," Meisner, G. P.; P012265, Record of Invention submitted April 8, 2010.
4. "Method of Controlling Temperature of a Thermoelectric Generator in an Exhaust System." Prior, G. P.; Reynolds, M. G.; Cowgill, J. D.; P011519, U.S. Patent Application filed April 2, 2010.
5. "Thermoelectric Generator Cooling System and Method of Control," Prior, G. P.; Meisner, G. P.; Glassford, D. B.; P011552-R&D, U.S. Patent Application Filed April 2, 2010.
6. "Formation of Thermoelectric Elements by Net Shape Sintering" Salvador, J. R.; Yang, J.; Wereszczak, A. A.; P009885-R&D, U.S. Patent Application Filed June 4, 2010.
7. "Thermoelectric Generators for Waste Heat Recovery from Engine Exhaust," Meisner, G. P.; Yang, J.; P012262, U.S. Patent Application filed September 2010.

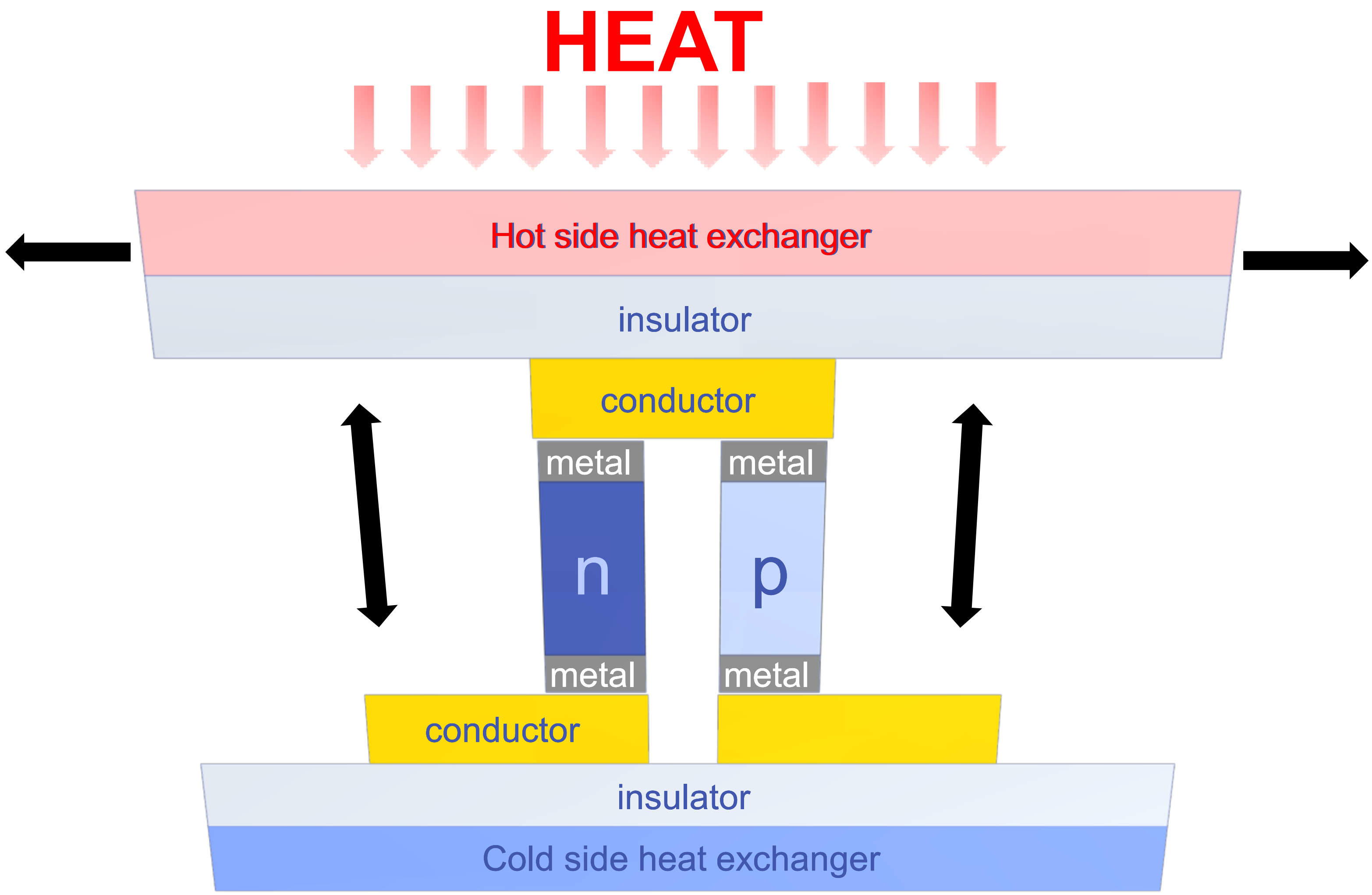
TE Materials Research

Schematic Diagram of a TE Module



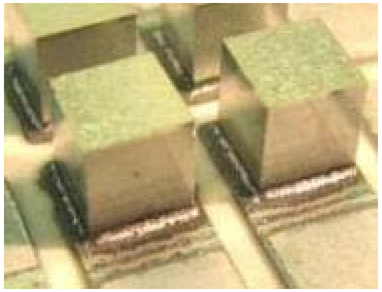
TE Materials Research

Schematic Diagram of a TE Module



TE Module Fabrication: PbTe
(Marlow)

- Evaluated braze methods for electrical connections to PbTe .

