

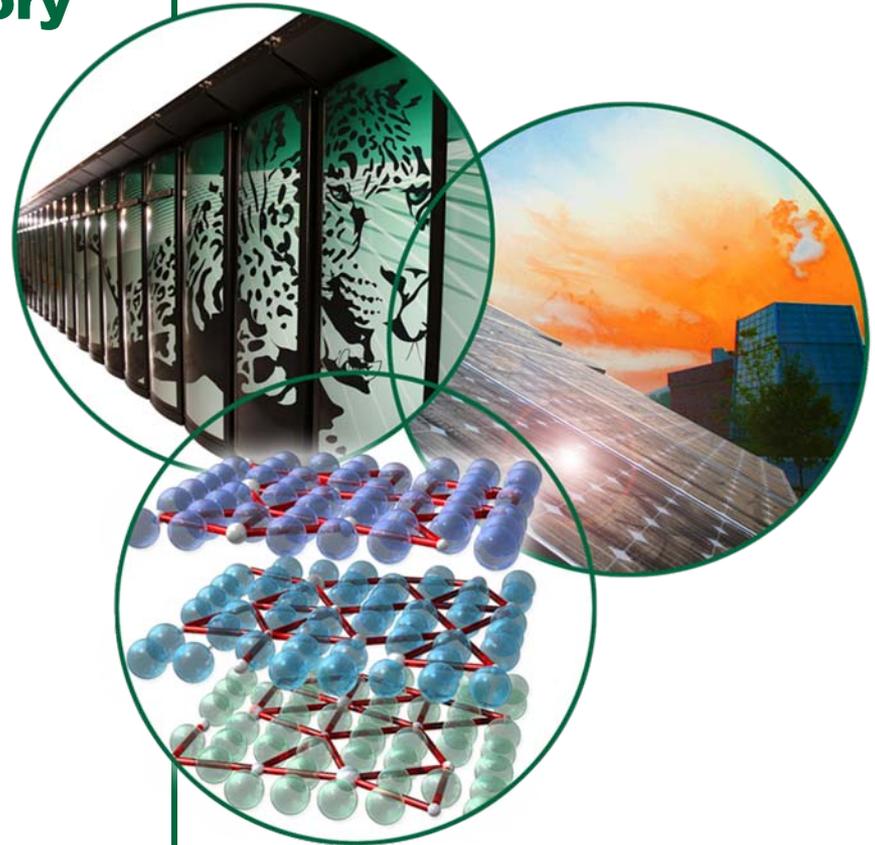
High Temperature Thermoelectric Materials Characterization for Automotive Waste Heat Recovery: Success Stories from the High Temperature Materials Laboratory (HTML) User Program

DOE 2009 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

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The HTML User Program - Background

The HTML is a National User Facility that supports the missions of DOE, EERE and the Vehicle Technologies Program in particular, by working with industry, universities and other national laboratories to develop energy efficient technologies that will enable the U.S. to use less petroleum. The HTML is organized into six user centers, which are clusters of highly skilled staff and sophisticated, often one-of-a-kind instruments for materials characterization.

Access to the HTML is provided through the HTML User Program proposal process. Research proposals are reviewed by a committee and approved based on scientific merit, relevance of the proposed research to the mission of DOE's Vehicle Technologies Program, and feasibility. Research is completed within 24 months and normally involves one or more user visits to the HTML.

Both nonproprietary and proprietary research is conducted within the HTML User Program. There are generally no charges for nonproprietary research projects, and users conducting nonproprietary research must agree to submit research results for publication in the open, refereed literature. For proprietary research, the user owns the research data and all costs at the HTML are paid by the user based on DOE guidelines for ORNL costs. A nonproprietary project is complete when the results are published in the open literature and/or presented at a professional conference.

The HTML User Program – FY2008 Activity

During FY2008, the HTML User Program managed 76 user projects from 53 different organizations.

The FY2008 budget for the HTML was \$6,072,283 and was allocated as follows:

- \$1,567,500 for capital equipment purchases
- \$3,879,483 to support staff participation in user projects
- \$626,000 for the operation of the user program

Users cost-share user projects through:

- 1) their direct involvement with HTML staff members during the development of the user project;
- 2) funding their travel to the HTML to perform research;
- 3) costs of materials provided by the user or the research performed prior to the user project;
- 4) their subsequent collaboration with HTML staff members to analyze the data and publish the results.

