National Institute of Standards & Technology

Certificate

Standard Reference Material® 3451

Low-Temperature Seebeck Coefficient Standard (10 K to 390 K)

This Standard Reference Material (SRM) is intended primarily for use in calibrating Seebeck coefficient measurement equipment (for bulk materials) in the temperature range 10 K to 390 K. A unit of SRM 3451 consist of a bar-shaped artifact (approximately 3.5 mm × 2.5 mm × 8.0 mm) of non-stoichiometric bismuth telluride (n-type, Te rich, Bi/Te mole ratio approximately 2/3, formula Bi_2Te_{3+x}).

Certified Values and Uncertainties: A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [1]. Certified values were obtained using a differential steady-state (DC) technique on a Quantum Design Physical Property Measurement System (PPMS) and can be found in Table 1.

Uncertainty analysis was conducted in accordance with recommendations contained in the ISO Guide [2]. Uncertainties associated with the results of the Seebeck coefficient measurements were categorized as components that can be evaluated statistically (type A) and those that cannot (type B). Type A components include sample-to-sample variations and non-systematic voltage and/or thermal offsets that are best treated statistically based on our combined series of measurements, while type B components are systematic in origin and derive from instrumentation, data acquisition, and thermometer calibration errors, arising from the measurement of the hot and cold temperatures and the electric potential. To derive the Seebeck coefficient uncertainty component for the average base temperature, the Seebeck coefficient data was parameterized, and the derivative of this Seebeck coefficient data, $S_m(T)$, multiplied by the base temperature and the combined uncertainty for individual temperatures. The final combined standard uncertainty for the Seebeck coefficient is the root sum of squares of the combined type A and type B uncertainty components. The expanded uncertainty intervals were obtained by multiplying the combined standard uncertainty by $k = 2$, i.e., $S_m \pm k\sigma$, under the normal distribution assumption.

Expiration of Certification: The certification of **SRM 3451** is valid, within the measurement uncertainty specified, until **01 September 2021**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). This certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The overall direction and coordination of the technical measurements leading to the certification of this SRM were performed by W. Wong-Ng and N. Lowhorn of the NIST Ceramics Division.

Statistical analysis was provided by J. Lu of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

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Ceramics Division

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Gaithersburg, MD 20899
Certificate Issue Date: 13 October 2011

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Storage: SRM 3451 should be stored in a low-moisture environment (e.g., a desiccator), in the container provided.

Handing and Use: Seebeck coefficient measurements should be performed in a vacuum cryostat ($<10^{-5}$ Pa), using appropriate thermal gradient control and voltage instrumentation, by mounting the artifact in a two-probe arrangement, with one probe connected to each coated end of the artifact with solder. These connections should allow for the attachment of both a thermometer and voltage probe. In addition, a heater should be connected to one of these probes, while the other is connected to a heat sink. For additional details see Figure 1 [4].

