International Round-Robin on Transport Properties of Bismuth Telluride

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This project is supported by the International Energy Agency (IEA) under the Implementing Agreement on Advanced Materials for Transportation (AMT) and DOE EERE VT Program - Propulsion Materials: Jerry Gibbs
Annex VIII Participants

• IEA-AMT Thermoelectric Annex
  – Annex lead: Oak Ridge National Laboratory (H. Wang)
  – USA: Clemson (T. Tritt, S. Zhu); Marlow (J. Sharp); Corning (A. Mayolet, C. Smith, J. Senawiratne) and ZT-Plus (F. Harris)
  – China: SICCAS (S.Q. Bai, L. Chen)
  – Canada: Natural Resource Canada (J. Lo); University of Waterloo (Holger Kleinke); University of Quebec at Chicoutimi (Laszlo Kiss)
  – Germany: Fraunhofer IPM (H. Böttner, J. König)

• IEA-AMT members countries:
  – UK: NPL
  – Finland: VTT (discussion on October 20)
  – Israel:
  – Australia:
  – International Observer: Korea: KERI (H. W. Lee)
Annex VIII on Thermoelectric: Oct. 2009 - present:

- Support DOE VT thermoelectric programs for vehicle applications
- Transport properties measurements
- Measurement standards and reliability
- Support the commercialization of thermoelectrics
- Annex VIII on thermoelectrics led by ORNL
  - Round robin 1: 2009-2010 on n-type and p-type bismuth telluride
  - Round robin 2: 2010-2011 on p-type bismuth telluride
  - Round robin 3: 2012 at high temperatures n-type PbTe
IEA-AMT Focus: Bulk Thermoelectrics Used for Automotive Waste Heat Recovery

- Significant gaps exist between literature ZT values and scalable materials

Possible Issues:
- Measurement errors
- No standards for calibration
- Incomplete measurements
- Data extrapolation
- Materials non-uniformity
- Orientation effect
- Measurements on different samples
Marlow Materials Selected for Transport Properties Round-Robin Tests

- Materials: $\text{Bi}_2\text{Te}_{3.005}$ (n-type) $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (p-type)

- Four-sample Sets
  - Thermal diffusivity: 12.7 mm diameter disk
  - Specific heat: 4 mm diameter disk
  - Seebeck coefficient and electrical resistivity: $2 \times 2 \times 15 \, \text{mm}^3 \, \text{bar}$, $3 \times 3 \times 12 \, \text{m}^3 \, \text{bar}$

- Temperature range: 20-200°C

- Round-robin plans:
  1. Use best practice in each lab
  2. Focusing on one specific material
  3. Develop test procedures
NIST Standards and Thermoelectrics

- Five internationally recognized standards:
  - Temperature (K); Distance (m); Current (A); Frequency (Hz) and Mass (Kg)

- Thermoelectric properties for ZT:
  - Seebeck coefficient: V/K
  - Electrical resistivity: Ohm-m
  - Thermal conductivity: (W/mK)
    - Thermal diffusivity: m²/sec
    - Specific heat: J/gK
    - Density: Kg/m³

- All TE properties are “derived”

\[
ZT = \frac{s^2 T}{\rho k}
\]
\[
k = \alpha C_p D
\]
Round-robin 1: Thermal Diffusivity

Results from 8 labs
Round-robin 1: Seebeck Coefficient

-300 -200 -100 0 100 200 300

0 50 100 150 200 250 300 350

Temperature (ºC)

Seebeck Coefficient (µV/K)

Lab #1 N 2x2
Lab #1 N 3x3
Lab #1 P 2x2
Lab #1 P 3x3
Lab #2 N 2x2
Lab #2 N 3x3
Lab #2 P 2x2
Lab #2 P 3x3
Lab #3 N 2x2
Lab #3 N 3x3
Lab #3 P 2x2
Lab #3 P 3x3
Lab #4 N 2x2
Lab #4 N 3x3
Lab #4 P 2x2
Lab #4 P 3x3
Lab #5 N1
Lab #5 N2
Lab #5 P1
Lab #5 P2
Lab #6 N 2x2
Lab #6 N 3x3
Lab #6 P 2x2
Lab #6 P 3x3
Lab #7 N 2x2
Lab #7 N 3x3
Lab #7 P 2x2
Lab #7 P 3x3
Round-robin 1: Electrical Resistivity