The HTML also supports the education and preparation of a new generation of scientists and engineers.

During FY2008, students and professors from 32 universities participated in the HTML User Program. Four of those students received their Ph.D. degree in FY2008 based in part on research performed through the HTML User Program.

General Motors R&D Center



“Thermoelectric properties of Yb-filled skutterudites prepared by spark plasma sintering”

Timeline

- Start date: 10/1/07
- End date: 9/30/08
- % complete: 80%

Budget

- Included in the user center allocations from the annual budget of the HTML User Program; users cost-share as previously noted.

Barriers

- Materials performance: Figure of Merit
- Reliable property measurements
- Understanding of the property-structure relationships

Collaborators

- Users: General Motors R&D Center
Jihui Yang, Xun Shi, James Salvador
- HTML Staff: Hsin Wang
- GM Partners at University of South Florida and University of Michigan

Relevance to the VT Program

- The Vehicle Technologies Program supports the HTML User Program and provides an annual budget to address a wide range of materials-related issues in ground transportation systems arising from R&D needs in U.S. industry.
- The user project highlighted in this poster presentation address the need for developing techniques for measuring key thermophysical and transport properties of thermoelectric materials. Materials with high ZT value are essential to achieving the goal of improving fuel efficiency by 10% or more by recovering energy from engine exhaust and/or engine cooling system.

Project ID: IMP06, Wang

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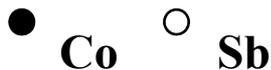
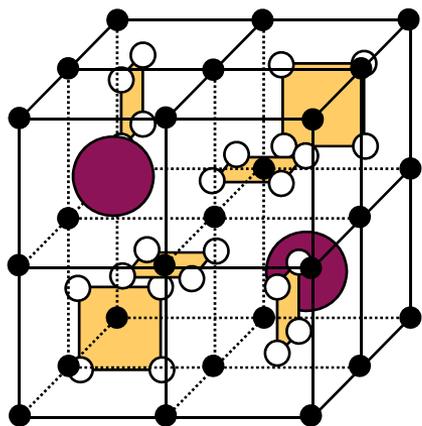
User Project with General Motors R&D Center



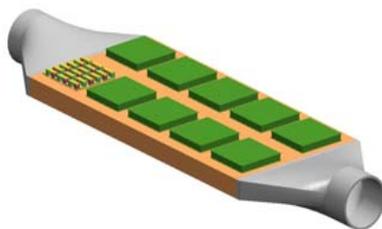
Research Problem: To determine the high-temperature transport properties of bulk thermoelectric materials including thermal conductivity, electrical resistivity and Seebeck coefficient.

Technical Approach: Work with HTML users to improve the performance of thermoelectric materials and provide critical properties at the application temperature range

Materials



Devices



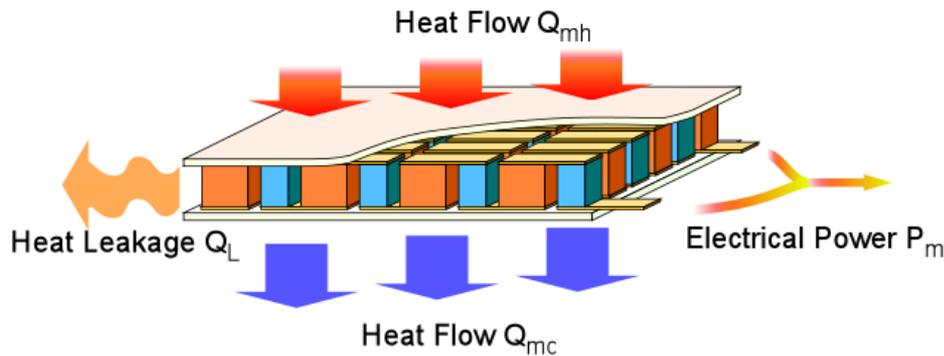
Vehicle Application



Photo courtesy of General Motors R&D Center.