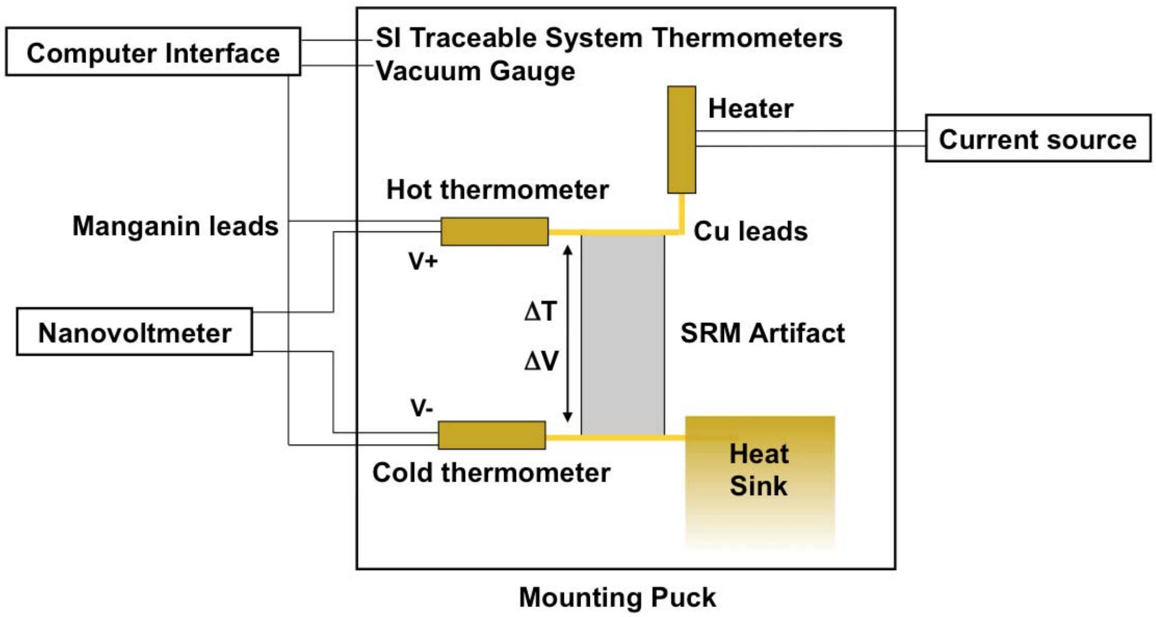

Figure 1. Schematic depicting SRM artifact mounting for Seebeck coefficient measurement

SOURCE, PREPARATION, AND ANALYSIS[(1)]

SRM 3451 was custom prepared involving ingot solidification, cutting, and polishing of the bar-shaped pieces and metal coating of their ends by Marlow Industries, Inc.

The Seebeck effect is the conversion of a temperature difference, ΔT, maintained between the two interfaces formed of two dissimilar conductors (i.e., the artifact and the lead wires), into an electric potential, $\Delta V = V^{+} - V^{-}$, where V^{+} is measured at the hot thermometer. The voltage produced is directly proportional to the temperature difference, and the proportionality constant, S, is defined as the Seebeck coefficient: $\Delta V = S\Delta T$.

Measurement Procedure: Certification measurements were obtained using a differential steady-state (DC) technique [3]. Ten artifacts were selected randomly from the batch received from the manufacturer. Five of these artifacts were measured once. The remaining five artifacts were measured twice: for the second measurement, the contact leads were removed and reattached on the opposite ends of the artifacts. Thus, a total of 15 data sets were obtained. Measurements were performed under a vacuum of $<10^{-5}$ Pa. During the measurements, each artifact was maintained at a constant base temperature while a range of ΔT values ($\Delta T \leq 0.01T$) were applied, and the corresponding ΔV values measured. For each ΔT, the artifact was stabilized for a period ranging from 25 s to 400 s, depending on the base temperature. Corresponding ΔT and ΔV measurements were then made over an additional time period of 25 s to 100 s and averaged over that period. The time-averaged values of ΔV were plotted as a function of the corresponding ΔT for each base temperature; the Seebeck coefficient was derived from the unconstrained linear fit of these data. This method of fitting the data, obtained from multiple ($\Delta T, \Delta V$) measurements, avoids the assumption that any given data point and the origin ($\Delta V = 0$, $\Delta T = 0$) are collinear, thus effectively eliminating any offset voltage. The mean Seebeck coefficient (S_m) was then computed at each base temperature using the values obtained from the unconstrained linear fit for each of the fifteen data sets. S_m is defined as the certified Seebeck coefficient [4].

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

The thermometers were calibrated by the manufacturer, Quantum Design, using a NIST-traceable thin film resistance thermometer (for temperatures <100 K) and a NIST-traceable platinum thermometer (for temperatures >100 K). The electric potential measurement instrument was calibrated by the manufacturer, Keithley Instruments, with NIST-traceable standards.

The NIST certified Seebeck coefficient values (S_m) for SRM 3451, type A (σ_A) and type B (σ_B) uncertainty components, the combined standard uncertainty (σ), and the expanded uncertainty are listed in Table 1 in units of µV/K.

In order for the user to obtain the Seebeck coefficient of the artifact at temperatures in between the 32 base temperature values at which it was measured, the 32 (S_m, T) data points (Table 1) can be fit to a fourth order polynomial function, expanded around a temperature A:

$$S_m(T) = S_A + aT\left(1-\frac{A}{T}\right) + bT^2\left(1-\frac{A}{T}\right)^2 + cT^3\left(1-\frac{A}{T}\right)^3 + dT^4\left(1-\frac{A}{T}\right)^4 \qquad (1)$$

where $S_m(T)$ is the interpolated value of the Seebeck coefficient and $10\ \text{K} \le \text{A} \le 391\ \text{K}$. As an example, if A is chosen for utility to be approximately room temperature (295 K), the following values are found for the fitting coefficients:

$$\begin{aligned} a &= -2.2040 \times 10^{-1}\ \mu\text{V/K}^2 \\ b &= 3.9706 \times 10^{-3}\ \mu\text{V/K}^3 \\ c &= 7.2922 \times 10^{-6}\ \mu\text{V/K}^4 \\ d &= -1.0864 \times 10^{-9}\ \mu\text{V/K}^5 \end{aligned}$$