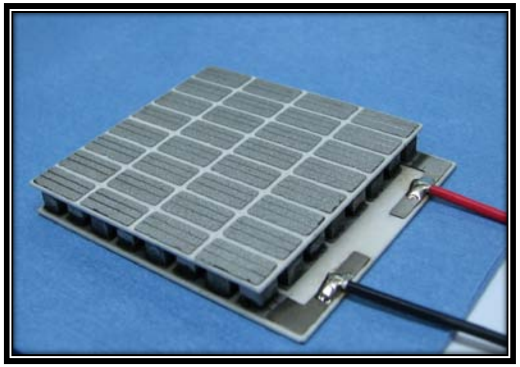
(a) 

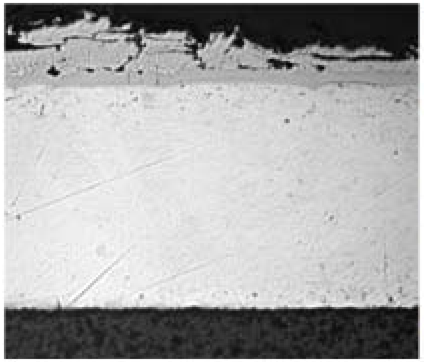
(b) 

(a) PbTe elements with a thick nickel end cap brazed to the metallization layer, and (b) shear test results with adhesion promoting heat treatment (failure is in bulk material.)

- Designed tooling for fabricating ceramic headers for TE modules.
- Synthesized several n-type PbTe ingots and explored processing variables to reduce cracking and fragility, and to improve adhesion of electrical and thermal contacts.

Prototype PbTe module





TE Generator Development

Incorporate New Advanced TE materials into Operational Devices & Vehicle Systems

Improve TE materials (Skutterudites) (ZT = 1.6 at 850 K, ZT_{ave}= 1.2)

Develop models and computational tools to design TE generators (TEGs) which include heat transfer physics at heat exchanger and interfaces; TE material properties; mechanical reliability, and cost

Develop thermoelectric modules for TEG

Finalize design, fabricate, and assemble prototype TEG

Complete vehicle modification for controls and integration of TEG

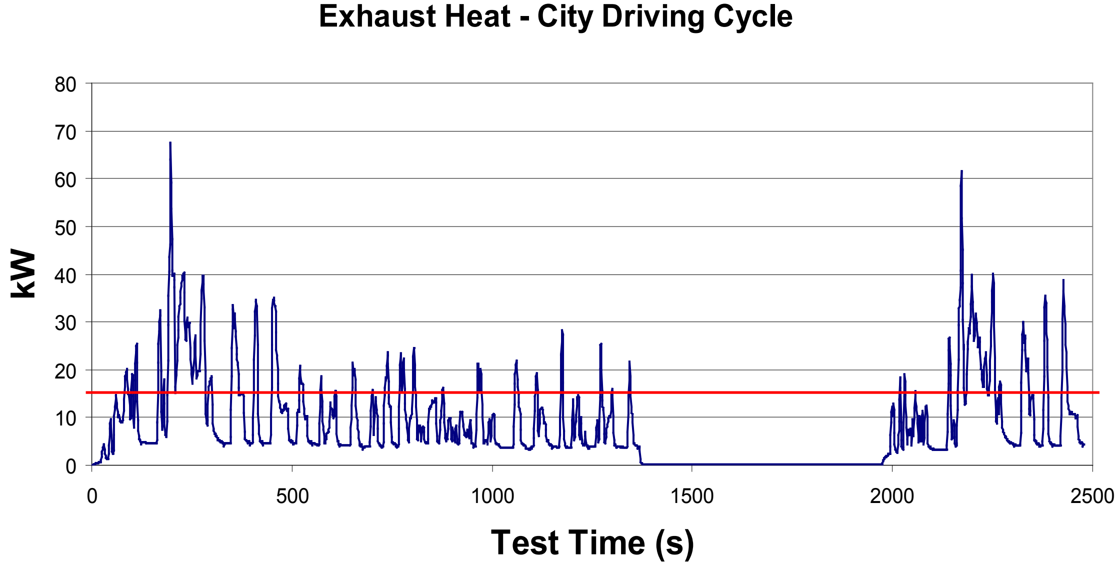
Develop power electronics design for power conditioning

Develop system control algorithms for improved thermal-to-electrical conversion efficiency

Assess TEG performance

TE Generator Development

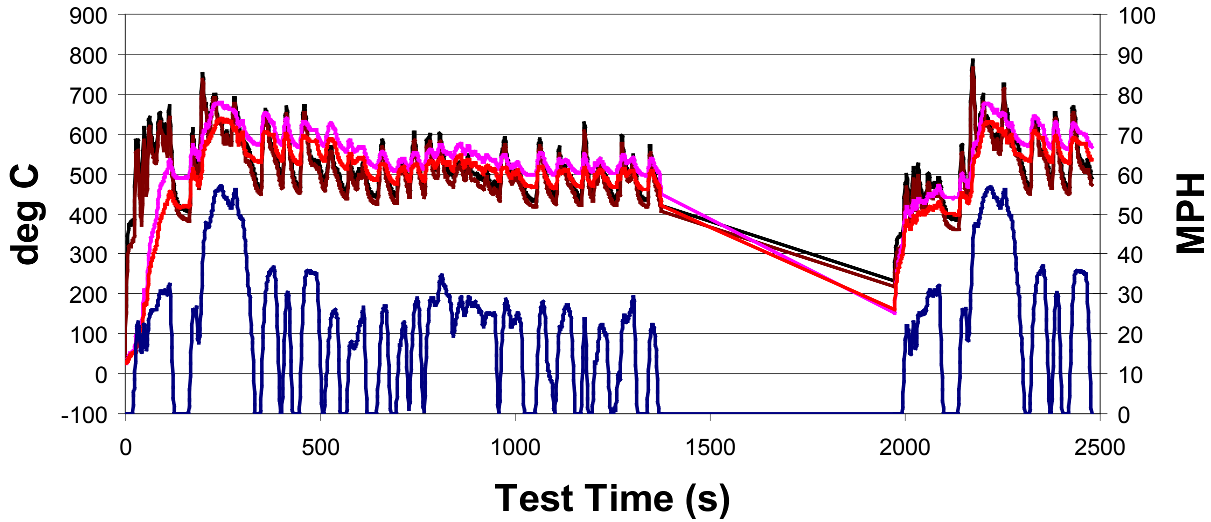
TE Automotive Waste Heat Recovery Vehicle Selection – Chevy Suburban



The Suburban was selected as a test vehicle because it simplified the vehicle modification and installation of the prototype.

