National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 3452

High-Temperature Seebeck Coefficient Standard (295 K to 900 K)

This Standard Reference Material (SRM) 3452 is intended primarily for use in instrument validation and interlaboratory data comparison in the temperature range of 295 K to 900 K to support the research, development, and production of materials and devices related to thermoelectric based energy conversion applications. The Seebeck coefficient is the proportionality constant that quantifies the thermoelectric energy conversion of an applied temperature difference into an electric potential [1,2]. A unit of SRM 3452 is a bar-shaped artifact (with nominal dimensions of 2.5 mm x 2.5 mm x 14.0 mm) of p-type boron-doped polycrystalline silicon-germanium (with a nominal composition of $Si_{80}Ge_{20}$).

Certified Values: Certified values are provided in Table 1. Data sets described in the Measurement Procedure section were used to determine the certified Seebeck coefficient values and the measurement uncertainty using the opensource software environment for statistical computing, R [3], and the generic function for linear models *lm*(). 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 [4].

Expiration of Certification: The certification of SRM 3452 is valid, within the measurement uncertainty specified, until **01 September 2030**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see “Instructions for Handling, Storage, and Use”). The certification is nullified if the SRM is damaged, contaminated, improperly stored, 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 or register online) will facilitate notification.

Coordination of the production and measurements leading to the certification of this SRM was performed by J. Martin and W. Wong-Ng of the NIST Materials Measurement Science Division. Instrumentation, development and execution of measurement protocols, and Type B uncertainty analysis were conducted by J. Martin.

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

Support aspects involved in the issuance of this SRM were coordinated through the Office of Reference Materials.

David Holbrook, Chief
Materials Measurement Science Division

Gaithersburg, MD 20899
Certificate Issue Date: 04 February 2021

Steven J. Choquette, Director
Office of Reference Materials

Certified Values Analysis: An expanded quadratic polynomial model was used to fit the measured data sets, described in the Measurement Procedures section, for curve analysis:

$$S_m(T) = S_A + a(T - 295) + b(T - 295)^2 \tag{1}$$

where $S_m(T)$ is the value of the artifact Seebeck coefficient at temperature T, a and b are the coefficients for the linear and quadratic terms, respectively, and 295 is the temperature around which the polynomial is expanded, such that S_A is the Seebeck coefficient value at 295 K. This form allows physical interpretation for the units of the coefficients: μV/K for S_A and $\mu V/K^{i+1}$ for each coefficient a and b, where i is the degree of the corresponding term.

Analysis of covariance (ANCOVA), a hybrid of the analysis of variance model and regression analysis [5,6], was applied to generate parameter estimates, provide an analysis of variance for the function data, and assess which variant of the model parameters and interaction terms was the most appropriate to describe the measured data. The quadratic polynomial model was then fit to each artifact data set. The coefficient values for the intercept and linear terms were given directly by the model output. Based on the analysis of covariance, the coefficient for the quadratic term was defined as common for the combined data set. The mean coefficient values were obtained by the mean of each regression coefficient:

$S_A = 1.162\,467\,64 \times 10^{2}$ μV/K,
$a = 2.343\,158 \times 10^{-1}$ $\mu V/K^2$
$b = -8.781\,594 \times 10^{-5}$ $\mu V/K^3$.

Since the Seebeck coefficients were measured at marginally dissimilar base temperatures, a set of shared temperatures were defined common to all artifact curves between 295 K and 900 K. The certified Seebeck coefficient values were computed at these defined temperatures using the quadratic polynomial model (equation 1) and the mean coefficient values.

Uncertainty Analysis: Uncertainty analysis was conducted in accordance with the procedures and definitions contained in the Guide to the Expression of Uncertainty in Measurement (GUM) [7] and the NIST Technical Note 1900 [8]. Uncertainties associated with the results of the Seebeck coefficient measurements were categorized as components that can be evaluated by the application of statistical methods to experimental data (Type A) and evaluations that are not derived from repeated observations (Type B). The Type A uncertainty was calculated using the covariance matrix for the fitted model coefficients S_A, a, and b. The covariance matrix comprises two component covariance matrices: M_1, the variance-covariance matrix of the coefficient parameters from the least square fit of the quadratic polynomial model; and M_2, the sample covariance matrix from the six sets of coefficient vectors that represent the sample-to-sample variability. The final covariance matrix is the sum $M_F = M_1 + M_2$. The variance of the fitted quadratic model prediction values is then given by:

$$var[S_m(T)] = \begin{bmatrix} 1 & (T-295) & (T-295)^2 \end{bmatrix} M_F \begin{bmatrix} 1 \\ (T-295) \\ (T-295)^2 \end{bmatrix} \tag{2}$$

The Type A standard uncertainty components for the certified Seebeck coefficient values are obtained as the square root of the variance function $var[S_m(T)]$.