Milestones

- Characterize and obtain accurate thermophysical and transport properties for thermoelectric materials during the user visit
- Jointly report via papers and presentations the results of the user project
- Build larger projects in thermoelectrics based on positive results from the user projects



User Project with General Motors R&D Center



ULVAC ZEM-3 for electrical resistivity and Seebeck coefficient



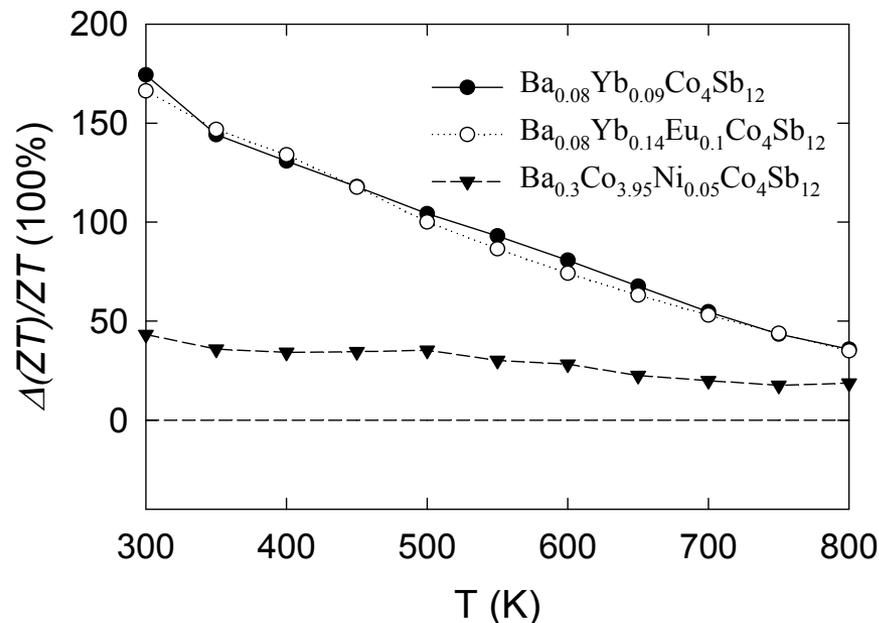
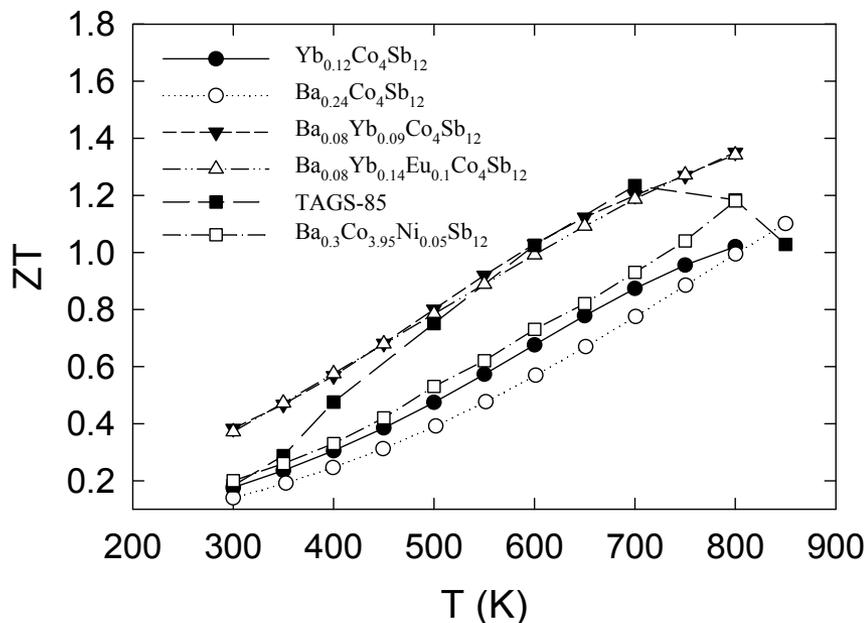
Anter flash diffusivity system for thermal conductivity measurements

Utilize the world-leading capabilities at the HTML to determine reliable thermophysical and transport properties for thermoelectric materials from 20°C to 800°C



Accomplishments

Double-filled Skutterudites Exhibit Significantly Improved Figure of Merit



- ZT: 1.36 at 800K for n-type Ba_xYb_yCo₄Sb₁₂
- Compared to single-filled skutterudites (Ba), double-filled skutterudites (Ba and Yb) exhibit more than 150% improvement at room temperature and up to 40% improvement at high temperature.