TE Generator Development

TE Automotive Waste Heat Recovery Vehicle Selection – Chevy Suburban



The Suburban was selected as a test vehicle because it simplified the vehicle modification and installation of the prototype.

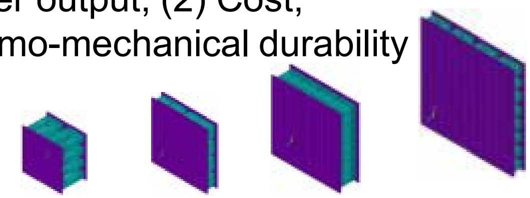
TE Generator Development

Subsystems Modeling and Design (With General Electric)

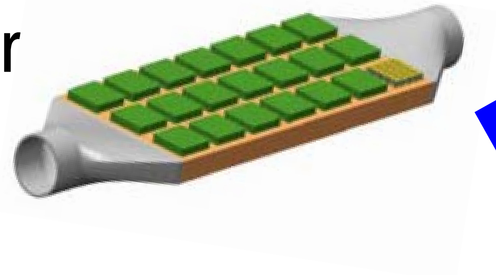
TE Module Design:

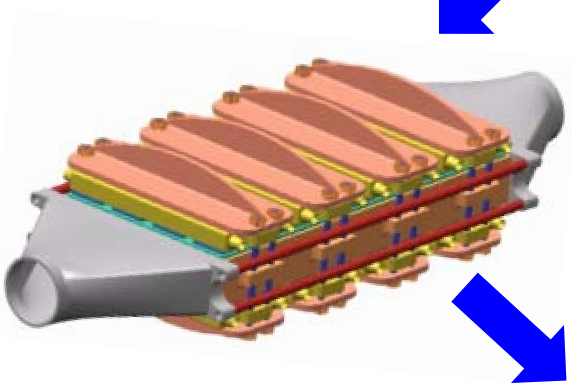
Identify primary module design variables

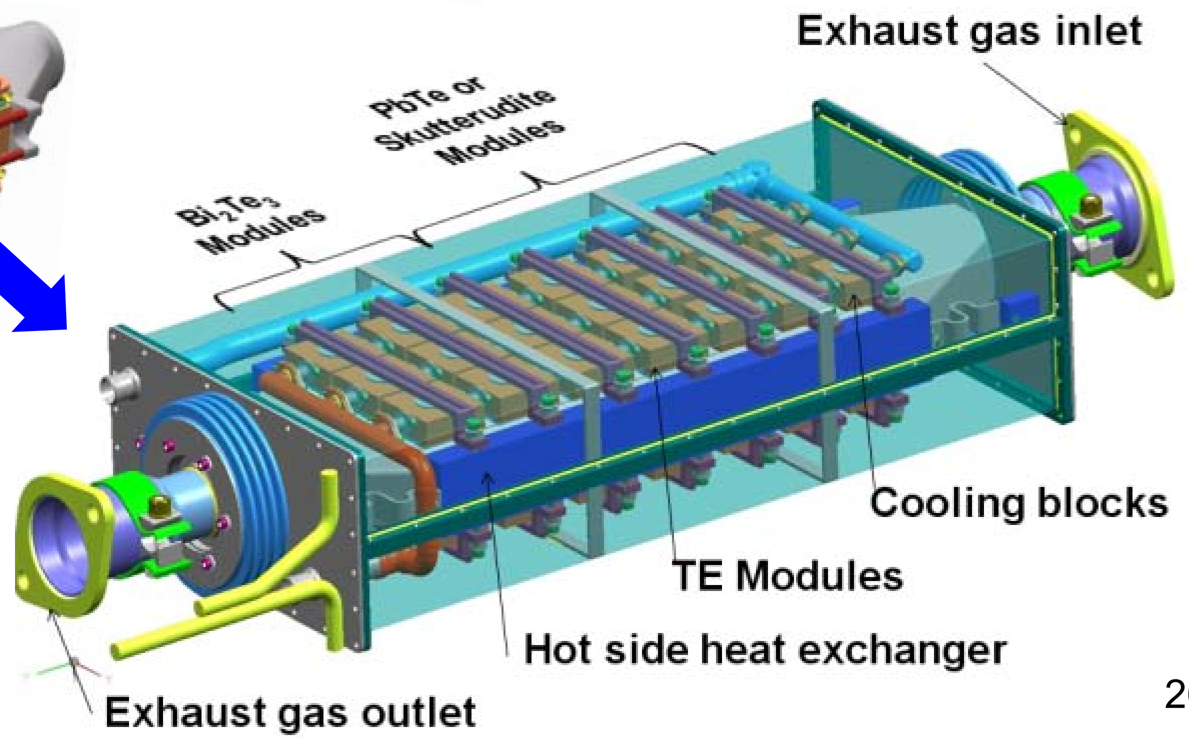
Examine effect on primary output variables:
(1) Power output, (2) Cost,
(3) Thermo-mechanical durability



Heat Exchanger Design:





