Appl Phys A (2009) 96: 511–514
DOI 10.1007/s00339-009-5191-5

Applied Physics A
Materials Science & Processing

Development of a Seebeck coefficient Standard Reference Material

Nathan D. Lowhorn · W. Wong-Ng · Z.Q. Lu · E. Thomas · M. Otani · M. Green · N. Dilley · J. Sharp · T.N. Tran

Received: 17 December 2008 / Accepted: 9 February 2009 / Published online: 24 March 2009

Abstract We have successfully developed a Seebeck coefficient Standard Reference Material (SRM™), Bi_2Te_3, that is crucial for inter-laboratory data comparison and for instrument calibration. Certification measurements were performed using two different techniques on 10 samples randomly selected from a batch of 390 bars. The certified Seebeck coefficient values are provided from 10 to 390 K. The availability of this SRM will validate the measurement accuracy, leading to a better understanding of the structure/property relationships, and the underlying physics of new and improved thermoelectric materials. An overview of the measurement techniques and data analysis is given.

PACS 66.70.Df · 72.15.Jf · 72.15.Eb · 72.00.00 · 72.15.-v

N.D. Lowhorn · W. Wong-Ng (✉) · E. Thomas · M. Otani · M. Green
Ceramics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
e-mail: winnie.wong-ng@nist.gov
Fax: +1-301-975-5334

Z.Q. Lu
Statistical Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

N. Dilley
Quantum Design, San Diego, CA 92126, USA

J. Sharp
Marlow Industries, Inc., Dallas, TX 75238, USA

T.N. Tran
Naval Surface Warfare Center, Bethesda, MD 20817, USA

1 Introduction

Efficient thermoelectric materials are critical for direct energy conversion applications. Thermoelectric materials research requires evaluation of the thermoelectric figure of merit ZT given by $\alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature [1, 2]. Thermoelectric materials with desirable properties ($ZT \gg 1$) are characterized by high electrical conductivity, high Seebeck coefficient, and low thermal conductivity. Until recently, only a small number of materials have been found which have practical industrial applications because of generally low thermoelectric efficiencies. Increased attention to research and development of thermoelectric materials has been partly due to the soaring energy demand and also due to the dramatic increase of the ZT values being discovered in bulk materials and thin films.

The development of standard reference materials for thermoelectric research is essential for U.S. industries. Standard reference materials (SRM™) exist for thermal conductivity and electrical conductivity (NIST SRM™ 8420/8421-electrolytic iron and 8424/8426-graphite), and there are reliable low Seebeck coefficient materials such as Pb or Pt. However, a moderate to high Seebeck coefficient standard reference material does not exist [3]. The Seebeck coefficient is an important indicator for power conversion efficiency.

The main mission of the National Institute of Standards and Technology (NIST) is to promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology. To enable inter-laboratory data comparison and validation of measurements, we have certified a SRM™ for the Seebeck coefficient with high Seebeck coefficient values typical of those measured in this field.

A round-robin measurement survey was first conducted to determine the appropriate material and to examine different measurement techniques. Two candidate materials, constantan and undoped-Bi_2Te_3, were circulated between 12 laboratories actively involved in thermoelectric research. The details and results from this survey are presented elsewhere [4, 5]. As a result of the round-robin study, Bi_2Te_3 was chosen as the prototype SRM.

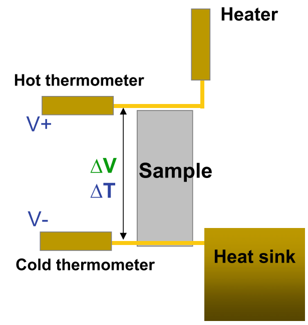

Fig. 1 A schematic of sample mounting for Seebeck coefficient measurements

2 Experimental

The SRM material, provided by Marlow Industries, is a bar-shaped sample of Te-doped Bi_2Te_3 [$(Bi_{1.998}Te_{0.002})Te_3$] which measures ($3.5 \times 2.5 \times 8.0$ mm). The ends are coated with a layer of nickel and then gold. Nickel acts as a barrier to diffusion of external material when soldering to the end of the sample. Gold provides a good surface for wetting with solder making it easier to attach leads to the sample. The materials were acquired from Marlow Industries.[1]