The primary Type B standard uncertainty sources include: the thermocouple accuracy, the measurement of the T_1 and T_2 thermocouple voltages that determine the temperature difference, the interpolation of the platinum wire Seebeck coefficient correction, the reference temperature to reference voltage conversion, the two thermocouple voltage to temperature conversions, the calibrated platinum resistor reference temperature accuracy, and the thermoelectric voltage measurement.

The Type A and Type B standard uncertainty components are combined using the root-sum-of-the-squares (RSS) method for a total uncertainty, u_c. The total expanded uncertainty for the certified Seebeck coefficient values is $\pm k u_c$ with a normal distribution coverage factor $k = 2$ for an approximately 95 % confidence interval (Table 1). Figure 1 plots the Certified Seebeck coefficient values, the individual Seebeck coefficient values for each of the six artifact curves, the mean quadratic polynomial regression, and the expanded uncertainty intervals. The uncertainty for any Seebeck coefficient value interpolated between the discrete certification temperatures (obtained using equation 1 and the mean coefficient values) is given approximately by the uncertainty value at a proximate certified temperature value in Table 1. The relative expanded uncertainty $[2u_c/S_m(T)]$ is ≈ ± 3 % for all temperatures.

Table 1. Certified Seebeck Coefficient Values, Type A and Type B Uncertainty Components, the Total Uncertainty, and the Expanded Uncertainty (*k* = 2) as a Function of Defined Temperature

Temperature (K)	Certified Values (μV/K)	Type A Uncertainty (μV/K)	Type B Uncertainty (μV/K)	Total Uncertainty (μV/K)	Expanded Uncertainty (μV/K)
295	116.25	1.24	1.33	1.82	3.63
350	128.87	1.34	1.48	1.99	3.99
400	139.88	1.44	1.60	2.16	4.31
450	150.46	1.55	1.72	2.32	4.63
500	160.59	1.66	1.84	2.48	4.95
550	170.29	1.77	1.95	2.63	5.26
600	179.54	1.88	2.05	2.78	5.57
650	188.36	1.99	2.15	2.93	5.86
700	196.74	2.11	2.24	3.08	6.15
750	204.68	2.22	2.33	3.22	6.44
800	212.18	2.34	2.41	3.36	6.72
850	219.24	2.46	2.48	3.49	6.99
900	225.87	2.58	2.55	3.63	7.26

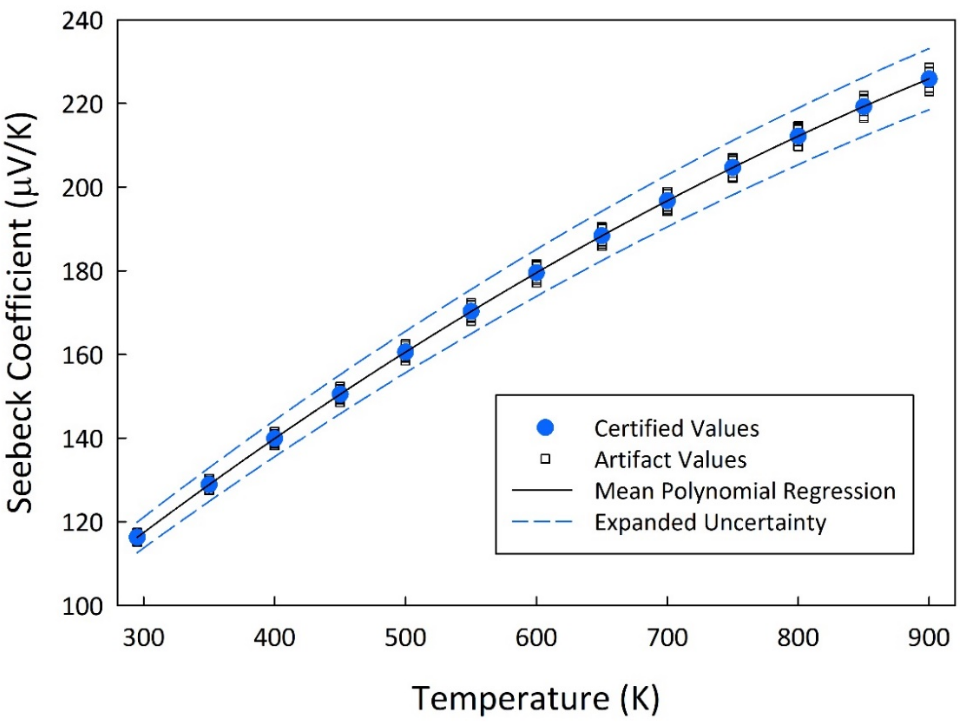

Figure 1. The Certified Seebeck coefficient values, the individual Seebeck coefficient values for each of the six artifact curves, the mean quadratic polynomial regression, and the expanded uncertainty intervals.