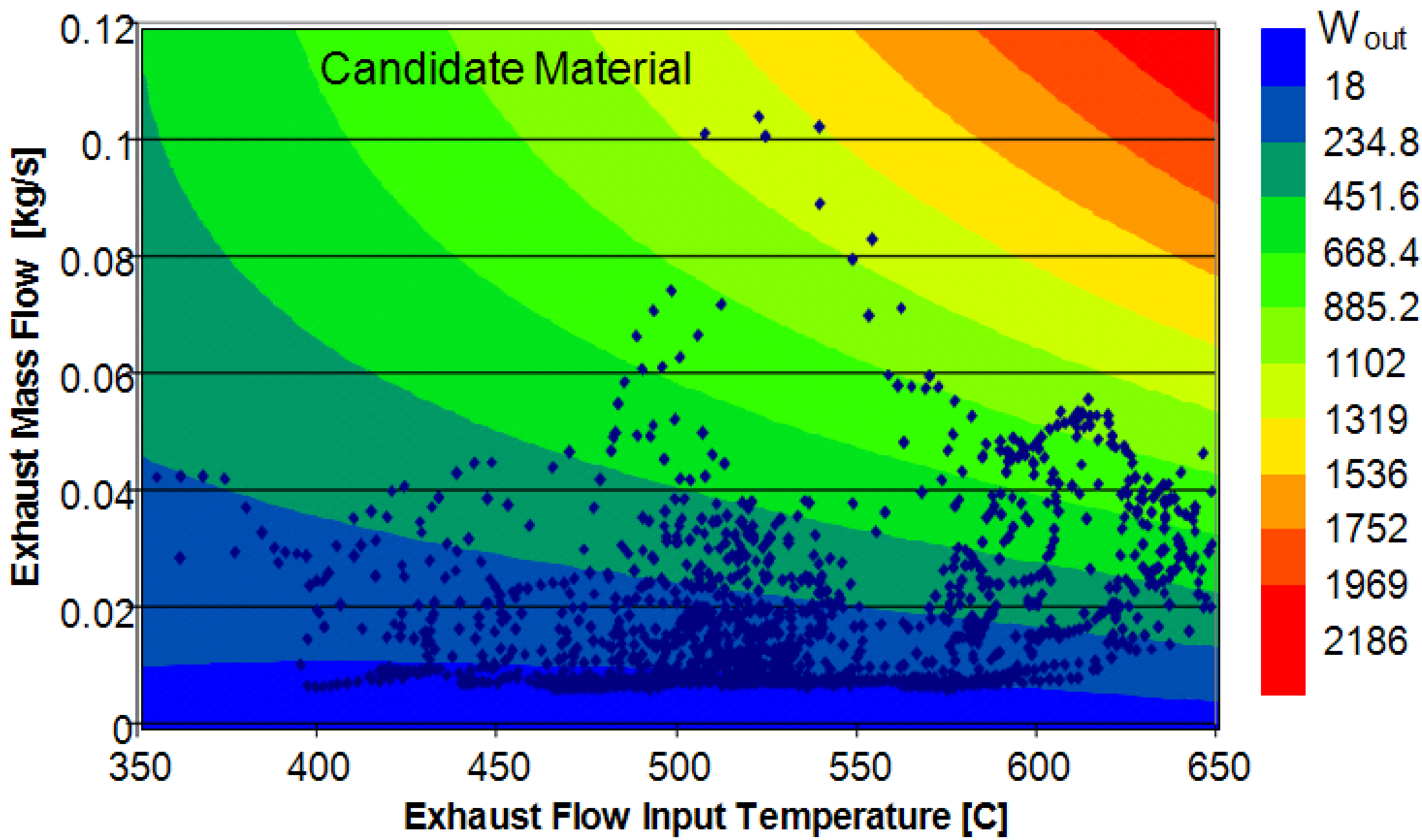


TEG Design:

Program metric: $/Watt

TE Generator Development

TE Model System Expected Efficiency and Urban Cycle Exhaust Conditions



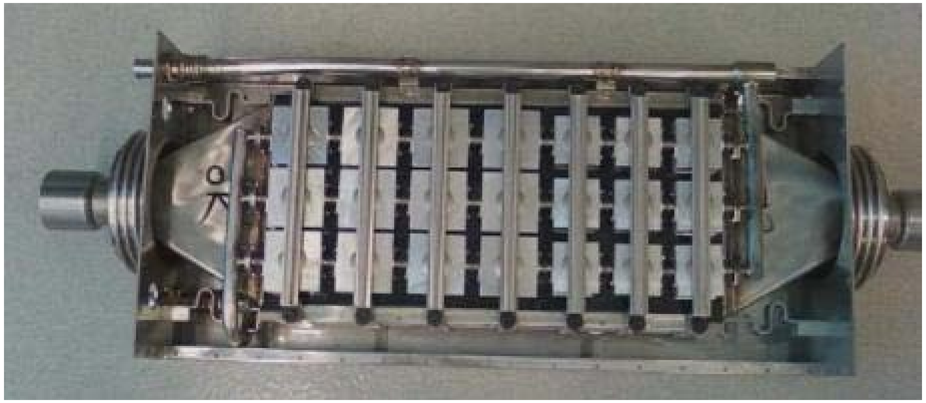
TE Generator Development

- We expect ~ 1 mpg (~ 5 %) fuel economy improvement for Suburban (average 350 W and 600 W for the FTP city and highway driving cycles, respectively.)
- This technology is well-suited to other vehicle platforms such as passenger cars and hybrids.