The Seebeck coefficient is defined as the ratio of the Seebeck voltage (ΔV) to the applied temperature gradient (ΔT). The basic concept of a typical Seebeck measurement only requires the creation of a ΔT and measurement of the ΔT and resulting ΔV. This concept is approached in many different ways by different researchers. For our certification measurements, we used two different measurement techniques which used completely different measurement software while sharing much of the same hardware.

The primary technique was a custom, steady-state, sweep technique using a modified Quantum Design Physical Property Measurement System (PPMS) (Model PPMS-9) (see footnote 1). In this technique, the sample was held at a constant temperature while a range of ΔT values were created and the corresponding ΔV values measured. Graphing this data produced a line from which the slope yielded the Seebeck coefficient. We took this a step further by stabilizing at each ΔT and measuring for a period of time. The ΔT and ΔV measurements during this time were averaged to give the final values for calculation of the Seebeck coefficient. Two 3rd party instruments had to be interfaced with the typical PPMS hardware for this technique. A Keithley 2182A nanovoltmeter (see footnote 1) was used to measure the ΔV, and a Kepco ABC125DM power supply (see footnote 1) was used to supply the heater current for creating the ΔT. Custom software was written using LabVIEW[2] to automate the measurements and data collection.

The secondary technique used the standard PPMS Thermal Transport Option (TTO) Seebeck measurement technique. This is the standard technique provided as part of the Quantum Design PPMS Thermal Transport Option (TTO). This method continuously monitors the ΔT and ΔV along the sample while supplying a heat pulse to one end and slowly varying the sample temperature. This approach gives the ability to measure the Seebeck coefficient as a function of temperature without having to wait for stability and data collection at each temperature. The steady-state values for ΔT and ΔV are found by extrapolating the data from a relatively short heat pulse.

Ten samples were selected randomly from the SRM batch of 390 received from Marlow Industries. Five of the samples were measured twice using the primary technique with the contact leads and thermometers removed and attached to the opposite end of the sample for the second measurement. The other five samples were measured once with this same technique. All ten samples were measured once using the secondary technique.

Samples were mounted in the same 2-probe configuration for both techniques. A schematic of the sample mounting configuration used for both techniques is shown in Fig. 1. The details of the sample mounting will be discussed elsewhere [6]. In summary, the sample and attached leads were mounted on the Quantum Design Thermal Transport Option puck. The hot and cold thermometer shoes, which also act as electrical probes for measuring the ΔV along the sample, were calibrated to the PPMS system thermometer prior to starting the certification measurements using the calibration routine in the Quantum Design software and TTO calibration fixture assembly. The system thermometer is calibrated to a NIST-traceable primary Cernox thermometer for low

[1]Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

[2]LabVIEW is a programming language produced by National Instruments which is commonly used for experiment control.

temperatures[3] and a NIST-traceable platinum thermometer for temperatures greater than 100 K.[4]

3 Results and discussion

The Seebeck coefficient data from the primary technique has 32 rows representing 32 temperature values for 15 measurements, each of which consists of a column of temperature values and measured Seebeck coefficient values. The mean $m(t)$ of the Seebeck coefficient is computed, along with the standard deviation $\sqrt{v(t)}$, at each of the 32 temperature values. The confidence band, which is computed based on the prescription

$$m(t) \pm c\sqrt{v(t)} \tag{1}$$

with $c = 2$, gives the nominal 95% confidence interval at each temperature value, or 95% average coverage, if averaged across different t values.