METROLOGICAL TRACEABILITY:[1]

The 78 measured Seebeck coefficient data points comprise 78 reference temperature voltage measurements, 3,120 thermoelectric voltage measurements, and 6,240 thermocouple voltage measurements (one each for the hot and cold thermocouple voltage for T_2 and T_1, respectively, that determine the temperature difference ΔT), for 9,438 unique voltage measurements in total. Prior to certification measurements, all three Keithley 2182A Nanovoltmeters were calibrated (accredited) by Keithley (a Tektronix Company) using measurement standards traceable to the International System of Units (SI) through the National Institute of Standards and Technology (NIST) and meets the requirements of the International Organization for Standardization/International Electrotechnical Commission (ISO/IEC) 17025:2005 and American National Standard Institute/National Conference of Standards Laboratories (ANSI/NCSL) Z540.3-2006. The quality system is registered to ISO 9001. The SRM 3452 certification measurements were conducted within 8 months post calibration, such that the Type B uncertainty components were obtained using the one-year post-calibration accuracy values in the manufacturer's published specifications.

The reference temperature was measured using a calibrated platinum resistor (Lake Shore Cryotronics, Inc. Model PT-103-AM-70H). The platinum resistor was calibrated in the temperature range 70.0 K to 500 K. This temperature sensor has been calibrated to the International Temperature Scale of 1990 (ITS-90) or the Provisional Low Temperature Scale (PLTS-2000) as appropriate. The calibrations are traceable to the National Institute of Standards and Technology, the National Physical Laboratory (NPL, United Kingdom), the Physikalisch-Technische Bundesanstalt (PTB, Germany), or natural physical constants. Lake Shore Cryotronics, Inc. maintains ITS-90 and PLTS-2000 on standard platinum (PRT), rhodium-iron (RIRT), and germanium (GRT) resistance thermometers that have been calibrated directly by an internationally recognized national metrology institute (NIST, NPL, PTB) for $T < 330$ K or an ISO 17025 accredited metrology laboratory for $330 \text{ K} < T < 800$ K. These standards are routinely intercompared to verify consistency and accuracy of the temperature scale. The sensor calibrations are performed by comparison to laboratory standard resistance thermometers and tested in accordance with Lake Shore Cryotronics, Inc. Quality Assurance Manual. The quality system of Lake Shore Cryotronics Inc. is registered to ISO 9001.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE:

Storage: SRM 3452 should be stored in a low-moisture environment (e.g., a desiccator) at room temperature (21 ºC to 30 ºC), in the container provided.

Handling and Use: To prevent dopant precipitation, the Seebeck coefficient should not be measured above 900 K. Although no reference data is provided, SRM 3452 may be measured below 295 K.

For Seebeck coefficient measurements, the 2-probe arrangement is recommended [9,10]. Measurements using the 4-probe arrangement may have asymmetric thermal errors that result in overestimation of the Seebeck coefficient. It is further recommended to conduct measurements under vacuum ($< 10^{-4}$ Pa) to reduce convective and conductive thermal errors. Thermal interface materials may be used. The thermal interface quality may be evaluated by comparing the Seebeck coefficient measured at atmospheric pressure (S_A) and under vacuum (S_V). It is recommended that $|S_A - S_V| \leq 0.5\, u_B$, where u_B is the Type B uncertainty component of the measurement system in use. Current-voltage (IV) sweeps may also be conducted to verify Ohmic behavior of the electrical contact between the probes and SRM 3452.

The Seebeck coefficient should be measured using the differential method [1,9]. In this method, a small temperature difference ΔT is applied to the artifact at an average temperature of interest $T_o = (T_1 + T_2)/2$, where $T_1 = T_o - \Delta T/2$, and $T_2 = T_o + \Delta T/2$. The Seebeck coefficient can be obtained by the ratio of the voltage and the temperature difference: $S = V/\Delta T$, where $V = V^+ - V^-$ is the voltage, and $\Delta T = T_2 - T_1$ is the applied temperature difference, provided that $T_2 > T_1$, $\Delta T/T_o << 1$, and V^+ (V^-) is measured at T_2 (T_1) and at the same time. To reduce voltage offsets, it is further recommended to calculate the Seebeck coefficient as the slope of the unconstrained linear fit of multiple voltage and temperature difference ordered pairs $\{(\Delta T, V)\}$. The measured Seebeck coefficient must be corrected using the absolute Seebeck coefficient of the reference wires used to measure the thermoelectric voltage.