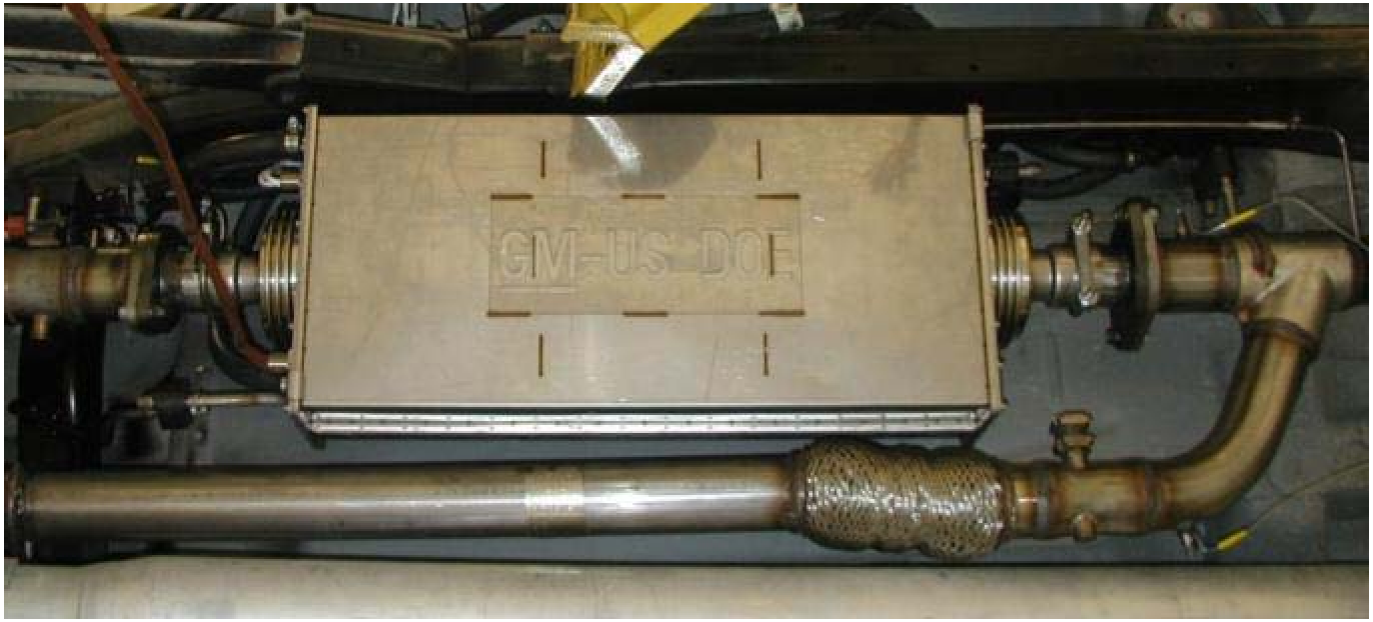
TE Generator Development

Finalize design, fabricate, & assemble prototype TEG

- Completed thermoelectric generator design and fabrication of heat exchanger subassemblies. Prototype TEG #1 completed, TEG#2 installed.



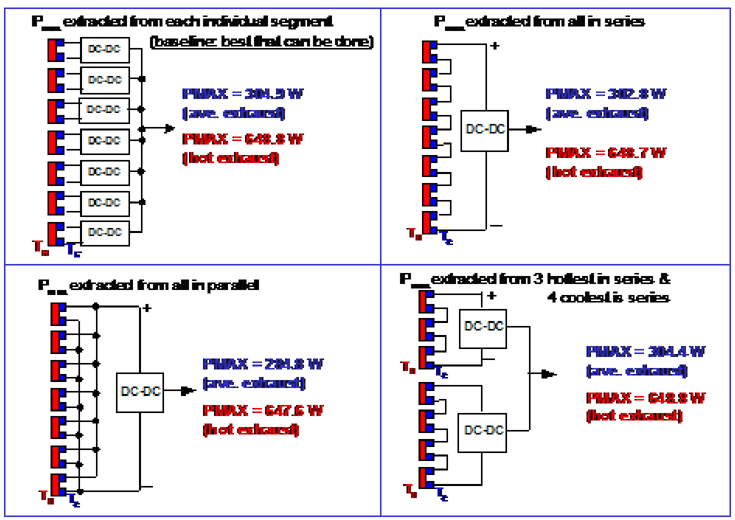
TEG Installation

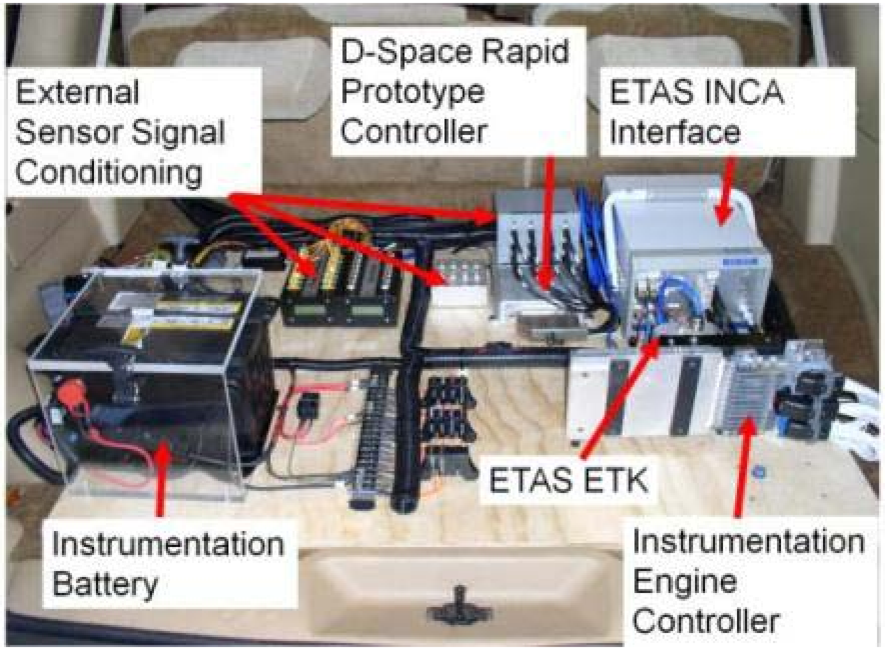


TE Generator Development

Vehicle Integration

- Power electronics designed for power conditioning and vehicle control





- Control algorithms developed for improved thermal-to-electrical conversion efficiency