![Graph showing the relationship between electrical resistivity (mOhm-cm) and temperature (°C) for various labs and lab configurations.]
Round-robin 1: Specific Heat

![Graph showing specific heat vs. temperature for different laboratories and conditions.](image-url)
Round-robin #2 Started October 2010

- Procedures for DSC prepared by ORNL
- Two sets of p-type samples
  - Set #1: ORNL -> Clemson-> Corning -> ZT-Plus -> Germany -> China -> Canada
  - Set #2: China -> (Japan) -> Germany -> ORNL -> Clemson-> Corning -> ZT-Plus -> Canada
- Completed in September 2011
- Report to IEA-AMT: October 2011
- IEA-AMT Topical report November 2011
Discussion on Seebeck Measurements

![Seebeck Coefficient vs Temperature Graph](image)

- **Seebeck Coefficient** ($\mu$V/K) vs **Temperature** ($^\circ$C)
- Data from Labs 1 to 7, with Lab #1 to #7 P1-1 to P2-2
- Marlow and Contacts markers
Comments on Seebeck coefficient measurement with ZEM 3 (M10) and IPM-SR1

- **ZEM-3 (M10)**
  Configuration of measurement:

- **IPM-SR1**
  Configuration of measurement:

Assuming the real temperature gradient is the same, the temperature gradient measured with the ZEM-3 tends to be smaller than the one measured with the Fraunhofer IPM-SR1 because of the difference of configurations.
Round-robin 2: Electrical Resistivity

Electrical Resistivity

Resistivity (mOhm-cm) vs. Temperature (°C)

Legend:
- Lab #1 P1-1
- Lab #1 P1-2
- Lab #1 P2-1
- Lab #1 P2-2
- Lab #2 P1-1
- Lab #2 P1-2
- Lab #2 P2-1
- Lab #2 P2-2
- Lab #3 P1-1
- Lab #3 P1-2
- Lab #3 P2-1
- Lab #3 P2-2
- Lab #4 P1-1
- Lab #4 P1-2
- Lab #4 P2-1
- Lab #4 P2-2
- Lab #5 P1-1
- Lab #5 P1-2
- Lab #5 P2-1
- Lab #5 P2-2
- Lab #6 P1-1
- Lab #6 P1-2
- Lab #6 P2-1
- Lab #6 P2-2
- Lab #7 P1-1
- Lab #7 P1-2
- Lab #7 P2-1
- Lab #7 P2-2

Marlow
Round-robin 2: Thermal Diffusivity

Thermal Diffusivity (cm$^2$/sec) vs. Temperature (°C)
Round-robin 2: Specific Heat

![Graph showing the specific heat (Cp) as a function of temperature (°C) for different labs.](image-url)
Round Robin 3 (Spring-Summer 2012)

- Temperature range: RT-500C
- Materials n-type: lead telluride
  - Difficult to machine, especially small disk for DSC
  - Professional cutting for thermoelectrics
  - Back-up materials is n-type skutterudite

- Test Plan: Germany-> China-> US (ORNL, ZT-Plus, GMZ, Clemson, Corning) -> Canada
  - Alternate methods: Marlow, ARL
Summary

- IEA-AMT is addressing the important issue of measurement standardization of thermoelectrics.
- Significant measurement issues were observed, especially in specific heat and electrical resistivity.
- Good agreements in Seebeck coefficient, electrical resistivity.
- Thermal diffusivity in good agreement expect for one test (data analysis).
- Specific heat remains an issue for reliable ZT.
- Round-robin 3 underway.