X. Shi, et al. H. Wang, *Appl. Phys. Lett.* **92**, 182101 (2008)

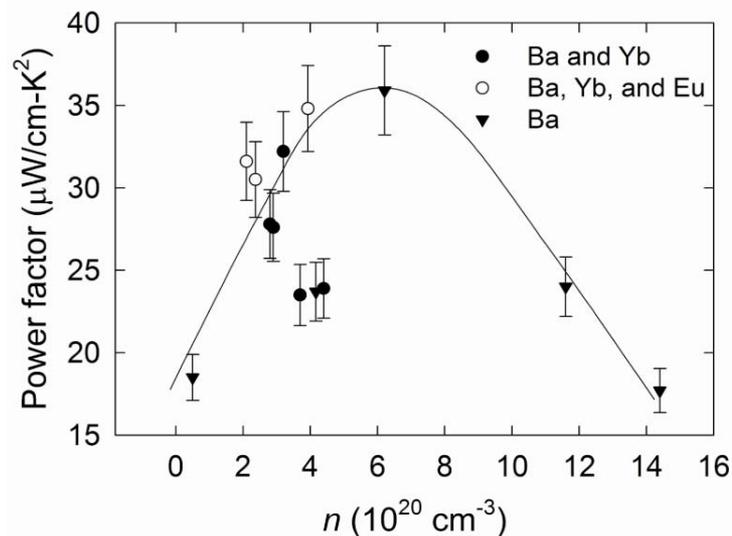
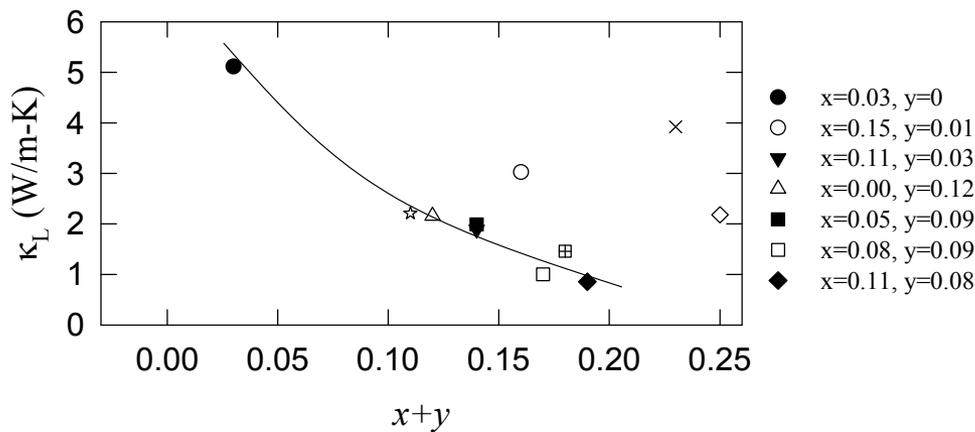
Project ID: IMP06, Wang

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Accomplishments

Double-filling leads to a significant reduction in thermal conductivity without deterioration of Power factor

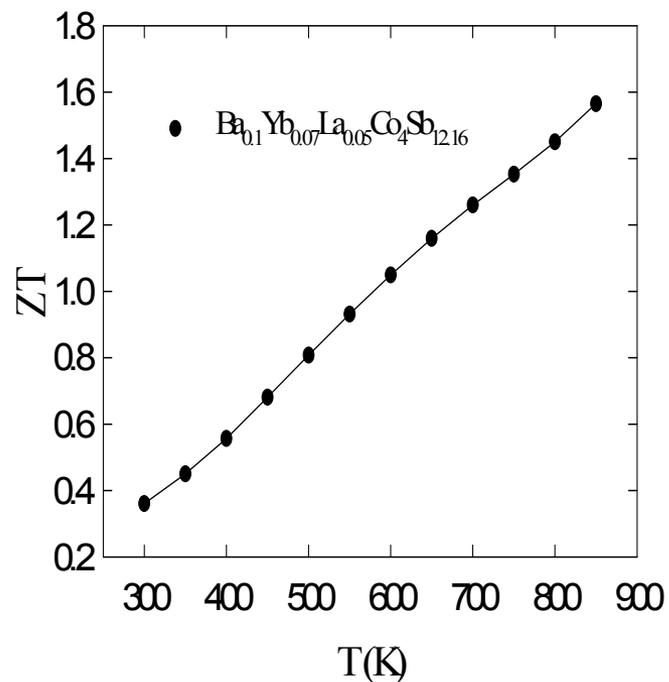
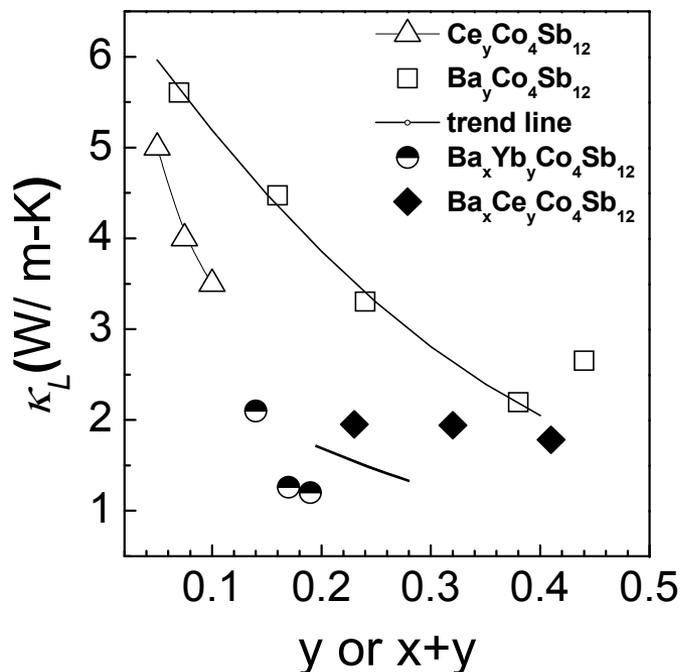