TEG Testing & Validation

- <u>Assess TEG Performance</u>

  Start-Cart

  - First step in integration development
  - Provides a decoupled testing environment
  - Provides easy access for modification and debugging

  Chassis-Rolls Dynamometer

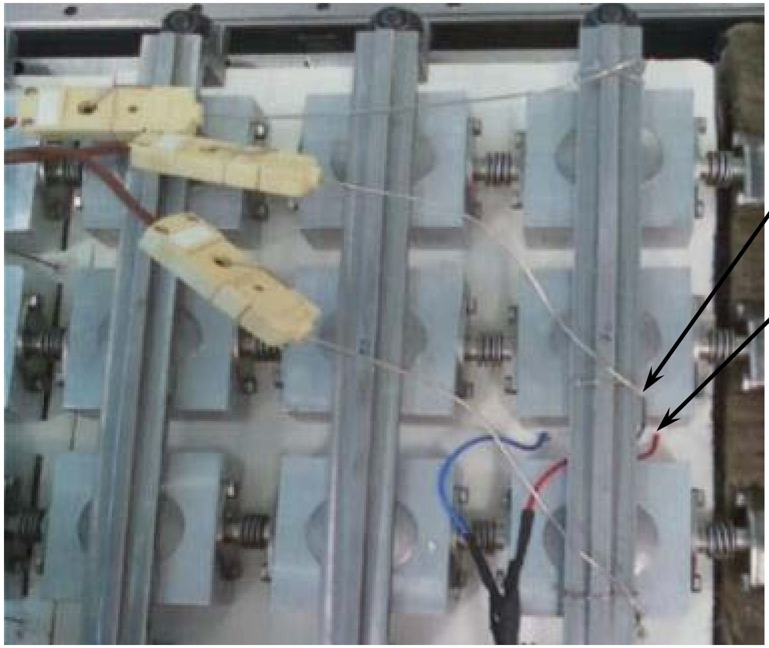
  - Provide a realistic loading and repeatable environment, though not a realistic environment
  - Precise data collection
  - Standard test method for fuel economy and emissions measurements

