System for the simultaneous Harman based measurement of all thermoelectric parameters from 240 K to 720 K with novel calibration procedure

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Topics

1. Introduction
2. ZT-Scanner and Bipolar Transient Harman Measurement
3. Influence of the parasitic thermal phenomena on the $ZT$ and $\lambda$ measurement
4. Novel Two Sample System Calibration (2SSC)
5. ZT-Scanner application on different TE materials
6. Accuracy and precision of measurement
7. Conclusions
Introduction

“The inherent difficulty in thermoelectrics is that direct efficiency measurements require nearly as much complexity as building an entire device”*. 

\[ ZT = T \frac{\alpha^2}{\rho\lambda} \]

* G. JEFFREY SNYDER AND ERIC S. TOBERER
Materials Science, California Institute of Technology,
nature materials | VOL 7 | FEBRUARY 2008
Separate measurements on different samples

- ULVAC ZEM-3
- NETZSCH DSC
- NETZSCH FLA

The uncertainty in $ZT$ * 50% 

The uncertainty in $ZT$ ** $\pm$ 20%

* G. JEFFREY SNYDER AND ERIC S. TOBERER
  nature materials | VOL 7 | FEBRUARY (2008)

**H. WANG, W.D. PORTER, H. BOTNER, J. KÖNIG at al,
ZT-measurement on the same sample

Fraunhofer Institute for Physical Measurement Technique IPM

IPM-ZT-Meter-870K

Measurement accuracy

\[ \alpha < \pm 5\% \]
\[ \rho < \pm 10\% \]
\[ \lambda < \pm 10\% \]
\[ ZT \pm 25\% \]
Bipolar Transient Harman Measurement

Marlow test setup

From 220 K to 525 K

R. MCCARTY, J. THOMPSON, J. SHARP, A. THOMPSON
Journal of ELECTRONIC MATERIALS,
Vol. 41, No. 6, (2012)
Bipolar Transient Harman Measurement

ZT-Scanner by TEMTE Inc.
From 240 K to 720 K

Ambitious !?

Measurement accuracy:

\[ \alpha < \pm 0.5\% \]
\[ \rho < \pm 1.0\% \]
\[ \lambda < \pm 1.0\% \]
\[ ZT < \pm 1.0\% \]
Bipolar Transient Harman Measurement*

\[ ZT = \left( \frac{\Delta V_S}{\Delta V_{\Omega}} \right) \]

\[ \alpha = \frac{\Delta V_S}{\Delta T} \quad \rho = (SF)^{-1} \times \frac{\Delta V_{\Omega}}{I_{DC}} \quad \lambda = \alpha^2 / Z\rho \]

\[ SF = A/l \quad \text{sample Shape Factor, } A \text{ – cross-section} \]

\[ l \quad \text{sample thickness} \]

* R. J. Buist, Handbook of Thermoelectrics (1995)
Influence of parasitic thermal phenomena on $ZT$ and $\lambda$ Harman measurement. The problem is well known for almost 60 years!*

the Thermoelectric Performance of
Materials and Components at High Temperature
A. Jacquot, M. Jägle, J. König, D.G. Ebling, H. Böttner, ECT2007

Figure 1: Arrangement of the sample

Derivation of the correction factor $\beta$

\[ Z_{\alpha;e} T = \frac{V_{\alpha}}{V_{\rho}} \beta \]

Method of calculation of $\beta$

The equation (7) comes also as:

\[ \frac{ZT V_{\alpha;e}}{V_{\alpha}} = a_1 a_2 V_{\alpha;\rho}^2 + a_3 + a_4 + a_5 \quad (12) \]

- $a_1$ represents the effect of the contact resistance.
- $a_2$ arises from the effect of the difference of the contact resistances.
- $a_3$ account for the heat losses along the feed lines.
- $a_4$ represents the heat radiated by the feed lines.
- $a_5$ represents the heat radiated by the sample.

Table 1b: Effect of the sample geometry and emissivity on $\beta$. The data used for the calculation are reported in the Table 1a.

<table>
<thead>
<tr>
<th>$L_{c;e}$</th>
<th>$\gamma$</th>
<th>$V_{\alpha;e} = 9.989e-4$</th>
<th>$\beta = 1.002$</th>
<th>$a_1 (\Delta r_{\gamma}) = 1$</th>
<th>$a_2 (\Delta r_{\gamma}) = 0$</th>
<th>$a_3 (\Delta r_{\gamma}) = 2e-3$</th>
<th>$a_4 (h_{\gamma}) = 0$</th>
<th>$a_5 (\varepsilon_{\gamma}) = 1,000$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 cm</td>
<td>0</td>
<td>$V_{\alpha;e} = 1,036e-3$</td>
<td>$\beta = 1.049$</td>
<td>$a_1 (\Delta r_{\gamma}) = 1$</td>
<td>$a_2 (\Delta r_{\gamma}) = 0$</td>
<td>$a_3 (\Delta r_{\gamma}) = 2e-3$</td>
<td>$a_4 (h_{\gamma}) = 4,1e-2$</td>
<td>$a_5 (\varepsilon_{\gamma}) = 1,005$</td>
</tr>
<tr>
<td></td>
<td>0,5</td>
<td>$V_{\alpha;e} = 1,061e-3$</td>
<td>$\beta = 1.095$</td>
<td>$a_1 (\Delta r_{\gamma}) = 0$</td>
<td>$a_2 (\Delta r_{\gamma}) = 2e-3$</td>
<td>$a_3 (\Delta r_{\gamma}) = 8,3e-2$</td>
<td>$a_4 (h_{\gamma}) = 1,011$</td>
<td></td>
</tr>
</tbody>
</table>

