An instrument for the high temperature measurement of the Seebeck coefficient and electrical resistivity

Murat Gunes¹, Macit Ozenbas²

¹Dept. of Physics, Erzincan University, Erzincan, Turkey
¹SP2M, ICMMO, University of Paris Sud 11, Orsay, France
²Dept. of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey

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Outline

- Thermoelectric Properties Measurement System
  + Temperature measurement of the Seebeck coefficient and electrical resistivity

- Example Measurement except for standard samples
  + Nanostructured Ca$_3$Co$_4$O$_9$ (C-349)

- Summary
Developments in the Measurement System

Figure 1 Timeline of vacuum chamber, sample probe designs and contact configurations.
High Temperature Seebeck Coefficient & Electrical Resistivity Measurement System

- **System Components**
  - Vacuum Chamber
  - Vacuum Pump
  - Sample Probe
  - Micro Heaters
  - Beadless Thermocouples
  - Electronics
    - Temperature Controller
    - Nanovoltmeter
    - Source Measure Unit
    - Data Acquisition card and PC

*Figure 2* Schematic illustration of the measurement system.
1. Advantages of the Sample Probe

Figure 3 General design of the sample probe.
2. Advantages of the Micro Heaters

Figure 4 A commercial Seebeck coefficient and resistivity measurement system

Figure 5 The image of a micro heater with applied current follow direction.

Magnetic Field Elimination
No need a Furnace
3. Cold-Finger Effect Elimination using Beadless Thermocouple

**Figure 6** Homemade and commercially preferred contact profile

**Figure 7 (a)** The form of common thermocouple  
**Figure 7 (b)** The form of mutually placed thermocouple  
**Figure 7 (c)** A picture of a beadless thermocouple.  
**Figure 7 (d)** Contact diagram showing the measurement points for voltages and temperature on the sample  
**Figure 7 (e)** 3-beadless thermocouple design.
4. Contact Configurations

**Figure 8** (a) and (b) The type of contacts and configurations for Seebeck coefficient and differential temperature measurements for 1SC, (c) and (d) for Seebeck coefficient and 4-point probe resistivity measurements for 2SC.
5. Differential Temperature Measurement

Figure 9 Temperature gradient created by pulsing the micro heater during heating and cooling.

Figure 10 The comparison of temperature gradient data measured via differential method ($\Delta T_1$) and the subtraction of hot and cold side temperatures ($\Delta T_2$).
Possible Temperature Profiles of the System

Step-by-step mode

Temperature (K)

Time (h)

Step-by-step mode

Temperature (K)

Time (h)
Seebeck Coefficient Measurement Method

- Integral Method (50 K gradient)
  - Curve fitting is necessary!

\[ S_{AB}(T_H) = S_B(T_H) - S_A(T_C) = \frac{dV_{AB}(T_C, T_H)}{dT} \]

- Differential Method (5 K gradient)
  - Steady state
  - Quasi steady-state

\[ \frac{\Delta V_{AB}}{\Delta T} = S_{AB}(T_o) + \Delta S_{AB}(T_o) \]

**Figure 11** The illustration of integral (left) and differential (right) methods comparison chart. J. Martin, et.al., J. Appl.Phys. 108 (2010) pp 121101
Electrical Resistivity Measurement Method

+ **2-point Probe (2pp)**
  × wire resistance is problem

+ **4-point Probe (4pp)**
  × emf should be eliminated

+ **Van der Pauw**
  × contact and thickness limited

+ **Developed Van der Pauw**
  × Axial contact
  × 4-pp
  × Non-destructive
  × Eliminate possible source of errors: thermal-emf

\[
R_{12,34} = \frac{V_{34} - V'_{34}}{2I_{av}} = \frac{(V_{IR} + V_{EMF}) - (-V_{IR} + V_{EMF})}{I_{12} - I'_{12}} = \frac{V_{IR}}{I_{av}}
\]

\[
R = \frac{R_{12,34} + R_{23,41} + R_{34,12} + R_{41,23}}{4}
\]
Reference Seebeck Coefficient Measurements
Standard Samples: Platinum and Niobium

Figure 12 Data and linear fit graphs for $\Delta V$ versus $\Delta T$ for platinum wire (a) and niobium rod (b) at room temperature. The estimated measurement error is less than 2.6 % for both Pt wire and Nb rod.
Figure 13 Temperature dependent absolute Seebeck coefficient values of platinum wire (black solid circle) and niobium rod (blue solid square) with respect to theoretical reference data. Error bars for both samples are indicated with red color.

# Reference Electrical Resistivity Measurements

**Table 1** Resistivity values of platinum wire and niobium rode. Percentage difference of measurements is calculated based on each earlier report and represented by their reference numbers.

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<thead>
<tr>
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<td>1000</td>
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Error calculation «Error in the system»

For Seebeck coefficient Measurement

Keithley-2182 Nanovoltmeter;

- For 10 mV range we have 50 ppm of reading and 4 ppm of range. Generally, we are measuring a «5 mV signal», in this case our uncertainty is;

\[50 \times 10^{-6} \times 5 \times 10^{-3} \text{V} + 4 \times 10^{-6} \times 10^{-2} \text{V}\]

that is **290 nanovolts (0.29 µV)**.