X. Shi, et al. H. Wang, *Appl. Phys. Lett.* **92**, 182101 (2008)



Accomplishments

Findings suggest that even greater reductions in thermal conductivity and increased ZT can be achieved by filling (chemically distinct) ions into the voids of the skutterudite structure.



ZT = 1.56, highest value reported in skutterudites has been obtained for triple-filled structures (Ba, Yb, La)

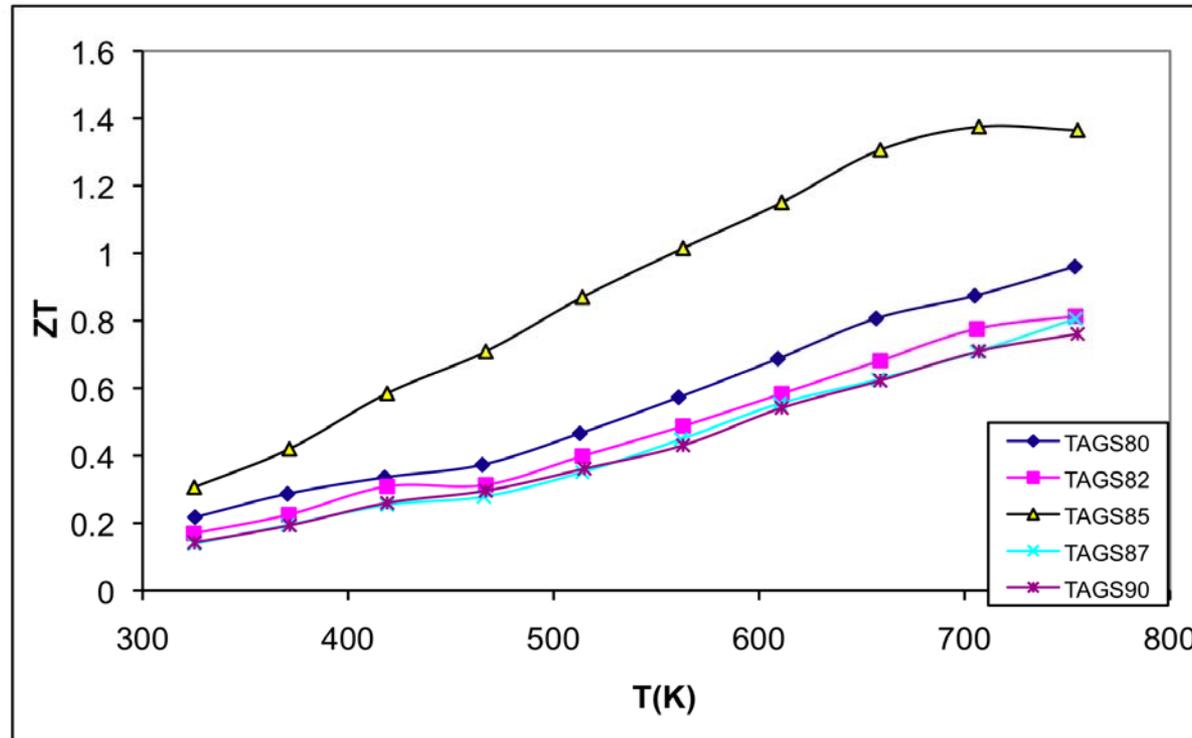
User Project with General Motors R&D Center