---

[1] Certain commercial instruments, materials, or processes 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 instruments, materials, or processes identified are necessarily the best available for the purpose.

SOURCE, PREPARATION, AND ANALYSIS

Source and Preparation: SRM 3452 comprises p-type boron-doped polycrystalline silicon-germanium, with a nominal composition of $Si_{80}Ge_{20}$. A 50 mm diameter, 18 mm thick ingot was produced using a combination of tribochemistry and hot pressing. The constituent elements were used as received without further purification or alteration. Elemental silicon (99.999 % purity, granular), germanium (99.999 % purity, 3-9 mm pieces), and boron (98 % purity, powder) were combined in stoichiometric quantities and mechanically alloyed under an inert argon atmosphere for 11 hours using a high-kinetic rotor ball mill and stainless steel balls. The resulting powders were hot pressed using direct current sintering under a uniaxial pressure of 35 MPa and thermal treatment at 1420 K for 5 min. The ingot density was 2.93 g/cm^3, > 99 % of the theoretical density. The ingot was fixed using natural beeswax and then diced into parallelepipeds using a webbed (net of parallel wires) slurry abrasive wire saw. The nominal dimensions for SRM 3452 are 2.5 mm x 2.5 mm x 14.0 mm to accommodate longer sample requirements in both custom-built and commercial instrumentation. All parallelepipeds were treated using an anneal-quench procedure to ensure homogeneous redissolution of the dopants into solid solution by sealing the artifacts in 16 mm diameter quartz ampoules under a 25 kPa argon atmosphere, immersing in a 1275 K furnace for 24 hours, then promptly removing and quenching in ice-water.

Measurement Procedures: Seebeck coefficient measurements were conducted in a custom developed apparatus [10]. Six artifacts were selected at random from the 70 unit batch for certification measurements. The Seebeck coefficient was measured at 13 base temperatures in 50 K intervals between 295 K and 900 K in the 2-probe arrangement using the quasi-steady-state condition of the differential method. Measurements were conducted under vacuum (< 10^{-4} Pa) following a triple purge and backfill cycle (99.999 % UHP He). Graphitic interface foil was inserted between the artifact and each tungsten electrode to enhance the thermal contact interface. The artifact and the two foil inserts were then compressed between the tungsten electrodes using defined current, velocity, and revolutions of the step motor. This ensured that the pressing force applied to each measured artifact was consistent. The thermal interface quality was verified by comparing the Seebeck coefficient measured at atmospheric pressure (S_A) and under vacuum (S_V), according to $|S_A - S_V| \leq 0.5\ u_B$, where u_B is the Type B measurement uncertainty component (typically << 0.4 µV/K). Current-voltage (IV) sweeps were conducted to verify Ohmic behavior of the tungsten-artifact contact interfaces, where the $R^2 \geq 0.9999$ for the IV least square fits and the voltage offsets at $I = 0$ were < 0.5 µV.

The thermal stability of the base temperature (the temperature of interest at which the artifact was stabilized prior to measurement) was between 10 mK to 50 mK throughout the 295 K to 900 K temperature range. At each stabilized base temperature, a small thermal flux was applied to the artifact with heating rates between 5 mK/s and 50 mK/s. The maximum temperature difference was $\leq 0.01\ T_B$, where T_B is the base temperature. Forty corresponding voltage (V) and temperature difference (ΔT) ordered pairs were simultaneously measured using 3 bus-triggered Keithley 2182A Nanovoltmeters [number of power line cycles (NPLC) = 5; aperture time = 83.3 ms] in 5 s intervals, where $V = V^+ - V^-$, $\Delta T = T_2 - T_1$, $T_2 > T_1$, and V^+ (V^-) was measured at T_2 (T_1) and at the same time (Figure 2). The thermocouple reference temperature was measured once at each base temperature.

The total average artifact temperature was calculated as the compound average of the 40 $(T_1 + T_2)/2$ individual average temperatures. The Seebeck coefficient was calculated as the slope of the unconstrained linear fit of the collection of voltage and temperature difference ordered pairs $\{(\Delta T, V)\}$, where $R^2 \geq 0.9999$. This avoids the assumption that the experimental data are collinear with the origin ($V = 0$, $\Delta T = 0$) and eliminates extraneous voltage offsets.