Further, $S_A = -230.03$ µV/K and $R^2 = 0.99994649$. Expansion of equation 1 around other values of A led to insignificant differences in interpolated values over the entire temperature range. Figure 2 is a plot of equation 1 for A = 295 K.

The Seebeck coefficient uncertainty for any interpolated temperature value is given approximately by the expanded uncertainty value at a nearby measured temperature value (Table 1).

Table 1. Certified Seebeck Coefficients for SRM 3451

Temperature (K)	Seebeck Coefficient, S_m, (μV/K)	Type-A Uncertainty σ_A (μV/K)	Type-B Uncertainty σ_B (μV/K)	Combined Standard Uncertainty σ[(a)] (μV/K)	Expanded Uncertainty[(b)] (μV/K)	Coefficient of Variation[(c)]
10.09	–20.83	0.39	0.18	0.43	0.85	0.021
12.58	–22.98	0.47	0.2	0.52	1.03	0.022
15.1	–24.56	0.41	0.22	0.47	0.93	0.019
17.6	–25.95	0.42	0.23	0.48	0.96	0.018
20.09	–27.3	0.25	0.24	0.35	0.71	0.013
25.1	–29.79	0.35	0.27	0.44	0.88	0.015
30.11	–33.36	0.17	0.30	0.35	0.7	0.010
40.14	–40.42	0.27	0.37	0.46	0.92	0.011
50.16	–48.01	0.39	0.44	0.59	1.18	0.012
60.25	–56.26	0.60	0.52	0.80	1.60	0.014
70.29	–65.28	0.93	0.61	1.11	2.22	0.017
80.33	–74.1	0.94	0.69	1.17	2.34	0.016
100.34	–92.79	1.30	0.88	1.57	3.13	0.017
120.37	–111.6	1.69	1.06	1.99	3.99	0.018
140.38	–129.6	1.95	1.23	2.31	4.61	0.018
160.4	–147.22	2.21	1.39	2.61	5.22	0.018
180.41	–163.81	2.41	1.53	2.85	5.70	0.017
200.43	–179.4	2.61	1.65	3.09	6.19	0.017
220.49	–193.96	2.71	1.76	3.23	6.46	0.017
240.52	–206.22	2.73	1.84	3.03	6.59	0.016
260.52	–217.26	2.73	1.91	3.33	6.66	0.015
280.71	–226.11	2.64	1.95	3.28	6.56	0.015
300.73	–231.36	2.43	1.98	3.13	6.26	0.014
310.74	–232.82	2.27	1.98	3.01	6.03	0.013
320.74	–233.48	2.08	1.98	2.87	5.75	0.012
330.87	–232.99	1.81	1.98	2.68	5.37	0.012
340.84	–231.45	1.55	1.98	2.51	5.02	0.011
350.81	–228.93	1.26	1.97	2.34	4.67	0.010
360.76	–225.28	1.03	1.96	2.21	4.42	0.010
370.9	–220.43	0.80	1.94	2.10	4.21	0.010
381.04	–214.58	0.79	1.93	2.08	4.16	0.010
391	–208.17	0.90	1.92	2.12	4.23	0.010

[(a)] The total Seebeck coefficient measurement uncertainty is $\sigma = (\sigma_A^2 + \sigma_B^2)^{1/2}$.
[(b)] Expanded uncertainty is calculated as $k\sigma$, with coverage factor, k, and $k = 2$.
[(c)] Coefficient of variation is σ/S_m.