  Environmental Dynamometer

  - Chassis-rolls dynamometer which simulates grades, atmospheric environment

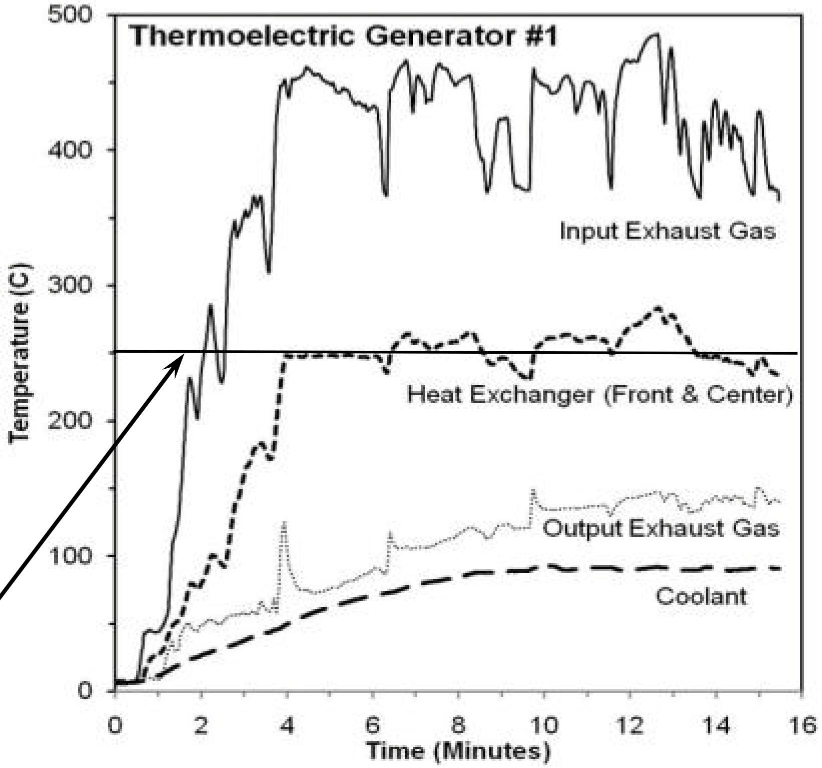
  Real World Driving

Results: TEG #1



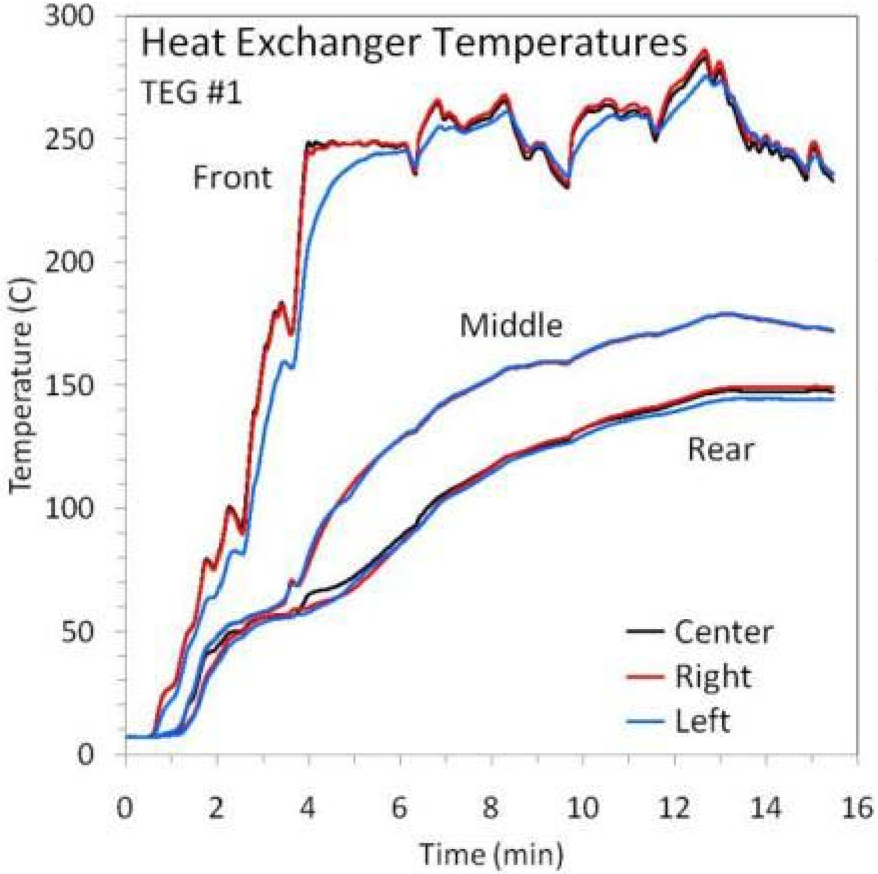
Front & Center thermocouple

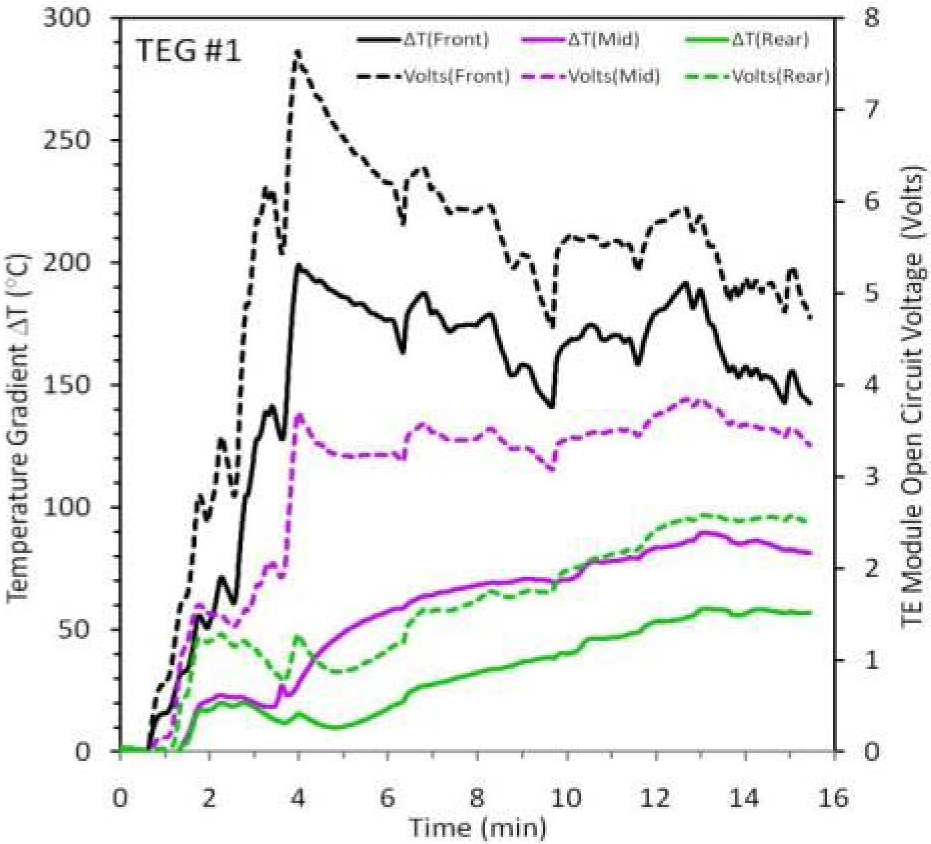
Front & Center TE module



The by-pass valve set point temperature for the heat exchanger was 250°C.