Accomplishments

Thermoelectric material developed by General Motors and characterized at the HTML

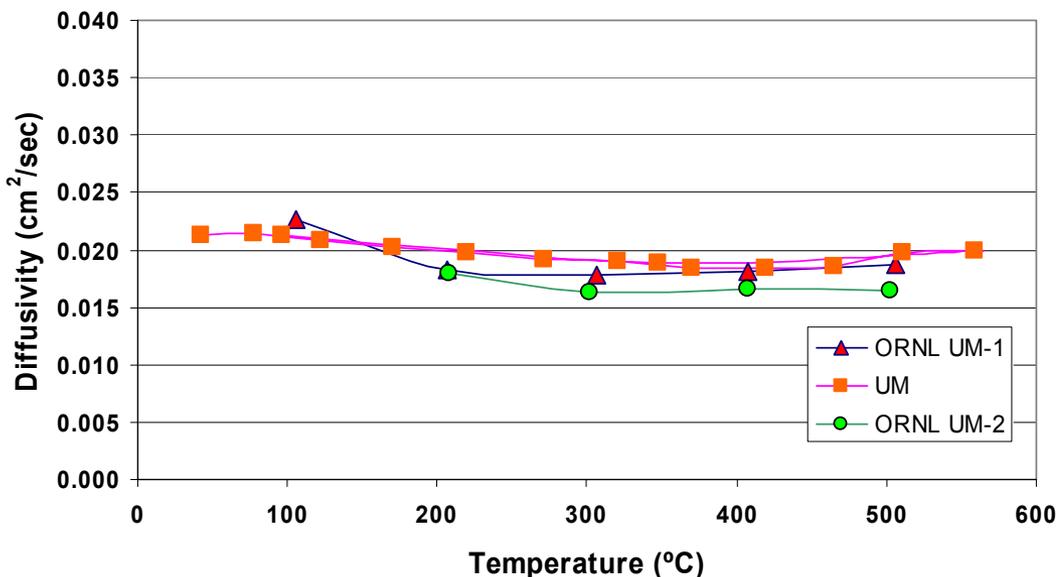
ZT of GM TAGS Reached 1.4 at 700K



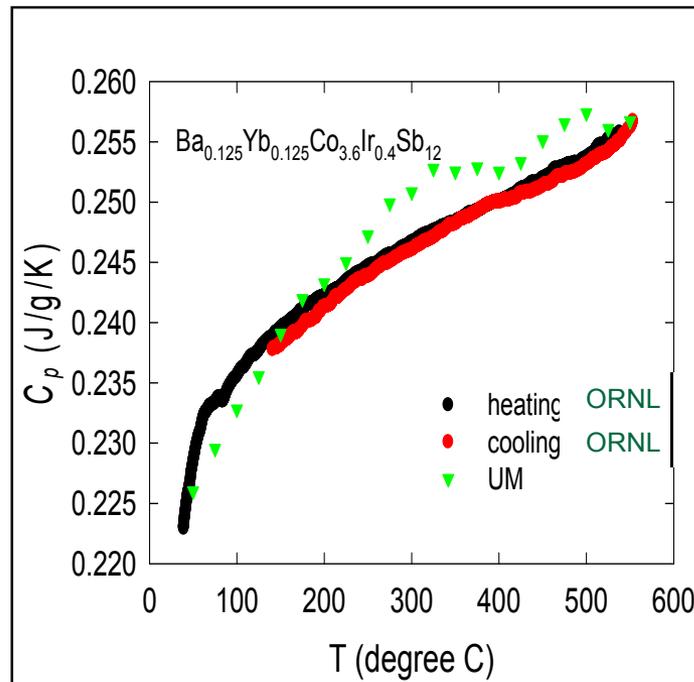


Accomplishments

Values of thermophysical properties obtained at the HTML for thermoelectric materials synthesized by General Motors are comparable to values obtained by the University of Michigan for the same materials.