| 1 cm     | $V_{\alpha;e} = 9.866e-4$ | $\beta = 1.347$ | $a_1 (\Delta r_{\gamma}) = 1$ | $a_2 (\Delta r_{\gamma}) = 0$ | $a_3 (\Delta r_{\gamma}) = 1e-2$ | $a_4 (h_{\gamma}) = 2,07e-1$ | $a_5 (\varepsilon_{\gamma}) = 1,130$ |

| 2 cm     | $V_{\alpha;e} = 1,007e-3$ | $\beta = 1.915$ | $a_1 (\Delta r_{\gamma}) = 1$ | $a_2 (\Delta r_{\gamma}) = 0$ | $a_3 (\Delta r_{\gamma}) = 2e-2$ | $a_4 (h_{\gamma}) = 4,13e-1$ | $a_5 (\varepsilon_{\gamma}) = 1,248$ |

|          | $V_{\alpha;e} = 1,892e-3$ | $\beta = 2,710$ | $a_1 (\Delta r_{\gamma}) = 0$ | $a_2 (\Delta r_{\gamma}) = 2e-2$ | $a_3 (\Delta r_{\gamma}) = 8,27e-1$ | $a_4 (h_{\gamma}) = 2,677e-3$ | $a_5 (\varepsilon_{\gamma}) = 2,710$ |
We accepted that it is **impossible**:

- Total practical elimination of parasitic thermal phenomena
- Precise theoretical prediction of thermal interaction between the sample and its environment

We believe that it is **possible**:

- Experimental evaluation with high precision of the total impact of all parasitic phenomena for any given temperature
- Compensation of its impact by proper system calibration
Two Samples System Calibration (2SSC)

We introduced novel calibration procedure which we call 2SSC

(Two Sample System Calibration)
Two Samples System Calibration (2SSC)

Basic hypothesis

Peltier heat $\alpha TI$ during the Harman test generates a temperature difference $\Delta T$ across the sample which is inversely proportional to the thermal conductance of the sample $K_s$ and the total equivalent thermal conductance $K_p$ of all parasitic phenomena.

$$\alpha TI = \Delta T (K_s + K_p)$$

Parasitic conductance $K_p$ is the distinctive system parameter which varies with temperature but is independent of the sample size and its nature.
For two samples of the same material and the same DC electrical current

\[
\begin{align*}
\alpha TI &= \Delta T_1 (K_{s1} + K_p) \\
\alpha TI &= \Delta T_2 (K_{s2} + K_p)
\end{align*}
\]

For \( A_1 = A_2 \) and \( l_1 = n l_2 \)

Shape factors \( nSF_1 = SF_2 \)

Thermal conductances \( nK_{s1} = K_{s2} \)

Solving system for \( K_p \)

\[
K_p = K_{s1} \frac{n\Delta T_2 - \Delta T_1}{\Delta T_1 - \Delta T_2}
\]

Parasitic Thermal Conductance
1st step of the Two Samples System Calibration (2SSC)

True value ($Z$)

\[ Z = \frac{\alpha^2}{\rho \lambda} = \frac{\alpha^2}{R_{s1} K_{s1}} \]

Measured value ($Z_{\text{meas}}$)

\[ Z_{\text{meas}} = \frac{\alpha^2}{R_{s1}(K_{s1} + K_p)} \]

\[ ZT = Z_{\text{meas}} T \left( 1 + \frac{n\Delta T_2 - \Delta T_1}{\Delta T_1 - \Delta T_2} \right) \]

\[ \lambda = \lambda_{\text{meas}} / \left( 1 + \frac{n\Delta T_2 - \Delta T_1}{\Delta T_1 - \Delta T_2} \right) \]

This result needs experimental validation.
Experimental Validation of 2SSC

\[ l_1 = n l_2 \]