The voltage was measured between the negative T_2 and T_1 thermocouple wires (platinum). The measured Seebeck coefficient was subtracted from the absolute Seebeck coefficient of the platinum reference wires to obtain the corrected Seebeck coefficient of the artifact, according to: $S_{measured} = S_{Pt} - S_{artifact}$. The absolute Seebeck coefficient of platinum was obtained by using an empirical interpolation function [11].

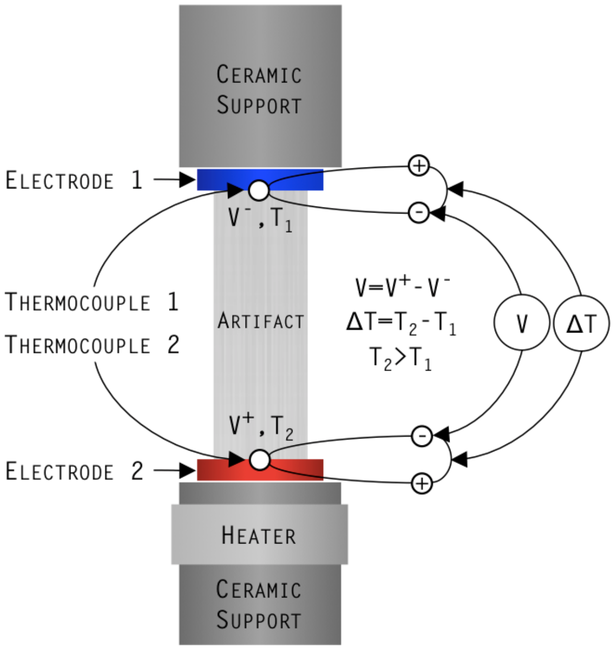

Figure 2. Graphic representation of the Seebeck coefficient measurement depicting the voltage and temperature measurement locations, the ceramic supports, the tungsten electrodes, the two thermocouples, the sample heater, and the artifact.

REFERENCES

[1] Martin, J.; Tritt, T.; Uher, C.; *High Temperature Seebeck Coefficient Metrology*; J. Appl. Phys., Vol. 108, pp. 121101–121112 (2010).

[2] Nolas, G.S.; Sharp, J.; Goldsmid, H.J.; *Thermoelectrics: Basic Principles and New Materials Developments*; Springer: New York, NY (2001).

[3] R Core Team; *R: A Language and Environment for Statistical Computing*; R Foundation For Statistical Computing; Vienna, Austria (2020); available at https://www.R-project.org/ (accessed Feb 2021).

[4] Beauchamp, C.R.; Camara, J.E.; Carney, J.; Choquette, S.J.; Cole, K.D.; DeRose, P.C.; Duewer, D.L.; Epstein, M.S.; Kline, M.C.; Lippa, K.A.; Lucon, E.; Phinney, K.W.; Polakoski, M.; Possolo, A.; Sharpless, K.E.; Sieber, J.R.; Toman, B.; Winchester, M.R.; Windover, D.; *Metrological Tools for the Reference Materials and Instruments of the NIST Material Measurement Laboratory*; NIST Special Publication 260-136-2020; U.S. Government Printing Office: Washington, DC (2020); available at https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.260-136-2020.pdf (accessed Feb 2021).

[5] Scheffé, H.; *The Analysis of Variance*; John Wiley & Sons: New York, NY (1999).

[6] Seber, G.A.F.; *Linear Regression Analysis*; John Wiley & Sons: New York, NY (1977).

[7] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Feb 2021).

[8] Possolo, A.; *Simple Guide for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1900; U.S. Government Printing Office: Washington, DC (2015); available at https://dx.doi.org/10.6028/NIST.TN.1900 (accessed Feb 2021).

[9] Martin, J.; *Protocols for the High Temperature Measurement of the Seebeck Coefficient in Thermoelectric Materials*; Meas. Sci. Technol., Vol. 24, 085601 (2013).

[10] Martin, J.; *Apparatus for the High Temperature Measurement of the Seebeck Coefficient in Thermoelectric Materials*; Rev. Sci. Instrum., Vol. 83, 065101 (2012).

[11] Burkov, A.T.; Heinrich, A.; Konstantinov, P.P.; Nakama, T.; Yagasaki, K.; *Experimental Set-Up for Thermopower and Resistivity Measurements at 100–1300 K*; Meas. Sci. Technol., Vol. 12, pp. 264–272 (2001).

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