Thermal Diffusivity of Double-Filled Skutterudite



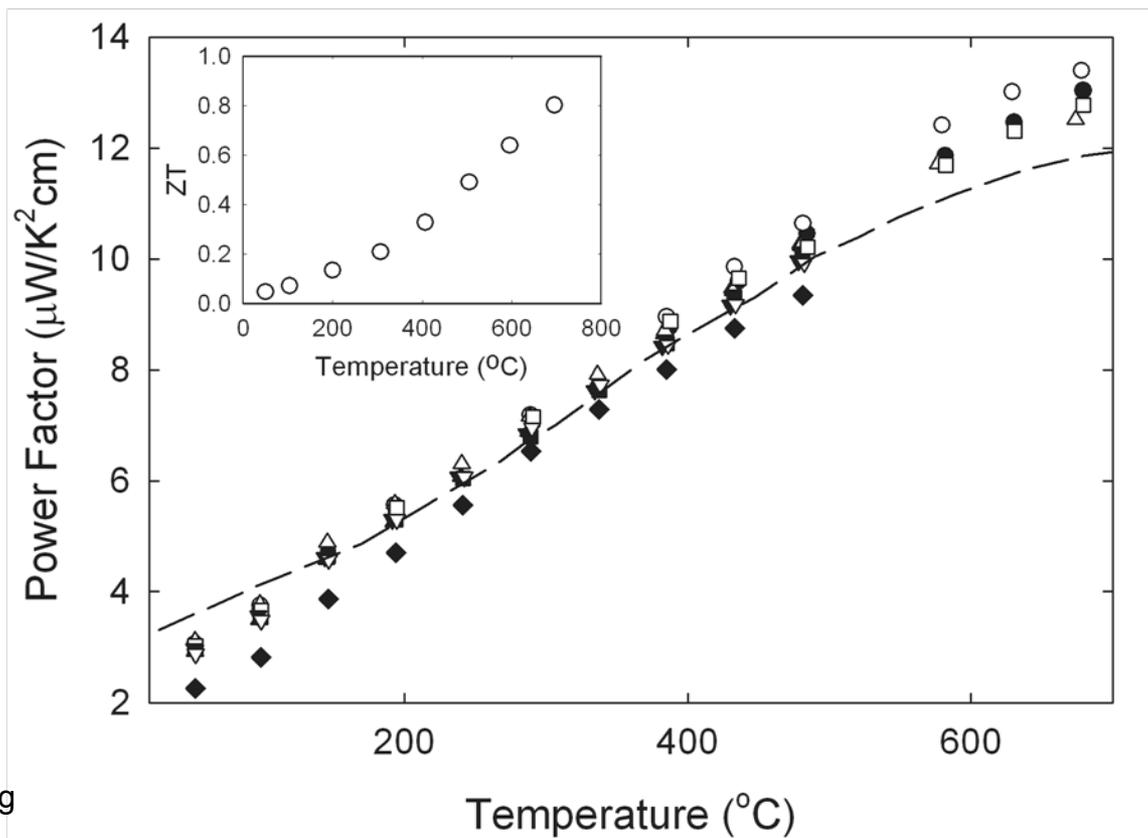
Specific Heat of Double-Filled Skutterudite

These results are relevant to establish reliable property measurements



Accomplishments

Polycrystalline BaGaGe clathrates developed at the University of South Florida showed comparable properties to those of single-crystals.



Project ID: IMP06, Wang

Martin J, Wang H, Nolas GS, "Optimization of the thermoelectric properties of Ba₈Ga₁₆Ge₃₀", *Applied Physics Letters* Volume: 92 Issue: 22 Article Number: 222110, JUNE 2008



Future Work

Utilize the world-leading characterization capabilities at the HTML (e.g.- aberration corrected electron microscope (ACEM)) to image with sub-Angstrom resolution the crystal structure of clathrates and skutterudites

- When filling the “cages” with multiple atoms, it is not clear how the atoms are distributed. ACEM is likely the best tool to answer this question. This follow-on work will help to answer some fundamental issues in thermoelectrics

Improve measurement reliability through system upgrade and through collaboration with other research labs to develop standardized testing protocols.

User Project with General Motors R&D Center Summary



- Bulk thermoelectrics developed by General Motors and its materials partners were evaluated.
- General Motors and its partners used the world-leading characterization capabilities at the HTML through the HTML User Program to determine the thermophysical and transport properties of a wide range of thermoelectric materials, including filled skutterudites and clathrates.
- The transport properties obtained through this user project have helped the GM team to select materials for waste heat power generators