The mean Seebeck coefficient curve can be parameterized by a 4th-order polynomial,

$$m(t) = a_0 + a_1 t + a_2(t-200)^2 + a_3(t-200)^3 + a_4(t-200)^4. \tag{2}$$

Here, by the least squares estimation, the parameters a_0, a_1, a_2, a_3, a_4 are identified as −25.02319, −0.7739003, 0.001841421, 7.723781e–006, −1.065563e–009.

In addition, the variance (or standard deviation) appears to vary with the mean signal. Since the variability of CV (coefficient of variation = standard deviation divided by the absolute mean value) over temperature is within a very narrow range, being between 0.36 to 1.87%, a reasonable model for the variance function is

$$v(t) = cm(t), \tag{3}$$

where c is a constant.

The Seebeck coefficient data from the secondary technique consists of 10 measurement curves with many more temperature values compared to the data from the primary technique. The primary custom sweep SRM measurements have only 32 temperature values while there are more temperature measurements for the secondary TTO SRM data. The most effective way to analyze these data sets was to focus on the 32 temperature values and use interpolated values from the TTO SRM data for comparison and combined mean analysis. S-plus[5] has a function, called *approx*, which allows us to calculate the interpolation based on a simple linear interpolation routine. One can also compute the mean and standard deviation of the Seebeck coefficient data based on the derived data matrix.

[3]NIST-traceable primary Cernox thermometer for low temperatures.

[4]NIST-traceable platinum thermometer for temperatures greater than 100 K.

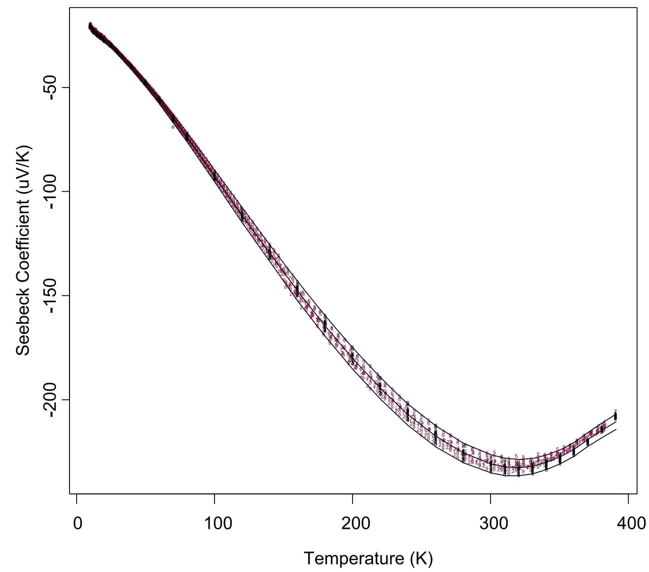

Fig. 2 Plot of data from primary technique (*dots in black*), secondary technique (*dots in red*), and final mean and 95% confidence band (*solid lines in black*)

The measurement results of the two techniques agree very well with each other. The primary and secondary SRM data can be combined to produce a final mean and uncertainty (Fig. 2, Table 1). We can also fit a parametric model to the final mean value by a 4th-order polynomial,

$$m(t) = a_0 + a_1 t + a_2(t-200)^2 + a_3(t-200)^3 + a_4(t-200)^4. \tag{2}$$

Here, by the least squares estimation, the parameters a_0, a_1, a_2, a_3, a_4 are identified as −27.55699, −0.7653341, 0.00201416, 7.443016e–006, and −5.758658e–009. It is noted that the 4th-order polynomial model used in this paper gives a better fit for the mean SRM data than the parametric model used early in our round-robin study [4, 5]. In addition, the data from the two measurement techniques are very similar, as evidenced from a t-test based on the two data sets at each of the 32 temperature values. There is only one t-ratio value outside the pre-specified 95% confidence band, assuming the null hypothesis of no difference between the

[5]S-plus is a trademark of Insightful Corporation. Mention of a software product in this paper is only to illustrate and to make explicit the statistical procedures used in our data analysis, and does not imply in anyway the endorsements of NIST, nor that the product is the best available for the purpose.