- An instrumental uncertainty of ± 290 nanovolts for each point that we measure.
- We can plot the dV vs. dT with this error (S=dV/dT). This value can be ignored when the Seebeck coefficient of material is more than **5.8 µV /K** because generally the 5 % error is acceptable in thermoelectric area.
- The temperature error is larger (typically 1 or 2K) but that will not change Seebeck coefficient, because we are calculating the slope (dV/dT). There is no any other way that we can obtain systematical errors.

For Electrical Resistivity Measurement;

Keithley-238 Current Source;

- Systematic error calculated as ± **0.46 µΩ cm** including the error contribution of K-2182 and K-238 devices together.

Ref: Keithley, Keithley 2181 and Keithley 238 device’ standart manual.
"I performed 33 measurements. I obtained a mean of 133.4 µV/K with a standard deviation 1.47 µV/K. I have a measurement error ± 0.29 µV/K. Multiplying my standard deviation with 3, and adding the measurement error, I obtained the sampling error of my measurements as ±4.70 µV/K adding and subtracting the sampling error to my mean value, I obtained my specification limits as the interval within 128.70 µV/K to 138.10 µV/K. Then I wondered how much of the observations that my interval should include. According to statistical theory, Chebyschew asserts that 89% of the observations should lie within this interval. However, if my data follows a Gaussian Distribution, I could infer that 99.7% of the observations must be within this interval. So, I performed an Anderson Darling normality test to my data, and obtained a p_value of 0.773. So, my data follows a normal distribution with high confidence, and corresponding normality test cannot be rejected at any acceptable significance level."

Mean= Average ±3*standart deviation (±*error

- Data strongly supports normal data at any acceptable significance level.
- According to the statistical theory, we can safely assert that 99.7% of the measurements are within lower and upper limits.
An instrument for the high temperature measurement of the Seebeck coefficient and electrical resistivity

Murat Gunes¹, Mehmet Parlak² and Macit Ozenbas³

¹ Micro and Nanotechnology Graduate Program, Middle East Technical University, 06800 Ankara, Turkey
² Department of Physics, Middle East Technical University, 06800 Ankara, Turkey
³ Department of Metallurgical and Materials Engineering, Middle East Technical University, 06800 Ankara, Turkey

E-mail: gunes.mu@metu.edu.tr

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Abstract
A system for the simultaneous measurement of thermoelectric power and resistivity of one and/or two samples over a temperature range of 300–1000 K in a vacuum chamber is designed and implemented. A sample probe is developed to provide its easy mounting and usage. In addition, two samples can be measured at the same time. Measurement accuracy has been enhanced by beadless thermocouples and micro-heaters that are specifically designed in order to minimize the ‘cold-finger effect’ and to eliminate some possible source of contact, design and measurement errors. A broad range of physical types and shapes of samples, such as bulk, bar or disc, can be measured by a software controlled system. A differential steady-state method has been applied for Seebeck coefficient measurement. Resistivity measurement is conducted with the axial technique of the four-point probe method. Platinum wire and a niobium rod are chosen as the standard samples. The total data error for the Seebeck coefficient and resistivity measurements is estimated to be less than 2.6% and 1%, respectively.
Nanostructured C-349

Figure 14 XRD patterns of C-349 compounds.

Figure 15 The particle size of the samples calculated using FE-SEM images vs % PEG 400 in solution.

Table 2 The result of measured and calculated particle size and density.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(%) Theoretical Density</th>
<th>Size</th>
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<tbody>
<tr>
<td>S0</td>
<td>79.5</td>
<td>2.0 µm</td>
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<tr>
<td>S3</td>
<td>74.2</td>
<td>68 nm</td>
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<tr>
<td>S5</td>
<td>72.5</td>
<td>30 nm</td>
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<tr>
<td>S7</td>
<td>66.0</td>
<td>18 nm</td>
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Ref: 10.1016/j.jallcom.2014.12.004
Figure 16  (A) Seebeck coefficient and (B) electrical resistivity measurements. (C) power factor (D) (ZT).

Ref: 10.1016/j.jallcom.2014.12.004
Summary

Table 3 The summary of improvements on high temperature Seebeck coefficient and resistivity measurement device

<table>
<thead>
<tr>
<th>High Temperature Seebeck Coefficient &amp; Resistivity Measurement Device</th>
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<tbody>
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<td><strong>System Properties</strong></td>
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<tr>
<td>Seebeck Coefficient</td>
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<td>Resistivity</td>
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<tr>
<td>Differential Temperature</td>
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<tr>
<td><strong>Measurements</strong></td>
</tr>
<tr>
<td>High</td>
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<tr>
<td>Low</td>
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<tr>
<td><strong>Error</strong></td>
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<tr>
<td>Cold-finger effect is limited to the thickness of the contact wire</td>
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<tr>
<td>External magnetic field</td>
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<tr>
<td>Thermal &amp; electrical contact</td>
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<tr>
<td><strong>Atmosphere</strong></td>
</tr>
<tr>
<td>Any inert gas</td>
</tr>
<tr>
<td><strong>Differences &amp; Achievements</strong></td>
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<tr>
<td>Simultaneously 2-sample measurement option</td>
</tr>
<tr>
<td>2- and 4-point probe resistivity measurement</td>
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<tr>
<td>Large contact area</td>
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<tr>
<td>Axial force for good thermal &amp; electrical contact</td>
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<tr>
<td>Modular</td>
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<tr>
<td>Software control</td>
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<tr>
<td>Easy to use</td>
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**Thermocouple Design**
Triple Beadless thermocouple design