**PbTe Hot Extruded**  \( n=1.76 \)

<table>
<thead>
<tr>
<th>“Short”</th>
<th>“Long”</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.96 mm</td>
<td>6.98 mm</td>
</tr>
</tbody>
</table>

\[ Z_{1\text{meas}} T (1 + \frac{n \Delta T_2 - \Delta T_1}{\Delta T_1 - \Delta T_2}) = ZT = Z_{2\text{meas}} T (1 + \frac{1}{n} \frac{n \Delta T_2 - \Delta T_1}{\Delta T_1 - \Delta T_2}) \]

\[ \lambda_{1\text{meas}} / (1 + \frac{n \Delta T_2 - \Delta T_1}{\Delta T_1 - \Delta T_2}) = \lambda = \lambda_{2\text{meas}} / (1 + \frac{1}{n} \frac{n \Delta T_2 - \Delta T_1}{\Delta T_1 - \Delta T_2}) \]
Pros & Cons

Pros.
- True $ZT$ and $\lambda$ values for an unknown material
- No need in reference sample

Cons.
- Time consuming procedure
- Potential problem for preparation of two samples with the same properties

There is another option - the 2\textsuperscript{nd} step of 2SSC
With \( K_p = K_{s1} \frac{n \Delta T_2 - \Delta T_1}{\Delta T_1 - \Delta T_2} \) and \( K_{s1} = SF_1 \times \lambda \) for different \( T \), we define absolute values of \( K_p(T) \).

\( K_p(T) \) is the distinctive signature of the system (ZT-Scanner) setup.

We consider now the 1st sample as the Reference one with \( \lambda_{Ref} \equiv \lambda \).
2\textsuperscript{nd} step of the Two Samples System Calibration (2SSC)

X-sample differs from the reference one not only by the shape factor, but also by its thermal conductivity with \( K_X = n \frac{\lambda_X}{\lambda_{Ref}} K_{Ref} \)

\[
Z_X T = Z_{X,meas} T \left( 1 + \frac{1}{n} \frac{\lambda_{Ref}}{\lambda_X} \frac{K_p}{K_{Ref}} \right)
\]

\[
\lambda_X = \frac{\lambda_{X,meas}}{1 + \frac{1}{n} \frac{\lambda_{Ref}}{\lambda_X} \frac{K_p}{K_{Ref}}}
\]

Second equation can be solved for \( \lambda_X \), which then is used in the first one for true \( Z_X T \) value calculation

\[
\lambda_X = \lambda_{X,meas} - \frac{\lambda_{Ref}}{n} \frac{K_p}{K_{Ref}}
\]
Application of the ZT-Scanner with the 2SSC on different TE materials

- BiSbTe - p
- PbTe - n
- SiGe - p
- Skutterudite - n
Application of the ZT-Scanner with the 2SSC on different TE materials

Graph showing the application of the ZT-Scanner with the 2SSC on different TE materials. The graph plots ZT (ZT = zT) against temperature (T) in Kelvin (K). The materials Bi,Sb,Te EPM, Skutterudite Evident Tech., PbTe EPM, JPL ref. data, and SiGe JPL are compared. The graph indicates the thermal conductivity and thermoelectric power of these materials as functions of temperature.
Precision of Measurement

Three consecutive $\rho(T)$ and $\alpha(T)$ measurements on SiGe sample

Measurement precision

$\alpha$ - $< \pm 0.5\%$

$\rho$ - $< \pm 0.5\%$

Specific contact resistivity

PbSn solder $R_C = 6 \times 10^{-7} \ \Omega \ cm^2$

Silver Paste $R_C = 9 \times 10^{-7} \ \Omega \ cm^2$
Accuracy of Measurement

Data Acquisition by ZT-Scanner with:
Keithley 2401 power source
Agilent 34420a nano-voltmeter

Combined error on sample size (5×5×6 mm³)

Relative overestimation of ρ for
(ρ ≥ 10 μΩ m ) and $R_c = 9 \times 10^{-7} \, \Omega \, \text{cm}^2$

Accuracy of 2SSC is based on

\[ K_p = K_{s1} \frac{n\Delta T_2 - \Delta T_1}{\Delta T_1 - \Delta T_2} \, < \, \pm \, 1.0\% \]

Measurement accuracy

\[ \alpha \, < \, \pm \, 0.5\% \]
\[ \rho \, < \, \pm \, 1.0\% \]
\[ \lambda \, < \, \pm \, 1.0\% \]
\[ ZT \, < \, \pm \, 1.0\% \]

Accuracy

\[ \Delta V \, < \, \pm \, 0.1\% \]
\[ \Delta T \, < \, \pm \, 0.2\% \]
\[ SF \, < \, \pm \, 0.6\% \]
Conclusions

- Parasitic thermal interactions is not a critical factor anymore for Harman measurements

- Its impact can be properly compensated by 2SSC procedure

- \(ZT, \alpha, \rho\) and \(\lambda\) values can be defined with the accuracy of 1\% from 240K to 720K with the ZT-Scanner

- The problem with almost 60 years history of accurate Harman measurement is now solved
Conclusions

ZT-Scanner is available from TEMTE Inc.

Visit us at www.temte.ca

Contact us at info@temte.ca