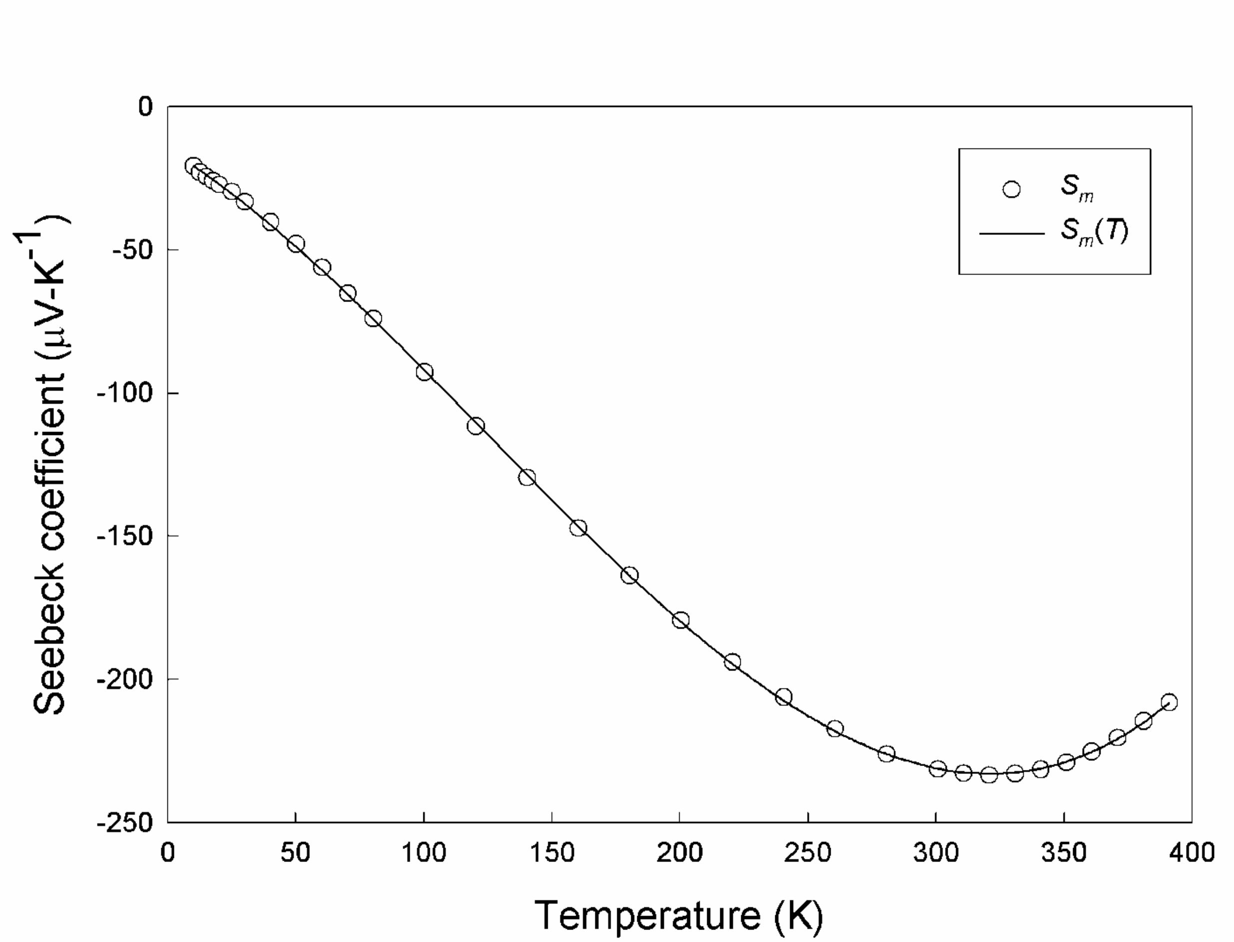

Figure 2. Fourth-order polynomial fit to the measured data (Table 1)

REFERENCES

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[2] JCGM 100:2008; *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement*; (ISO GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Oct 2011); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at http://www.nist.gov/pml/pubs/index.cfm (accessed Oct 2011).

[3] Martin, J.; Tritt, T.; Uher, C.; *High temperature Seebeck coefficient metrology*; J. Appl. Phys., Vol. 108, No. 12 (2010).

[4] Lowhorn, N.D; Wong-Ng, W; Lu, Z.Q.; Martin, J.; Green; M.L.; Thomas, E.L.; Bonevich, J.E.; Dilley, N.R.; Sharp, J.; *Development of a Seebeck Coefficient Standard Reference Material (SRM)*; J. Mater. Res., Vol. 26 (15), pp.1983-1992 (2011).

Users of this SRM should ensure that the Certificate in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.