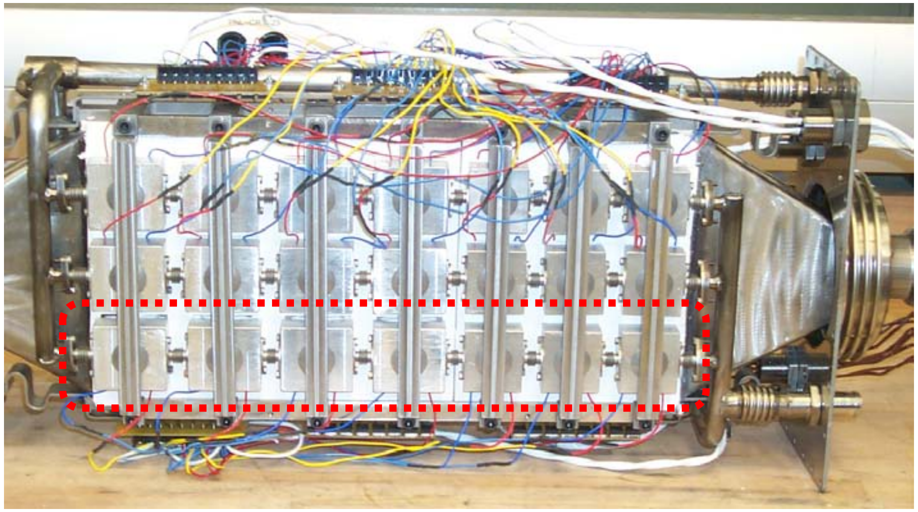
Results: TEG #1

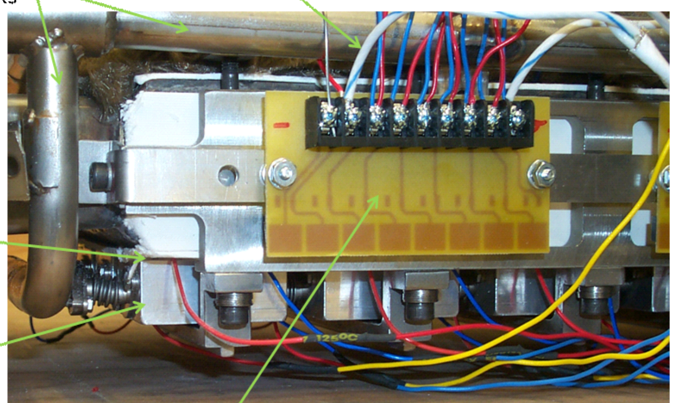


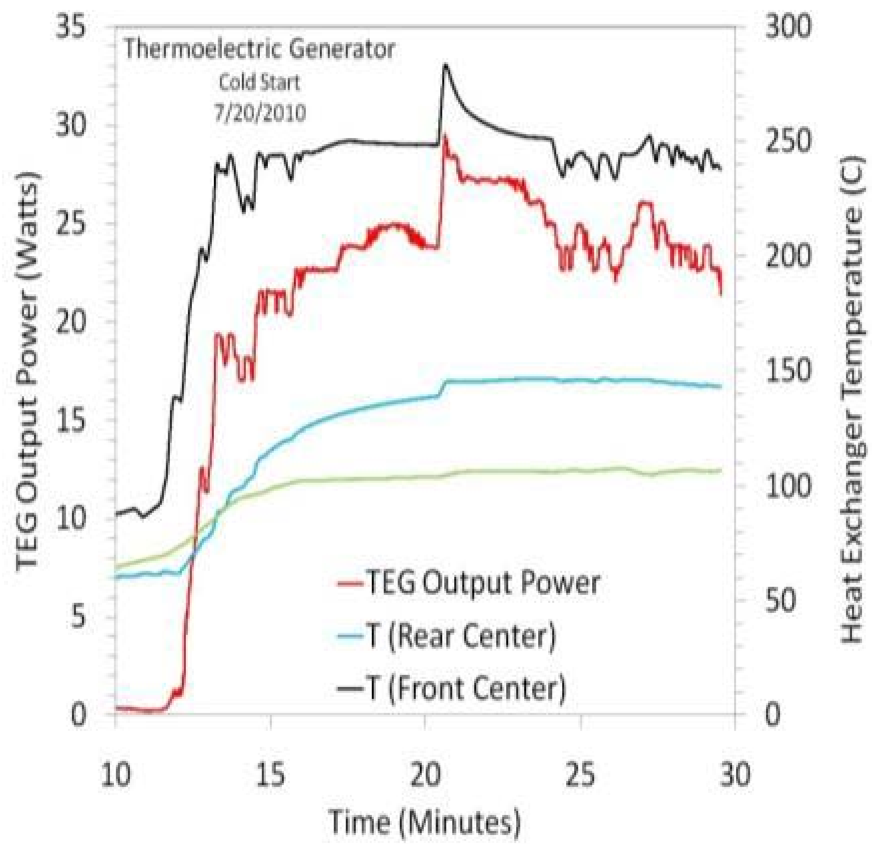


- Substantial temperature drop along the length of the TEG: 250°C (Front), 178°C (Middle), and 148°C (Rear)
- Temperature variation across the TEG: < 3°C.
- TE output voltage is consistent with a 50°C smaller ΔT than measured between the hot side heat exchanger and the coolant

Results: TEG #2





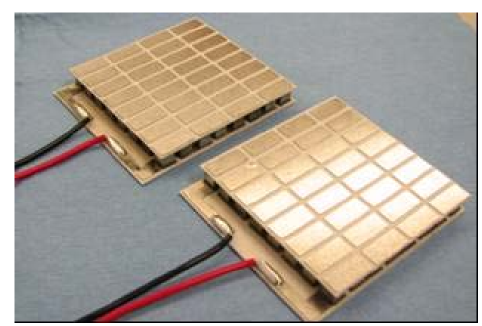


Summary: Current Work

- Completed TEG #2 assembly (42 Bi-Te TE modules) and installation on the vehicle.
- Finalized and implemented vehicle integration with TE waste heat recovery system.
- Achieved improvements in the performance of TE materials, particularly for Skutterudites.
- Developing higher temperature Skutterudite TE modules for final prototype: TEG #3.

Synthesize n- and p-type ingots (GM):

Fabricate modules (Marlow):



GM

Future Work

- Complete fabrication of high temperature TE modules for TEG #3.
- Conduct dynamometer tests and proving ground tests for vehicle equipped with the TEG waste heat recovery system (TEG #2 and TEG #3).
- Demonstrate fuel economy gain using TE waste heat recovery technology (TEG #3).

FINANCIAL ASSISTANCE
FUNDING OPPORTUNITY ANNOUNCEMENT

U. S. Department of Energy

National Energy Technology Laboratory

FY 2011 Vehicle Technologies Program Wide

Funding Opportunity Announcement

Funding Opportunity Number: DE-FOA-0000239

Announcement Type: Initial

CFDA Number: 81.086 Conservation Research and Development

Issue Date:	December 16, 2010
Letter of Intent Due Date:	January 18, 2011
Pre-Application Due Date:	Not Applicable
Application Due Date:	February 28, 2011 at 8:00:00 PM Eastern Standard Time

Area of Interest 6-- Thermoelectrics and Enabling Engine Technologies:

The goal of this AOI is to achieve improved efficiency and reduced emissions in advanced combustion engines for passenger and commercial vehicle applications through: 1) accelerated development of cost competitive advanced second generation thermoelectric devices for vehicle applications…

Subtopic 6A: Solid State Thermoelectric Energy Conversion Devices