Table 1 Certified reference values for SRM 3451

Temperature (K)	Seebeck coefficient (μV/K)	Expanded Uncertainty (coverage factor = 2)
10.09	−20.82	1.08
12.58	−23.02	1.05
15.01	−24.56	1.00
17.60	−25.89	1.03
20.09	−27.27	0.93
25.10	−29.94	0.89
30.11	−33.42	0.85
40.14	−40.50	1.05
50.16	−48.13	1.32
60.25	−56.50	1.74
70.29	−65.20	2.63
80.32	−74.17	2.47
100.34	−92.83	3.33
120.36	−111.79	4.13
140.37	−129.79	4.85
160.40	−147.97	5.59
180.41	−164.81	5.95
200.43	−180.37	6.20
220.48	−194.56	6.37
240.51	−207.33	6.18
260.52	−217.65	6.18
280.70	−225.67	5.81
300.73	−230.82	5.38
310.74	−232.28	5.19
320.74	−232.61	4.71
330.87	−231.89	4.35
340.84	−229.96	3.96
350.81	−227.33	3.67
360.76	−223.75	3.54
370.89	−218.94	3.53
381.04	−214.62	3.70
391.00	−210.58	3.94

two measurement methods. Given that there are 32 temperature values being considered, the probability of having at least one value outside the confidence band is very common, with probability 0.806. Therefore, we conclude that there is no significant difference between these two measurement techniques.

For additional information, the resistivity values of these samples, which were obtained using a conventional four probe technique, were determined to be 0.63 and 1.26 Ω at 200 and 300 K. The carrier concentration at 200 K is 1.61×10^{19} cm^{-3} using a Hall measurement technique [7].

4 Conclusion

In conclusion, we have certified an important Standard Reference Material for low temperature Seebeck coefficient measurements. This SRM is currently in production and will be made available to the public in the near future. The availability of this SRM will improve and validate measurement accuracy, leading to a better understanding of the structure/property relationships and the underlying physics of new and improved thermoelectric materials.

References

1. T.M. Tritt, M.A. Subramanian (eds.), *Thermoelectric Materials, Phenomena, and Applications: A Bird's Eye View, Harvesting Energy through Thermoelectrics: Power Generation and Cooling*. MRS Bulletin, Materials Research Soc. (2006), pp. 188–195
2. G.S. Nolas et al., *Thermoelectrics: Basic Principles and New Materials Developments* (Springer, New York, 2001)
3. NIST Standard Reference Materials Home Page. http://ts.nist.gov/ts/htdocs/230/232/232.htm
4. N.D. Lowhorn, W. Wong-Ng, Z.Q.J. Lu, W. Zhang, E. Thomas, M. Otani, M. Green, T.N. Tran, C. Caylor, N. Dilley, A. Downey, B. Edwards, N. Elsner, S. Ghamaty, T. Hogan, Q. Jie, Q. Li, J. Martin, G. Nolas, H. Obara, J. Sharp, R. Venkatasubramanian, R. Willigan, J. Yang, T. Tritt, Appl. Phys. A **94**, 231–234 (2009)
5. Z.Q.J. Lu, N.D. Lowhorn, W. Wong-Ng, W. Zhang, E. Thomas, M. Otani, M. Green, T.N. Tran, C. Caylor, N. Dilley, A. Downey, B. Edwards, N. Elsner, S. Ghamaty, T. Hogan, Q. Jie, Q. Li, J. Martin, G. Nolas, H. Obara, J. Sharp, R. Venkatasubramanian, R. Willigan, J. Yang, T. Tritt, J. Res. Natl. Inst. Stand. Tech. **114**(1), 37–55 (2009)
6. N.D. Lowhorn, W. Wong-Ng, Z.Q. Lu, E. Thomas, M. Otani, M. Green, N. Dilley, J. Sharp, T.N. Tran, J. Res. Natl. Inst. Stand. Tech. (2008 to be submitted)
7. NIST website on Hall effect measurements. http://www.eeel.nist.gov/812/hall.html